AB INITIO CONFIGURATION INTERACTION (CI) CALCULATION OF THE CHARGE-DENSITY SUSCEPTIBILITY OF MOLECULAR HYDROGEN AND HIGHER-ORDER VAN DER WAALS INTERACTIONS FROM PERTURBATION THEORY

By

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ABSTRACT

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The charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$ of a molecule is defined as the change in the ω-frequency component $\delta\rho^e(\mathbf{r},\omega)$ of the electronic charge-density at a point $\mathbf{r}$ within a molecule, due to a perturbing potential $v_e(\mathbf{r}',\omega)$ of frequency ω applied at a point $\mathbf{r}'$ (within linear response). This work includes a derivation of an *ab initio* expression for the charge-density susceptibility and its application to calculate $\chi(\mathbf{r},\mathbf{r}';\omega)$ of the H_2 molecule as a function of $\mathbf{r}$, $\mathbf{r}'$, and ω in the aug-cc-pVDZ basis set using a configuration interaction wavefunction with single and double excitations (CISD). Since CISD theory is equivalent to full configuration interaction (CI) theory in a two-electron case, the results are exact within a given basis set. Results of the calculations of $\chi(\mathbf{r},\mathbf{r}';\omega)$ for the H_2 molecule are analyzed, with emphasis on the behavior of the function when the frequency ω is close to a molecular transition frequency from the ground electronic state.

In order to test the calculations of $\chi(\mathbf{r},\mathbf{r}';\omega)$ for the H_2 molecule, the result for $\chi(\mathbf{r},\mathbf{r}';\omega)$ has been used to calculate the frequency-dependent polarizabilities $\alpha_{xx}(\omega)$, $\alpha_{yy}(\omega)$, and $\alpha_{zz}(\omega)$ of H_2 as a function of ω in the DZ, DZP and aug-cc-PVDZ basis sets. Excellent agreement has been obtained between our results for static polarizabilities and the corresponding finite-field polarizabilities obtained with the MOLPRO quantum chemistry software package.

Following a review of known results for the second-order and third-order corrections to the energy of interaction of two molecules in the polarization approximation, complex contour integration is used to derive a new equation for the third-order dispersion energy of two interacting molecules. The results for the second- and third-order interaction energies are used to obtain approximations to these energies for pairs and clusters of hydrogen fluoride molecules, in terms of the properties of the individual molecules.

In Loving Memory

of

Juan M. Lafuente

June 27, 1940 - September 11, 2001

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1.1 Introduction

The charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$ gives the change in the ω-frequency component $\delta\rho^e(\mathbf{r},\omega)$ of the electronic charge density at point $\mathbf{r}$ within a molecule, due to a perturbing potential $v_e(\mathbf{r}',\omega)$ of frequency ω applied at $\mathbf{r}'$ (within linear response),[1]

$$\delta\rho^e(\mathbf{r},\omega) = \int \chi(\mathbf{r},\mathbf{r}';\omega)\; v_e(\mathbf{r}',\omega)\; d\mathbf{r}'. \tag{1}$$

Molecular properties, such as dipole and higher-order polarizabilities, Sternheimer electric field shielding tensors,[5] induction energies for interacting molecules,[8–10] van der Waals dispersion energies,[11] infrared intensities,[5] electronic reorganization terms in vibrational force constants,[6,7] and intramolecular dielectric functions[4] depend on the charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$.

The dipole polarizability $\alpha_{\alpha\beta}(\omega)$ of a molecule is the first moment of the charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$, with respect to both $\mathbf{r}$ and $\mathbf{r}'$,

$$\alpha_{\alpha\beta}(\omega) = \int r_\alpha\, r'_\beta\; \chi(\mathbf{r},\mathbf{r}';\omega)\; d\mathbf{r}\, d\mathbf{r}', \tag{2}$$

where r_α and r'_β are the α and β components of $\mathbf{r}$ and $\mathbf{r}'$, respectively ($(\alpha,\beta = x,y,z)$).[3] Similarly, the quadrupole polarizability $C_{\alpha\beta,\gamma\delta}(\omega)$ is related to $\chi(\mathbf{r},\mathbf{r}';\omega)$ by

$$C_{\alpha\beta,\gamma\delta}(\omega) = 3\int \frac{1}{2}\,(3\,r_\alpha\, r_\beta - \delta_{\alpha\beta}\, r^2)\;\frac{1}{2}(3\,r'_\gamma\, r'_\delta - \delta_{\gamma\delta}\, r'^2)\;\chi(\mathbf{r},\mathbf{r}';\omega)\; d\mathbf{r}\, d\mathbf{r}'. \tag{3}$$

In Eq. (3), r_α and r_β are the α and β components of $\mathbf{r}$, and r'_γ and r'_δ are the γ and δ components of $\mathbf{r}'$.[3]

When a molecule is subject to an external electric field $\mathbf{F}^e$, the net electric field experienced by nucleus I within that molecule depends on the unperturbed electric field within the molecule and the screening of the applied field resulting from rearrangements in the molecular electronic charge distribution. If the applied field $\mathbf{F}^e$ is both static and uniform, the shielding tensor $\gamma^I_{\alpha\beta}$ determines screening effects which are linear in $\mathbf{F}^e$. The shielding tensor $\gamma^I_{\alpha\beta}$ depends on the static nonlocal polarizability density $\alpha(\mathbf{r}, \mathbf{r}')$,[5]

$$\gamma^I_{\alpha\beta} = -\int d\mathbf{r}\ d\mathbf{r}'\ T_{\alpha\beta}(\mathbf{R}^I, \mathbf{r})\ \alpha(\mathbf{r}, \mathbf{r}'). \tag{4}$$

In Eq. (4), $T_{\alpha\beta}(\mathbf{R}^I, \mathbf{r})$ is the $\alpha\beta$ component of the dipole-propagator tensor $T(\mathbf{R}^I, \mathbf{r})$ with coordinates $\mathbf{R}^I$ of nucleus I. Also, the static nonlocal polarizability density determines the static susceptibility,[3]

$$\nabla\nabla' : \alpha(\mathbf{r}, \mathbf{r}') = -\chi(\mathbf{r}, \mathbf{r}'), \tag{5}$$

where ∇ and ∇' are the gradients with respect to $\mathbf{r}$ and $\mathbf{r}'$.

When a pair of molecules interact at long range (where the overlap between the charge clouds is weak), the permanent and fluctuating charge distributions of each molecule give rise to a perturbing potential $v_e(\mathbf{r}, \omega)$ that acts on the neighboring molecule. Thus, both induction and dispersion energies depend on $\chi(\mathbf{r}, \mathbf{r}'; \omega)$. Specifically, the dispersion energy of a pair of molecules A and B depends on the charge-density susceptibility at imaginary frequencies.[2,3] Several researchers have derived equations for the second-order dispersion energy of interaction between two atoms or molecules that depend on the charge-density susceptibilities of the interacting atoms or molecules. In 1963, McLachlan[12] derived the first equation of this type. Specifically, McLachlan derived an equation for the second-order dispersion energy of interaction of two atoms that is given in terms of implicit forms of the charge-density susceptibilities of the two molecules. Following the work of McLachlan, Longuet-Higgins derived the first equation for the second-order dispersion energy of interaction of two molecules that has an explicit dependence on the charge-density susceptibilities of the two molecules. Specifically, according to Longuet-Higgins' work, the second-order dispersion energy of interaction W between two molecules is[13]

$$\begin{aligned} W &= -\frac{h}{4\pi^2}\int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}'_1 \int d\mathbf{r}'_2 \\ &\times \int_0^\infty d\xi \frac{\alpha\left(\mathbf{r}_1, \mathbf{r}_2, \imath\xi\right) \alpha'\left(\mathbf{r}'_1, \mathbf{r}'_2, \imath\xi\right)}{|\mathbf{r}_1 - \mathbf{r}'_1||\mathbf{r}_2 - \mathbf{r}'_2|}, \end{aligned} \tag{6}$$

In Eq. (6), $\alpha\left(\mathbf{r}_1, \mathbf{r}_2, \imath\xi\right)$ and $\alpha'\left(\mathbf{r}'_1, \mathbf{r}'_2, \imath\xi\right)$ are the charge-density susceptibilities of the first and second molecules, respectively. Note that we are using Longuet-Higgins' notation in Eq. (6); α and α' correspond to the function $\chi(\mathbf{r}, \mathbf{r}'; \omega)$

in this work. In Eq. (6), $\mathbf{r}_1$ and $\mathbf{r}_2$ are points in the first molecule, $\mathbf{r}'_1$ and $\mathbf{r}'_2$ are points in the second molecule, and $\imath\xi$ is an imaginary frequency. Longuet-Higgins' α susceptibility measures the response of the electronic charge-density at $\mathbf{r}_1$ to an exponentially increasing perturbation at $\mathbf{r}_2$ with $e^{(\xi t)}$ time dependence. The α' susceptibility measures the corresponding response at $\mathbf{r}'_1$ to an exponentially increasing perturbation at $\mathbf{r}'_2$ with $e^{(\xi t)}$ time dependence.

Langhoff[14] has expressed the second-order Coulomb energy in terms of the Fourier integral of the Coulomb potential and uses the contour integration techniques of Casimir and Polder[106] to simplify the energy denominators contained in this expression for the Coulomb energy. The resulting expression gives the second-order Coulomb energy in terms of the response functions of the two systems, which are essentially Fourier transforms of the charge-density susceptibilities of those systems. Jacobi and Csanak used a similar procedure to write the second-order dispersion energy of interaction between two closed-shell atoms in terms of implicit forms of the Fourier-transformed charge-density susceptibilities of those atoms.[15] Langhoff's work is similar to Jacobi and Csanak's work in that both involve transforming susceptibilities from configuration to momentum space. Langhoff transforms the susceptibilities in the second-order Coulomb energy from configuration to momentum space, and Jacobi and Csanak transform the susceptibilities in the second-order dispersion energy similarly. The momentum-space expressions for the second-order Coulomb and dispersion energies contain integrals over fewer variables than the configuration-space expressions.

Following the work of Jacobi and Csanak, several researchers developed approximate methods for calculating the second-order dispersion energy of interaction of two atoms or molecules from the charge-density susceptibilities of those systems. Koide[18] developed the first approximation to the second-order dispersion energy of interaction of two spherically symmetric atoms by deriving a convergent expansion for the interaction energy where V is written in terms of spherical wave interactions. This expansion for the second-order dispersion energy ΔE gives

$$\begin{aligned}\Delta E &= -\frac{1}{4\pi^2}\int\frac{d^3\mathbf{k}}{k^2}e^{\imath\mathbf{k}\dot{\mathbf{r}}}\int\frac{d^3\mathbf{k}'}{k'^2}e^{-\imath\mathbf{k}'\dot{\mathbf{r}}} \\ &\times\frac{\hbar}{2\pi}\int_0^\infty du\,\alpha_A\left(\mathbf{k},\mathbf{k}';\imath u\right)\alpha_B\left(-\mathbf{k},-\mathbf{k}';\imath u\right) \qquad (7)\end{aligned}$$

where we have used Koide's notation for Eq. (7). In Eq. (7), $\alpha_A\left(\mathbf{k},\mathbf{k}';\imath u\right)$ and $\alpha_B\left(-\mathbf{k},-\mathbf{k}';\imath u\right)$ are the polarizabilities of atoms A and B, respectively. Also, $\mathbf{k}$ and $\mathbf{k}'$ are wavenumber vectors, and $\imath u$ is an imaginary frequency. These polarizabilies correspond to Fourier transforms of charge-density susceptibilities of atoms A and B, which depend on spatial coordinates $\mathbf{r}$ and $\mathbf{r}'$, as well as on the imaginary frequency $\imath u$. Koide derived the polarizability $\alpha\left(\mathbf{k},\mathbf{k}';\imath u\right)$ in terms of spherical harmonics and polarizabilities $\alpha_l\left(k,k';\imath u\right)$, for angular momentum quantum numbers $l=0,1,2,...$; $\alpha_l\left(k,k';\omega\right)$ is defined as

$$\begin{aligned}\alpha_l\left(k,k';\omega\right) &= \frac{2}{\hbar}\sum_{\rho\neq0}\frac{\omega_\rho}{\omega_\rho^2-\omega^2} \\ &\times \langle0|Q_l^m(k)^*|\rho\rangle\langle\rho|Q_l^m\left(k'\right)|0\rangle, \qquad (8)\end{aligned}$$

where we have let $\imath u=\omega$. The states $|\rho\rangle$ are the eigenstates of the unperturbed atom (which is either atom A or B in this case), and $|0\rangle$ is the ground state of the unperturbed atom. Again, we are using Koide's notation in Eq. (8). Also, $\hbar\omega_\rho = E_\rho - E_0$, where E_ρ and E_0 are the energies of states $|\rho\rangle$ and $|0\rangle$. Finally, $Q_l^m\left(k\right)$ and $Q_l^m\left(k'\right)$ are multipole moment operators which are defined in Koide's work in terms of spherical harmonics and Bessel functions. The polarizability $\alpha_l\left(k,k';\omega\right)$ in Eq. (8) can be approximated using the variational method of Karplus and Kolker[19] or other variational methods. After calculating $\alpha_l\left(k,k';\omega\right)$, one can use his or her results for $\alpha_l\left(k,k';\omega\right)$ and the appropriate spherical harmonics to obtain $\alpha_A\left(\mathbf{k},\mathbf{k}';\imath u\right)$ and $\alpha_B\left(-\mathbf{k},-\mathbf{k}';\imath u\right)$. Finally, using the resulting expressions for $\alpha_A\left(\mathbf{k},\mathbf{k}';\imath u\right)$ and $\alpha_B\left(-\mathbf{k},-\mathbf{k}';\imath u\right)$ and Eq. (7), one can obtain an approximate dispersion energy of interaction of atoms A and B. References 1, 25–30 and 31 give equations for second-order dispersion energies that depend on approximate charge-density susceptibilities and include other derivations and calculations that are related to these equations.

Recently, Kohn, Meir, and Makarov[20] have used density functional theory (DFT) to derive a seamless expression for the van der Waals interaction energy of two atomic or molecular systems. The expression is seamless in the sense that it yields accurate van der Waals energies at any intersystem distance. They began their derivation by using either the local-density approximation (LDA) or the generalized-gradient approximation (GGA) to describe the electron density $\eta(\mathbf{r})$. Next, they separated the Coulomb potential into short and long-range parts, and assumed that the van der Waals energies could be completely attributed to the long-range interactions. At this point, they used the adiabatic connection formula to write the long-range interaction energy. After transforming this expression into the time domain, they obtained the correct long-range limit for the van der Waals energy E_{vdW} of two spherically symmetric atoms A and B,

$$E_{vdW} = -\frac{C_6}{R^6}, \tag{9}$$

with the following expression for C_6 :

$$C_6 = \frac{3}{\pi} \int_0^\infty dt_1 \int_0^\infty dt_2 \frac{\chi_A^{zz}(t_1)\,\chi_B^{zz}(t_2)}{t_1 + t_2}. \tag{10}$$

In Eq. (9), $R = |\mathbf{R}_A - \mathbf{R}_B|$, where $\mathbf{R}_A$ and $\mathbf{R}_B$ are the coordinates of the nuclei of atoms A and B, respectively. In Eq. (10), χ^{zz} is the z component of the response of the electron density to a perturbation applied in the z direction. In equation form, this response is

$$\chi^{zz} = \int d\mathbf{r}_1 d\mathbf{r}_2\, \chi(\mathbf{r}_1, \mathbf{r}_2)\, z_1 z_2, \tag{11}$$

where $\chi(\mathbf{r}_1, \mathbf{r}_2)$ is the static charge-density susceptibility.

Dobson and co-workers[21–23] have developed a seamless density functional for calculating the van der Waals interaction energy of atomic, molecular or other physical systems. The functional is defined by four equations, and Dobson and Wang give specific forms of these equations for the interaction of two jellium metal slabs in reference 21. The first equation gives the average ground-state electron density $\overline{\eta}^{IGA}(z, z')$ of the interacting system. The second equation, which depends on $\overline{\eta}^{IGA}\left(z, z'\right)$ and the Kohn-Sham polarization response α_{KS}^{hom} of the system, gives the Kohn-Sham density-density response function $\chi_{KS}\left(z, z', q_{||}, \imath s\right)$ of the interacting system. The third equation is the Dyson-like screening equation for the Kubo density-density response function $\chi_{\lambda}\left(\mathbf{r}, \mathbf{r}'; \omega = \imath s\right)$ of the interacting system. When $\lambda = 1$ in the Kubo density-density response function, we obtain the frequency-dependent charge-density susceptibility $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ defined in this work. The equation which gives the Kubo density-density response function depends on the Kohn-Sham density-density response function, the exchange-correlation kernel $f_{xc\lambda}\left(\mathbf{r}, \mathbf{r}'; \omega = \imath s\right)$ of the system, and a modified electron-electron interaction λV_{Coul} . Finally, the fourth equation for the van der Waals density functional is the adiabatic connection fluctuation-dissipation (ACFD) formula. This equation uses V_{Coul}, χ_{λ}, and χ_{KS} as input, and gives the correlation energy of the system. In this work, we have used Dobson and Wang's[21] notation to refer to all quantities contained in the four equations that yield their seamless density functional for van der Waals interactions. Also, all quantities mentioned in this work that appear in Dobson and Wang's equations are defined in reference 21. Dobson and Wang have carried out a related derivation (and calculations) in reference 24.

Equations for the second-order dispersion energy that depend on charge-density susceptibilities are superior to the corresponding point-multipole expressions for the second-order dispersion energy because the former equations account for charge-overlap effects that are neglected in the latter expressions. Because charge-overlap effects are accounted for, the dispersion energy as defined in terms of charge-density susceptibilities is finite as $R \longrightarrow 0$, whereas the corresponding infinite series for the point-multipole dispersion energy diverges.

The static charge-density susceptibility $\chi(\mathbf{r}, \mathbf{r}')$ determines the derivative of the electronic charge density with respect to nuclear coordinates,[5]

$$\frac{\partial \rho_0^e(\mathbf{r})}{\partial \mathbf{R}^A} = Z^A \left(4\pi\epsilon_o\right)^{-1} \int d\mathbf{r}' \, \chi(\mathbf{r}, \mathbf{r}') \nabla^A \left|\mathbf{r}' - \mathbf{R}^A\right|^{-1}, \qquad (12)$$

where Z^A is the charge of nucleus A with coordinates $\mathbf{R}^A$, and ∇^A denotes the derivative with respect to $\mathbf{R}^A$. Eq. (12) holds because the electronic charge density responds via the same susceptibility to an applied potential and to the change in the nuclear Coulomb potential when a nucleus shifts.[5] Changes in the electronic dipole moment as a molecule vibrates depend on linear combinations of the derivatives $\partial\rho_0^e(\mathbf{r})/\partial\mathbf{R}^A$; thus the intensities of vibrational transitions are related to the internal charge redistribution in the molecule by Eq. (12). Similarly, the electronic charge redistribution term in harmonic force constants depends on $\chi(\mathbf{r},\mathbf{r}')$; this term corresponds to the induction energy energy of the molecule, due to changes in the nuclear Coulomb field, as the molecule vibrates.[7]

A non-local intramolecular dielectric function $\epsilon_v{}^{-1}(\mathbf{r},\mathbf{r}';\omega)$ characterizes the screening of an applied potential $v_e(\mathbf{r};\omega)$ by the electronic charge redistribution, to give an effective potential $v_{eff}(\mathbf{r},\omega)$ within the molecule

$$v_{eff}(\mathbf{r},\omega) = \int \epsilon_v^{-1}(\mathbf{r},\mathbf{r}';\omega)\, v_e(\mathbf{r}',\omega)\, d\mathbf{r}'. \qquad (13)$$

The dielectric function is related to $\chi(\mathbf{r},\mathbf{r}';\omega)$ by[4]

$$\epsilon_o\,\epsilon_v^{-1}(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}') + (4\pi\epsilon_o)^{-1}\int d\mathbf{r}''\,|\mathbf{r}-\mathbf{r}''|^{-1}\,\chi(\mathbf{r}'',\mathbf{r}';\omega). \quad (14)$$

The correlations of the spontaneous quantum mechanical fluctuations in charge density are determined by the imaginary part of the charge-density susceptibility $\chi''(\mathbf{r},\mathbf{r}';\omega)$ via the fluctuation-dissipation theorem,[57]

$$\frac{1}{2}\left\langle \delta\rho_e(\mathbf{r},\omega)\,\delta\rho_e(\mathbf{r}',\omega') + \delta\rho_e(\mathbf{r}',\omega')\,\delta\rho_e(\mathbf{r},\omega)\right\rangle = \left(\frac{\hbar}{2\pi}\right)\chi''(\mathbf{r},\mathbf{r}';\omega)$$
$$\times\delta\left(\omega+\omega'\right)\coth\left(\frac{\hbar\omega}{2kT}\right). \qquad (15)$$

For this reason, the total electronic energy of a molecule is determined by $\chi(\mathbf{r},\mathbf{r}';i\omega)$ and the permanent molecular charge density,[58]

$$E = \frac{1}{2}\sum_N Z_N \int d\mathbf{r}\,\frac{\langle\rho_e(\mathbf{r})\rangle}{|\mathbf{r}-\mathbf{R}_N|} + \frac{1}{4}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{\langle\rho_e(\mathbf{r})\rangle\langle\rho_e(\mathbf{r}')\rangle}{|\mathbf{r}-\mathbf{r}'|}$$

$$+ \left(\frac{\hbar}{4\pi}\right) \int d\mathbf{r}\, d\mathbf{r}' \int_0^\infty d\omega\, \frac{\chi(\mathbf{r}, \mathbf{r}'; \imath\omega)}{|\mathbf{r} - \mathbf{r}'|} - \left(\frac{1}{2}\right) \Sigma_{ee}$$

$$+ \left(\frac{1}{2}\right) \sum_{K,\alpha} Z_K\, R_{K\alpha} \int d\mathbf{r}\, \frac{\langle \rho_e(\mathbf{r}) \rangle (\mathbf{R}_K - \mathbf{r})_\alpha}{|\mathbf{r} - \mathbf{R}_K|^3}. \tag{16}$$

In Eq. (16), Σ_{ee} is an electronic self-energy. Additionally, the charge-density susceptibility $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is related to the softness kernel as defined in density functional theory.[33,34]

The static charge-density susceptibility $\chi(\mathbf{r}, \mathbf{r}')$ has been calculated *ab initio* using a finite field CI approach for water by Li, Ahuja, Hunt, and Harrison.[32] Ando,[35] Zangwill and Soven,[36], Gross and Kohn,[37,38] and van Gisbergen and coworkers[39] have developed techniques for calculating the charge-density susceptibility within density functional theory (DFT). The charge-density susceptibililty can also be calculated *ab initio* using time-dependent perturbation methods, pseudo-state techniques,[40,44,41–43,45–50] or by quantum Monte Carlo methods.[51–53] Furthermore, an *ab initio* expression for the charge-density susceptibility $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ can be formulated by deriving the linear response function within coupled-cluster (CC) theory.[54]

1.2 $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ at CI Level: Derivation

Quantum mechanically,

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}'; \omega) &= \langle \Psi_0 | \rho_e(\mathbf{r})\, G(\omega)\, \rho_e(\mathbf{r}') | \Psi_0 \rangle \\ &+ \langle \Psi_0 | \rho_e(\mathbf{r}')\, G(-\omega)\, \rho_e(\mathbf{r}) | \Psi_0 \rangle, \end{aligned} \tag{17}$$

where Ψ_0 is the ground-state wavefunction, $\rho_e(\mathbf{r})$ is the electronic charge-density operator at $\mathbf{r}$,

$$\rho_e(\mathbf{r}) = -\sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i), \tag{18}$$

$\rho_e(\mathbf{r}')$ is the charge-density operator at $\mathbf{r}'$, and $G(\omega)$ is the reduced resolvent,

$$G(\omega) = (1 - \wp_0)(H - E_0 - \hbar\omega)^{-1}(1 - \wp_0) = \sum_{K \neq 0} \frac{|\Psi_K\rangle\langle\Psi_K|}{E_K - E_0 - \hbar\omega}. \tag{19}$$

In Eq. (19), H is the electronic Hamiltonian for the unperturbed molecule, $\wp_0$ is the projection operator for the ground-state wavefunction, and Ψ_K is the K^{th} excited-state wavefunction. Also, E_0 and E_K denote the energies of the ground and K^{th} excited states, respectively. Thus

$$\begin{aligned}\chi(\mathbf{r},\mathbf{r}';\omega) &= \sum_{K\neq 0} \frac{\langle\Psi_0|\rho_e(\mathbf{r})|\Psi_K\rangle\langle\Psi_K|\rho_e(\mathbf{r}')|\Psi_0\rangle}{E_K - E_0 - \hbar\omega} \\ &+ \sum_{K\neq 0} \frac{\langle\Psi_0|\rho_e(\mathbf{r}')|\Psi_K\rangle\langle\Psi_K|\rho_e(\mathbf{r})|\Psi_0\rangle}{E_K - E_0 + \hbar\omega}. \end{aligned} \tag{20}$$

At CI level, the ground and K^{th} excited- state wavefunctions Ψ_0 and Ψ_K have the form

$$\begin{aligned}|\Psi_0\rangle &= c_0(0)|\Phi\rangle + \sum_{i,a} c_a^i(K)|\Phi_i^a\rangle + \sum_{i>j,a>b} c_{ab}^{ij}(K)|\Phi_{ij}^{ab}\rangle \\ &+ \ldots = \sum_J c_J(0)|\Phi_J\rangle, \\ |\Psi_K\rangle &= \sum_J c_J(K)|\Phi_J\rangle. \end{aligned} \tag{21}$$

In Eq. (21), $|\Phi\rangle$ is the reference determinant for the ground state, $|\Phi_i^a\rangle$ is a singly-excited determinant, and $|\Phi_{ij}^{ab}\rangle$ is a doubly-excited determinant. Additionally, $|\Phi_J\rangle$ represents all possible determinants in the full CI expansion. The coefficients $c_J(K)$ are the CI coefficients, determined by solving the Schrödinger equation at CI level,

$$H|\Psi_K\rangle = E_K|\Psi_K\rangle. \tag{22}$$

From Eqs. (20) and (21),

$$\chi(\mathbf{r},\mathbf{r}';\omega) = A(\mathbf{r},\mathbf{r}';\omega) + A(\mathbf{r}',\mathbf{r};-\omega), \tag{23}$$

where

$$\begin{aligned}A(\mathbf{r},\mathbf{r}';\omega) = & \sum_{K\neq 0} \sum_{J,J',J'',J'''} c_J(0)c_{J'}(K)c_{J''}(K)c_{J'''}(0) \\ & \frac{\langle\Phi_J|\rho_e(\mathbf{r})|\Phi_{J'}\rangle\langle\Phi_{J''}|\rho_e(\mathbf{r}')|\Phi_{J'''}\rangle}{E_K - E_0 - \hbar\omega}. \end{aligned} \tag{24}$$

Since $\rho_e(\mathbf{r})$ is a one-electron operator, the matrix elements in Eq. (24) vanish unless J and J' differ by at most one orbital occupancy. We separate $A(\mathbf{r},\mathbf{r}';\omega)$ into four sets of terms, based on the relationship between the determinants $|\Phi_J\rangle$, $|\Phi_{J'}\rangle$, $|\Phi_{J''}\rangle$, and $|\Phi_{J'''}\rangle$,

$$\begin{aligned}
A(\mathbf{r},\mathbf{r}';\omega) &= \sum_{J=J',J''=J'''} A_{J,J''}(\mathbf{r},\mathbf{r}';\omega) + \sum_{J=J',J''\neq J'''} A_{J,J''\neq J'''}(\mathbf{r},\mathbf{r}';\omega) \\
&+ \sum_{J\neq J',J''=J'''} A_{J\neq J',J''}(\mathbf{r},\mathbf{r}';\omega) \\
&+ \sum_{J\neq J',J''\neq J'''} A_{J\neq J',J''\neq J'''}(\mathbf{r},\mathbf{r}';\omega). \qquad (25)
\end{aligned}$$

Terms in Eq. (24) with $J = J'$ and $J'' = J'''$ are included in $A_{J,J''}(\mathbf{r},\mathbf{r}';\omega)$, etc. In terms of the atomic spin orbitals ϕ_p , ϕ_q, ϕ_t , and ϕ_u and the expansion coefficients d_{ls} that relate molecular orbital l to atomic orbital ϕ_s ,

$$\begin{aligned}
A_{J,J''}(\mathbf{r},\mathbf{r}';\omega) &= \sum_{p,q,t,u} \phi_p(\mathbf{r})\phi_q(\mathbf{r})\phi_t(\mathbf{r}')\phi_u(\mathbf{r}') \\
&\times \sum_{K\neq 0} \sum_{i(J),j(J''),occ} c_J(0)c_J(K)c_{J''}(K)c_{J''}(0) \\
&\times \frac{d_{ip}d_{iq}d_{jt}d_{ju}}{E_K - E_0 - \hbar\omega} \\
&= \sum_{p,q,t,u} B^{pqtu}_{J,J''}(\omega)\,\phi_p(\mathbf{r})\,\phi_q(\mathbf{r})\,\phi_t(\mathbf{r}')\,\phi_u(\mathbf{r}'). \qquad (26)
\end{aligned}$$

In Eq. (26), the sum over $i(J)$ runs over all molecular orbitals i that are occupied in determinant J and similarly for the sum over $j(J'')$. The sum over p, q, t , and u runs over all atomic orbitals. For $J \neq J'$, we define $l(J,J')$ as the molecular orbital occupied in J but not in J', $r(J,J')$ as the molecular orbital that is occupied in J' but not in J , $d_{l(J,J')p}$ is the coefficient of atomic orbital p in molecular orbital l, and $d_{r(J,J')q}$ is the coefficient of atomic orbital q in molecular orbital r (and similarly for $J'' \neq J'''$). We obtain

$$\begin{aligned}
A_{J=J',J''\neq J'''} &\equiv A_{J,J''\neq J'''}(\mathbf{r},\mathbf{r}';\omega) = \sum_{p,q,t,u} \phi_p(\mathbf{r})\,\phi_q(\mathbf{r})\,\phi_t(\mathbf{r}')\,\phi_u(\mathbf{r}') \\
&\times \sum_{K\neq 0} \sum_{i(J),occ} c_J(0)c_J(K)c_{J''}(K)c_{J'''}(0) \\
&\times \frac{d_{ip}d_{iq}d_{l(J'',J''')t}d_{r(J'',J''')u}}{E_K - E_0 - \hbar\omega} \\
&= \sum_{p,q,t,u} B^{pqtu}_{J,J''\neq J'''}(\omega)\,\phi_p(\mathbf{r})\,\phi_q(\mathbf{r})\,\phi_t(\mathbf{r}')\,\phi_u(\mathbf{r}') \qquad (27)
\end{aligned}$$

$$\begin{aligned} A_{J\neq J',J''=J'''}(\mathbf{r},\mathbf{r}';\omega) &= \sum_{p,q,t,u} \phi_p(\mathbf{r})\,\phi_q(\mathbf{r})\,\phi_t(\mathbf{r}')\,\phi_u(\mathbf{r}') \\ &\times \sum_{K\neq 0}\sum_{j(J''),occ} c_J(0)c_{J'}(K)c_{J''}(K)c_{J''}(0) \\ &\times \frac{d_{l(J,J')p}d_{r(J,J')q}d_{jt}d_{ju}}{E_K-E_0-\hbar\omega} \\ &= \sum_{p,q,t,u} B^{pqtu}_{J\neq J',J''}(\omega)\phi_p(\mathbf{r})\phi_q(\mathbf{r})\phi_t(\mathbf{r}')\phi_u(\mathbf{r}') \end{aligned} \tag{28}$$

$$\begin{aligned} A_{J\neq J',J''\neq J'''}(\mathbf{r},\mathbf{r}';\omega) &= \sum_{p,q,t,u} \phi_p(\mathbf{r})\,\phi_q(\mathbf{r})\,\phi_t(\mathbf{r}')\,\phi_u(\mathbf{r}') \\ &\times \sum_{K\neq 0}\frac{d_{l(J,J')p}d_{r(J,J')q}d_{l(J'',J''')t}d_{r(J'',J''')u}}{E_K-E_0-\hbar\omega} \\ &\times c_J(0)c_{J'}(K)c_{J''}(K)c_{J'''}(0) \\ &= \sum_{p,q,t,u} B^{pqtu}_{J\neq J',J''\neq J'''}(\omega) \\ &\times \phi_p(\mathbf{r})\phi_q(\mathbf{r})\phi_t(\mathbf{r}')\phi_u(\mathbf{r}'). \end{aligned} \tag{29}$$

The calculations of the charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$ in this work are based on Eqs. (26) - (29).

To check the calculations of $\chi(\mathbf{r},\mathbf{r}';\omega)$, we have calculated $\alpha_{\alpha\beta}(\omega)$ from $\chi(\mathbf{r},\mathbf{r}';\omega)$ and Eq. (25). The frequency-dependent polarizability $\alpha_{\alpha\beta}(\omega)$ is given by

$$\begin{aligned} \alpha_{\alpha\beta}(\omega) &= \sum_{K\neq 0}\frac{\langle\Psi_0|\mu_\alpha|\Psi_K\rangle\langle\Psi_K|\mu_\beta|\Psi_0\rangle}{E_K-E_0-\hbar\omega} \\ &+ \sum_{K\neq 0}\frac{\langle\Psi_0|\mu_\beta|\Psi_K\rangle\langle\Psi_K|\mu_\alpha|\Psi_0\rangle}{E_K-E_0+\hbar\omega} \end{aligned} \tag{30}$$

where μ_α and μ_β denote the α and β components of the dipole moment operator, given by $\hat{\mu}_\alpha = \sum_{i=1}^{N} e_i r_{i\alpha} + \sum_{j=1}^{M} Z_j R_{j\alpha}$ where N is the total number of electrons in the molecule and M is the total number of nuclei. Also, e_i is the charge on the i^{th} electron, Z_j is the charge on the j^{th} nucleus, $r_{i\alpha}$ is the α component of the vector from the origin to the i^{th} electron, and $R_{j\alpha}$ is the α component of the vector from the origin to the j^{th} nucleus. Eq. (2) follows from Eqs. (20) and (30). From Eqs. (25) - (29),

$$\alpha_{\alpha\beta}(\omega) = \sum_{J,J',J'',J'''} B^{pqtu}_{J,J',J'',J'''}(\omega)\, \mu^{pq}_{\alpha}\, \mu^{tu}_{\beta}, \tag{31}$$

where

$$\begin{aligned} B^{pqtu}_{J,J',J'',J'''}(\omega) &= B^{pqtu}_{J,J''}(\omega)\, \delta_{JJ'}\, \delta_{J''J'''} + B^{pqtu}_{J,J''\neq J'''}(\omega)\, \delta_{JJ'}\, (1-\delta_{J''J'''}) \\ &+ B^{pqtu}_{J\neq J',J''}(\omega)\, (1-\delta_{JJ'})\, \delta_{J''J'''} \\ &+ B^{pqtu}_{J\neq J',J''\neq J'''}(\omega)\, (1-\delta_{JJ'})\, (1-\delta_{J''J'''})\,; \end{aligned} \tag{32}$$

μ^{pq}_{α} and μ^{tu}_{β} are dipole moment integrals in the atomic orbital basis, defined as $\mu^{pq}_{\alpha} = \langle p|\hat{\mu}_{\alpha}|q\rangle$ and $\mu^{tu}_{\beta} = \langle t|\hat{\mu}_{\beta}|u\rangle$.

1.3 Algorithm for $\chi(\mathbf{r}, \mathbf{r}'; \omega)$

We have used the General Atomic and Molecular Electronic Software System (GAMESS)[16] to calculate the one- and two-electron integrals, to find the molecular orbitals at restricted Hartree-Fock (RHF) level, and to transform the one- and two-electron integrals from the atomic orbital basis to the molecular orbital basis. Then we have solved the CISD (CI singles and doubles) equations to find the CISD coefficients $c_J(K)$, the ground-state energy E_0 , and the excited-state energies E_K . Using these quantities, the atomic orbitals, and the transformation coefficients from the atomic orbital to molecular orbital basis, we have calculated $A_{J,J''}$, $A_{J\neq J',J''}$, $A_{J,J''\neq J'''}$ and $A_{J\neq J',J''\neq J'''}$ and then summed to obtain the charge-density susceptibility $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ of the molecule.

To calculate $\alpha_{\alpha\beta}(\omega)$, we have used dipole moment integrals $\int r_{\alpha}\, \phi_p(\mathbf{r})\, \phi_q(\mathbf{r})\, d\mathbf{r}$ and $\int r'_{\beta}\, \phi_t(\mathbf{r}')\, \phi_u(\mathbf{r}')\, d\mathbf{r}'$ computed in the linear-response coupled-cluster program written by Kondo and co-workers.[55,56]

1.4 Results of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ Calculations

We have calculated the charge-density susceptibility of the H_2 molecule at the CISD level as a function of frequency ω and points $\mathbf{r}$ and $\mathbf{r}'$ using a program based on the algorithm presented here. Since CISD is equivalent to full CI in a two-electron case, our results are exact within the basis set that we used. Each plot of the charge-density susceptibility that we will present here was generated by fixing ω, $\mathbf{r}'$, and x , and calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ for all y and z included in $-3.25 \leq y \leq +3.25$ and $-3.25 \leq z \leq +3.25$ a.u. with $\Delta y = \Delta z = 0.05$. The aug-cc-pVDZ basis set was used for the plots. Note that the internuclear axis was aligned with the z -axis for all calculations, and that we used the equilibrium geometry of the H_2 molecule (the equilibrium bond length of H_2 is 1.40126 a.u.).

Before presenting the results of our calculations, let us discuss some important properties of the charge-density susceptibility that we will use to understand the behavior of $\chi(\mathbf{r},\mathbf{r}';\omega)$. Recall Eq. (20) from Sect. 1.2,

$$\begin{aligned}\chi(\mathbf{r},\mathbf{r}';\omega) &= \sum_{K\neq 0}\frac{\langle\Psi_0|\rho_e(\mathbf{r})|\Psi_K\rangle\langle\Psi_K|\rho_e(\mathbf{r}')|\Psi_0\rangle}{E_K - E_0 - \hbar\omega} \\ &+ \sum_{K\neq 0}\frac{\langle\Psi_0|\rho_e(\mathbf{r}')|\Psi_K\rangle\langle\Psi_K|\rho_e(\mathbf{r})|\Psi_0\rangle}{E_K - E_0 + \hbar\omega}. \end{aligned} \qquad (33)$$

According to Eq. (33), $\chi(\mathbf{r},\mathbf{r}';\omega)$ is singular for energies $\hbar\omega$ that are equal to $\pm(E_K - E_0)$, if the corresponding terms in the numerator do not vanish. We have verified this property of $\chi(\mathbf{r},\mathbf{r}';\omega)$ by calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 at $\mathbf{r}' = 0,0,0$, $x = 0$, and $\omega = E_1 - E_0$ (data not shown). For these conditions, $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 was approaching infinity at $-3.25 \leq y \leq 3.25$ and $-3.25 \leq z \leq 3.25$ with $\Delta y = \Delta z = 0.05$.

If Ψ_0 is a singlet state and Ψ_K is a triplet state, then the matrix elements $\langle\Psi_0|\rho_e(\mathbf{r})|\Psi_K\rangle$, $\langle\Psi_0|\rho_e(\mathbf{r}')|\Psi_K\rangle$, $\langle\Psi_K|\rho_e(\mathbf{r})|\Psi_0\rangle$, and $\langle\Psi_K|\rho_e(\mathbf{r}')|\Psi_0\rangle$ vanish. This holds because $\rho_e(\mathbf{r})$ and $\rho_e(\mathbf{r}')$ are spin-independent operators, so that it is impossible for $\rho_e(\mathbf{r})$ and $\rho_e(\mathbf{r}')$ to change the spin of Ψ_K to a singlet. Therefore, triplet states will not contribute to $\chi(\mathbf{r},\mathbf{r}';\omega)$, and $\chi(\mathbf{r},\mathbf{r}';\omega)$ will not be singular at energies which correspond to transitions to triplet states. This will be true for all of our data, since Ψ_0 is a CI singlet ground state for all of our calculations.

In the aug-cc-pVDZ basis, H_2 has 18 spatial orbitals and 36 spin orbitals. Eighteen of the spin orbitals have α spin functions, and the other eighteen have β spin functions. We label α spin orbitals with odd integers, and β spin orbitals with even integers. In terms of spatial orbitals, the lowest energy spatial orbital (the $1\sigma_g$ orbital) is doubly occupied in the ground-state configuration of H_2. In terms of spin orbitals, the lowest energy α and β spin orbitals are occupied in the ground-state configuration of H_2. Recall from Eq. (21) that the ground- and excited-state CISD wavefunctions are generated from a linear combination of all possible singly- and doubly-excited determinants. Therefore, according to Eq. (21), the ground-state wavefunction for H_2 in the aug-cc-pVDZ basis is:

$$\begin{aligned}
|\Psi_0\rangle &= c_0(0)|\Phi\rangle + c_3^1(0)|\Phi_1^3\rangle + c_5^1(0)|\Phi_1^5\rangle \\
&+ c_4^2(0)|\Phi_2^4\rangle + c_6^2(0)|\Phi_2^6\rangle + \dots + c_{34}^{12}(0)|\Phi_{12}^{34}\rangle + c_{36}^{12}(0)|\Phi_{12}^{36}\rangle + \dots \\
&= c_0(0)|\Phi\rangle + c_5^1(0)\left[|\Phi_1^5\rangle - |\Phi_2^6\rangle\right] + \dots + c_{34}^{12}(0)|\Phi_{12}^{34}\rangle + \dots \qquad (34)
\end{aligned}$$

where Φ_1^3, Φ_1^5, Φ_2^4 , and Φ_2^6 are singly-excited determinants which correspond to exciting an electron from spin orbital 1 $(1\sigma_{g\alpha})$ to spin orbital 3 $(1\sigma_{u\alpha})$, from spin orbital 1 $(1\sigma_{g\alpha})$ to spin orbital 5 $(2\sigma_{g\alpha})$, from spin orbital 2 $(1\sigma_{g\beta})$ to spin orbital 4 $(1\sigma_{u\beta})$, and from spin orbital 2 $(1\sigma_{g\beta})$ to spin orbital 6 $(2\sigma_{g\beta})$, respectively. Also, Φ_{12}^{34} and Φ_{12}^{36} are doubly-excited determinants corresponding to exciting electrons from spin orbitals 1 and 2 to spin orbitals 3 and 4, and from spin orbitals 1 and 2 to spin orbitals 3 and 6, respectively. In Eq. (34), the quantity $|\Phi_1^5\rangle - |\Phi_2^6\rangle$ is a singlet spin-adapted configuration state function. This is because each determinant involved in the linear combination in either quantity involves exciting an electron from the same lower energy spatial orbital to the same higher energy spatial orbital, and the resulting determinantel configuration is an eigenfunction of S^2 and $S = 0$. If we write configuration $|\Phi_1^5\rangle - |\Phi_2^6\rangle$ in terms of spatial orbitals ψ_i and spin functions α and β, where $\langle\psi_i|\psi_j\rangle = \delta_{ij}$ and $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$, we have:

$$\begin{aligned}
|\Phi_1^5\rangle - |\Phi_2^6\rangle &= [\psi_1(1)\beta(1)\psi_3(2)\alpha(2) - \psi_1(2)\beta(2)\psi_3(1)\alpha(1)] \\
&- [\psi_1(1)\alpha(1)\psi_3(2)\beta(2) - \psi_1(2)\alpha(2)\psi_3(1)\beta(1)] \\
&= [\psi_1(1)\psi_3(2) + \psi_1(2)\psi_3(1)] \\
&\times [\beta(1)\alpha(2) - \beta(2)\alpha(1)]. \qquad (35)
\end{aligned}$$

According to Eq. (35), the spin part of $|\Phi_1^5\rangle - |\Phi_2^6\rangle$ is antisymmetric with respect to electron exchange. We can carry out a similar analysis on each excited-state Ψ_K

in the aug-cc-pVDZ basis set in order to determine whether a particular Ψ_K is a singlet or a triplet state.

Let us return to our discussion of the properties of $\chi(\mathbf{r},\mathbf{r}';\omega)$. To do this, consider the symmetry of the H_2 molecule. Since H_2 belongs to the $D_{\infty h}$ point group, there are an infinite number of irreducible representations that can be used to classify the symmetries of its orbitals and states, including Σ_g^+, Σ_g^-, Σ_u^+, Σ_u^-, Π_g, Π_u, Δ_g , and Δ_u . If $\mathbf{r}' = 0$ and Ψ_0 is a ${}^1\Sigma_g$ state, then matrix elements $\langle\Psi_0|\rho_e(\mathbf{r})|\Psi_K\rangle$, $\langle\Psi_0|\rho_e(\mathbf{r}')|\Psi_K\rangle$, $\langle\Psi_K|\rho_e(\mathbf{r})|\Psi_0\rangle$, and $\langle\Psi_K|\rho_e(\mathbf{r}')|\Psi_0\rangle$ are nonzero only for Ψ_K states that have ${}^1\Sigma_g$ symmetry. Therefore, when $\mathbf{r}' = 0$, $\chi(\mathbf{r},\mathbf{r}';\omega)$ will only be singular for energies $\hbar\omega$ approaching the energy of transition to Σ_g states. In order to understand why this is true, we need to consider the composition of the charge-density susceptibility. According to Eqs. (25) - (29) in Sect. 1.2, the charge-density susceptibility is essentially a sum of products of atomic orbitals evaluated at $\mathbf{r}$ and $\mathbf{r}'$ which is weighted by CI coefficients, coefficients for converting atomic orbitals to molecular orbitals, and energy denominators. Although we have not done so here, we can also write the charge-density susceptibility as a sum of products of molecular orbitals evaluated at $\mathbf{r}$ and $\mathbf{r}'$ and weighted by CI coefficients and energy denominators. Now, consider the molecular orbitals of H_2 as a function of $\mathbf{r}'$. The σ_g orbital is nonzero at $z' = 0$, and the σ_u orbital is zero when $z' = 0$. The π_g and π_u orbitals are also zero when $z' = 0$. Therefore, the only orbitals and states which will contribute to $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 when $\mathbf{r}' = (0,0,0)$ are σ_g-type orbitals and Σ_g -type states. Note that this property of $\chi(\mathbf{r},\mathbf{r}';\omega)$ is also true when $\mathbf{r} = 0$.

If $\mathbf{r}'$ lies along the molecular axis and Ψ_0 is ${}^1\Sigma_g$ state, then matrix elements $\langle\Psi_0|\rho_e(\mathbf{r})|\Psi_K\rangle$, $\langle\Psi_0|\rho_e(\mathbf{r}')|\Psi_K\rangle$, $\langle\Psi_K|\rho_e(\mathbf{r})|\Psi_0\rangle$, and $\langle\Psi_K|\rho_e(\mathbf{r}')|\Psi_0\rangle$ will only be nonzero for ${}^1\Sigma_g$ and ${}^1\Sigma_u$ states. Therefore, when $\mathbf{r}'$ lies along the molecular axis, the only singularities in $\chi(\mathbf{r},\mathbf{r}';\omega)$ will occur at transitions to ${}^1\Sigma_g$ or ${}^1\Sigma_u$ states. This property of $\chi(\mathbf{r},\mathbf{r}';\omega)$ can also be explained in terms of the molecular orbitals of H_2. The $\sigma_g(\mathbf{r}')$ and $\sigma_u(\mathbf{r}')$ orbitals are nonzero for all z' except $z' = 0$. Therefore, these orbitals will contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ for all $\mathbf{r}' = (0, 0, \pm z)$ except $\mathbf{r}' = (0, 0, 0)$. Since the $\pi_g(\mathbf{r}')$ and $\pi_u(\mathbf{r}')$ orbitals are zero for all z' , they will not contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ when $\mathbf{r}'$ is on the large z' axis. This property of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is also true for $\mathbf{r} = 0$. Note these results hold when the molecular axis is along the z' (or z) axis, which applies for all of our calculations.

If $\mathbf{r}'$ is somewhere in the xz plane, then the matrix elements $\langle \Psi_0 | \rho_e(\mathbf{r}) | \Psi_K \rangle$, $\langle \Psi_0 | \rho_e(\mathbf{r}') | \Psi_K \rangle$, $\langle \Psi_K | \rho_e(\mathbf{r}) | \Psi_0 \rangle$, and $\langle \Psi_K | \rho_e(\mathbf{r}') | \Psi_0 \rangle$ will only be nonzero for ${}^1\Pi_x$ and ${}^1\Delta_{x^2-y^2}$-type states (of the states generated by the basis set used). As a result, if $\mathbf{r}'$ is in the xz plane, $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ will only blow up for energies which correspond to transitions to ${}^1\Pi_x$ and ${}^1\Delta_{x^2-y^2}$ states in these calculations.

Figure 1 shows the charge-density susceptibility of the H_2 molecule with $\omega = 0$ and $\mathbf{r}' = (0, 0, 0)$. As expected, $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ does not become singular when $\omega = 0$, since we are not near any transition energies. Also, note that $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ has the general shape of a σ_g molecular orbital of H_2. This is as expected, since $\mathbf{r}' = (0, 0, 0)$, for which only σ_g type orbitals and Σ_g type states contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$.

Figure 2 shows the charge-density susceptibility of the H_2 molecule when $\mathbf{r}' = (0, 0, 0)$ and $\omega = 0.3858668352248763$ a.u. Note that $\hbar\omega$ is near $(E_1 - E_0)$ in the aug-cc-pVDZ basis set. As in Fig. 1, the susceptibility has the general shape of a σ_g molecular orbital of H_2. Again, this is observed because $\mathbf{r}' = (0, 0, 0)$; since only σ_g - type orbitals and Σ_g -type states contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ for $\mathbf{r}' = (0, 0, 0)$. Also, although $\hbar\omega$ is near $(E_1 - E_0)$, $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ of H_2 does not become singular at any $\mathbf{r}$. This is because Ψ_1 is a triplet state, and, as we have discussed, triplet states will not contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ at any frequency, $\mathbf{r}$ or $\mathbf{r}'$ value.

The charge-density susceptibility of the H_2 molecule at $\mathbf{r}' = (0, 0, 0)$ and

$\omega = 0.4812104263202694$ a.u. is shown in Fig. 3. This value of $\hbar\omega$ is near $(E_4 - E_0)$ for the aug-cc-pVDZ basis set. As was the case for $\omega = 0$ and $\omega = 0.3858668352248763$ a.u., $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ has the general shape of a σ_g molecular orbital of H_2 because $\mathbf{r}' = (0, 0, 0)$. However, in contrast to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ at $\omega = 0$ and at $\omega = 0.3858668352248763$ a.u., $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is singular near $\omega = 0.4812104263202694$ a.u. This happens because Ψ_4 is a $^1\Sigma_g$ state.

Figure 4 shows the charge-density susceptibility of the H_2 molecule at $\mathbf{r}' = (0, 0, +0.07)$ and $\omega = 0.3858668352248763$ a.u., which is near $(E_1 - E_0)$. This is the same frequency that was used to calculate $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ as shown in Fig. 2. As was the case for $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ as shown in Fig. 2, $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is not singular at this frequency, since Ψ_1 is a triplet state. However, the shape of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ in Fig. 2 is different from the shape of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ in Fig. 4. Whereas $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ as shown in Fig. 2 has the general shape of a σ_g molecular orbital of H_2, $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ as shown in Fig. 4 resembles a σ_u molecular orbital of H_2. This results from the fact that $\mathbf{r}'$ lies on the molecular axis. Recall that when $\mathbf{r}'$ lies on the molecular axis, both σ_g and σ_u-type orbitals can contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$. Therefore, both σ_g and σ_u-type orbitals contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ when $\mathbf{r}' = (0, 0, 0.7)$, and the overall shape of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ depends on a sum of products of σ_g and σ_u orbitals.

The charge-density susceptibility of the H_2 molecule at $\mathbf{r}' = (0, 0, 0.7)$ and $\omega = 0.4648380650856789$ a.u., which is near $(E_3 - E_0)$, is shown in Fig. 5. According to Fig. 5, $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is singular near this frequency. This results from the fact that Ψ_3 is a $^1\Sigma_u$ state, since $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ of H_2 at $\mathbf{r}' = (0, 0, 0.7)$ is singular for transitions to Σ_u or Σ_g states. Notice also that the charge-density susceptibility of H_2 in Fig. 5 resembles a σ_u molecular orbital of H_2. Again, this occurs because both σ_g-type and σ_u-type orbitals contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ when $\mathbf{r}'$ lies on the molecular axis, but $\mathbf{r}' \neq (0, 0, 0)$.

1.5 Results of $\alpha_{\alpha\beta}(\omega)$ Calculations

In order to test our calculations of the charge-density susceptibility of H_2, we have calculated the $\alpha_{xx}(\omega)$, $\alpha_{yy}(\omega)$ and $\alpha_{zz}(\omega)$ components of the static and frequency-dependent polarizabilities of the H_2 molecule at the CISD level in the DZ, DZP and aug-cc-pVDZ basis sets. Table 2 provides a comparison of the $\alpha_{xx}(\omega)$, $\alpha_{yy}(\omega)$, and $\alpha_{zz}(\omega)$ components of the frequency-dependent polarizability $\alpha_{\alpha\beta}(\omega)$ obtained by integration of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ (using the algorithm described here) and by finite-field calculations carried out with the MOLPRO[17] quantum chemistry software package. There is excellent agreement between the $\alpha_{xx}(\omega)$, $\alpha_{yy}(\omega)$, and $\alpha_{zz}(\omega)$ values calculated here and the corresponding values calculated with MOLPRO[17].

Figure 6 shows the $\alpha_{zz}(\omega)$ component of the polarizability of H_2 in the DZ, DZP and aug-cc-pVDZ basis sets as a function of frequency for various frequencies within the range from 0 to 1.5 atomic units (a.u.). Note that for these calculations, the bond length of H_2 was set to 1.40126 a.u. (the equilibrium bond length of the H_2 molecule). According to Fig. 6, $\alpha_{zz}(\omega)$ in the DZ basis set becomes singular at approximately 0.58 a.u., and $\alpha_{zz}(\omega)$ in the DZP basis has a singularity at approximately 0.57 a.u. In the aug-cc-pVDZ basis set, $\alpha_{zz}(\omega)$ is singular at frequencies of approximately 0.47 and 0.6 a.u. Figure 7 shows the same data as shown in Fig. 6, however, the range of the $\alpha_{zz}(\omega)$ values in Fig. 7 is restricted to ± 200 a.u.

We will now explain the singularities of $\alpha_{xx}(\omega)$, $\alpha_{yy}(\omega)$, and $\alpha_{zz}(\omega)$ in the DZ, DZP and aug-cc-pVDZ basis sets in terms of the spin states which contribute to $\alpha_{\alpha\beta}(\omega)$ of H_2 and the symmetries of these states. According to Eq. (30), $\alpha_{\alpha\beta}(\omega)$ can be written in terms of matrix elements $\langle\Psi_0|\mu_\alpha|\Psi_K\rangle$ and $\langle\Psi_K|\mu_\beta|\Psi_0\rangle$ of dipole moment operators μ_α and μ_β , respectively. Because μ_α and μ_β are spin independent and Ψ_0 is a singlet state, matrix elements $\langle\Psi_0|\mu_\alpha|\Psi_K\rangle$ and $\langle\Psi_K|\mu_\beta|\Psi_0\rangle$ will be nonzero only if the Ψ_K states are singlet states. Therefore, only singlet Ψ_K's will contribute to $\alpha_{\alpha\beta}(\omega)$.

We can determine which singlet excited states contribute to $\alpha_{\alpha\beta}(\omega)$ by analyzing the symmetries of the matrix elements which contribue to $\alpha_{\alpha\beta}(\omega)$. To begin this analysis, consider Eqs. (21) and (30). If Eq. (21) is substituted for $|\Psi_0\rangle$ and $|\Psi_K\rangle$, then $\alpha_{\alpha\beta}(\omega)$ becomes

$$\alpha_{\alpha\beta}(\omega) = P(\alpha,\beta,\omega) + P(\beta,\alpha,-\omega) \tag{36}$$

and

$$\begin{aligned} P(\alpha,\beta,\omega) &= \sum_{K>0} \sum_{J,J',J'',J'''} c_J(0)c_{J'''}(0)c_{J''}(K)c_{J'}(K) \\ &\times \frac{\langle\Phi_J|\hat{\mu}_\alpha|\Phi_{J'}\rangle\langle\Phi_{J''}|\hat{\mu}_\beta|\Phi_{J'''}\rangle}{E_K - E_0 - \hbar\omega} \end{aligned} \tag{37}$$

where all quantities in Eq. (37) have been defined previously. According to group theory, the matrix element $\langle\Phi_J|\hat{\mu}_\alpha|\Phi_{J'}\rangle$ will be nonzero only if the direct product of the irreducible representations of Φ_J , $\hat{\mu}_\alpha$, and $\Phi_{J'}$ equals or contains the totally symmetric irreducible representation for the molecular point group. We will determine the symmetries of Φ_J, $\hat{\mu}_\alpha$, and $\Phi_{J'}$ that make $\langle\Phi_J|\hat{\mu}_\alpha|\Phi_{J'}\rangle$ nonzero for $\alpha = x$, $\alpha = y$, and $\alpha = z$.

Let us begin by determining the symmetries of Φ_J, $\Phi_{J'}$, and $\hat{\mu}_z$ that make $\langle\Phi_J|\hat{\mu}_z|\Phi_{J'}\rangle$ nonzero when $J = J'$. Eqs. (21) and (37) indicate that determinants Φ_J are contained within the ground state CI wavefunction Ψ_0 . Because all determinants within a CI wavefunction must have the same symmetry as the overall wavefunction, determinants Φ_J must have the same symmetry as the wavefunction Ψ_0. Therefore, since we have required that Ψ_0 has Σ_g^+ symmetry (in the $D_{\infty h}$ point group), Φ_J must also have Σ_g^+ symmetry. If we let $\hat{\mu}_z = -(e\,z_1 + e\,z_2)$ in $\langle\Phi_J|\hat{\mu}_z|\Phi_J\rangle$, we have

$$\langle\Phi_J|\hat{\mu}_z|\Phi_J\rangle = -e\,\langle\Phi_J|z_1|\Phi_J\rangle - e\,\langle\Phi_J|z_2|\Phi_J\rangle. \tag{38}$$

In the $D_{\infty h}$ point group, z transforms as Σ_u^+ . Therefore, the direct product corresponding to either $\langle\Phi_J|z_1|\Phi_J\rangle$ or $\langle\Phi_J|z_2|\Phi_J\rangle$ is $\Sigma_g^+\,\Sigma_u^+\,\Sigma_g^+ = \Sigma_u^+$, which does not equal or contain Σ_g^+ . Therefore, matrix elements $\langle\Phi_J|\hat{\mu}_z|\Phi_{J'}\rangle$ vanish for all $J = J'$. Now, let us determine the symmetries of Φ_J, $\Phi_{J'}$ and $\hat{\mu}_z$ that make $\langle\Phi_J|\hat{\mu}_z|\Phi_{J'}\rangle$ nonzero when $J \neq J'$. If we let $\hat{\mu}_z = -(e\,z_1 + e\,z_2)$ in $\langle\Phi_J|\hat{\mu}_z|\Phi_{J'}\rangle$, we have

$$\langle\Phi_J|\hat{\mu}_z|\Phi_{J'}\rangle = -e\,\langle\Phi_J|z_1|\Phi_{J'}\rangle - e\,\langle\Phi_J|z_2|\Phi_{J'}\rangle. \tag{39}$$

Let us assume that $\Phi_{J'}$ has Σ_u^+ symmetry. Since Φ_J has Σ_g^+ symmetry and z_1 has Σ_u^+ symmetry, the direct product corresponding to either $\langle\Phi_J|z_1|\Phi_{J'}\rangle$ or $\langle\Phi_J|z_2|\Phi_{J'}\rangle$ is $\Sigma_g^+\,\Sigma_u^+\,\Sigma_u^+ = \Sigma_g^+$, which is the totally symmetric representation. Therefore, $\langle\Phi_J|\hat{\mu}_z|\Phi_{J'}\rangle$ will contribute to $\alpha_{zz}(\omega)$ when $\Phi_{J'}$ has Σ_u^+ symmetry. Since the excited states Ψ_K that contain $\Phi_{J'}$ must have the same symmetry as $\Phi_{J'}$, we can also conclude that excited states with Σ_u^+ symmetry will contribute to $\alpha_{zz}(\omega)$. If $\Phi_{J'}$ has a non-zero projection of the angular momentum along the z axis, $\langle\Phi_J|\hat{\mu}_z|\Phi_{J'}\rangle$ vanishes. Therefore, only states of Σ_u^+ symmetry contribute to $\alpha_{zz}(\omega)$.

At this point, let us determine the symmetries of Φ_J, $\Phi_{J'}$, and $\hat{\mu}_x$ that make $\langle\Phi_J|\hat{\mu}_x|\Phi_{J'}\rangle$ nonzero when $J = J'$. If we let $\hat{\mu}_x = -(e\,x_1 + e\,x_2)$ in $\langle\Phi_J|\hat{\mu}_x|\Phi_J\rangle$, we have

$$\langle\Phi_J|\hat{\mu}_x|\Phi_J\rangle = -e\,\langle\Phi_J|x_1|\Phi_J\rangle - e\,\langle\Phi_J|x_2|\Phi_J\rangle. \tag{40}$$

In the $D_{\infty h}$ point group, x transforms as Π_u . Therefore, the direct product corresponding to either $\langle\Phi_J|x_1|\Phi_J\rangle$ or $\langle\Phi_J|x_2|\Phi_J\rangle$ is $\Sigma_g^+\,\Pi_u\,\Sigma_g^+ = \Pi_u$, which does not equal or contain Σ_g^+. Therefore, matrix elements $\langle\Phi_J|\hat{\mu}_x|\Phi_{J'}\rangle$ vanish for all $J = J'$. Let us determine the symmetries of Φ_J, $\Phi_{J'}$ and $\hat{\mu}_x$ that make $\langle\Phi_J|\hat{\mu}_x|\Phi_{J'}\rangle$ nonzero when $J \neq J'$. If we let $\hat{\mu}_x = -(e\,x_1 + e\,x_2)$ in $\langle\Phi_J|\hat{\mu}_x|\Phi_{J'}\rangle$, we have

$$\langle\Phi_J|\hat{\mu}_x|\Phi_{J'}\rangle = -e\,\langle\Phi_J|x_1|\Phi_{J'}\rangle - e\,\langle\Phi_J|x_2|\Phi_{J'}\rangle. \tag{41}$$

Let us assume that $\Phi_{J'}$ has Π_u symmetry. Since Φ_J has Σ_g^+ symmetry and x_1 has Π_u symmetry, the direct product corresponding to either $\langle\Phi_J|x_1|\Phi_{J'}\rangle$ or $\langle\Phi_J|x_2|\Phi_{J'}\rangle$ is $\Sigma_g^+\,\Pi_u\,\Pi_u = \Sigma_g^+ + \Sigma_g^- + \Delta_g$, which contains the totally symmetric representation. The matrix element $\langle\Phi_J|\hat{\mu}_x|\Phi_{J'}\rangle$ will contribute to $\alpha_{xx}(\omega)$ when $\Phi_{J'}$ has Π_{u_x} symmetry. Since the excited states Ψ_K that contain $\Phi_{J'}$ must have the same symmetry as $\Phi_{J'}$, we can also conclude that excited states with Π_{u_x} symmetry will contribute to $\alpha_{xx}(\omega)$. Excited states of other symmetries do not contribute. In the $D_{\infty h}$ point group, y also transforms as Π_u. Therefore, matrix elements $\langle\Phi_J|\hat{\mu}_y|\Phi_J\rangle$ will also vanish, matrix elements $\langle\Phi_J|\hat{\mu}_y|\Phi_{J'}\rangle$

will also be nonzero when $\Phi_{J'}$ has Π_{u_y} symmetry, and excited states with Π_{u_y} symmetry will be the only ones to contribute to $\alpha_{yy}(\omega)$. In Fig. 7, we see that $\alpha_{zz}(\omega)$ in the DZ basis set is singular at two frequencies, approximately 0.58 and 1.47 a.u. We also see that $\alpha_{zz}(\omega)$ in the DZP basis set is singular at 0.57 and at 1.43 a.u.

For the three basis sets, each of the frequencies where $\alpha_{zz}(\omega)$ blows up corresponds to a specific $(E_K - E_0)$ value. In the DZ basis, 0.58 a. u. and 1.47 a. u. correspond to $(E_2 - E_0)$ and $(E_7 - E_0)$, respectively. In the DZP basis, 0.57 a. u. and 1.43 a. u. correspond to $(E_2 - E_0)$ and $(E_7 - E_0)$. Finally, 0.47 a.u. and 0.6 a.u. correspond to $(E_3 - E_0)$ and $(E_{10} - E_0)$ in the aug-cc-pVDZ basis set. According to an analysis of the spins and symmetries of states 2 and 7 in the DZ and DZP basis sets, state 2 corresponds to the $1^1\Sigma_u^+$ of H_2, and state 7 corresponds to the $2^1\Sigma_u^+$ state of H_2. A similar analysis of states 3 and 10 in the aug-cc-pVDZ basis set shows that these states correspond to the $1^1\Sigma_u^+$ and $2^1\Sigma_u^+$ states of H_2, respectively.

Figure 8 shows the $\alpha_{xx}(\omega)$ component of the polarizability of the H_2 molecule in the DZP and aug-cc-pVDZ basis sets as as a function of ω, where ω varies from 0 to 1.75 a.u. Note that the $\alpha_{xx}(\omega)$ component of the polarizability of H_2 in the DZ basis set vanishes, since there are no *p*-type atomic orbitals on either of the H atoms in the DZ basis set. According to Fig. 8, $\alpha_{xx}(\omega)$ of H_2 in the aug-cc-pVDZ basis set is singular at approximately 0.57 a.u. Figure 9 shows the $\alpha_{xx}(\omega)$ component of the polarizability of H_2 as a function of ω in the DZP basis set, where ω varies from 0 to 1.75 a.u. Note that these data were also shown in Fig. 8, however, in Fig. 8, the $\alpha_{xx}(\omega)$ scale is too large to show the behavior of $\alpha_{xx}(\omega)$ in the DZP basis. According to Fig. 9, the $\alpha_{xx}(\omega)$ component of the polarizability of H_2 in the DZP basis is not singular within the 0 to 1.5 a.u. frequency range.

Only Π_u-type states will contribute to the $\alpha_{xx}(\omega)$ component of the polarizability of H_2. The energy $\hbar\omega$ of the frequency at which $\alpha_{xx}(\omega)$ is singular in the aug-cc-pVDZ basis set corresponds to the degenerate energy differences $(E_8 - E_0)$

and $(E_9 - E_0)$. According to an analysis of the spins and symmetries of Ψ_8 and Ψ_9, these states are the $1^1\Pi_{u_x}$ and $1^1\Pi_{u_y}$ states of H_2, respectively. Transitions to the $1^1\Pi_{u_x}$ state account for the singularity of $\alpha_{xx}(\omega)$.

The $\alpha_{yy}(\omega)$ component of the frequency-dependent polarizability of H_2 in the DZP and aug-cc-pVDZ basis sets as a function of ω, where $0 \leq \omega \leq 1.75$ a.u., is shown in Fig. 10. Note that the $\alpha_{yy}(\omega)$ component of the frequency-dependent polarizability of H_2 in the DZ basis set vanishes. Fig. 10 shows us that the $\alpha_{yy}(\omega)$ component of the polarizability of H_2 in the aug-cc-pVDZ basis set also has a singularity at $\omega = 0.57$ a.u.

Only Π_u-type states will contribute to $\alpha_{yy}(\omega)$ of the H_2 molecule. As was the case for the $\alpha_{xx}(\omega)$, the energy $\hbar\omega$ corresponding to the frequency at which $\alpha_{yy}(\omega)$ has a singularity corresponds to the degenerate energy differences $(E_8 - E_0)$ and $(E_9 - E_0)$. As mentioned above, Ψ_8 and Ψ_9 in the aug-cc-pVDZ basis are the $1^1\Pi_{u_x}$ and $1^1\Pi_{u_y}$ states of H_2, respectively.

2 Higher-Order van der Waals Interactions from Perturbation Theory

2.1 Introduction

This chapter provides an introduction to intermolecular interaction phenomena and a brief summary of the methods used to calculate these interactions, within perturbation theory. In chemistry, the interaction energy E_{int} of molecules A and B is given by

$$E_{int} = E_{AB} - E_A - E_B \tag{42}$$

where E_{AB} is the total energy of the two interacting molecules. Also, in Eq. (42), E_A and E_B are the energies of molecules A and B when they are separated from one another.

In comparison to covalent bond energies, intermolecular interaction energies are weak. Whereas covalent bond energies are on the order of one hundred kilocalories per mole, intermolecular interaction energies range from fractions of kilocalories per mole to kilocalories per mole. Despite the relatively small magnitudes of intermolecular interaction energies, several phenomena are affected by these interactions. Some of these phenomena include the structures and properties of intermolecular complexes, molecular dynamics, solvation, and the behavior of bulk gases, liquids, and solids. This chapter is organized as follows: In Sect. 2.1, we introduce the idea of an intermolecular interaction energy and briefly discuss the importance of this kind of interaction in chemistry, biology, and physics. In Sect. 2.2, we present the basic quantum mechanical theory of intermolecular interactions. In Sects. 2.3 and 2.4, we present and discuss the polarization and the multipole approximations, respectively. We use Sect. 2.5 to introduce various formulations of the bipolar expansion. Finally, we discuss symmetry-adapted pertubation theory and many-body perturbation theory in Sects. 2.6 and 2.7.

2.2 The Quantum Mechanical Theory of Intermolecular Interactions

In the Born-Oppenheimer approximation, the time-independent electronic Schrödinger equation is

$$H|\Psi_k\rangle = E_k|\Psi_k\rangle. \tag{43}$$

In Eq. (43), H is the Hamiltonian for the system, $|\Psi_k\rangle$ is the exact electronic wavefunction for the k^{th} state of the system, and E_k is the exact energy for the k^{th} state of the system. If the system consists of two interacting molecules A and B, then Eq. (43) becomes

$$H|\Psi_{k_{AB}}\rangle = E_{k_{AB}}|\Psi_{k_{AB}}\rangle, \tag{44}$$

where $\Psi_{k_{AB}}$ and $E_{k_{AB}}$ are the exact wavefunction and energy for the k^{th} state of the interacting system. In Eq. (44), the overall Hamiltonian H is

$$H = H^A + H^B + V, \tag{45}$$

where H^A and H^B are the Hamiltonians for molecules A and B when they are isolated from one another. The Hamiltonians H^X are given by

$$\begin{aligned} H^X &= -\left(\frac{1}{2}\right)\sum_{i\in X}\nabla_i^2 - \sum_{i\in X}\sum_{\alpha\in X}\frac{Z_\alpha}{r_{i\alpha}} \\ &+ \sum_{i,j\in X, i<j}\frac{1}{r_{ij}}, \end{aligned} \tag{46}$$

where $X = A$ for molecule A, and $X = B$ for molecule B. Indices i and j run over all electrons in X, and α runs over all nuclei in X. Also, $\left(\frac{1}{2}\right)\nabla_i^2$ is the kinetic energy operator for the i^{th} electron in molecule X, Z_α is the charge on nucleus α of molecule X, and $r_{i\alpha}$ is the distance between the i^{th} electron and nucleus α in molecule X. Additionally, r_{ij} is the distance between the i^{th} and j^{th} electrons in molecule X. The Hamiltonians H^A and H^B satisfy the time-independent electronic Schrödinger equation

$$H^X|\Psi_{l_X}\rangle = E_{l_X}|\Psi_{l_X}\rangle, \tag{47}$$

with $X = A$ for molecule A, and $X = B$ for molecule B. In Eq. (47), $|\Psi_{l_X}\rangle$ is the exact wavefunction for the l^{th} state of molecule X , and E_{l_X} is the corresponding energy of that state. Finally, in Eq. (45), V is the intermolecular interaction operator, which is

$$
\begin{aligned}
V &= \sum_{\gamma\in A}\sum_{\delta\in B}\frac{Z_\gamma Z_\delta}{r_{\gamma\delta}} - \sum_{n\in B}\sum_{\gamma\in A}\frac{Z_\gamma}{r_{n\gamma}} \\
&- \sum_{m\in A}\sum_{\delta\in B}\frac{Z_\delta}{r_{m\delta}} + \sum_{m\in A}\sum_{n\in B}\frac{1}{r_{mn}}.
\end{aligned} \tag{48}
$$

Indices γ and δ run over all nuclei in A and B, respectively, and m and n run over all electrons in A and B. Also, Z_γ is the charge on nucleus γ in molecule A, and Z_δ is the charge on nucleus δ in molecule B. We also use $r_{\gamma\delta}$ to denote the distance between nucleus γ in A and nucleus δ in B, $r_{n\gamma}$ to denote the distance between nucleus γ in A and the n^{th} electron in B, and $r_{m\delta}$ to denote the distance between nucleus δ in B and the m^{th} electron in A. Here, r_{mn} is the distance between the m^{th} electron in A and the n^{th} electron in B. When we combine Eqs. (44) and (45), we have

$$
\left(H^A + H^B + V\right)|\Psi_{k_{AB}}\rangle = E_{k_{AB}}|\Psi_{k_{AB}}\rangle. \tag{49}
$$

Eq. (49) can only be solved exactly for the interaction between a hydrogen atom and a proton. The energy of interaction between two larger systems can be obtained by solving Eq. (49) approximately, using either perturbation theory or variational theory.[280] Although variational methods have successfully been used to calculate intermolecular interaction energies,[280] these methods will not be discussed in this work. For the remainder of this chapter, we will briefly discuss various perturbative schemes for solving Eq. (49). For more detailed descriptions of each of the methods mentioned here, we refer the reader to several reviews.[70–73,?,75]

2.3 The Polarization Approximation

2.3.1 Introduction

In Rayleigh-Schrödinger perturbation theory, the Hamiltonian for any perturbed atomic or molecular system is

$$
H = H^0 + V, \tag{50}
$$

where H^0 is the Hamiltonian for the unperturbed system, and V is the term that describes the perturbation which is being applied to the system. If we assume that the Hamiltonian in Eq. (49) has the form of Eq. (50), then $H^A + H^B = H^0$ in Eq. (49) and we can solve Eq. (49) with perturbation theory. This specific partitioning of the Hamiltonian in Eq. (49) is known as the polarization approximation (PA).[69,76,70] In this formulation of Eq. (49), V is the potential of interaction between A and B. When A and B are infinitely far apart, $V = 0$ and $H = H^0$, since there is no interaction between A and B when they are isolated from one another. Let us consider only the ground-state Schrödinger equation for the interacting system. In this case, Eq. (49) becomes

$$\left(H^A + H^B + V\right)|\Psi_{0_{AB}}\rangle = E_{0_{AB}}|\Psi_{0_{AB}}\rangle. \tag{51}$$

Now, let us derive expressions for the exact ground-state wavefunction and energy of the interacting system. Let us introduce an ordering parameter λ into the expression for the Hamiltonian of the interacting system, so that H becomes

$$H = H^0 + \lambda V. \tag{52}$$

Then, let us expand both $\Psi_{0_{AB}}$ and $E_{0_{AB}}$ in a power series in λ . When we do this, $\Psi_{0_{AB}}$ becomes

$$\Psi_{0_{AB}} = \sum_{n=0}^{\infty} \lambda^n \Psi_{0_{AB}}^{(n)}, \tag{53}$$

where

$$\Psi_{0_{AB}}^{(n)} = \lim_{\lambda \to 0} \frac{1}{n!} \frac{\partial^n \Psi_{0_{AB}}}{\partial \lambda^n} \tag{54}$$

and, $E_{0_{AB}}$ becomes

$$E_{0_{AB}} = \sum_{n=0}^{\infty} \lambda^n E_{0_{AB}}^{(n)}. \tag{55}$$

In Eq. (53), $\Psi_{0_{AB}}^{(n)}$ is the n^{th}-order correction to the exact wavefunction for the interacting system, $\Psi_{0_{AB}}$. Similarly, in Eq. (55), $E_{0_{AB}}^{(n)}$ is the n^{th} -order correction to the exact energy for the interacting system, $E_{0_{AB}}$. Now, let us impose the intermediate normalization condition, so that

$$\langle \Psi_{0_{AB}}^{(0)} | \Psi_{0_{AB}} \rangle = 1. \tag{56}$$

Then, substituting Eq. (53) for $|\Psi_{0_{AB}}\rangle$ in Eq. (56), we obtain

$$\sum_{n=1}^{\infty} \lambda^n \langle \Psi_{0_{AB}}^{(0)} | \Psi_{0_{AB}}^{(n)} \rangle = 0. \tag{57}$$

Since $\lambda \neq 0$, Eq. (57) simplifies to

$$\sum_{n=1}^{\infty} \langle \Psi_{0_{AB}}^{(0)} | \Psi_{0_{AB}}^{(n)} \rangle = 0. \tag{58}$$

If we substitute Eqs. (53) and (55) into Eq. (51) and combine terms of the same order in λ , we obtain a system of equations of infinite order. The general form of an equation in this system for a given n is

$$\begin{aligned} \left(H^A + H^B\right) | \Psi_{0_{AB}}^{(n)} \rangle + V | \Psi_{0_{AB}}^{(n-1)} \rangle &= E_{0_{AB}}^{(0)} | \Psi_{0_{AB}}^{(n)} \rangle + E_{0_{AB}}^{(1)} | \Psi_{0_{AB}}^{(n-1)} \rangle + \ldots \\ &+ E_{0_{AB}}^{(n-1)} | \Psi_{0_{AB}}^{(1)} \rangle + E_{0_{AB}}^{(n)} | \Psi_{0_{AB}}^{(0)} \rangle, \end{aligned} \tag{59}$$

where $n = 1, 2, \ldots \infty$. If we multiply each term in Eq. (59) by $\langle \Psi_{0_{AB}}^{(0)} |$ and use Eq. (54), we obtain

$$E_{0_{AB}}^{(n)} = \langle \Psi_{0_{AB}}^{(0)} | V | \Psi_{0_{AB}}^{(n-1)} \rangle. \tag{60}$$

The n^{th} -order energy $E_{0_{AB}}^{(n)}$ is known as the n^{th} -order polarization energy. The ground state energy for the interacting system is the sum of the n^{th}-order polarization energies for all possible values of n , that is,

$$E_{0_{AB}} = \sum_{n=0}^{\infty} E_{0_{AB}}^{(n)}. \tag{61}$$

Also, the n^{th} -order polarization wavefunction $\Psi_{0_{AB}}^{(n)}$ is calculated recursively from

$$\Psi_{0_{AB}}^{(n)} = -GV\Psi_{0_{AB}}^{(n-1)} + \sum_{k=1}^{n-1} E_{0_{AB}}^{(k)} G \Psi_{0_{AB}}^{(n-k)}, \tag{62}$$

where G is the reduced resolvent given by Eq. (19) in Chap. 1. The 1^{st}, 2^{nd} and 3^{rd} -order polarization energies have been studied extensively, and their physical interpretations are well understood. In the next section of this chapter, we will present the equations for each of these energies and briefly discuss their physical interpretations.

2.3.2 The First-, Second-, and Third-Order Polarization Energies

The 1^{st}-order polarization energy is obtained by letting $n = 1$ in Eq. (60),

$$E^{(1)}_{0_{AB}} = \langle \Psi^{(0)}_{0_{AB}} | V | \Psi^{(0)}_{0_{AB}} \rangle. \tag{63}$$

We approximate $\Psi^{(0)}_{0_{AB}}$ by the product of the exact ground-state wavefunctions Ψ_{0_A} and Ψ_{0_B} of A and B, so that

$$\Psi^{(0)}_{0_{AB}} = \Psi_{0_A} \Psi_{0_B}. \tag{64}$$

Using Eq. (64) in Eq. (63), we obtain

$$E^{(1)}_{0_{AB}} = \langle \Psi_{0_A} \Psi_{0_B} | V | \Psi_{0_A} \Psi_{0_B} \rangle. \tag{65}$$

The energy given by Eq. (65) is called the *electrostatic* energy. Classically, $E^{(1)}_{0_{AB}}$ is interpreted as the Coulombic interaction energy between the charge distributions of A and B.[70,95] When the distance between A and B is large enough that the potential energy of interaction of A and B is asymptotically approaching zero, the electrostatic energy is the sum of the energies due to the interactions between the permanent multipole moments of A and B. When A and B are relatively close together, the electrostatic energy contains terms that can be attributed to the overlap of the charge distributions of A and B. These terms are largely responsible for stabilizing van der Waals complexes that consist of an atom and a diatomic molecule.[77–80] Also, the structures of dimers of polar molecules, especially of hydrogen-bonded dimers, are largely determined by the electrostatic energies of these complexes.[81–85,94,86–93]

We obtain the 2^{nd}-order polarization energy by letting $n = 2$ in Eq. (60),

$$E^{(2)}_{0_{AB}} = \langle \Psi^{(0)}_{0_{AB}} | V | \Psi^{(1)}_{0_{AB}} \rangle. \tag{66}$$

Using Eqs. (64) and (62) in Eq. (66), we obtain

$$E^{(2)}_{0_{AB}} = -\langle \Psi_{0_A} \Psi_{0_B} | VGV | \Psi_{0_A} \Psi_{0_B} \rangle. \tag{67}$$

If we allow excitations of A or B only in Eq. (67), we obtain the *induction* contribution to $E^{(2)}_{0_{AB}}$. The term that arises from excitations in A can be physically interpreted as the polarization of molecule A due to the static electric field produced by B. Similarly, the term that arises from excitations in B can be interpreted as the polarization of molecule B due to the static electric field produced by A. It is important to note that the induction energy does not account for intermonomer electron correlation, that is, the correlation of the motion of the electrons in A with the motion of the electrons in B. When the distance between A and B is such that interaction energy is asymptotically approaching zero, the induction energies of A and B can be calculated using the permanent multipole moments and static multipole polarizabilities of A and B. At shorter distances, where the charge distributions of A and B overlap, the polarization propagators[96,97] of A and B are also needed to calculate $E^{(2)}_{0_{AB}}$. Equations that express the second-order induction energy in terms of polarization propagators are given in references 95 and 187. Distributed multipole moments and polarizabilities are often used in calculations of induction energies generated by the interaction of two larger molecules.[98–100] However, because the polarizabilities used in these calculations are non-unique, these calculations are often inaccurate.[100] Ángyán *et. al.* have improved these types of calculations by defining distributed multipole polarizabilities so that they are basis set independent, and have also used these polarizabilities to calculate induction energies.[101]

We obtain the 3^{rd}-order polarization energy by letting $n = 3$ in Eq. (60),

$$E^{(3)}_{0_{AB}} = \langle \Psi^{(0)}_{0_{AB}} | V | \Psi^{(2)}_{0_{AB}} \rangle. \tag{68}$$

Using Eqs. (64) and (62) in Eq. (68), we obtain

$$E^{(3)}_{0_{AB}} = \langle \Psi_{0_A} \Psi_{0_B} | V G \overline{V} G V | \Psi_{0_A} \Psi_{0_B} \rangle, \tag{69}$$

where $\overline{V} = V - \langle \Psi_{0_A} \Psi_{0_B} | V | \Psi_{0_A} \Psi_{0_B} \rangle$. We obtain the 3^{rd}-order induction energy in the same way that we obtain the 2^{nd}-order induction energy. When we allow excitations in states of A or B in Eq. (69), we obtain the 3^{rd}-order induction energy as a sum of four terms. The first two terms represent the polarization of molecule B due to the static electric field produced by A and *vice versa.* The second two terms represent the mutual polarization of A and B by the fields of B and A, respectively. As was the case for the 2^{nd}-order induction energy, the 3^{rd}-order induction energy can also be calculated using the permanent multipole moments and static multipole polarizabilities at large intermonomer distances. At distances where the charge-densities of A and B overlap, the static polarization propagators of A and B are also needed to calculate the 3^{rd}-order induction energy. Moszynski *et. al.* has derived an expression for the 3^{rd}-order induction energy that expresses this energy in terms of the static polarization propagators of A and B,[187] including the quadratic polarization propagators[97,102–105] of A and B.

We have discussed the terms that arise in the expressions for $E^{(2)}_{0_{AB}}$ and $E^{(3)}_{0_{AB}}$ when we allow excitations in A or B only. If we allow simultaneous excitations of A and B in the expressions for $E^{(2)}_{0_{AB}}$ and $E^{(3)}_{0_{AB}}$, we obtain the *dispersion* contributions to these energies. The dispersion energy appearing in $E^{(2)}_{0_{AB}}$ can be physically interpreted as a consequence of the correlation of the motion of the electrons in A with the motion of the electrons in B. At large intermonomer distances, the 2^{nd}-order dispersion energy $E^{(2,disp)}_{0_{AB}}$ can be calculated from the dynamic multipole polarizabilities of A and B.[106] At distances where charge overlap is important, the polarization propagators of A and B are also needed to calculate $E^{(2,disp)}_{0_{AB}}$.[95,107–109] The 3^{rd} -order polarization energy contains terms corresponding to a combined induction-dispersion effect as well as terms corresponding to a pure dispersion effect. Moszynski *et. al.* have derived an equation which expresses the induction-dispersion energy $E^{(3,ind-disp)}_{0_{AB}}$ in terms of the electron densities and polarization propagators of A and B.[187] In this work, the dispersion energy $E^{(3,disp)}_{0_{AB}}$ is expressed in terms of frequency-dependent monomer susceptibilities for the first time. It should be noted, however, that our result is correct only for large distances between A and B, where exchange can be neglected. Previous attempts to express $E^{(3,disp)}_{0_{AB}}$ in terms of monomer properties were made by Chan *et. al.*[110]

2.3.3 The Convergence of the Polarization Expansion

The convergence of the polarization expansion has been thoroughly studied.[111–125] The polarization expansions for the interaction energies of H-H$^+$ and H-H systems converge. According to studies performed by Chalanski *et. al.*, Jeziorski *et. al.*, and others, the polarization expansion for the H-H$^+$ interaction energy slowly converges to the energy of the $1s\sigma_g$ ground state of the system at large H-H$^+$ distances. Additionally, at small intermonomer distances, calculations of the polarization expansion for the interaction energy of two ground-state He atoms carried to high order show that the series is convergent. However, in general, the polarization expansions for the interaction energy of other many-electron systems either converge to energies of unphysical states or diverge.

2.3.4 Summary

There are two major advantages to using the polarization approximation to study intermolecular interactions. The first advantage is that the polarization approximation is conceptually simple, relative to other perturbative methods for calculating intermolecular interactions.[280] The second advantage, which is more important than the first, is that the energetic expressions which result from these calculations have physically meaningful interpretations, as discussed earlier in this chapter.[280] However, there are also several drawbacks to using the polarization approximation to study intermolecular interactions. One major problem with the polarization approximation is that the unperturbed Hamiltonian H^0 has the wrong symmetry with respect to electron exchange. Although H^0 is symmetric with respect to the exchange of electrons within molecule A or B, H^0 is not symmetric with respect to electron exchange between A and B.[72] As a result, the polarization approximation does not account for exchange effects.[280] The inability of the polarization approximation to account for exchange effects inspired the development of symmetry-adapted perturbation theory, which will be discussed later in this chapter.

2.4 The Multipole Approximation

2.4.1 Introduction

Another common method for calculating intermolecular interaction energies is known as the multipole approximation. In the multipole approximation, we express both the intermolecular interaction operator and interaction energy as infinite series in inverse powers of R_{AB} , where R_{AB} is defined as the distance between the centers of mass of A and B. The multipole expansion for the intermolecular interaction operator V in an arbitrary space-fixed coordinate system is

$$V = \sum_{n=1}^{\infty} \frac{V_n}{(R_{AB})^n}, \tag{70}$$

where V_n is given by[280]

$$V_n = \sum_{l=0}^{n-1} V_{l,n-l-1}. \tag{71}$$

In turn, $V_{l,n-l-1}$ describes the interaction between the 2^l instantaneous moment on A with the 2^{n-l-1} instantaneous moment on B. When we express the intermolecular interaction operator V as a multipole expansion in powers of $\frac{1}{R_{AB}}$, we can write the interaction energy of A and B as[282,284,283]

$$E_{int}\left(R_{AB}, \zeta_A, \zeta_B, \hat{\mathbf{R}}\right) \sim \sum_{n=1}^{\infty} \frac{C_n\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)}{(R_{AB})^n}. \tag{72}$$

In Eq. (72), ζ_X ($X = A$ for monomer A and $X = B$ for monomer B) is the Euler angle that describes the rotation of a coordinate system fixed on X with respect to the spaced-fixed coordinate system in which V and $E_{int}\left(R_{AB}, \zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$ are defined. Also, $\hat{\mathbf{R}} = (\theta, \phi)$ are the polar angles that indicate the orientations of the molecular axes of A and B with respect to the space-fixed coordinate system. The functions $C_n\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$ appearing in Eq. (72) contains coefficients that are called van der Waals constants.

In the following sections, we will discuss various formulations of the intermolecular interaction operator, van der Waals constants, and intermolecular interaction energy in the multipole approximation. Finally, we will discuss the convergence properties of many of the expansions that we will discuss.

2.4.2 The Cartesian and Spherical Formulations of the Intermolecular Interaction Operator in the Multipole Approximation

We can write the multipole expansion of the intermolecular interaction operator as described by Eqs. (70) and (71) in terms of irreducible spherical[126–136] or Cartesian tensors[137–145] of the multipole moments on monomers A and B. First, we will write the multipole expansion of the intermolecular interaction operator in terms of the irreducible spherical tensors. Let us begin by noting that we will refer to the operator $V_{n,n-l-1}$ in the following presentations as a specific form of V_{l_A,l_B}, with $l_A = n$ and $l_B = n - l - 1$. The quantities l_A and l_B refer to multipole moments on monomers A and B, respectively. In the spherical tensor formalism, V_{l_A,l_B} is

$$\begin{aligned} V_{l_A,l_B} &= X_{l_A,l_B}(R_{AB})^{-l_A-l_B-1} \sum_{m=-l_A-l_B}^{l_A+l_B} (-1)^m C_{l_A+l_B}^{-m}\left(\hat{\mathbf{R}}\right) \\ &\times \left[\mathbf{M}_{l_A} \otimes \mathbf{M}_{l_B}\right]_{l_A+l_B}^{m}. \end{aligned} \tag{73}$$

where X_{l_A,l_B} is a constant, and the equation for this constant is

$$X_{l_A,l_B} = (-1)^{l_B} ||\mathbf{S}||^{\frac{1}{2}}, \tag{74}$$

where $\mathbf{S}$ is given by

$$\mathbf{S} = \begin{pmatrix} 2l_A + 2l_B \\ 2l_A \end{pmatrix} \tag{75}$$

In Eq. (73), we also have that $C_{l_A+l_B}^{-m}\left(\hat{\mathbf{R}}\right)$ are complex spherical harmonics which are often replaced by real tesseral harmonics.[144] We note that equations for the real tesseral harmonics are given in reference 145. The quantities $\mathbf{M}_{l_A} = \left\{M_{l_A}^{m_A}, m_A = -l_A, ..., +l_A\right\}$ and $\mathbf{M}_{l_B} = \left\{M_{l_B}^{m_B}, m_B = -l_B, ..., +l_B\right\}$ are multipole moment tensors on A and B, respectively. The $M_{l_A}^{m_A}$ and $M_{l_B}^{m_B}$ components of the multipole moment tensors $\mathbf{M}_{l_A}$ and $\mathbf{M}_{l_B}$ on A and B are given by

$$M_{l_X}^{m_X} = \sum_{p \in X} Z_p r_p^{l_X} C_{l_X}^{m_X}\left(\hat{\mathbf{r}}_p\right) \tag{76}$$

where $X = A$ for monomer A and $X = B$ for monomer B. In Eq. (76), p runs over all nuclei and electrons in monomer X, Z_p is the charge of the p^{th} particle in X , and $C_{l_X}^{m_X}(\hat{\mathbf{r}}_p)$ is a spherical harmonic. Finally, the tensor product $[\mathbf{M}_{l_A} \otimes \mathbf{M}_{l_B}]^m_{l_A+l_B}$ is

$$[\mathbf{M}_{l_A} \otimes \mathbf{M}_{l_B}]^m_l = \sum_{m_A=-l_A}^{l_A} \sum_{m_B=-l_B}^{l_B} M_{l_A}^{m_A} M_{l_B}^{m_B} \langle l_A, m_A; l_B, m_B | l, m\rangle, \quad (77)$$

where $\langle l_A, m_A; l_B, m_B | l, m\rangle$ is a Clebsch-Gordon coefficient, and where we have let $l_A + l_B = l$.[143]

Now, let us write the multipole expansion of the intermolecular interaction operator as given in Eqs. (70) and (71) in terms of Cartesian multipole moment tensors on A and B. In the Cartesian formalism, V_{l_A,l_B} is

$$V_{l_A,l_B} = \sum_{\{\alpha\}} \sum_{\{\beta\}} M_{l_A}^{\{\alpha\}} T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]} M_{l_B}^{\{\beta\}}. \quad (78)$$

Here, the $M_{l_A}^{\{\alpha\}}$ and $M_{l_B}^{\{\beta\}}$ components of the multipole moment tensors on A and B are

$$M_{l_X}^{\{\gamma\}} = \sum_{p \in X} Z_p r_{p,\gamma_1} r_{p,\gamma_2} ... r_{p,\gamma_{l_X}}, \quad (79)$$

where $X = A$ and $\gamma = \alpha$ for monomer A, and $X = B$ and $\gamma = \beta$ for monomer B. As in Eq. (76), p runs over all nuclei and electrons in monomer X, and Z_p is the charge on the p^{th} particle in X. Also, r_{p,γ_1}, $r_{p,\gamma_2} ... r_{p,\gamma_{l_X}}$ are the Cartesian coordinates of particle p. In Eq. (78), the tensor $T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]}$ is given by

$$\begin{aligned} T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]} &= (R_{AB})^{l_A+l_B+1} \frac{(-1)^{l_A}}{l_A! l_B!} \left(\nabla_{\alpha_1} \nabla_{\alpha_2} ... \nabla_{\alpha_{l_A}} \nabla_{\beta_1} \nabla_{\beta_2} ... \nabla_{\beta_{l_B}}\right) \\ &\times \left(\frac{1}{R_{AB}}\right). \end{aligned} \quad (80)$$

Mulder *et. al.* give general expressions for $T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]}$ for $l_A + l_B \leq 6$ in reference 142, and Isnard and co-workers give specific expressions for $T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]}$ for tetrahedral and linear molecules in reference 246. One can convert between the spherical and Cartesian formulas for V_{l_A,l_B} using equations derived by Coope *et. al.*[146–148] and Stone.[149,150]

2.4.3 The van der Waals Constants

In this section, we will discuss various methods for calculating the van der Waals functions $C_n\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$. We obtain the first expression for $C_n\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$ by solving the Schrödinger equation for the energy of interaction of A and B in Rayleigh-Schrödinger perturbation theory with the normalized Hamiltonian H^N, which is

$$H^N = H_0 + V^N. \tag{81}$$

In Eq. (81), V^N is a truncated form of the multipole expansion that is given by

$$V^N = \sum_{n=1}^{N} \frac{V_n}{\left(R_{AB}\right)^n}, \tag{82}$$

with $N = N_A + N_B$, where N_A and N_B are the total number of electrons in monomers A and B, respectively. The operator V_n appearing in Eq. (82) is defined in Eq. (71). When the Schrödinger equation containing H^N is solved, we obtain an asymptotic expansion for the energies of the AB dimer which is expressed in powers of $\frac{1}{R_{AB}}$ and contains the van der Waals functions $C_n\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$.[112] According to Ahlrichs,[160] one can calculate the van der Waals functions $C_n\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$ recursively. Jeziorski *et. al.* give the equations needed to perform these calculations in reference 280.

We obtain another expression for the van der Waals coefficients by asymptotically expanding the polarization energies $E_{0_{AB}}^{(n)}$ as

$$E_{0_{AB}}^{(n)}\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right) \sim \sum_{m=1}^{\infty} \frac{C_m^{(n)}\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)}{\left(R_{AB}\right)^m}. \tag{83}$$

Then, each van der Waals coefficient $C_m\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$ is obtained from

$$C_m\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right) = \sum_{n=1}^{M} C_m^{(n)}\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right), \tag{84}$$

where M is an integer whose value depends on whether the interacting molecules A and B are neutral or charged.[280]

We can also use the standard Rayleigh-Schrödinger perturbation equations of the polarization approximation to write expressions for the $C_m^{(n)}$ coefficients. One obtains these expressions by substituting Eq. (82) for the intermolecular interaction operator into the standard RSPT equations of the polarization approximation. In this approximation, $C_m^{(1)}\left(\zeta_A,\zeta_B,\hat{\mathbf{R}}\right)$ and $C_m^{(2)}\left(\zeta_A,\zeta_B,\hat{\mathbf{R}}\right)$ are

$$C_m^{(1)}\left(\zeta_A,\zeta_B,\hat{\mathbf{R}}\right) = \langle\Psi^{(0)}_{0_{AB}}|V_n|\Psi^{(0)}_{0_{AB}}\rangle, \tag{85}$$

and[280]

$$C_m^{(2)}\left(\zeta_A,\zeta_B,\hat{\mathbf{R}}\right) = \sum_{k=\kappa}^{n-\kappa}\langle\Psi^{(0)}_{0_{AB}}|V_k G_{AB} V_{n-k}|\Psi^{(0)}_{0_{AB}}\rangle. \tag{86}$$

where G_{AB} is the reduced resolvent for the AB complex. The expression for G_{AB} is given by Eq. (19) with index K replaced by k, Ψ_K replaced by $\Psi_{k_{AB}}$, E_K replaced by $E_{k_{AB}}$, and E_0 replaced by $E_{0_{AB}}$. Finally, if the interaction energy is known, then the van der Waals coefficients can be computed from

$$C_1\left(\zeta_A,\zeta_B,\hat{\mathbf{R}}\right) = \lim_{R_{AB}\to\infty} R_{AB}E_{int}\left(R_{AB},\zeta_A,\zeta_B,\hat{\mathbf{R}}\right) \tag{87}$$

and

$$\begin{aligned} C_n\left(\zeta_A,\zeta_B,\hat{\mathbf{R}}\right) &= \lim_{R_{AB}\to\infty}\left(R_{AB}\right)^n\left(E_{int}\left(R_{AB},\zeta_A,\zeta_B,\hat{\mathbf{R}}\right)\right. \\ &\quad \left. - \sum_{k=1}^{n-1}\frac{C_k\left(\zeta_A,\zeta_B,\hat{\mathbf{R}}\right)}{\left(R_{AB}\right)^k}\right). \end{aligned} \tag{88}$$

2.4.4 Removing the Angular Dependence from the Multipole Expansion for the Interaction Energy

The irreducible spherical and Cartesian expressions for the interaction energy presented in Sect. 2.4.2, as well as the equations for the van der Waals constants presented in Sect. 2.4.3, are very useful. However, since all of these expressions depend on the Euler and polar angles $\zeta_A,\zeta_B,\hat{\mathbf{R}}$, they need to be re-evaluated every time the geometry of the AB dimer is changed. Fortunately, we can also write an expression for the interaction energy in the multipole approximation which separates the dependence on $\zeta_A,\zeta_B,\hat{\mathbf{R}}$ from the rest of the expression for the interaction energy. In this equation, the non-angular part of the interaction energy (which contains the van der Waals constants) depends only on the distance R_{AB} between the centers of mass of A and B, so that this portion of the interaction energy only needs to be re-computed if the distance between monomers is changed. In the polarization approximation, the equation for the n^{th} -order correction to the energy of the interacting system which separates the angular and radial components of the intermolecular interaction energy is

$$E^{(n)}_{0_{AB}} = \sum_{\{\Lambda\}} {}^{\{\Lambda\}}\tilde{\varepsilon}^{(n)}_{0_{AB}} \left(R_{AB}\right) A_{\{\Lambda\}} \left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right). \tag{89}$$

In Eq. (89), ${}^{\{\Lambda\}}\tilde{\varepsilon}^{(n)}_{0_{AB}} \left(R_{AB}\right)$ is the radial expansion coefficient which depends on the intermonomer distance R_{AB} . Additionally, $A_{\{\Lambda\}} \left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$ is a function containing the angular dependence of $E^{(n)}_{0_{AB}}$. The equation for this function is

$$\begin{aligned} A_{\{\Lambda\}} \left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right) &= \sum_{M_A=-L_A}^{L_A} \sum_{M_B=-L_B}^{L_B} \sum_{M=-L}^{L} S_{ML} D^{L_A}_{M_A,K_A}(\zeta_A)^* \\ &\times D^{L_B}_{M_B,K_B}(\zeta_B)^* C^M_L \left(\hat{\mathbf{R}}\right), \end{aligned} \tag{90}$$

where

$$S_{ML} = \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} \tag{91}$$

is a $3j$ symbol,[143] $C^M_L \left(\hat{\mathbf{R}}\right)$ is a complex spherical harmonic, and $D^{L_A}_{M_A,K_A}(\zeta_A)^*$ and $D^{L_B}_{M_B,K_B}(\zeta_B)^*$ are elements of the Wigner rotation matrix as functions of the orientation angles of monomers A and B.[143] References 247, 248, 133–135 and 249 also contain derivations of equations (89) and (90). To obtain this energy in the multipole approximation, we replace the intermolecular interaction operator that appears in the equation for the radial expansion coefficients ${}^{\{\Lambda\}}\tilde{\varepsilon}^{(n)}_{0_{AB}} \left(R_{AB}\right)$ with the multipole expansion of the intermolecular operator, as given by Eqs. (70) and (71). When we do this, we can write approximations for the radial expansion coefficients ${}^{\{\Lambda\}}\tilde{\varepsilon}^{(n)}_{0_{AB}} \left(R_{AB}\right)$ that are determined by the irreducible spherical tensors of the polarizabilities and multipole moments of A and B.[130,132] Van der Avoird *et. al.* have reviewed these derivations in reference 75. We will present the equations for the electrostatic, second-order induction, and second-order dispersion radial expansion coefficients in the multipole approximation. Note that we will denote these approximations to the exact radial expansion coefficients ${}^{\{\Lambda\}}\tilde{\varepsilon}^{(n)}_{0_{AB}}\left(R_{AB}\right)$ by ${}^{\{\Lambda\}}\varepsilon^{(n)}_{0_{AB}}\left(R_{AB}\right)$.

The electrostatic radial expansion coefficient in the multipole approximation is

$$\begin{aligned} {}^{\{\Lambda\}}\varepsilon^{(1)}_{0_{AB}}\left(R_{AB}\right) &= (-1)^{L_A}\delta_{L_A+L_B,L}\left[\frac{(2L_A+2L_B+1)!}{(2L_A)!\,(2L_B)!}\right]^{\frac{1}{2}} \\ &\times \frac{Q^{K_A}_{L_A}Q^{K_B}_{L_B}}{\left(R_{AB}\right)^{L_A+L_B+1}}. \end{aligned} \tag{92}$$

In Eq. (92), $Q^{K_A}_{L_A}$ and $Q^{K_B}_{L_B}$ are the spherical portions of the 2^{L_A} and 2^{L_B} multipole moments on A and B. The equations for $Q^{K_A}_{L_A}$ and $Q^{K_B}_{L_B}$ are

$$Q^{K_A}_{L_A} \equiv \langle\Psi_{0_A}|\tilde{M}^{K_A}_{L_A}|\Psi_{0_A}\rangle \tag{93}$$

and

$$Q^{K_B}_{L_B} \equiv \langle\Psi_{0_B}|\tilde{M}^{K_B}_{L_B}|\Psi_{0_B}\rangle. \tag{94}$$

In Eqs. (93) and (94), $\tilde{M}^{K_A}_{L_A}$ and $\tilde{M}^{K_B}_{L_B}$ are multipole moment operators of A and B, as defined in their respective molecular coordinate systems.

The second-order induction radial expansion coefficient in the multipole approximation is[130,132–135]

$$\begin{aligned} {}^{\{\Lambda\}}\varepsilon^{(2,ind)}_{0_{AB}}\left(R_{AB}\right) = &- \frac{1}{2}\sum_{l_A=1}^{\infty}\sum_{l'_A=1}^{\infty}\sum_{l_B=0}^{\infty}\sum_{l'_B=0}^{\infty}\frac{C^{\{\Lambda\}}_{\{\lambda\},ind-A}}{\left(R_{AB}\right)^{n}} \\ &- \frac{1}{2}\sum_{l_A=0}^{\infty}\sum_{l'_A=0}^{\infty}\sum_{l_B=1}^{\infty}\sum_{l'_B=1}^{\infty}\frac{C^{\{\Lambda\}}_{\{\lambda\},ind-B}}{\left(R_{AB}\right)^{n}} \end{aligned} \tag{95}$$

where $\{\lambda\}$ is a set of indices given by $\{\lambda\}=\{l_A,l'_A,l_B,l'_B\}$, and

$$n = l_A + l'_A + l_B + l'_B + 2. \tag{96}$$

Also, $C^{\{\Lambda\}}_{\{\lambda\},ind-A}$ and $C^{\{\Lambda\}}_{\{\lambda\},ind-B}$ are long-range induction coefficients, where $C^{\{\Lambda\}}_{\{\lambda\},ind-A}$ is

$$C^{\{\Lambda\}}_{\{\lambda\},ind-A} = \xi^{L_A L_B L}_{l_A l'_A l_B l'_B}\,\alpha^{K_A}_{(l_A l'_A)L_A}(0)\left[\mathbf{Q}_{l_B}\otimes\mathbf{Q}_{l'_B}\right]^{K_B}_{L_B}. \tag{97}$$

The long-range induction coefficient for B is given by Eq. (97) with A and B interchanged. The irreducible product $\left[\mathbf{Q}_{l_B} \otimes \mathbf{Q}_{l'_B}\right]^{K_B}_{L_B}$ is given by Eq. (77) with $\mathbf{M}_{l_A} = \mathbf{Q}_{l_B}$, $\mathbf{M}_{l_B} = \mathbf{Q}_{l'_B}$, $m = K_B$, and $l = L_B$. The quantity $\xi^{L_A L_B L}_{l_A l'_A l_B l'_B}$ is a constant, given by

$$\begin{aligned}
\xi^{L_A L_B L}_{l_A l'_A l_B l'_B} &= (-1)^{l_A + l'_A} \left[\frac{(2l_A + 2l_B + 1)!\,(2l'_A + 2l'_B + 1)!}{(2l_A)!\,(2l_B)!\,(2l'_A)!\,(2l'_B)!} \right]^{\frac{1}{2}} l_{AB} \\
&\times \left[(2L_A + 1)\,(2L_B + 1)\,(2L + 1) \right]^{\frac{1}{2}} \\
&\times \langle l_A + l_B, 0; l'_A + l'_B, 0 | L, 0 \rangle. \qquad (98)
\end{aligned}$$

where

$$l_{AB} = \left\{ \begin{array}{ccc} l_A & l'_A & L_A \\ l_B & l'_B & L_B \\ l_A + l_B & l'_A + l'_B & L \end{array} \right\} \qquad (99)$$

is a 9j symbol,[143] and $\langle l_A + l_B, 0; l'_A + l'_B, 0 | L, 0 \rangle$ is a Clebsh-Gordan coefficient. Finally, $\alpha^{K_A}_{(l_A l'_A) L_A}(0)$ is the irreducible spherical tensor portion of the frequency-dependent polarizability on A,

$$\begin{aligned}
\alpha^{K_A}_{(l_A l'_A) L_A}(\omega) &= \sum_{n \neq 0} \frac{2\left(E_{n_A} - E_{0_A}\right)}{\left(E_{n_A} - E_{0_A}\right)^2 - \omega^2} \\
&\times \left[\langle \Psi_{0_A} | \tilde{\mathbf{M}}_{l_A} | \Psi_{n_A} \rangle \otimes \langle \Psi_{n_A} | \tilde{\mathbf{M}}_{l'_A} | \Psi_{0_A} \rangle \right]^{K_A}_{L_A} \qquad (100)
\end{aligned}$$

with the frequency $\omega = 0$. In this equation, Ψ_{n_A} and E_{n_A} are the n^{th} excited-state wavefunction and energy of A, respectively. The irreducible product $\left[\langle \Psi_{0_A} | \tilde{\mathbf{M}}_{l_A} | \Psi_{n_A} \rangle \otimes \langle \Psi_{n_A} | \tilde{\mathbf{M}}_{l'_A} | \Psi_{0_A} \rangle \right]^{K_A}_{L_A}$ is given by Eq. (77) with $\mathbf{M}_{l_A} = \langle \Psi_{0_A} | \tilde{\mathbf{M}}_{l_A} | \Psi_{n_A} \rangle$, $\mathbf{M}_{l_B} = \langle \Psi_{n_A} | \tilde{\mathbf{M}}_{l'_A} | \Psi_{0_A} \rangle$, $m = K_A$, $l = L_A$. We obtain the equation for the irreducible spherical component of the frequency-dependent polarizability on B by replacing A with B in Eq. (100).

The second-order dispersion radial expansion coefficient in the multipole approximation is[130,132–135]

$${}^{\{\Lambda\}}\varepsilon^{(2,disp)}_{0_{AB}}\left(\mathbf{R_{AB}}\right) = -\sum_{l_A=1}^{\infty} \sum_{l'_A=1}^{\infty} \sum_{l_B=1}^{\infty} \sum_{l'_B=1}^{\infty} \frac{C^{\{\Lambda\}}_{\{\lambda\},disp}}{\left(R_{AB}\right)^n} \qquad (101)$$

with

$$C^{\{\Lambda\}}_{\{\lambda\},disp} = \frac{1}{2\pi}\xi^{L_A L_B L}_{l_A l'_A l_B l'_B} \int_0^\infty \alpha^{K_A}_{(l_A l'_A)L_A}(\imath\omega)\, \alpha^{K_B}_{(l_B l'_B)L_B}(\imath\omega)\, d\omega. \tag{102}$$

Van der Avoird and co-workers[281] have reviewed the calculations of the electrostatic, second-order induction, and second-order dispersion radial expansion coefficients. Since the electrostatic and induction coefficients are determined only by the multipole moments and static polarizabilities of the monomers, it is relatively straightforward to calculate these coefficients.[280] However, because the second-order radial dispersion coefficients are determined by the polarizabilities of the monomers at imaginary frequency, calculating these coefficients is relatively difficult. To date, these coefficients have been calculated with several different methods, including many-body perturbation theory,[236,251,237,238,240,239] the second-order polarization propagator approach (SOPPA),[250] and the multiconfigurational time-dependent Hartree-Fock (MCTDHF) technique.[259–261] Other methods that have been used to calculate these coefficients are the limited CI technique,[244,252] the random-phase approximation (RPA), or the time-dependent coupled Hartee-Fock (TDCHF) approach.[241,243,253,254,242]

2.4.5 The Convergence of the Multipole Expansions of the Intermolecular Interaction Operator and Interaction Energy

In general, the multipole expansion of the intermolecular interaction operator as defined by Eqs. (70) and (71) is divergent. However, there is a small region of configuration space where the multipole expansion of V is convergent. The exact specifications of this region are given in reference 151.[280]

Like the multipole expansion of the intermolecular interaction operator V, the multipole expansion of the interaction energy is also divergent. Although the divergence of this expansion has only been proven for the H_2^+ system,[154–156] it is expected that the expansion will also diverge for multi-electron systems. Additionally, Damburg *et. al.*[158] and Cizek and co-workers[159] have shown that Eq. (72) is not summable for H_2^+ using conventional summation techniques,[157] so it is also expected that the expansion will not be summable for any multi-electron complexes.

Some of the methods used to define and calculate the van der Waals constants also have divergent expansions of the intermolecular interaction energy.[280] For example, the multipole expansion of the intermolecular interaction energy that is produced when the Schrödinger equation is solved using RSPT with H^N and V^N (as defined in Eqs. (81) and (82)) is divergent.[280] This divergence results from the fact that V^N cannot be treated as a small perturbation, which is a direct consequence of the fact that the spectrum of H^N is continuous.

The convergence properties of the asymptotic expansion given by Eq. (72) are not well understood. Although researchers have studied the convergence properties of the expansions for the first- and second-order polarization energies, no one has investigated the convergence properties of the expansions for higher-order polarization energies. Jeziorski *et. al.* have studied the convergence properties of the asymptotic expansion for the electrostatic energy $E_{0_{AB}}^{(1)}$ for the water dimer,[209] and Berns and co-workers have studied the convergence properties of the same expansion for the N_2 dimer.[262] The expansions of $E_{0_{AB}}^{(1)}$ for both the water dimer and the N_2 dimer converge. However, neither expansion converges to the correct physical value of the electrostatic energy for the appropriate system. Vigné-Maeder *et. al* have shown that in general, the asymptotic expansion of the electrostatic energy is convergent for any system when Gaussian functions are used to approximate the unperturbed charge distributions of the monomers.[263] Again, however, the expansion does not converge to the physical ground-state electrostatic energy of the system of interest. Several researchers[264–267] have studied the convergence properties of the asymptotic expansion for the electrostatic energy for each of various large molecules using the distributed multipole analysis. Stone has reviewed this method in reference 98. Dalgarno *et. al.*[268] have studied the convergence properties of the asymptotic expansion for the 2^{nd}-order polarization energy of H_2^+. Specifically, they showed that the asymptotic expansion for the 2^{nd}-order induction energy of H_2^+ is divergent. Young[269] studied the convergence properties of the asymptotic expansion for the 2^{nd}-order polarization energy of the H_2 molecule. The author showed that the asymptotic expansion for the 2^{nd}-order dispersion energy of H_2 is divergent. We should also mention that neither Dalgarno's final expression for the 2^{nd}-order induction energy of H_2^+ nor Young's final expression for the 2^{nd}-order dispersion energy of H_2 are Borel or Páde summable.[157] One might be able to use distributed polarizabilities[99,270–272] to make these series convergent. To date, however, no one has done these studies.

2.4.6 The Multipole Approximation and Nonadditive Interactions

Stogryn[273,274] was the first to use the multipole approximation in the study of nonadditive intermolecular interactions. Piecuch[275] has derived equations in the spherical tensor formalism for the interaction energy of M molecules to any order of pertubation theory. These equations are based on Wormer's perturbation equations in the spherical tensor formalism for the energy of interaction of two molecules.[130,132] Piecuch has also derived an expression for the anisotropic induction energy of M molecules through third-order in perturbation theory.[63] The author has also used his equations to derive expressions for the isotropic interaction energy[65] and anisotropic dispersion energy[64] of M molecules through third-order in perturbation theory. Following this work, the author derived expressions for the induction energies of M molecules through fourth-order in pertubation theory.[276,277] Finally, Piecuch used the equations presented in reference 275 to calculate the nonadditive induction energies of the Ar_2-HF and Ar_2-HCl systems. We refer the reader to reference 278 for a review of these derivations and calculations.

2.4.7 Summary

There are significant advantages and disadvantages of using the multipole approximation to calculate intermolecular interaction energies. Probably the most significant advantage of using the multipole approximation to calculate intermolecular interaction energies is that it is easier to evaluate multipole interaction energies than it is to evaluate the corresponding polarization energies. This is because the expression for any particular polarization correction must be completely re-evaluated any time the Euler or polar angles between monomers are changed, while only part of the corresponding expression in the multipole approximation needs to be re-evaluated when these angles are changed. As discussed in Sect. 2.4.4, we can write the multipole expansion of the intermolecular interaction energy as a product of radial expansion coefficients and angular functions. When one changes the Euler or polar angles between monomers, only the angular functions need to be re-evaluated.

Although the multipole expansion of the interaction energy is easier to evaluate than the corresponding energy in the polarization approximation, there are also significant disadvantages of using the multipole approximation to calculate intermolecular interaction energies. The most significant disadvantage of using the multipole approximation to calculate intermolecular interaction energies is that by definition, the multipole expansion does not account for charge-overlap effects. Charge-overlap effects are contributions to the intermolecular interaction energy that are caused by the overlap of the electron density on A with the electron density on B, and these effects are largest when the intermonomer distance is near or below the van der Waals minimum for the dimer. There is another method for calculating intermolecular interaction energies that has the many of the same advantages as the multipole approximation, and also accounts for charge-overlap effects. This method is known as the bipolar expansion, and this method is the subject of the next section.

2.5 The Bipolar Expansion

2.5.1 Introduction

Another method for calculating intermolecular interaction energies involves using the bipolar expansion for the intermolecular interaction operator. There are several advantages to using this method to calculate intermolecular interaction energies. Like the multipole expansion, the bipolar expansion of the intermolecular interaction energy can be separated into a radial component and an angular component. Also, intermolecular interaction energies computed using the bipolar expansion of the intermolecular interaction operator include contributions from charge-overlap effects.

2.5.2 The Bipolar Expansion of Buehler and Hirschfelder

The exact bipolar expansion of the intermolecular interaction operator proposed by Buehler and Hirschfelder is[255,256]

$$\frac{1}{r_{12}} = \sum_{l_A, l_B = 0}^{\infty} \sum_{m=-l_<}^{l_<} J_{l_A l_B}^{|m|}\left(r_1, r_2, R_{AB}\right) Y_{l_A}^{m}\left(\tilde{\theta}_1, \tilde{\phi}_1\right) Y_{l_B}^{-m}\left(\tilde{\theta}_2, \tilde{\phi}_2\right). \quad (103)$$

In Eq. (103), r_{12} is the distance between particles 1 and 2, where particle 1 belongs to monomer A, and particle 2 belongs to monomer B. Also, $l_< = l_A$ if $l_A < l_B$, and $l_< = l_B$ if $l_B < l_A$. The quantities r_1, $\tilde{\theta}_1$, $\tilde{\phi}_1$ and r_2, $\tilde{\theta}_2$, $\tilde{\phi}_2$ are polar coordinates of particles 1 and 2, respectively. Finally $Y_{l_A}^{m}\left(\tilde{\theta}_1, \tilde{\phi}_1\right)$ and $Y_{l_B}^{-m}\left(\tilde{\theta}_2, \tilde{\phi}_2\right)$ are spherical harmonics defined with respect to particles 1 and 2, respectively.

Buehler and Hirschfelder[255,256] derived Eq. (103) after assigning coordinate systems to monomers A and B. The coordinate systems that they assigned to A and B have their origins at the centers of mass of A and B, and their z axes are co-aligned. Also, the x and y axes of the system on A are parallel to the x and y axes of the system on B. The x, y , and z axes in both of these coordinate systems are parallel to the corresponding axes of an arbitrarily selected spaced-fixed coordinate system. Note that we have written Eq. (103) with the notation used by Meath and co-workers in reference 257. Note also that although Ng *et. al.*[257] use $J_{l_A l_B}^{|m|}\left(r_1, r_2, R_{AB}\right)$ in place of the $B_{l_A l_B}^{|m|}\left(r_1, r_2, R_{AB}\right)$ quantities used by Buehler and Hirschfelder, these functions are proportional to each other.

There are four different expressions for $J_{l_A l_B}^{|m|}\left(r_1, r_2, R_{AB}\right)$, and the form of this function that we use in Eq. (103) depends on the intermonomer distances of interest. Specifically, the form of $J_{l_A l_B}^{|m|}(r_1, r_2, R_{AB})$ depends on whether we are interested in calculating intermolecular interaction energies for $R_{AB} > r_1 + r_2$, $r_1 > R_{AB} + r_2$, $r_2 > R_{AB} + r_1$, or $|r_1 - r_2| \leq R_{AB} \leq |r_1 + r_2|$. For $R_{AB} > r_1 + r_2$, $r_1 > R_{AB} + r_2$, and $r_2 > R_{AB} + r_1$, the equations for $J_{l_A l_B}^{|m|}(r_1, r_2, R_{AB})$ are combinatorial expressions containing l_A and l_B. Each of these combinatorial expressions also consists of a product of powers of R_{AB}, r_1, and r_2, and this product is also multiplied by m. For $|r_1 - r_2| \leq R_{AB} \leq |r_1 + r_2|$, the equation for $J_{l_A l_B}^{|m|}(r_1, r_2, R_{AB})$ is a finite sum of different powers of R_{AB}, r_1, and r_2. The exact expressions for $J_{l_A l_B}^{|m|}(r_1, r_2, R_{AB})$ are given in reference 257. If we neglect the contribution of the $J_{l_A l_B}^{|m|}(r_1, r_2, R_{AB})$ functions to $\frac{1}{r_{12}}$ when $r_1 > R_{AB} + r_2$, $r_2 > R_{AB} + r_1$, $|r_1 - r_2| \leq R_{AB} \leq |r_1 + r_2|$, then $\frac{1}{r_{12}}$ reduces to the multipole expansion.

2.5.3 The Fourier Integral Formulation of the Bipolar Expansion

We can also express the bipolar expansion of the intermolecular interaction operator in terms of a Fourier transform. In this formulation of the bipolar expansion, $1/r_{12}$ is[258]

$$\frac{1}{r_{12}} = \frac{1}{2\pi^2} \int \frac{d^3\mathbf{k}}{k^2} e^{i\mathbf{k}\cdot\mathbf{R}} e^{-i\mathbf{k}\cdot\tilde{\mathbf{r}}_1} e^{i\mathbf{k}\cdot\tilde{\mathbf{r}}_2}. \tag{104}$$

Kay and co-workers[258] assigned the same coordinate systems to monomers A and B as Buehler and Hirschfelder assigned to A and B. Kay *et. al.*[258] also chose the same laboratory frame as chosen by Buehler and Hirschfelder. In Eq. (104), $e^{i\mathbf{k}\cdot\mathbf{R}}$, $e^{i\mathbf{k}\cdot\tilde{\mathbf{r}}_1}$, and $e^{i\mathbf{k}\cdot\tilde{\mathbf{r}}_2}$, are given by

$$e^{i\mathbf{k}\cdot\tilde{\mathbf{r}}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l \frac{2^l l!}{(2l)!} C_l^{-m}\left(\hat{\mathbf{k}}\right) q_l^m\left(k, \tilde{\mathbf{r}}\right), \tag{105}$$

with $\tilde{\mathbf{r}} = \mathbf{R}$ for $e^{i\mathbf{k}\cdot\mathbf{R}}$, $\tilde{\mathbf{r}} = \tilde{\mathbf{r}}_1$ for $e^{i\mathbf{k}\cdot\tilde{\mathbf{r}}_1}$, and $\tilde{\mathbf{r}} = \tilde{\mathbf{r}}_2$ for $e^{i\mathbf{k}\cdot\tilde{\mathbf{r}}_2}$. Note that the equation for $e^{i\mathbf{k}\cdot\tilde{\mathbf{r}}}$ is expressed in terms of the arbitrarily selected spaced-fixed coordinate system. In Eq. (105), the unit vector $\hat{\mathbf{k}} = \frac{\mathbf{k}}{k}$, and its orientation angles are θ_k and ϕ_k . Also, $C_l^{-m}\left(\hat{\mathbf{k}}\right)$ is a Racah spherical harmonic, and it is given by[143]

$$C_l^m\left(\hat{\mathbf{k}}\right) = \left(\frac{4\pi}{2l+1}\right)^{\frac{1}{2}} Y_l^m\left(\theta_k, \phi_k\right). \tag{106}$$

Finally, the k-dependent multipole operator $q_l^m\left(k, \hat{\mathbf{r}}\right)$ is

$$q_l^m\left(k, \hat{\mathbf{r}}\right) = \frac{(2l+1)!}{2^l l!} C_l^m\left(\hat{\mathbf{r}}\right) j_l\left(kr\right). \tag{107}$$

The $j_l\left(kr\right)$ quantity contained in Eq. (107) is a spherical Bessel function. If we substitute Eq. (105) into the Fourier integral given by Eq. (104) and integrate over θ_k and ϕ_k , we obtain

$$\begin{aligned} \frac{1}{r_{12}} &= \sum_{l_A l_B\, j\, k_A k_B} i^{l_A - l_B - j}\left(2j+1\right) 2^{l_A + l_B + 1} \\ &\times \frac{l_A! l_B!}{\pi (2l_A)!(2l_B)!} J_{AB} A_{l_A l_B j}^{k_A k_B}\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right) \\ &\times \int_0^\infty dk\, j_l\left(kR_{AB}\right) q_{l_A}^{m_A}\left(k, \tilde{\mathbf{r}}_1\right) q_{l_B}^{m_B}\left(k, \tilde{\mathbf{r}}_2\right), \end{aligned} \tag{108}$$

where we have expressed $\frac{1}{r_{12}}$ in terms of the coordinate systems centered on A and B. Also

$$J_{AB} = \begin{pmatrix} l_A & l_B & j \\ 0 & 0 & 0 \end{pmatrix} \tag{109}$$

The quantity $A_{l_A l_B j}^{k_A k_B}\left(\zeta_A, \zeta_B, \hat{\mathbf{R}}\right)$ is given by Eq. (90) with $\{\Lambda\} = \{l_A, k_A, l_B, k_B, j\}$. If we select a space-fixed coordinate system that has $\mathbf{R}$ along z and replace V in Eq. (60) with Eq. (108), we obtain an expression for the n^{th}-order correction to the energy of interaction of A and B where the angular and radial components are completely separate from each other.

2.6 Symmetry-Adapted Perturbation Theory

2.6.1 Introduction

Although polarization theory lends itself to physically meaningful interpretations of each term in the interaction energy of A and B, it cannot be used to obtain quantitatively correct interaction energies. This is because polarization theory does not account for the exchange of electrons between monomers. This, in turn, is because the zeroth-order approximation to the exact ground-state wavefunction $\Psi_{0_{AB}}^{(0)}$ violates the Pauli-exclusion principle. This problem can be overcome by using $\mathcal{A}\Psi_{0_{AB}}^{(0)}$ rather than $\Psi_{0_{AB}}^{(0)}$ as the zeroth-order approximation to the exact ground-state wavefunction of the AB complex, where $\mathcal{A}$ is the antisymmetrizing operator for the system, defined as

$$\mathcal{A} = \frac{N_A!N_B!}{(N_A + N_B)!}\mathcal{A}_A\mathcal{A}_B\left(1 + \mathcal{P}\right). \tag{110}$$

In Eq. (110), $\mathcal{A}_A$ and $\mathcal{A}_B$ are the antisymmetrizing operators for monomers A and B. Also, $\mathcal{P}$ represents the sum of all possible permutations which exchange an electron between A and B, where the appropriate sign factors have been assigned to all permutations. However, since $\mathcal{A}\Psi_{0_{AB}}^{(0)}$. is not an eigenfunction of $H^0 = H^A + H^B$, this wavefunction cannot be used as the zeroth-order approximation to the exact ground-state wavefunction in conventional Rayleigh-Schrödinger Perturbation Theory. This problem has lead to the development of several new symmetry-adapted perturbation theories which maintain the definition of H^0 used in polarization theory and use $\mathcal{A}\Psi_{0_{AB}}^{(0)}$ as the zeroth-order approximation to the exact ground-state wavefunction of the system.

The first formulation of symmetry-adapted perturbation theory (SAPT) was published in 1930 by Eisenschitz and London.[161] Other foundational works in this field include those of Murrell, Randic, and Williams;[162] Hirschfelder and Sibley;[163] Hirschfelder;[76,164] van der Avoird;[165–168] Murrell and Shaw;[169] Musher and Amos;[170] Kirtman;[172] and Carr.[171] We will summarize the most important features of these works here. We refer the reader to several reviews for thorough discussions of these works.[72,73,120,173,174]

In general, there are two classes of symmetry-adapted perturbation theories. The first class of symmetry-adapted perturbation theories include those theories which were developed using weak symmetry forcing.[175,173] The energy expressions resulting from the development of these theories contain the antisymmetrizing operator $\mathcal{A}$

. However, the equations used to derive these energy expressions do not contain the antisymmetrizing operator. These theories have been used to calculate interaction energies between one-electron as well as many-electron monomers.[280] The second class of symmetry-adapted perturbation theories contains those theories which were developed using strong symmetry forcing.[175,173] In these theories, the equations used to derive the energy of the system contain the antisymmetrizing operator $\mathcal{A}$. These theories have only been used to calculate interaction energies between one- or two-electron monomers.[280]

2.6.2 Weak Symmetry Forcing: Symmetrized Perturbation Theories

The first kind of SAPT that employs weak symmetry forcing which we will discuss is called symmetrized Rayleigh-Schrödinger (SRS) perturbation theory.[175] In SRS theory, the exact ground-state energy of the interacting system $E_{0_{AB}}^{SRS}$ is the sum of all n^{th}-order SRS energies $E_{0_{AB}}^{(n,SRS)}$,

$$E_{0_{AB}}^{SRS} = \sum_{n=0}^{\infty} E_{0_{AB}}^{(n,SRS)}, \tag{111}$$

where $E_{0_{AB}}^{(n,SRS)}$ is given by[175,176]

$$E_{0_{AB}}^{(n,SRS)} = \frac{\langle \Psi_{0_{AB}}^{(0)} | V\mathcal{A} | \Psi_{0_{AB}}^{(n-1)} \rangle}{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(0)} \rangle} - \sum_{k=1}^{n-1} E_{0_{AB}}^{(k,SRS)} \frac{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(n-k)} \rangle}{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(0)} \rangle}. \tag{112}$$

It can also be shown that the n^{th} -order SRS energy is the sum of the corresponding n^{th}-order polarization energy $E_{0_{AB}}^{(n)}$ and an exchange term $E_{0_{AB}}^{(n,SRS-exch)}$, that is,

$$E_{0_{AB}}^{(n,SRS)} = E_{0_{AB}}^{(n)} + E_{0_{AB}}^{(n,SRS-exch)}. \tag{113}$$

The exchange term $E_{0_{AB}}^{(n,SRS-exch)}$ included in Eq. (113) represents the energy resulting from intermonomer electron exchange. The energy resulting from intramonomer electron exchange is included in $E_{0_{AB}}^{(n)}$.

The generalized Heitler-London method is another weak symmetry forcing method which expresses the n^{th}-order perturbation exchange energy in terms of the wavefunctions of polarization theory.[193] Cwiok and co-workers[176] have shown that the generalized Heitler-London energies are equivalent to the SRS energies.

The next weak symmetry forcing symmetry-adapted method that we will discuss is called Murrell-Shaw, Musher-Amos (MSMA).[169,170,164] Jeziorski and co-workers[173] have shown that the n^{th}-order correction to the exact ground-state energy $E_{0_{AB}}^{(n,MSMA)}$ of the interacting system in MSMA theory can be written as

$$\begin{aligned} E_{0_{AB}}^{(n,MSMA)} &= \frac{\langle \Psi_{0_{AB}}^{(0)} | V\mathcal{A} | \Psi_{0_{AB}}^{(n-1,MSMA)} \rangle}{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(0)} \rangle} \\ &- \sum_{k=1}^{n-1} E_{0_{AB}}^{(k,MSMA)} \frac{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(n-k,MSMA)} \rangle}{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(0)} \rangle}. \end{aligned} \tag{114}$$

The first- and second-order corrections to the exact ground-state energy of the interacting system in MSMA theory are equivalent to the corresponding corrections in SRS theory.[280] Higher-order MSMA corrections are not equivalent to the corresponding corrections in SRS theory because the MSMA energies $E_{0_{AB}}^{(n,MSMA)}$ rather than the polarization energies $E_{0_{AB}}^{(n)}$ are used in calculating $\Psi_{0_{AB}}^{(n,MSMA)}$.[280]

2.6.3 Strong Symmetry Forcing: Hirschfelder-Silbey Perturbation Theory

There are two categories of theories that employ strong symmetry forcing. The first category contains what are known as one-state theories,[161,164–168,181,194–198] and the second category contains what are known as multi-state theories.[163,180,174,172,199–204] In one-state theories, only one state is included in the perturbation equations in order to account for intermonomer electron exchange and that state is included via the antisymmetrizing operator $\mathcal{A}$.[280] In multi-state theories, such as Hirschfelder-Silbey (HS) theory,[163] all possible states that can be produced by intermonomer electron exchange are included in the perturbation equations.[280] Each state is accounted for by the inclusion of the specific permutation operator that generates the state.[280] Although one-state theories are significantly less complicated than multi-state theories, one-state theories do not have the correct asymptotic behavior in the intermonomer distance R_{AB}. Speficially, several calculations carried out on H_2^+ have shown that energies resulting from one-state calculations do not reduce to the appropriate polarization energies at large R_{AB}.[181,173,202,205–207]

2.6.4 The First and Second-Order Energies in Symmetrized Rayleigh-Schrödinger Perturbation Theory

In this section, we will write the specific expressions for the first- and second-order corrections to the exact ground-state energy of the interacting system in SRS perturbation theory. Then, we will discuss the physical origin of each term in these expressions. If we let $n = 1$ in Eq. (112), we obtain

$$E_{0_{AB}}^{(1,SRS)} = \frac{\langle \Psi_{0_{AB}}^{(0)} | V \mathcal{A} | \Psi_{0_{AB}}^{(0)} \rangle}{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(0)} \rangle}. \tag{115}$$

Then, using Eq. (110) in Eq. (115), we can show that

$$E_{0_{AB}}^{(1,SRS)} = E_{0_{AB}}^{(1)} + E_{0_{AB}}^{(1,SRS-exch)}. \tag{116}$$

In Eq. (116), the exchange term $E_{0_{AB}}^{(1,SRS-exch)}$ is given by

$$E_{0_{AB}}^{(1,SRS-exch)} = \frac{\langle \Psi_{0_{AB}}^{(0)} | \left(V - \bar{V} \right) \mathcal{P} | \Psi_{0_{AB}}^{(0)} \rangle}{1 + \langle \Psi_{0_{AB}}^{(0)} | \mathcal{P} | \Psi_{0_{AB}}^{(0)} \rangle}, \tag{117}$$

Eq. (117) represents the largest component of the total exchange energy in SRS theory. Specifically, at the van der Waals minimum, $E_{0_{AB}}^{(1,SRS-exch)}$ comprises at least 90 percent of the total exchange energy for many molecules.[280] Eq. (117) corresponds to the expectation value of the Hamiltonian for the interacting system over the wavefunction $\mathcal{A}\Psi_{0_{AB}}^{(0)}$, where $\mathcal{A}\Psi_{0_{AB}}^{(0)}$ is the wavefunction which accounts for electron exchange between A and B.

Jeziorski and co-workers have developed a method for calculating exact values of $E_{0_{AB}}^{(1,SRS-exch)}$.[211] Additionally, by restricting the types of electron exchanges to include single exchanges only, Jeziorski *et.al.* and Williams and co-workers have written an equation which approximates $E_{0_{AB}}^{(1,SRS-exch)}$.[211,212] Moszynski *et. al.* have rewritten the approximation to $E_{0_{AB}}^{(1,SRS-exch)}$ in terms of the properties of monomers A and B.[186] Specifically, they have rewritten the approximation to $E_{0_{AB}}^{(1,SRS-exch)}$ in terms of the one- and two-particle density matrices of A and B. The resulting equations have been used to calculate $E_{0_{AB}}^{(1,SRS-exch)}$ for various systems.[186,78,80]

If we let $n = 2$ in Eq. (112), we obtain the second-order correction to the exact ground-state energy of the interacting system in SRS theory. The expression for this energy is

$$E_{0_{AB}}^{(2,SRS)} = \frac{\langle \Psi_{0_{AB}}^{(0)} | V \mathcal{A} | \Psi_{0_{AB}}^{(1)} \rangle}{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(0)} \rangle} - E_{0_{AB}}^{(1,SRS)} \frac{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(1)} \rangle}{\langle \Psi_{0_{AB}}^{(0)} | \mathcal{A} | \Psi_{0_{AB}}^{(0)} \rangle}. \tag{118}$$

We can separate $E_{0_{AB}}^{(2,SRS)}$ into the second-order polarization energy $E_{0_{AB}}^{(2)}$ and an exchange component $E_{0_{AB}}^{(2,SRS-exch)}$[280]

$$E_{0_{AB}}^{(2,SRS)} = E_{0_{AB}}^{(2)} + E_{0_{AB}}^{(2,SRS-exch)}. \tag{119}$$

Also, the second-order exchange energy $E_{0_{AB}}^{(2,SRS)}$ in SRS theory is given by[280]

$$E_{0_{AB}}^{(2,SRS-exch)} = E_{0_{AB}}^{(2,SRS-exch-ind)} + E_{0_{AB}}^{(2,SRS-exch-disp)}, \tag{120}$$

where $E_{0_{AB}}^{(2,SRS-exch-ind)}$ is the induction contribution to the second-order exchange energy, and $E_{0_{AB}}^{(2,SRS-exch-disp)}$ is the dispersion contribution to the second-order exchange energy.[280] The exchange-induction contribution $E_{0_{AB}}^{(2,SRS-exch-ind)}$ to the second-order exchange energy in SRS theory corresponds to the induction energy that arises when electrons are exchanged between monomers A and B.[280] Williams and co-workers have shown that the second-order induction-exchange energy in SRS theory is a significant portion of the overall induction energy, especially at intermonomer distances R_{AB} which are smaller than the van der Waals minimum.[78]

Due to the complexity of the expression for $E_{0_{AB}}^{(2,SRS-exch-ind)}$, the second-order exchange-induction energy in SRS theory is also difficult to evaluate. However, Chalasinski *et. al.* have derived an equation which is an approximation to the second-order exchange-induction energy $E_{0_{AB}}^{(2,SRS-exch-ind)}$.[214] They obtained this approximation by ignoring the energetic contributions of higher than single-electron exchanges to the second-order induction-exchange energy $E_{0_{AB}}^{(2,SRS-exch-ind)}$. Chalasinski and co-workers have shown that this approximation is valid at and around the van der Waals minimum for the helium dimer.[213] Similar calculations need to be performed on larger systems in order to determine whether this approximation is valid in a general sense.

The exchange-dispersion contribution $E_{0_{AB}}^{(2,SRS-exch-disp)}$ to the second-order exchange energy in SRS theory corresponds to the dispersion energy that arises when electrons are exchanged between monomers A and B.[280] This energy, however, is not a significant portion of the overall dispersion energy. Specifically, the magnitude of $E_{0_{AB}}^{(2,SRS-exch-disp)}$ comprises only about a few percent of the overall dispersion energy.[280] Like the exact expression for $E_{0_{AB}}^{(2,SRS-exch-ind)}$, the exact expression for $E_{0_{AB}}^{(2,SRS-exch-disp)}$ is also very complicated and difficult to evaluate. Chalasinski and Jeziorski have also derived an approximation to $E_{0_{AB}}^{(2,SRS-exch-disp)}$.[214] They obtained this expression by making the same assumption that they made when deriving the approximation to $E_{0_{AB}}^{(2,SRS-exch-ind)}$. In other words, they ignored the energetic contribution of greater than single-electron exchanges to $E_{0_{AB}}^{(2,SRS-exch-disp)}$. Unfortunately, however, even the evaluation of the approximation to $E_{0_{AB}}^{(2,SRS-exch-disp)}$ is difficult. This is because the wavefunction used in calculating the approximation to $E_{0_{AB}}^{(2,SRS-exch-disp)}$ must contain charge-transfer terms,[215] and it is also because the approximation cannot be simplified so that it depends only on the properties of A and B.[280]

2.6.5 The Convergence of the Symmetrized Rayleigh-Schrödinger and Hirschfelder-Silbey Perturbation Theories

Several researchers have studied the convergence properties of the SRS and HS symmetry-adapted pertubation theories. In particular, these groups have studied the convergence properties of SRS and HS expansions for several states and intermolecular distances of H_2^+,[111,112,175] H_2,[176,208] and He_2.[285] The calculations of the convergence properties of H_2 and He_2 were performed with very large basis sets. Therefore, it is very likely that the results of these calculations are close to the results that would be obtained if an infinite basis set were used.

In general, both the SRS and HS perturbation expansions for H_2^+, H_2, and He_2 converge rapidly.[280] However, according to the results of the calculations performed on H_2^+ and H_2, the convergence of the HS expansion is better than the convergence of the SRS expansion. Also, because the convergence radii for the HS expansions of H_2 and He_2 are similar,[208,285] it is likely that the HS convergence for He_2 will also be better than the corresponding SRS convergence for He_2 when expansions are carried out to high order in n.[280]

The most important difference between the convergence properties of the SRS and HS theories is that the two expansions converge to different energies.[280] While the HS expansion converges to the physically correct energy of the system, the SRS expansion does not.[280] If we subtract the energy that the SRS expansion converges to from the correct physical energy of the system, we obtain what is known as the residual exchange energy.[113,175] However, according to Jeziorski *et. al*, the residual exchange energy is so small that it does not affect the accuracy of the SRS method.[280]

2.7 Many-Body Perturbation Theory

2.7.1 Introduction

The polarization approximation, the multipole expansion, and symmetry-adapted perturbation theory are useful theories for calculating intermolecular interaction energies and determining the physical origins of each term in the equations for these energies. If the full configuration interaction (FCI) wavefunctions of monomers A and B are used in the polarization approximation expressions for the interaction energies, the intramonomer correlation effects are accounted for in these energies. However, these wavefunctions are rarely used when calculating these energies. This is because the sizes of these wavefunctions increase very quickly as the corresponding system sizes increase, so that these wavefunctions are impractical to work with for systems in which monomers A and B have more than two electrons. Instead, the wavefunctions of monomers A and B are usually approximated by their corresponding Hartree-Fock determinants. However, if the Hartree-Fock determinants are used to calculate the interaction energies of the system within the polarization approximation, the multipole expansion, or SAPT, then the effects of intramonomer correlation are not accounted for.

A new theory has been developed which accounts for intramonomer correlation. This theory is known as many-body perturbation theory (MBPT) or double perturbation theory.[217,218] In double perturbation theory, we assume that there are two perturbations acting on monomers A and B. The first perturbation is the intermolecular interaction, and the second is the intramonomer correlation. We use the intermolecular interaction operator V which is given by Eq. (48) in the double perturbation theory equations to represent the intermolecular interaction perturbation. Additionally, we represent the intramolecular correlation perturbation with a second perturbation operator W, where W is given by

$$W = W^A + W^B. \tag{121}$$

In Eq. (121), W^A represents the intramolecular correlation in A, and W^B represents the intramolecular correlation in B. In this formulation, the Hamiltonian for unperturbed monomer X is[183]

$$H^X = F^X + W^X, \tag{122}$$

where F^X is the Fock operator for monomer X. To obtain the equations for H^A and H^B, we let $X = A$ and $X = B$ in Eq. (122), respectively. Using Eq. (122), with $X = A$ and with $X = B$ in Eq. (45), we obtain

$$H = F^A + W^A + F^B + W^B + V. \tag{123}$$

In the polarization approximation, we partition Eq. (123) so that $F^A + F^B = H^0$. Letting $F^A + F^B = F$ and $W^A + W^B = W$ in Eq. (123), we have that

$$H = F + W + V. \tag{124}$$

Now, let us introduce the ordering parameters ζ and λ into the overall Hamiltonian for the interacting system, which is given by Eq. (124). When we do this, H

becomes

$$H = F + \zeta W + \lambda V. \tag{125}$$

Then, if we substitute Eq. (125) into Eq. (44), with $k = 0$, the result is[182]

$$(F + \zeta W + \lambda V)\,|\Psi_{0_{AB}}\rangle = E_{0_{AB}}|\Psi_{0_{AB}}\rangle. \tag{126}$$

If we expand both $\Psi_{0_{AB}}$ and $E_{0_{AB}}$ in powers of ζ and λ and collect terms of the same power in λ, we obtain the following double perturbation theory expressions for the n^{th}-order corrections to the ground-state wavefunction and energy of the AB complex in the polarization approximation,[182]

$$\Psi_{0_{AB}}^{(n)} = \sum_{i=0}^{\infty} \Psi_{0_{AB}}^{(ni)} \tag{127}$$

and

$$E_{0_{AB}}^{(n)} = \sum_{i=0}^{\infty} E_{0_{AB}}^{(ni)}. \tag{128}$$

In Eq. (127), $\Psi_{0_{AB}}^{(ni)}$ is the n^{th}-order correction in V and the i^{th}-order correction in W to the exact ground-state wavefunction of the interacting system. Also, in Eq. (128), $E_{0_{AB}}^{(ni)}$ is the n^{th}-order correction in V and the i^{th}-order correction in W to the exact ground-state wavefunction of the interacting system. Similarly, we obtain the SRS energy of the interacting system by introducing the ordering parameter ζ into Eq. (112), expanding this expression in powers of ζ and λ, and collecting terms of the same order in λ. When this is done, we find that the n^{th}-order correction in V to the SRS energy is given by[178]

$$E_{0_{AB}}^{(n,SRS)} = \sum_{i=0}^{\infty} E_{0_{AB}}^{(ni,SRS)}. \tag{129}$$

In Eq. (129), $E_{0_{AB}}^{(ni,SRS)}$ is the n^{th}-order correction in V and the i^{th}-order correction in W to the exact ground-state energy of the interacting system in SRS theory. Each $E_{0_{AB}}^{(ni,SRS)}$ has a polarization contribution $E_{0_{AB}}^{(ni)}$ and an exchange contribution $E_{0_{AB}}^{(ni,SRS-exch)}$, so that

$$E_{0_{AB}}^{(ni,SRS)} = E_{0_{AB}}^{(ni)} + E_{0_{AB}}^{(ni,SRS-exch)}. \tag{130}$$

The total exchange energy for the n^{th} -order correction to the energy of the interacting system is

$$E_{0_{AB}}^{(n,SRS-exch)} = \sum_{i=0}^{\infty} E_{0_{AB}}^{(ni,SRS-exch)}, \tag{131}$$

where $E_{0_{AB}}^{(ni,SRS-exch)}$ is the contribution to the overall exchange energy which is n^{th}- order in V and i^{th}-order in W .

Reference 280 reviews the evaluation of the MBPT expressions for $E_{0_{AB}}^{(ni)}$ and $\Psi_{0_{AB}}^{(ni)}$ in detail.[280] The procedures for evaluating these expressions were originally developed by Szalewicz and co-workers[182] and also by Tachikawa *et. al.*[219] The evaluation of the exchange energies $E_{0_{AB}}^{(ni,SRS-exch)}$ is much more difficult than the evaluation of the corresponding polarization energies because the MBPT expressions for $E_{0_{AB}}^{(ni,SRS-exch)}$ contain integrals formed by the overlap of nonorthogonal orbitals. Therefore, MBPT exchange energies $E_{0_{AB}}^{(ni,SRS-exch)}$ have only been evaluated under the assumption that intramonomer correlation has been neglected (that is, $i = 0$ in MBPT expressions for $E_{0_{AB}}^{(ni,SRS-exch)}$. Specifically, the first-order exchange energy $E_{0_{AB}}^{(10,SRS-exch)}$,[211,220] the second-order exchange-induction energy $E_{0_{AB}}^{(20,SRS-exch-ind)}$,[214] and the second-order exchange-dispersion energy $E_{0_{AB}}^{(20,SRS-exch-disp)}$ [214] have all been computed in this approximation.

If we write diagrammatic expressions for the MBPT equations for $E_{0_{AB}}^{(ni)}$ and $E_{0_{AB}}^{(ni,SRS-exch)}$, we see that these expressions include disconnected terms. As a result, these expressions scale improperly with the size of the interacting system. By manipulating these equations, one can eventually cancel the disconnected terms. Using this procedure, researchers have calculated $E_{0_{AB}}^{(10)}$,[209] $E_{0_{AB}}^{(10,SRS-exch)}$,[211] $E_{0_{AB}}^{(20,SRS-ind-exch)}$,[209] $E_{0_{AB}}^{(21,ind)}$,[221] $E_{0_{AB}}^{(20,disp)}$,[209] $E_{0_{AB}}^{(21,disp)}$,[71,222] and $E_{0_{AB}}^{(20,SRS-exch)}$.[214]

It is difficult to manipulate the diagrammatic expressions for the MBPT equations for $E_{0_{AB}}^{(ni)}$ and $E_{0_{AB}}^{(ni,SRS-exch)}$ in order to remove the disconnected terms that these expressions contain. Therefore, in order to avoid having to perform these manipulations, several researchers have used CC theory[217,218,223–230] to rewrite the diagrammatic expressions for the MBPT formulations of the RS and SRS perturbation equations.[177–179,216] Specifically, Rybak and co-workers have written CC equations for the MBPT formulation of the RS perturbation equations in the polarization approximation.[177] Additionally, Moszynski *et. al.* have derived CC equations that contain only connected diagrams for the first-order exchange energy in the MBPT formulation of SRS theory.[178] These authors used the connected CC expansion of the expectation value[232] and the single-exchange operator $\mathcal{P}_1$ to obtain the connected CC expression for the first-order exchange energy. Also, when deriving these equations, they also ignored the contribution of higher than single electron exchanges to the total exchange energy.[162,210,288] Finally, they used the CC equations for the MBPT first-order exchange energy to calculate $E_{0_{AB}}^{(10,SRS-exch)}$, $E_{0_{AB}}^{(11,SRS-exch)}$, and $E_{0_{AB}}^{(12,SRS-exch)}$, and they used a CC approximation to calculate $E_{0_{AB}}^{(1,SRS-exch)}$.[178] Other symmetry-adapted MBPT CC equations have been used to write orbital expressions for $E_{0_{AB}}^{(10)}$, $E_{0_{AB}}^{(11)}$, and $E_{0_{AB}}^{(12)}$,[177] and a symmetry-adapted MBPT coupled-cluster approximation has been used to derive a similar expression for $E_{0_{AB}}^{(2,disp)}$.[185]

Many-body perturbation theory can also be used to derive equations for various components of the interaction energies that express these energies in terms of the polarization propagators and electron densities of monomers A and B. Moszynski and co-workers[184] and Moszynski *et. al.*[77] have both derived MBPT equations for the electrostatic energy of interaction in terms of the electron densities and polarization propagators of A and B. Also, Moszynski, Cybulski, and Chalasinski[187] have written MBPT equations for the induction energy of interaction in terms of the electron densities and polarization propagators of A and B, and Moszynski *et. al.* have derived MBPT equations for the exchange energy in terms of the same properties of the interacting monomers.[186] These MBPT equations for the electrostatic energy, the induction energy, and the exchange energy can be formulated in terms of Møller-Plesset expansions for the polarization propagators and electron densities.[232,287,96,97,102,192] If these components of the total interaction energy are formulated in terms of the Møller-Plesset expansions for the polarization propagators and interaction energies, then the resulting energetic expressions are called nonrelaxed expansions.[280] The MBPT electrostatic, induction, and exchange energies can also be formulated in terms of what are known as relaxed expansions for the polarization propagators and electron densities. The expressions for these energies are called relaxed expansions.[280] In general, for a relaxed expansion of any particular polarization component of the interaction energy in MBPT, Eq. (128) is

$$E_{0_{AB}}^{(n,resp)} = \sum_{i=0}^{\infty} E_{0_{AB}}^{(ni,resp)}. \tag{132}$$

In Eq. (132), $E_{0_{AB}}^{(n,resp)}$ is the total n^{th}-order relaxed correction in V to the specified component of the interaction energy, and $E_{0_{AB}}^{(ni,resp)}$ is the n^{th}-order relaxed correction in V and the i^{th}-order correction in W to the specified component of the interaction energy.

2.7.2 The Electrostatic Energy in Many-Body Perturbation Theory

The MBPT expressions for the electrostatic energy in the polarization approximation and in SAPT contain contributions from the intramonomer correlation energies of monomers A and B. Rybak, Jeziorski and Szalewicz have derived an equation for the second-order intramonomer correlation correction $E_{0_{AB}}^{(12)}$ to the electrostatic energy in the polarization approximation.[177] Also, Moszynski *et. al.* have derived expressions for the third-order and fourth-order intramonomer correlation corrections to the electrostatic energy (given by $E_{0_{AB}}^{(13)}$ and $E_{0_{AB}}^{(14)}$, respectively) in the polarization approximation,[77] given in terms of the nonrelaxed expansions for the polarization propagators and electron densities.[96,287,97,102,192,232] Moszynski and co-workers[184] have derived an equation for the second-order relaxed intramonomer correlation correction $E_{0_{AB}}^{(12,resp)}$ to the electrostatic energy. Reference 77 also gives equations for the relaxed third- and fourth-order intramonomer correlation corrections $E_{0_{AB}}^{(13,resp)}$ and $E_{0_{AB}}^{(14,resp)}$ to the electrostatic energy.[77] Jeziorski and co-workers briefly review the derivations of the equations for $E_{0_{AB}}^{(1k)}$ and $E_{0_{AB}}^{(1k,resp)}$, where $k \leq 4$.[280]

The same researchers who derived the equations for these intramonomer correlation corrections to the electrostatic energy have also used these equations to calculate numerical values of these energies for several different dimers. They have used the results of their calculations to compare the magnitude of the intramonomer correlation correction to the electrostatic energy of the dimer to the magnitudes of the electrostatic energy and total interaction of the dimer. Rybak *et. al.* have used their equation for $E_{0_{AB}}^{(12)}$ to calculate the second-order intramonomer correlation correction to the electrostatic energy of the water dimer and of the hydrogen fluoride dimer.[177] The results of these calculations show that at or near the van der Waals minima of the dimers, the second-order intramonomer correlation correction $E_{0_{AB}}^{(12)}$ to the electrostatic energy is up to 10 percent of the total interaction energy. This indicates that for these dimers and at these distances, the intramonomer correlation energy is significant, and that one cannot neglect intramonomer correlation when trying to calculate the interaction energies of these dimers.

Williams and co-workers have also calculated the 2^{nd}-order intramonomer correlation correction $E_{0_{AB}}^{(12)}$ to the electrostatic energy of the water and hydrogen fluoride dimers.[286] They have also calculated the third-order intramonomer correlation correction $E_{0_{AB}}^{(13)}$ to the electrostatic energy of the same dimers.[286] Then, by adding $E_{0_{AB}}^{(12)}$ and $E_{0_{AB}}^{(13)}$ together, they obtained slightly more accurate estimates of the total intramonomer correlation energy of each dimer. The results of these calculations show that at intermonomer distances which are larger than the van der Waals minima, the second-order intramonomer correlation correction $E_{0_{AB}}^{(12)}$ is a much smaller component of the interaction energy for each dimer. Specifically, at the intermonomer distances specified in their work, the total intramonomer correlation energy was only two percent of the electrostatic energy of the water dimer, and five percent of the electrostatic energy of the hydrogen fluoride dimer. Although the intramonomer correlation energy of each dimer is a smaller portion of the corresponding total interaction energy at larger distances, intramonomer correlation is still a significant part of the total interaction energy. The authors of this work also computed the relaxed first-, third-, and fourth-order intramonomer correlation corrections $E_{0_{AB}}^{(12,resp)}$, $E_{0_{AB}}^{(13,resp)}$, and $E_{0_{AB}}^{(14,resp)}$, for the water and hydrogen fluoride dimers, and they provided another estimate of the total intramonomer correlation energy by adding $E_{0_{AB}}^{(12,resp)}$, $E_{0_{AB}}^{(13,resp)}$, and $E_{0_{AB}}^{(14,resp)}$ for each dimer. The results of these calculations were very similar to the results of the calculations of the nonrelaxed energies.

Other groups performed similar calculations on the helium dimer and on $(H_2)_2$. Specifically, Moszynski and co-workers calculated the second-order intramonomer correlation correction $E_{0_{AB}}^{(12)}$ and the corresponding relaxed correction $E_{0_{AB}}^{(12,resp)}$ for the $(H_2)_2$ dimer.[184] They performed these calculations in order to determine the convergence behavior of the nonrelaxed and relaxed MBPT expansions for the intramonomer correlation contributions to the electrostatic energy, which are given by Eqs. (128) and (132). They determined how quickly these equations (with $n = 1$) converge by comparing the values of $E_{0_{AB}}^{(12)}$ and $E_{0_{AB}}^{(12,resp)}$ with the electrostatic energy of the dimer as calculated with the FCI wavefunction. According to their calculations, the second-order intramonomer correlation corrections contain only between 50 percent and 70 percent of the FCI correlation energy. Therefore, higher-order intramonomer correlation corrections are large enough that they cannot be ignored in accurate calculations of the intramonomer correlation energy. Moszynski *et. al.* have also calculated $E_{0_{AB}}^{(12)}$ and $E_{0_{AB}}^{(12,resp)}$ for $(H_2)_2$.[77] However, they have also calculated higher-order intramonomer correlation corrections for this system, including $E_{0_{AB}}^{(13)}$, $E_{0_{AB}}^{(14)}$, $E_{0_{AB}}^{(13,resp)}$, and $E_{0_{AB}}^{(14,resp)}$.[77] Additionally, they have calculated $E_{0_{AB}}^{(1k)}$ and $E_{0_{AB}}^{(1k,resp)}$ where $n \leq 4$ for the helium dimer. Then, for each dimer, they computed the sum of $E_{0_{AB}}^{(1k)}$ for $k \leq 4$ and of $E_{0_{AB}}^{(1k,resp)}$ for $k \leq 4$, where the former sum is given by

$$\epsilon_{0_{AB}}^{(1)}(4) = E_{0_{AB}}^{(12)} + E_{0_{AB}}^{(13)} + E_{0_{AB}}^{(14)}, \tag{133}$$

and the latter sum is given by

$$\epsilon_{0_{AB}}^{(1,resp)}(4) = E_{0_{AB}}^{(12,resp)} + E_{0_{AB}}^{(13,resp)} + E_{0_{AB}}^{(14,resp)}. \tag{134}$$

In Eqs. (133) and (134), $\epsilon_{0_{AB}}^{(1)}(4)$ and $\epsilon_{0_{AB}}^{(1,resp)}(4)$ denote the sums given in each equation. In order to determine the convergence of both MBPT expansions for the intramonomer correlation contribution to the electrostatic energy of each dimer, they compared $\epsilon_{0_{AB}}^{(1)}(4)$ for each dimer to the corresponding total electrostatic-correlation energy. They also compared $\epsilon_{0_{AB}}^{(1,resp)}(4)$ for each dimer to the corresponding total relaxed electrostatic-correlation energy. The total electrostatic-correlation energy

$\epsilon_{0_{AB}}^{(1)}(FCI)$ is given by

$$\epsilon_{0_{AB}}^{(1)}(FCI) = E_{0_{AB}}^{(1)} - E_{0_{AB}}^{(10)}, \tag{135}$$

where $E_{0_{AB}}^{(1)}$ is the electrostatic energy of the dimer computed with its FCI wavefunction, and $E_{0_{AB}}^{(10)}$ is the electrostatic energy of the dimer in the Hartree-Fock (HF) approximation. The total relaxed electrostatic-correlation energy $\epsilon_{0_{AB}}^{(1,resp)}(FCI)$ is given by

$$\epsilon_{0_{AB}}^{(1,resp)}(FCI) = E_{0_{AB}}^{(1,resp)} - E_{0_{AB}}^{(10,resp)}, \tag{136}$$

where $E_{0_{AB}}^{(1,resp)}$ and $E_{0_{AB}}^{(10,resp)}$ are the same quantities as $E_{0_{AB}}^{(1)}$ and $E_{0_{AB}}^{(10)}$, respectively, except that $E_{0_{AB}}^{(1,resp)}$ and $E_{0_{AB}}^{(10,resp)}$ contain relaxed expansions for the polarization propagators and electron densities. When they compared the sum through the fourth-order of the intramonomer correlation correction $\epsilon_{0_{AB}}^{(1)}(4)$ to the total electrostatic-correlation energy $\epsilon_{0_{AB}}^{(1)}(FCI)$ for the dimer, they determined that over 90 percent of the total intramonomer correlation energy is included in $\epsilon_{0_{AB}}^{(1)}(4)$. They obtained similar results when they compared $\epsilon_{0_{AB}}^{(1,resp)}(4)$ to $\epsilon_{0_{AB}}^{(1,resp)}(FCI)$ for each dimer. These results indicate that the MBPT expansions for the intramonomer correlation contributions to the electrostatic energies of $(H_2)_2$ and He_2 converge quickly, and that for both dimers, $\epsilon_{0_{AB}}^{(1)}(4)$ and $\epsilon_{0_{AB}}^{(1,resp)}(4)$ are very good approximations to the total electrostatic-correlation energies $\epsilon_{0_{AB}}^{(1)}(FCI)$ and $\epsilon_{0_{AB}}^{(1,resp)}(FCI)$.[77]

2.7.3 The First-Order Exchange Energy in Many-Body Perturbation Theory

There are two methods for computing the intramonomer correlation contribution to the first-order exchange energy in SRS theory.[280] The first method involves using the approximation to $E_{0_{AB}}^{(1,SRS-exch)}$ developed in reference 73, which is given in terms of the one- and two-particle density matrices of monomers A and B. In order to account for the intramonomer correlation contribution to the first-order exchange energy, the one- and two-particle density matrices originally included in the expression for $E_{0_{AB}}^{(1,SRS-exch)}$ in reference 73 are expanded in powers of ζ.[186] The equations for these expansions are given in reference 280.

The second method for calculating the intramonomer correlation contribution to the first-order exchange energy in SRS theory is a coupled-cluster singles and doubles (CCSD) technique which involves infinite-order summation methods that are nonperturbative.[178,235] Jeziorski *et. al.* briefly review this method in reference 280.

Moszynski and co-workers have used the expressions which give the approximation for $E_{0_{AB}}^{(1,SRS-exch)}$ in terms of one- and two-particle density matrices expanded in powers of λ to calculate the first- and second-order intramonomer correlation corrections $E_{0_{AB}}^{(11,SRS-exch)}$ and $E_{0_{AB}}^{(12,SRS-exch)}$ to the first-order exchange energy of He_2, $(H_2)_2$, He-HF, and Ar-H_2.[186] Then, for each dimer, they added these two corrections. We will denote the sum of these corrections $\epsilon_{0_{AB}}^{(1,SRS-exch)}(2)$. In order to determine the convergence of the MBPT expansion for the intramonomer correlation contribution to the 1st-order exchange energy of each dimer, they compared $\epsilon_{0_{AB}}^{(1,SRS-exch)}(2)$ for each dimer to the corresponding total exchange-correlation energy $\epsilon_{0_{AB}}^{(1,SRS-exch)}(FCI)$, which is given by

$$\epsilon_{0_{AB}}^{(1,SRS-exch)}(FCI) = E_{0_{AB}}^{(1,SRS-exch)} - E_{0_{AB}}^{(10,SRS-exch)}. \qquad (137)$$

In Eq. (137), $E_{0_{AB}}^{(1,SRS-exch)}$ is the total 1st-order exchange energy of the dimer, as computed with its FCI wavefunction, and $E_{0_{AB}}^{(10,SRS-exch)}$ is the exchange energy of the dimer as calculated with its Hartree-Fock determinant. Moszynski, Jeziorski, and Szalewicz have calculated the intramonomer correlation correction to the first-order exchange energy in the CCSD approximation for He_2, $(H_2)_2$, He-HF, and Ar-H_2.[178] Jeziorski *et. al.* list and briefly discuss the results of these calculations.

According to the analysis of the convergence properties of the MBPT expansion (for the intramonomer correlation contribution to the first-order exchange energy), the convergence of the MBPT expansion is relatively slow. For example, for He_2, the sum of the first- and second-order intramonomer correlation corrections $\epsilon_{0_{AB}}^{(1,SRS-exch)}(2)$ to the first-order exchange energy constitutes only 50 percent of the corresponding total exchange-correlation energy $\epsilon_{0_{AB}}^{(1,SRS-exch)}(FCI)$.[186] For the H_2 dimer, $\epsilon_{0_{AB}}^{(1,SRS-exch)}(2)$ is 25 percent larger than the corresponding total exchange-correlation energy $\epsilon_{0_{AB}}^{(1,SRS-exch)}(FCI)$. However, for each dimer, the intramonomer correlation contribution to the 1^{st}-order exchange energy computed in the CCSD approximation is around 98 percent of the total exchange-correlation energy $\epsilon_{0_{AB}}^{(1,SRS-exch)}(FCI)$. Therefore, the CCSD-based method for computing the intramonomer correlation contribution to the first-order exchange energy is much more accurate than the corresponding MBPT method for computing the same quantity.

2.7.4 The Second-Order Induction Energy in Many-Body Perturbation Theory

Moszynski and co-workers have derived an equation for the induction energy that includes an MBPT expansion for the intramonomer correlation energy and depends on the polarization propagators and electron densities of the unperturbed monomers A and B.[187,232,287] This equation for the induction energy can also be written in terms of the relaxed expansions of the polarization propagators and electron densities.[103–105,188–190,233,234] The induction-correlation energy $\epsilon_{0_{AB}}^{(2,ind)}$ is given by

$$\epsilon_{0_{AB}}^{(2,ind)} = E_{0_{AB}}^{(2,ind)} - E_{0_{AB}}^{(20,ind)}. \tag{138}$$

In Eq. (138), $E_{0_{AB}}^{(2,ind)}$ is the exact second-order induction energy, and $E_{0_{AB}}^{(20,ind)}$ is the second-order induction energy in the Hartree-Fock approximation. Similarly, the relaxed induction-correlation energy $\epsilon_{0_{AB}}^{(2,resp-ind)}$ is given by

$$\epsilon_{0_{AB}}^{(2,resp-ind)} = E_{0_{AB}}^{(2,resp-ind)} - E_{0_{AB}}^{(20,resp-ind)}, \tag{139}$$

where $E_{0_{AB}}^{(2,resp-ind)}$ is the exact second-order relaxed induction energy, and $E_{0_{AB}}^{(20,resp-ind)}$ is the second-order relaxed induction energy in the Hartree-Fock approximation. Sadlej has shown that each intramonomer correlation correction $E_{0_{AB}}^{(2l,ind)}$ (which is second-order in V and l^{th}-order in W) can be written as[191]

$$E_{0_{AB}}^{(2l,ind)} = E_{0_{AB}}^{(2l,ind-a)} + E_{0_{AB}}^{(2l,ind-t)}. \tag{140}$$

In Eq. (140), $E_{0_{AB}}^{(2l,ind-t)}$ is what is called the true intramonomer correlation portion $E_{0_{AB}}^{(2l,ind)}$. Also, $E_{0_{AB}}^{(2l,ind-a)}$ is what is called the apparent intramonomer correlation portion of $E_{0_{AB}}^{(2l,ind)}$.[191] One can calculate the apparent intramonomer correlation portion $E_{0_{AB}}^{(2l,ind-a)}$ of $E_{0_{AB}}^{(2l,ind)}$ by using the random-phase approximation (RPA) propagator[280] in the expression for $E_{0_{AB}}^{(2l,ind)}$. Jeziorski, Moszynski, and Szalewicz (and references therein) discuss the apparent and true intramonomer correlation contributions to the second-order induction energy in more detail.[280] In summary of their discussion, the relaxed induction-correlation energy $\epsilon_{0_{AB}}^{(2,resp-ind)}$ is a more accurate representation of the second-order induction-correlation energy than the corresponding nonrelaxed induction-correlation energy $\epsilon_{0_{AB}}^{(2,ind)}$.

Moszynski, Cybulski, and Chalasinski as well as Moszynski *et. al.* have calculated $E_{0_{AB}}^{(20,resp-ind)}$ and $E_{0_{AB}}^{(22,resp-ind)}$ for the He-K$^+$, He-F$^-$, $(H_2O)_2$, and He-HCl dimers.[187,80] Note that they did not calculate the first-order relaxed intramonomer correlation energy $E_{0_{AB}}^{(21,resp-ind)}$ because this contribution is equal to zero by the Brillouin theorem.[280] According to the results of these calculations, the magnitude of $E_{0_{AB}}^{(22,resp-ind)}$ is very different for each of the different dimers. For dimers containing a rare gas atom and an ion, the magnitude of $E_{0_{AB}}^{(22,resp-ind)}$ is relatively large. For example, for the He-F$^-$ dimer, $E_{0_{AB}}^{(22,resp-ind)}$ is about 10 percent of the size of $E_{0_{AB}}^{(20,resp-ind)}$ at or near the van der Waals minimum of the dimer. For dimers containing two polar molecules, $E_{0_{AB}}^{(22,resp-ind)}$ is even larger, relative to the size of $E_{0_{AB}}^{(20,resp-ind)}$. For the water dimer, $E_{0_{AB}}^{(22,resp-ind)}$ is about 30 percent of the size of $E_{0_{AB}}^{(20,resp-ind)}$ at or near the van der Waals minimum of the dimer. Although the authors of references 74 and 93 did not calculate $E_{0_{AB}}^{(20,resp-ind)}$ and $E_{0_{AB}}^{(22,resp-ind)}$ for any dimers containing a rare gas atom and a nonpolar molecule, Jeziorski *et. al.* mention that $E_{0_{AB}}^{(22,resp-ind)}$ is so small for these types of dimers that it can usually be ignored in calculations of $E_{0_{AB}}^{(2,resp-ind)}$.

2.7.5 The Second-Order Dispersion Energy in Many-Body Perturbation Theory

In general, there are two ways of writing MBPT expansions for the intramonomer correlation contribution to the second-order dispersion energy in the polarization approximation.[280] Rybak and co-workers[177] have written completely connected CC equations for the first-order intramonomer correlation correction $E_{0_{AB}}^{(2l,disp)}$ to the second-order dispersion energy. Additionally, Jaszunski *et. al.* have written the original expression for the second-order dispersion energy in the polarization approximation as an MBPT expansion in the intramonomer correlation.[231] They did this by replacing the polarization propagators in the original expression for the second-order dispersion energy with MBPT expansions for these propagators.

One can also compute the second-order dispersion energy at large R_{AB} if the intermolecular interaction operator V is replaced with the multipole expansion in the MBPT perturbation equations for the dispersion energy. Recall from Sect. 2.4.4 that in the multipole approximation, the second-order dispersion energy is determined by the reciprocal of the distance R_{AB} between monomers and the van der Waals constants. In turn, the van der Waals constants are determined by the frequency-dependent polarizabilities of the monomers in the multipole approximation. Jeziorski and co-workers obtained a MBPT expansion for the l^{th}-order intramonomer correlation correction $E_{0_{AB}}^{(2l,disp)}$ to the second-order dispersion energy by substituting the expressions for the polarizabilities with the Møller-Plesset expansions for these quantities.[280] Specifically, Wormer *et. al.*[236–238,240,239] have derived diagrammatic MBPT equations for correlated frequency-dependent polarizabilities, and they have developed another MBPT method for calculating correlated van der Waals constants.

Moszynski, Jeziorski, and Szalewicz have developed a method for approximating the long-range second-order correlation-dispersion energy which is known as the ring approximation (RA).[185] One obtains the second-order correlation-dispersion energy

$E_{0_{AB}}^{(2,disp-RA)}$ in the ring approximation by replacing the expressions for the polarizabilities in the equation for the second-order dispersion energy with the expressions for the polarizabilities in the random-phase approximation.[241,243,244,242] If one writes the equation for the dispersion energy in the ring approximation in diagrammatic form, the resulting expression that he or she obtains will contain ring diagrams only.[185] One can obtain the diagrammatic expression for the dispersion-correlation energy $E_{0_{AB}}^{(2,disp-RA)}$ in the ring approximation by summing the ring diagrams included in each expression for $E_{0_{AB}}^{(2l,disp)}$ over all l.[185] Note that one can also obtain the second-order dispersion-correlation energy $E_{0_{AB}}^{(2,disp-RA)}$ in the ring approximation by replacing the polarization propagators in the expression for $E_{0_{AB}}^{(2,disp)}$ in the polarization approximation with the expressions for the polarization propagators in the random-phase approximation.[279,245] Finally, one can use CC equations derived by Moszynski, Jeziorski, and Szalewicz to calculate $E_{0_{AB}}^{(2,disp-RA)}$.[185]

Moszynski *et.al.* have used CC equations derived in the polarization approximation to calculate $E_{0_{AB}}^{(20,disp)}$, $E_{0_{AB}}^{(21,disp)}$, and $E_{0_{AB}}^{(22,disp)}$ for He_2, $(H_2)_2$, and $(HF)_2$.[185] Then, for each dimer, they used these results to calculate $\epsilon_{0_{AB}}^{(2,disp)}(2)$, which is the sum of the intramonomer correlation contributions to the second-order dispersion energy through second-order in W. They also calculated the $E_{0_{AB}}^{(22,disp-RA)}$ and the sum of all l^{th}-order intramonomer correlation corrections where $l \geq 3$ to the second-order dispersion energy in the ring approximation, which we will denote $\epsilon_{0_{AB}}^{(2,disp-RA)}(3 \longrightarrow \infty)$. The equation for this sum is

$$\epsilon_{0_{AB}}^{(2,disp-RA)}(3 \longrightarrow \infty) = \sum_{l=3}^{\infty} E_{0_{AB}}^{(2l,disp-RA)}. \tag{141}$$

According to the results of these calculations, the MBPT expansion for the intramonomer correlation contribution to the second-order dispersion energy converges relatively quickly. Specifically, for each dimer, the magnitude of $\epsilon_{0_{AB}}^{(2,disp-RA)}(3 \longrightarrow \infty)$ is very small in comparison to the value of $\epsilon_{0_{AB}}^{(2,disp)}(2)$, which indicates that most of the intramonomer correlation energy in included in the first-, second-, and third-order corrections to the total intramonomer correlation energy.

3 The Second-Order Correction to the Energy of Two Interacting Molecules A and B

This chapter provides a review of known results for the second-order intermolecular interaction energies in the polarization approximation, which is valid when molecules A and B are separated by a distance R_{AB} such that the overlap between their electronic charge distributions can be ignored. If the electronic overlap is non-negligable but A and B interact noncovalently, then the interaction energy can be obtained from exchange perturbation theory. However, the current work is limited to the polarization approximation. Then the second-order correction to the energy of interaction between the two molecules is

$$\Delta E^{(2)}_{0_{AB}} = \langle \Psi^{(0)}_{0_{AB}} | \hat{V}^{AB} \, G \, \hat{V}^{AB} \, | \Psi^{(0)}_{0_{AB}} \rangle, \tag{142}$$

where $|\Psi^{(0)}_{0_{AB}}\rangle$ denotes the ground-state wavefunction of the unperturbed system, which we approximate by the product of the ground-state wavefunctions $\Psi^{(0)}_{0_A}$ and $\Psi^{(0)}_{0_B}$ of molecules A and B,

$$|\Psi^{(0)}_{0_{AB}}\rangle = |\Psi^{(0)}_{0_A} \, \Psi^{(0)}_{0_B}\rangle. \tag{143}$$

In Eq. (142), $\hat{V}^{AB}$ is the interaction potential, and G is the reduced resolvent of $H^0 = H^A + H^B$, which was defined in Eq. (19) of Chap. 1. For the interaction between molecules A and B, G is a sum of three components,

$$G = G^A + G^B + G^{A \oplus B}, \tag{144}$$

where

$$G^A = \sum_{j \neq 0} \frac{|\Psi^{(0)}_{j_A} \Psi^{(0)}_{0_B}\rangle \langle \Psi^{(0)}_{j_A} \Psi^{(0)}_{0_B}|}{\left(E^{(0)}_{j_A} + E^{(0)}_{0_B}\right) - \left(E^{(0)}_{0_A} + E^{(0)}_{0_B}\right)}, \tag{145}$$

$$G^B = \sum_{r \neq 0} \frac{|\Psi^{(0)}_{0_A} \Psi^{(0)}_{r_B}\rangle \langle \Psi^{(0)}_{0_A} \Psi^{(0)}_{r_B}|}{\left(E^{(0)}_{0_A} + E^{(0)}_{r_B}\right) - \left(E^{(0)}_{0_A} + E^{(0)}_{0_B}\right)}, \tag{146}$$

and

$$G^{A \oplus B} = \sum_{j_A, r_B \neq 0} \frac{|\Psi^{(0)}_{j_A} \Psi^{(0)}_{r_B}\rangle \langle \Psi^{(0)}_{j_A} \Psi^{(0)}_{r_B}|}{\left(E^{(0)}_{j_A} + E^{(0)}_{r_B}\right) - \left(E^{(0)}_{0_A} + E^{(0)}_{0_B}\right)}. \tag{147}$$

In Eqs. (145), (146), and (147), $\Psi_{j_A}^{(0)}$ denotes the j^{th} excited state of molecule A, and $\Psi_{r_B}^{(0)}$ denotes the r^{th} excited state of molecule B. Similarly, $E_{j_A}^{(0)}$, $E_{r_B}^{(0)}$, $E_{0_A}^{(0)}$, and $E_{0_B}^{(0)}$ correspond to the energies of molecule A in excited state j , B in excited state r , A in its ground state, and B in its ground state. Eqs. (145), (146), and (147) are the reduced resolvents constructed when considering excitations in molecule A only, in B only, and in both A and B. In the following, we approximate V in terms of the dipole-dipole interaction and thus we have

$$\hat{V}^{AB} = -\hat{\mu}_\alpha^A \, T_{\alpha\beta} \, \hat{\mu}_\beta^B, \tag{148}$$

The dipole propagator $T_{\alpha\beta}$ is defined by

$$T_{\alpha\beta} = \nabla_\alpha \nabla_\beta \frac{1}{\mathbf{R}} = \frac{3\, R_\alpha \, R_\beta - \delta_{\alpha\beta}\, \mathbf{R}^2}{\mathbf{R}^5}. \tag{149}$$

In Eq. (149), R_α and R_β are the α and β components of $\mathbf{R}$, and ∇_α and ∇_β denote derivatives of $\mathbf{R}$ with respect to α and β , respectively. The full polarization approximation can be recovered by expressing V in terms of polarization density operators for the interacting molecules and a dipole propagator $T\left(\mathbf{r}, \mathbf{r}'\right)$ integrated over all space with respect to $\mathbf{r}$ and $\mathbf{r}'$. Using Eq. (142), (143), and Eqs. (144) - (147), we have

$$\begin{aligned}
\Delta E_{0_{AB}}^{(2)} = & -T_{\gamma\delta}\, T_{\epsilon\phi} \sum_{j_A \neq 0} \frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle 0_B|\hat{\mu}_\delta^B|0_B\rangle\langle j_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_B|\hat{\mu}_\phi^B|0_B\rangle}{\left(E_{j_A}^{(0)} + E_{0_B}^{(0)}\right) - \left(E_{0_A}^{(0)} + E_{0_B}^{(0)}\right)} \\
& -T_{\gamma\delta}\, T_{\epsilon\phi} \sum_{r_B \neq 0} \frac{\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle r_B|\hat{\mu}_\phi^B|0_B\rangle}{\left(E_{0_A}^{(0)} + E_{r_B}^{(0)}\right) - \left(E_{0_A}^{(0)} + E_{0_B}^{(0)}\right)} \\
& -T_{\gamma\delta}\, T_{\epsilon\phi} \sum_{j_A, r_B \neq 0} \frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle j_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle r_B|\hat{\mu}_\phi^B|0_B\rangle}{\left(E_{j_A}^{(0)} + E_{r_B}^{(0)}\right) - \left(E_{0_A}^{(0)} + E_{0_B}^{(0)}\right)},
\end{aligned} \tag{150}$$

where we have let $\Psi_{0_A}^{(0)} = 0_A$, $\Psi_{0_B}^{(0)} = 0_B$, $\Psi_{j_A}^{(0)} = j_A$, and $\Psi_{r_B}^{(0)} = r_B$, and we have replaced the first and second interaction operators with $\hat{V}^{AB} = -\hat{\mu}_\gamma^A \, T_{\gamma\delta} \, \hat{\mu}_\delta^B$ and $\hat{V}^{AB} = -\hat{\mu}_\epsilon^A \, T_{\epsilon\phi} \, \hat{\mu}_\phi^B$, respectively. Because $\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle = \mu_\gamma^{A0}$, $\langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle = \mu_\epsilon^{A0}$, $\langle 0_B|\hat{\mu}_\delta^B|0_B\rangle = \mu_\delta^{B0}$, and $\langle 0_B|\hat{\mu}_\phi^B|0_B\rangle = \mu_\phi^{B0}$, where μ_γ^{A0}, μ_ϵ^{A0}, μ_δ^{B0}, and μ_ϕ^{B0} are static dipole moments of molecules A and B, we can write Eq. (150) as

$$\begin{aligned}
\Delta E^{(2)}_{0_{AB}} &= -T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\delta}^{B0}\, \mu_{\phi}^{B0} \sum_{j_A \neq 0} \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)} \\
&-T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\gamma}^{A0}\, \mu_{\epsilon}^{A0} \sum_{r_B \neq 0} \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)} \\
&-T_{\gamma\delta}\, T_{\epsilon\phi} \\
&\times \sum_{j_A, r_B \neq 0} \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle\langle r_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)}
\end{aligned} \tag{151}$$

where we have also rearranged and simplified the denominators in Eq. (151). Now, consider the first term in Eq. (151). We can write the first term in Eq. (151) as a sum of two halves,

$$\begin{aligned}
&- \ T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\delta}^{B0}\, \mu_{\phi}^{B0} \sum_{j_A \neq 0} \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)} = \\
&- \ T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\delta}^{B0}\, \mu_{\phi}^{B0} \left(\frac{1}{2}\right) \sum_{j_A \neq 0} \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)} \\
&- \ T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\delta}^{B0}\, \mu_{\phi}^{B0} \left(\frac{1}{2}\right) \sum_{j_A \neq 0} \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)}.
\end{aligned} \tag{152}$$

Interchanging the labels ϵ with γ and ϕ with δ in the second term on the right-hand side of Eq. (152) gives

$$\begin{aligned}
&- \ T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\delta}^{B0}\, \mu_{\phi}^{B0} \sum_{j_A \neq 0} \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)} = \\
&- \ T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\delta}^{B0}\, \mu_{\phi}^{B0} \left(\frac{1}{2}\right) \sum_{j_A \neq 0} \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)} \\
&- \ T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu_{\phi}^{B0}\, \mu_{\delta}^{B0} \left(\frac{1}{2}\right) \sum_{j_A \neq 0} \frac{\langle 0_A|\hat{\mu}_{\epsilon}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\gamma}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)} \\
&= \ -T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\delta}^{B0}\, \mu_{\phi}^{B0} \left(\frac{1}{2}\right)
\end{aligned}$$

$$\times \left[\sum_{j_A \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\mu}_\epsilon^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} \right)} + \sum_{j_A \neq 0} \frac{\langle 0_A | \hat{\mu}_\epsilon^A | j_A \rangle \langle j_A | \hat{\mu}_\gamma^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} \right)} \right]. \tag{153}$$

The bracketed quantity in Eq. (153) is the definition of the static polarizability $\alpha_{\gamma\epsilon}^A$ of molecule A. Therefore, we can write the first term in Eq. (151) as

$$- T_{\gamma\delta} T_{\epsilon\phi} \mu_\delta^{B0} \mu_\phi^{B0} \sum_{j_A \neq 0} \frac{\langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\mu}_\epsilon^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} \right)} = -T_{\gamma\delta} T_{\epsilon\phi} \times \mu_\delta^{B0} \mu_\phi^{B0} \left(\frac{1}{2} \right) \alpha_{\gamma\epsilon}^A. \tag{154}$$

At this point, consider the second term in Eq. (151). We can also write the second term in Eq. (151) as a sum of two halves

$$\begin{aligned} - T_{\gamma\delta} T_{\epsilon\phi} \mu_\gamma^{A0} \mu_\epsilon^{A0} \sum_{r_B \neq 0} \frac{\langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\mu}_\phi^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} \right)} &= \\ - T_{\gamma\delta} T_{\epsilon\phi} \mu_\gamma^{A0} \mu_\epsilon^{A0} \left(\frac{1}{2} \right) \sum_{r_B \neq 0} \frac{\langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\mu}_\phi^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} \right)} & \\ - T_{\gamma\delta} T_{\epsilon\phi} \mu_\gamma^{A0} \mu_\epsilon^{A0} \left(\frac{1}{2} \right) \sum_{r_B \neq 0} \frac{\langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\mu}_\phi^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} \right)}. & \end{aligned} \tag{155}$$

If we interchange δ with ϕ and γ with ϵ in the second term on the right-hand side of Eq. (155), then Eq. (155) becomes

$$\begin{aligned} - T_{\gamma\delta} T_{\epsilon\phi} \mu_\gamma^{A0} \mu_\epsilon^{A0} \sum_{r_B \neq 0} \frac{\langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\mu}_\phi^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} \right)} &= \\ - T_{\gamma\delta} T_{\epsilon\phi} \mu_\gamma^{A0} \mu_\epsilon^{A0} \left(\frac{1}{2} \right) \sum_{r_B \neq 0} \frac{\langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\mu}_\phi^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} \right)} & \\ - T_{\epsilon\phi} T_{\gamma\delta} \mu_\epsilon^{A0} \mu_\gamma^{A0} \left(\frac{1}{2} \right) \sum_{r_B \neq 0} \frac{\langle 0_B | \hat{\mu}_\phi^B | r_B \rangle \langle r_B | \hat{\mu}_\delta^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} \right)} & \end{aligned}$$

$$= -T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\epsilon}^{A0}\, \mu_{\gamma}^{A0} \left(\frac{1}{2}\right)$$

$$\times \left[\sum_{r_B \neq 0} \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)}\right.$$

$$\left. + \sum_{r_B \neq 0} \frac{\langle 0_B|\hat{\mu}_{\phi}^{B}|r_B\rangle\langle r_B|\hat{\mu}_{\delta}^{B}|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)}\right]. \qquad (156)$$

The bracketed quantity in Eq. (156) is the static polarizability $\alpha_{\delta\phi}^{B}$ of molecule B. Therefore, we can write the second term in Eq. (151) as

$$-T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\gamma}^{A0}\, \mu_{\epsilon}^{A0} \sum_{r_B \neq 0} \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)} = -T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\gamma}^{A0}\, \mu_{\epsilon}^{A0} \times \left(\frac{1}{2}\right) \alpha_{\delta\phi}^{B}. \qquad (157)$$

Therefore, from Eqs. (151),(154), and (157), the second order correction to the energy of two interacting molecules A and B is

$$\Delta E_{0_{AB}}^{(2)} = - T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\delta}^{B0}\, \mu_{\phi}^{B0} \left(\frac{1}{2}\right) \alpha_{\gamma\epsilon}^{A} - T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\gamma}^{A0}\, \mu_{\epsilon}^{A0} \left(\frac{1}{2}\right) \alpha_{\delta\phi}^{B} - T_{\gamma\delta}\, T_{\epsilon\phi} \sum_{j_A, r_B \neq 0} \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle\langle r_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)}. \qquad (158)$$

We can simplify Eq. (158) by replacing the denominator in the third term of Eq. (158) with an integral,

$$\frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)} = \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega$$

$$\times \left[\frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} + \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)}\right]$$

$$\times \left[\frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} + \frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}\right]. \tag{159}$$

Before making this substitution, however, we will use complex contour integration to prove that Eq. (159) is true. Consider the integral $\int\limits_{-\infty}^{+\infty} du \left(a/\left(a^2+u^2\right)\right)\left(b/\left(b^2+u^2\right)\right)$. The integral over a semi-circular contour C of radius $\mathbf{R}_1$ in the upper complex half plane is given by

$$\begin{aligned}\int\limits_{C} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2} &= \int\limits_{\mathbf{R}_1}^{\mathbf{R}_1} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2} \\ &+ \int\limits_{S} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2},\end{aligned} \tag{160}$$

where S is the portion of C that lies off the real axis, as illustrated by Fig. 11. We take the limit as $\mathbf{R}_1$ approaches infinity. In this limit, the integral over S vanishes. Along S, $u = \mathbf{R}_1 e^{\imath\theta}$ and $du = \imath\mathbf{R}_1 e^{\imath\theta} d\theta$, so that

$$\begin{aligned}\lim_{\mathbf{R}_1 \to +\infty} \int\limits_{S} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2} &= \lim_{\mathbf{R}_1 \to +\infty} \int\limits_{0}^{\pi} \imath\mathbf{R}_1 e^{\imath\theta} \\ &\times\ d\theta \frac{a}{a^2+{\mathbf{R}_1}^2 e^{2\imath\theta}}\frac{b}{b^2+{\mathbf{R}_1}^2 e^{2\imath\theta}} \\ &= 0.\end{aligned} \tag{161}$$

Thus

$$\int\limits_{C} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2} = \int\limits_{-\infty}^{+\infty} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2}. \tag{162}$$

First, let us evaluate $\int\limits_{C} du \left(a/\left(a^2+u^2\right)\right)\left(b/\left(b^2+u^2\right)\right)$ assuming that $a \neq b$. The integrand of $\int\limits_{C} du \left(a/\left(a^2+u^2\right)\right)\left(b/\left(b^2+u^2\right)\right)$ has 4 singular points, which are $u = \pm a\imath$ and $u = \pm b\imath$. Because $-a\imath$ and $-b\imath$ are on the negative imaginary axis, they are not located within the contour C in Fig. 11. Therefore, according to the residue theorem,

$$\int\limits_{C} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2} = 2\pi\imath\left(K_1+K_2\right), \tag{163}$$

where K_1 and K_2 are the 2 residues at the poles within the contour C. If we let $f(u) = \left(a/\left(a^2+u^2\right)\right)\left(b/\left(b^2+u^2\right)\right)$, $p(u) = a \cdot b$, and $q(u) = \left(a^2+u^2\right)\left(b^2+u^2\right)$, then $f(u) = p(u)/q(u)$. Also, $q'(u) = 2a^2u + 2b^2u + 4u^3$, where $q'(u)$ is the derivative of $q(u)$ with respect to u. We can determine whether $a\imath$ and $b\imath$ are simple poles by evaluating $p(u)$, $q(u)$, and $q'(u)$ at each pole. Since $q(a\imath) = 0$, $q'(a\imath) = 2a^3\imath + 2ab^2\imath - 4a^3\imath \neq 0$, and $p(a\imath) = ab \neq 0$, $a\imath$ is a simple pole. Similarly, since $q(b\imath) = 0$, $q'(b\imath) = 2a^2b\imath + 2b^3\imath - 4b^3\imath \neq 0$, and $p(b\imath) = ab \neq 0$, $b\imath$ is also a simple pole. Since both $a\imath$ and $b\imath$ are simple poles, the residues of $f(u)$ at $a\imath$ and $b\imath$ are

$$\begin{aligned} K_1 &= \frac{p(a\imath)}{q'(a\imath)} = \frac{b}{2\imath(b+a)(b-a)} \\ K_2 &= \frac{p(b\imath)}{q'(b\imath)} = \frac{a}{2\imath(a+b)(a-b)}. \end{aligned} \tag{164}$$

Consequently,

$$\begin{aligned} \int_C du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2} &= 2\pi\imath\left(K_1+K_2\right) \\ &= 2\pi\imath\left[\frac{b}{2\imath(b+a)(b-a)} + \frac{a}{2\imath(a+b)(a-b)}\right] \\ &= \pi\left[\frac{1}{(a+b)}\right], \end{aligned} \tag{165}$$

and therefore

$$\int_{-\infty}^{+\infty} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2} = \pi\left[\frac{1}{(a+b)}\right]. \tag{166}$$

If we let $u = \hbar\omega$, then $du = \hbar d\omega$, and

$$\begin{aligned} \frac{1}{\pi}\int_{-\infty}^{+\infty} du \frac{a}{a^2+u^2}\frac{b}{b^2+u^2} &= \left(\frac{\hbar}{\pi}\right)\int_{-\infty}^{+\infty} d\omega \frac{a}{a^2+\hbar^2\omega^2}\frac{b}{b^2+\hbar^2\omega^2} \\ &= \frac{1}{(a+b)}. \end{aligned} \tag{167}$$

Now, we must manipulate Eq. (167) so that it resembles Eq. (159). Because

$$\frac{a}{a^2+\hbar^2\omega^2} = \left[\frac{1}{2(a+\imath\hbar\omega)} + \frac{1}{2(a-\imath\hbar\omega)}\right] \tag{168}$$

and

$$\frac{b}{b^2+\hbar^2\omega^2}=\left[\frac{1}{2\left(b+\imath\hbar\omega\right)}+\frac{1}{2\left(b-\imath\hbar\omega\right)}\right] \tag{169}$$

we can write

$$\left(\frac{\hbar}{\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega\frac{a}{a^2+\hbar^2\omega^2}\frac{b}{b^2+\hbar^2\omega^2}=\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega$$

$$\times\left[\frac{1}{\left(a+\imath\hbar\omega\right)}+\frac{1}{\left(a-\imath\hbar\omega\right)}\right]\left[\frac{1}{\left(b+\imath\hbar\omega\right)}+\frac{1}{\left(b-\imath\hbar\omega\right)}\right]. \tag{170}$$

Letting $a=\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)$ and $b=\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}\right)$ in Eq. (170) and using Eq. (167), we have

$$\left(\frac{\hbar}{\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega\left[\frac{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)^2+\hbar^2\omega^2}\right]\left[\frac{\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}\right)}{\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}\right)^2+\hbar^2\omega^2}\right]$$

$$=\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega\left[\frac{1}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)}+\frac{1}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)}\right]$$

$$\times\left[\frac{1}{\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}+\imath\hbar\omega\right)}+\frac{1}{\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}-\imath\hbar\omega\right)}\right]$$

$$=\frac{1}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)+\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}\right)}, \tag{171}$$

which is essentially Eq. (159).

To complete the proof, we will evaluate $\int\limits_C du\left(a/\left(a^2+u^2\right)\right)\left(b/\left(b^2+u^2\right)\right)$ for the case with $a=b$. Then $f\left(u\right)$ is

$$f\left(u\right)=\frac{a}{\left(a^2+u^2\right)}\frac{a}{\left(a^2+u^2\right)}, \tag{172}$$

and the two singular points for $f\left(u\right)$ are $u=\pm a\imath$. However, $a\imath$ is the only singular point within contour C. Therefore, by the residue theorem, we have

$$\int\limits_C du\frac{a}{\left(a^2+u^2\right)}\frac{a}{\left(a^2+u^2\right)}=2\pi\imath K_1, \tag{173}$$

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where K_1 is the residue at the pole $u = a\imath$. If we let $p(u) = a^2$ and $q(u) = (a^2 + u^2)(a^2 + u^2) = a^4 + 2a^2u^2 + u^4$, where $f(u) = p(u)/q(u)$, we can determine whether $a\imath$ is a simple pole by evaluating $p(u)$, $q(u)$, and $q'(u) = 4a^2u + 4u^3$ at $a\imath$. Because $p(a\imath) = a^2$, $q(a\imath) = 0$ and $q'(a\imath) = 0$, $a\imath$ is not a simple pole. In order to determine the order of $a\imath$, we need to rewrite $f(u)$. Factoring and rewriting $f(u)$, we have

$$\begin{aligned} f(u) &= \frac{a^2}{(a^2+u^2)(a^2+u^2)} \\ &= \frac{a^2}{(u+a\imath)^2(u-a\imath)^2}, \end{aligned} \tag{174}$$

which indicates that $a\imath$ is a pole of order two. At this point, consider $q''(u)$. Since $q''(u) = 4a^2 + 12u^2$, $q''(a\imath) = -8a^2 \neq 0$. Then, because $p(a\imath) \neq 0$, $q(a\imath) = 0$, $q'(a\imath) = 0$, and $q''(a\imath) \neq 0$, we can determine the residue K_1 of $f(u)$ from

$$K_1 = 2\left[\frac{p'(a\imath)}{q''(a\imath)}\right] - \left(\frac{2}{3}\right)\left\{\frac{p(a\imath)\,q'''(a\imath)}{[q''(a\imath)]^2}\right\}. \tag{175}$$

From $q''(u) = 4a^2 + 12u^2$, we have that $q'''(u) = 24u$. Using $p(a\imath) = a^2$, $p'(u) = p'(a\imath) = 0$, $q'(a\imath) = 0$, $q''(a\imath) = -8a^2$, and $q'''(a\imath) = 24a\imath$ in Eq. (175) gives $K_1 = -\imath/4a$. Substituting the value of K_1 into Eq. (173), we have

$$\int\limits_C du \frac{a}{(a^2+u^2)} \frac{a}{(a^2+u^2)} = \frac{\pi}{2a}. \tag{176}$$

Using Eqs. (162) with $b = a$ and (176), we can write

$$\int\limits_{-\infty}^{+\infty} du \frac{a}{a^2+u^2} \frac{a}{a^2+u^2} = \frac{\pi}{2a}. \tag{177}$$

Letting $u = \hbar\omega$ and $du = \hbar d\omega$ in Eq. (177) and rearranging, we have

$$\left(\frac{\hbar}{\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega \frac{a}{a^2+\hbar\omega^2} \frac{a}{a^2+\hbar\omega^2} = \frac{1}{2a}. \tag{178}$$

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Finally, recalling that $a = b$, we can write

$$\left(\frac{\hbar}{\pi}\right) \int_{-\infty}^{+\infty} d\omega \frac{a}{a^2 + \hbar\omega^2} \frac{b}{b^2 + \hbar\omega^2} = \frac{1}{a+b}, \tag{179}$$

which completes our proof of Eq. (159).

Having completed the proof of Eq. (159), we are ready to continue developing the second-order correction to the interaction energy $\Delta E^{(2)}_{0_{AB}}$ of A and B. Using Eqs. (158) and (159), we have

$$\begin{aligned}
\Delta E^{(2)}_{0_{AB}} &= -T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\delta}\, \mu^{B0}_{\phi} \left(\frac{1}{2}\right) \alpha^{A}_{\gamma\epsilon} \\
&- \; T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{A0}_{\gamma}\, \mu^{A0}_{\epsilon} \left(\frac{1}{2}\right) \alpha^{B}_{\delta\phi} \\
&- \; T_{\gamma\delta}\, T_{\epsilon\phi} \sum_{j_A, r_B \neq 0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \langle 0_A|\hat{\mu}^{A}_{\gamma}|j_A\rangle \langle 0_B|\hat{\mu}^{B}_{\delta}|r_B\rangle \\
&\times \; \langle j_A|\hat{\mu}^{A}_{\epsilon}|0_A\rangle \langle r_B|\hat{\mu}^{B}_{\phi}|0_B\rangle \\
&\times \; \left[\frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)} + \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)}\right] \\
&\times \; \left[\frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} + \frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}\right] .
\end{aligned} \tag{180}$$

Let us consider the third term in Eq. (180). Rearranging the components of this term allows us to write

$$\begin{aligned}
&- \; T_{\gamma\delta}\, T_{\epsilon\phi} \sum_{j_A, r_B \neq 0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \langle 0_A|\hat{\mu}^{A}_{\gamma}|j_A\rangle \langle 0_B|\hat{\mu}^{B}_{\delta}|r_B\rangle \\
&\times \; \langle j_A|\hat{\mu}^{A}_{\epsilon}|0_A\rangle \langle r_B|\hat{\mu}^{B}_{\phi}|0_B\rangle \\
&\times \; \left[\frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)} + \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)}\right] \\
&\times \; \left[\frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} + \frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}\right]
\end{aligned}$$

$$
\begin{aligned}
&= -T_{\gamma\delta}\,T_{\epsilon\phi}\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega \sum_{j_A\neq 0} \\
&\times \left[\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}+\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}\right] \\
&\times \sum_{r_B\neq 0}\left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}+\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right].
\end{aligned}
\tag{181}
$$

Since $\hat{\mu}^A_\gamma$, $\hat{\mu}^A_\epsilon$, $\hat{\mu}^B_\delta$, and $\hat{\mu}^B_\phi$ are Hermitian and $|0_A\rangle$, $|0_B\rangle$, $|j_A\rangle$ and $|r_B\rangle$ are real, $\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle = \langle j_A|\hat{\mu}^A_\gamma|0_A\rangle$, $\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle = \langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle$, $\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle = \langle r_B|\hat{\mu}^B_\delta|0_B\rangle$, and $\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle = \langle r_B|\hat{\mu}^B_\phi|0_B\rangle$. Using these relationships in Eq. (181) gives

$$
\begin{aligned}
&- T_{\gamma\delta}\,T_{\epsilon\phi}\sum_{j_A,r_B\neq 0}\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega \langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle \\
&\times \langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle r_B|\hat{\mu}^B_\phi|0_B\rangle \\
&\times \left[\frac{1}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}+\frac{1}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}\right] \\
&\times \left[\frac{1}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}+\frac{1}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right] \\
&= -T_{\gamma\delta}\,T_{\epsilon\phi}\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega \sum_{j_A\neq 0} \\
&\left[\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}+\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}\right] \\
&\times \sum_{r_B\neq 0}\left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}+\frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right].
\end{aligned}
\tag{182}
$$

In order to complete our analysis of the second-order correction to the energy of interaction between A and B, we need to derive expressions for the frequency-dependent polarizabilities $\alpha^{A}_{\gamma\epsilon}(\omega)$ and $\alpha^{B}_{\delta\phi}(\omega)$ of molecules A and B. According to Orr and Ward,[61] the first-order polarization $\mathbf{P}^{\omega}$ of an isolated molecule in the presence of an applied field of frequency ω is

$$\mathbf{P}^{\omega} = \sum_{n \neq 0} \left[\frac{\langle 0|\hat{P}|n\rangle\langle n|\hat{H}'^{\omega}|0\rangle}{E_n^{(0)} - E_0^{(0)} - \hbar\omega} + \frac{\langle 0|\hat{H}'^{\omega}|n\rangle\langle n|\hat{P}|0\rangle}{E_n^{(0)} - E_0^{(0)} + \hbar\omega} \right], \tag{183}$$

if damping is neglected. In Eq. (183), $|n\rangle$ is an excited state and $|0\rangle$ is the ground state of the unperturbed molecule, with energies $E_n^{(0)}$ and $E_0^{(0)}$. Also, $\hat{P}$ is a polarization operator, and $\hat{H}'^{\omega}$ is the perturbation due to the applied field of frequency ω. If we let $\omega = \imath\omega$, $\hat{H}'^{\omega} = \hat{H}'^{A,\imath\omega} = -\hat{\mu}^{A}_{\epsilon} F^{A,\imath\omega}_{\epsilon}$ and $\hat{P} = \hat{\mu}^{A}_{\gamma}$, then

$$\begin{aligned} \langle \hat{\mu}^{A}_{\gamma} \rangle^{\imath\omega} &= F^{A,\imath\omega}_{\epsilon} \sum_{j_A \neq 0} \left[\frac{\langle 0_A|\hat{\mu}^{A}_{\gamma}|j_A\rangle\langle j_A|\hat{\mu}^{A}_{\epsilon}|0_A\rangle}{E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega} + \frac{\langle 0_A|\hat{\mu}^{A}_{\epsilon}|j_A\rangle\langle j_A|\hat{\mu}^{A}_{\gamma}|0_A\rangle}{E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega} \right] \\ &= F^{A,\imath\omega}_{\epsilon} \alpha^{A,\imath\omega}_{\gamma\epsilon} = F^{A,\imath\omega}_{\epsilon} \alpha^{A}_{\gamma\epsilon}(\imath\omega). \end{aligned} \tag{184}$$

In Eq. (184), we have also let $|0\rangle = |0_A\rangle$, $|n\rangle = |j_A\rangle$, $E_0^{(0)} = E^{(0)}_{0_A}$, and $E_n^{(0)} = E^{(0)}_{j_A}$. Similarly, if we let $\omega = \imath\omega$, $\hat{H}'^{\omega} = \hat{H}'^{B,\imath\omega} = -\hat{\mu}^{B}_{\phi} F^{B,\imath\omega}_{\phi}$ and $\hat{P} = \hat{\mu}^{B}_{\delta}$, then

$$\begin{aligned} \langle \hat{\mu}^{B}_{\delta} \rangle^{\imath\omega} &= F^{B,\imath\omega}_{\phi} \sum_{r_B \neq 0} \left[\frac{\langle 0_B|\hat{\mu}^{B}_{\delta}|r_B\rangle\langle r_B|\hat{\mu}^{B}_{\phi}|0_B\rangle}{E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega} + \frac{\langle 0_B|\hat{\mu}^{B}_{\phi}|r_B\rangle\langle r_B|\hat{\mu}^{B}_{\delta}|0_B\rangle}{E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega} \right] \\ &= F^{B,\imath\omega}_{\phi} \alpha^{B,\imath\omega}_{\delta\phi} = F^{B,\imath\omega}_{\phi} \alpha^{B}_{\delta\phi}(\imath\omega), \end{aligned} \tag{185}$$

with $|0\rangle = |0_B\rangle$, $|n\rangle = |r_B\rangle$, $E_0^{(0)} = E^{(0)}_{0_B}$, and $E_n^{(0)} = E^{(0)}_{r_B}$. Therefore, according to Eqs. (184) and (185),

$$\begin{aligned} \alpha^{A}_{\gamma\epsilon}(\imath\omega) &= \sum_{j_A \neq 0} \left[\frac{\langle 0_A|\hat{\mu}^{A}_{\gamma}|j_A\rangle\langle j_A|\hat{\mu}^{A}_{\epsilon}|0_A\rangle}{E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega} \right. \\ &\quad \left. + \frac{\langle 0_A|\hat{\mu}^{A}_{\epsilon}|j_A\rangle\langle j_A|\hat{\mu}^{A}_{\gamma}|0_A\rangle}{E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega} \right], \end{aligned} \tag{186}$$

and

$$\begin{aligned} \alpha^B_{\delta\phi}(\imath\omega) &= \sum_{r_B\neq 0}\left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\phi|0_B\rangle}{E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega}\right. \\ &\left. + \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega}\right]. \end{aligned} \tag{187}$$

Using Eqs. (186) and (187) in Eq. (182), we have

$$\begin{aligned} &- T_{\gamma\delta}T_{\epsilon\phi}\sum_{j_A,r_B\neq 0}\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle \\ &\times \langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle r_B|\hat{\mu}^B_\phi|0_B\rangle \\ &\times \left[\frac{1}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}+\frac{1}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}\right] \\ &\times \left[\frac{1}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}+\frac{1}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right] \\ &= -T_{\gamma\delta}T_{\epsilon\phi}\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega\,\alpha^A_{\gamma\epsilon}(\imath\omega)\,\alpha^B_{\delta\phi}(\imath\omega). \end{aligned} \tag{188}$$

Finally, using Eqs. (180) and (188), we can write $\Delta E^{(2)}_{0_{AB}}$ as

$$\begin{aligned} \Delta E^{(2)}_{0_{AB}} = &- T_{\gamma\delta}T_{\epsilon\phi}\,\mu^{B0}_\delta\,\mu^{B0}_\phi\left(\frac{1}{2}\right)\alpha^A_{\gamma\epsilon} \\ &- T_{\gamma\delta}T_{\epsilon\phi}\,\mu^{A0}_\gamma\,\mu^{A0}_\epsilon\left(\frac{1}{2}\right)\alpha^B_{\delta\phi} \\ &- T_{\gamma\delta}T_{\epsilon\phi}\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega\,\alpha^A_{\gamma\epsilon}(\imath\omega)\,\alpha^B_{\delta\phi}(\imath\omega). \end{aligned} \tag{189}$$

The first two terms in $\Delta E^{(2)}_{0_{AB}}$ give the induction energy due to the polarization of each molecule by the field of the permanent dipole of the other (within linear response, and neglecting effects due to the non-uniformity of the field). The third term gives the dispersion energy.

4 The Third-Order Correction to the Energy of Two Weakly Interacting Molecules

In this chapter, the third-order interaction energy of a pair of moleculesis derived within the polarization approximation. Results for the induction, hyperpolarization, and induction-dispersion energies agree with earlier work, but the third-order dispersion energy is derived in a new form, as an integral of nonlinear response tensors over imaginary frequencies.

4.1 Non-Zero Contributions to $\Delta E^{(3)}_{0_{AB}}$

Again, we consider two molecules A and B, separated by a distance $\mathbf{R}$ such that the overlap between their electronic charge distributions can be ignored. The third-order correction to the energy of interaction between the two molecules is

$$\Delta E^{(3)}_{0_{AB}} = \langle \Psi^{(0)}_{0_{AB}} | \hat{V}^{AB} \, G \, \hat{\bar{V}}^{AB} \, G \, \hat{V}^{AB} | \Psi^{(0)}_{0_{AB}} \rangle, \tag{190}$$

where $|\Psi^{(0)}_{0_{AB}}$ denotes the ground-state wavefunction of the unperturbed system, which we approximate by the product of the ground-state wavefunctions $\Psi^{(0)}_{0_A}$ and $\Psi^{(0)}_{0_B}$ of molecules A and B. In Eq. (190), $\hat{V}^{AB}$ is the interaction potential, $\hat{\bar{V}}^{AB}$ is defined by

$$\hat{\bar{V}}^{AB} = \hat{V}^{AB} - \langle \Psi^{(0)}_{0_{AB}} | \hat{V}^{AB} | \Psi^{(0)}_{0_{AB}} \rangle, \tag{191}$$

and G is the reduced resolvent, given by Eq. (19) in Chap. 1. We split G into a sum of three terms, one with excitation in molecule A only (G^{A}), one with excitations in molecule B only (G^{B}), and one with excitations in both A and B ($G^{A\oplus B}$), as in Eqs. (145) - (147) of Chap. 3. Here we consider only the dipole-dipole contribution to the interaction potential, which was given in Eq. (148) of Chap. 3. We also have

$$\hat{\bar{V}}^{AB} = -\hat{\mu}^{A}_{\alpha} \, T_{\alpha\beta} \, \hat{\mu}^{B}_{\beta} + \langle \Psi^{(0)}_{0_A} \, \Psi^{(0)}_{0_B} | \hat{\mu}^{A}_{\alpha} \, T_{\alpha\beta} \, \hat{\mu}^{B}_{\beta} | \Psi^{(0)}_{0_A} \, \Psi^{(0)}_{0_B} \rangle. \tag{192}$$

Furthermore, since

$$\langle \Psi^{(0)}_{0_A} \, \Psi^{(0)}_{0_B} | \hat{\mu}^{A}_{\alpha} \, T_{\alpha\beta} \, \hat{\mu}^{B}_{\beta} | \Psi^{(0)}_{0_A} \, \Psi^{(0)}_{0_B} \rangle = T_{\alpha\beta} \, \mu^{A0}_{\alpha} \, \mu^{B0}_{\beta}, \tag{193}$$

then

$$\hat{\bar{V}}^{AB} = -\hat{\mu}^{A}_{\alpha} \, T_{\alpha\beta} \, \hat{\mu}^{B}_{\beta} + T_{\alpha\beta} \, \mu^{A0}_{\alpha} \, \mu^{B0}_{\beta}. \tag{194}$$

In Eq. (194), μ_α^{A0} and μ_β^{B0} are the permanent dipole moments of molecules A and B in the α and β directions, where the total permanent dipole moments μ^{A0} and μ^{B0} of molecules A and B are

$$\begin{aligned} \mu^{A0} &= \mu_x^{A0}\hat{\mathbf{x}} + \mu_y^{A0}\hat{\mathbf{y}} + \mu_z^{A0}\hat{\mathbf{z}} \\ \mu^{B0} &= \mu_x^{B0}\hat{\mathbf{x}} + \mu_y^{B0}\hat{\mathbf{y}} + \mu_z^{B0}\hat{\mathbf{z}} \end{aligned} \qquad (195)$$

and $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are unit vectors in the x,y and z directions. If we define $\hat{\overline{\mu}}_\alpha^A = \hat{\mu}_\alpha^A - \mu_\alpha^{A0}$ and $\hat{\overline{\mu}}_\beta^B = \hat{\mu}_\beta^B - \mu_\beta^{B0}$,

$$\hat{\overline{V}}^{AB} = -\overline{\mu}_\alpha^A T_{\alpha\beta} \overline{\mu}_\beta^B - \overline{\mu}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} - \mu_\alpha^{A0} T_{\alpha\beta} \overline{\mu}_\beta^B . \qquad (196)$$

Using Eqs. (144) - (147) from Chap. 3 for G and Eq. (196) for $\hat{\overline{V}}^{AB}$, we transform Eq. (190) into a sum of 27 terms, 15 of which are nonzero. Table 1 contains a list of the non-zero terms and the order of μ_{A0} and μ_{B0} in each of those terms.

4.2 Higher-Order Induction: Terms of First-Order in Both μ^{A0} and μ^{B0}

The static polarizability $\alpha_{\epsilon\delta}^A$ of molecule A is

$$\alpha_{\epsilon\delta}^A = \sum_{k_A \neq 0} \frac{\langle 0_A|\hat{\mu}_\epsilon^A|k_A\rangle\langle k_A|\hat{\mu_\delta}^A|0_A\rangle}{E_{k_A}^{(0)} - E_{0_A}^{(0)}} + \sum_{k_A \neq 0} \frac{\langle 0_A|\hat{\mu}_\delta^A|k_A\rangle\langle k_A|\hat{\mu_\epsilon}^A|0_A\rangle}{E_{k_A}^{(0)} - E_{0_A}^{(0)}}, \quad (197)$$

where $|k_A\rangle = \Psi_{k_A}^{(0)}$ is the k^{th} excited state of molecule A. Similarly, for molecule B,

$$\alpha_{\gamma\beta}^B = \sum_{t_B \neq 0} \frac{\langle 0_B|\hat{\mu}_\gamma^B|t_B\rangle\langle t_B|\hat{\mu_\beta}^B|0_B\rangle}{E_{t_B}^{(0)} - E_{0_B}^{(0)}} + \sum_{t_B \neq 0} \frac{\langle 0_B|\hat{\mu}_\beta^B|t_B\rangle\langle t_B|\hat{\mu_\gamma}^B|0_B\rangle}{E_{t_B}^{(0)} - E_{0_B}^{(0)}}, \quad (198)$$

where $|t_B\rangle$ denotes the t^{th} unperturbed excited state of B; then $\alpha_{\epsilon\delta}^A\,\alpha_{\gamma\beta}^B$ is

$$\begin{aligned} \alpha_{\epsilon\delta}^A\,\alpha_{\gamma\beta}^B &= \sum_{k_A, t_B \neq 0} \frac{1}{\left(E_{k_A}^{(0)} - E_{0_A}^{(0)}\right)\left(E_{t_B}^{(0)} - E_{0_B}^{(0)}\right)} \\ &\times \left[\langle 0_A|\hat{\mu}_\epsilon^A|k_A\rangle\langle k_A|\hat{\mu}_\delta^A|0_A\rangle\langle 0_B|\hat{\mu}_\gamma^B|t_B\rangle\langle t_B|\hat{\mu}_\beta^B|0_B\rangle\right. \\ &+ \langle 0_A|\hat{\mu}_\epsilon^A|k_A\rangle\langle k_A|\hat{\mu}_\delta^A|0_A\rangle\langle 0_B|\hat{\mu}_\beta^B|t_B\rangle\langle t_B|\hat{\mu}_\gamma^B|0_B\rangle \\ &+ \langle 0_A|\hat{\mu}_\delta^A|k_A\rangle\langle k_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_B|\hat{\mu}_\gamma^B|t_B\rangle\langle t_B|\hat{\mu}_\beta^B|0_B\rangle \\ &+ \left.\langle 0_A|\hat{\mu}_\delta^A|k_A\rangle\langle k_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_B|\hat{\mu}_\beta^B|t_B\rangle\langle t_B|\hat{\mu}_\gamma^B|0_B\rangle\right] . \quad (199) \end{aligned}$$

Now, let us evaluate each of the $(1,1)$ terms listed in Table 1. From Eq. (148) for the left-hand perturbation operator $\hat{V}^{AB}$, $\hat{V}^{AB} = -\hat{\mu}^A_\epsilon \, T_{\epsilon\phi} \, \hat{\mu}^B_\phi$, and Eqs. (145), (146), and (147) from Chap. 3, the $(1,1)$ terms 1, 4, 5, 7, 12, and 14 are

$$
\begin{aligned}
&- \ \langle 0_A 0_B | \hat{V}^{AB} \, G^A \, \hat{\bar{\mu}}^A_\alpha \, T_{\alpha\beta} \, \hat{\bar{\mu}}^B_\beta \, G^B \, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- \ \sum_{j_A, r_B \neq 0} T_{\alpha\beta} \, T_{\gamma\delta} \, T_{\epsilon\phi} \, \mu^{B0}_\delta \, \mu^{A0}_\epsilon \\
&\times \ \frac{\langle 0_A | \hat{\mu}^A_\gamma | j_A \rangle \langle j_A | \hat{\mu}^A_\alpha | 0_A \rangle \langle 0_B | \hat{\mu}^B_\beta | r_B \rangle \langle r_B | \hat{\mu}^B_\phi | 0_B \rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} \right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} \right)},
\end{aligned}
\tag{200}
$$

$$
\begin{aligned}
&- \ \langle 0_A 0_B | \hat{V}^{AB} \, G^A \, \mu^{A0}_\alpha \, T_{\alpha\beta} \, \hat{\bar{\mu}}^B_\beta \, G^{A \oplus B} \, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- \ \sum_{j_A, r_B \neq 0} T_{\alpha\beta} \, T_{\gamma\delta} \, T_{\epsilon\phi} \, \mu^{A0}_\alpha \, \mu^{B0}_\delta \\
&\times \ \frac{\langle 0_B | \hat{\mu}^B_\beta | r_B \rangle \langle r_B | \hat{\mu}^B_\phi | 0_B \rangle \langle 0_A | \hat{\mu}^A_\gamma | j_A \rangle \langle j_A | \hat{\mu}^A_\epsilon | 0_A \rangle}{\left[\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} \right) + \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} \right) \right] \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} \right)},
\end{aligned}
\tag{201}
$$

$$
\begin{aligned}
&- \ \langle 0_A 0_B | \hat{V}^{AB} \, G^B \, \hat{\bar{\mu}}^A_\alpha \, T_{\alpha\beta} \, \hat{\bar{\mu}}^B_\beta \, G^A \, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- \ \sum_{r_B, j_A \neq 0} T_{\alpha\beta} \, T_{\gamma\delta} \, T_{\epsilon\phi} \, \mu^{A0}_\gamma \, \mu^{B0}_\phi \\
&\times \ \frac{\langle 0_B | \hat{\mu}^B_\delta | r_B \rangle \langle r_B | \hat{\mu}^B_\beta | 0_B \rangle \langle 0_A | \hat{\mu}^A_\alpha | j_A \rangle \langle j_A | \hat{\mu}^A_\epsilon | 0_A \rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} \right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} \right)},
\end{aligned}
\tag{202}
$$

$$
\begin{aligned}
&- \ \langle 0_A 0_B | \hat{V}^{AB} \, G^B \, \hat{\bar{\mu}}^A_\alpha \, T_{\alpha\beta} \, \mu^{B0}_\beta \, G^{A \oplus B} \, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- \ \sum_{r_B, j_A \neq 0} T_{\alpha\beta} \, T_{\gamma\delta} \, T_{\epsilon\phi} \, \mu^{B0}_\beta \, \mu^{A0}_\gamma \\
&\times \ \frac{\langle 0_B | \hat{\mu}^B_\delta | r_B \rangle \langle r_B | \hat{\mu}^B_\phi | 0_B \rangle \langle 0_A | \hat{\mu}^A_\alpha | j_A \rangle \langle j_A | \hat{\mu}^A_\epsilon | 0_A \rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} \right) \left[\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} \right) + \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} \right) \right]},
\end{aligned}
\tag{203}
$$

$$
\begin{aligned}
&- \ \langle 0_A 0_B | \hat{V}^{AB} \, G^{A \oplus B} \, \hat{\bar{\mu}}^A_\alpha \, T_{\alpha\beta} \, \mu^{B0}_\beta \, G^B \, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- \ \sum_{j_A, r_B \neq 0} T_{\alpha\beta} \, T_{\gamma\delta} \, T_{\epsilon\phi} \, \mu^{B0}_\beta \, \mu^{A0}_\epsilon
\end{aligned}
$$

$$\times \quad \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\phi|0_B\rangle}{\left[\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)+\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\right]\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)}, \tag{204}$$

and

$$\begin{aligned} &- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \mu^{A0}_\alpha\, T_{\alpha\beta}\hat{\bar{\mu}}^B_\beta\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle = \\ &- \sum_{j_A, r_B \neq 0} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{A0}_\alpha\, \mu^{B0}_\phi \\ &\times \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left[\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)+\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\right]}. \end{aligned} \tag{205}$$

Since α, β, γ, δ, ϵ, and ϕ are dummy variables, we can rename them. If we convert ϵ to α , ϕ to β, β to γ, δ to ϕ, γ to ϵ, and α to δ , term 1 from Eq. (200) becomes

$$\begin{aligned} &- \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle = \\ &- \sum_{j_A, r_B \neq 0} T_{\delta\gamma}\, T_{\epsilon\phi}\, T_{\alpha\beta}\, \mu^{B0}_\phi\, \mu^{A0}_\alpha \\ &\times \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\mu}^A_\delta|0_A\rangle\langle 0_B|\hat{\mu}^B_\gamma|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)}. \end{aligned} \tag{206}$$

In term 4 from Eq. (201), we convert δ to ϕ, γ to ϵ, ϵ to δ , and ϕ to γ to give

$$\begin{aligned} &- \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \mu^{A0}_\alpha\, T_{\alpha\beta}\hat{\bar{\mu}}^B_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\ &- \sum_{j_A, r_B \neq 0} T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\delta\gamma}\, \mu^{A0}_\alpha\, \mu^{B0}_\phi \\ &\times \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\gamma|0_B\rangle\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\mu}^A_\delta|0_A\rangle}{\left[\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)+\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\right]\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)}. \end{aligned} \tag{207}$$

Similarly, in term 5 from Eq. (202), we convert γ to α, δ to β, β to γ, and α to δ which gives

$$\begin{aligned} &- \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle = \\ &- \sum_{r_B, j_A \neq 0} T_{\delta\gamma}\, T_{\alpha\beta}\, T_{\epsilon\phi}\, \mu^{A0}_\alpha\, \mu^{B0}_\phi \end{aligned}$$

$$\times \quad \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\gamma|0_B\rangle\langle 0_A|\hat{\mu}^A_\delta|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)}. \tag{208}$$

When we convert γ to α, δ to β, ϕ to γ, β to ϕ, α to ϵ, and ϵ to δ in term 7 from Eq. (203) we have

$$\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \mu^{B0}_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \sum_{r_B, j_A \neq 0} T_{\epsilon\phi}\, T_{\alpha\beta}\, T_{\delta\gamma}\, \mu^{B0}_\phi\, \mu^{A0}_\alpha \\
&\times \quad \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\gamma|0_B\rangle\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\mu}^A_\delta|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left[\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)+\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\right]}.
\end{aligned} \tag{209}$$

In term 12 from Eq. (204) we convert ϵ to α, ϕ to β, δ to γ, β to ϕ, α to ϵ and γ to δ, so that this term becomes

$$\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \mu^{B0}_\beta\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \sum_{j_A, r_B \neq 0} T_{\epsilon\phi}\, T_{\delta\gamma}\, T_{\alpha\beta}\, \mu^{B0}_\phi\, \mu^{A0}_\alpha \\
&\times \quad \frac{\langle 0_A|\hat{\mu}^A_\delta|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\gamma|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left[\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)+\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\right]\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)}.
\end{aligned} \tag{210}$$

Finally, in term 14 from Eq. (205), interchanging δ and γ gives

$$\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \mu^{A0}_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \sum_{j_A, r_B \neq 0} T_{\alpha\beta}\, T_{\delta\gamma}\, T_{\epsilon\phi}\, \mu^{A0}_\alpha\, \mu^{B0}_\phi \\
&\times \quad \frac{\langle 0_A|\hat{\mu}^A_\delta|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\gamma|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left[\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)+\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\right]}.
\end{aligned} \tag{211}$$

If we add terms 4 and 7 as specified by Eqs. (207) and (209), we have

$$\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \mu^{A0}_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^B \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \mu^{B0}_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \sum_{j_A, r_B \neq 0} T_{\alpha\beta}\, T_{\delta\gamma}\, T_{\epsilon\phi}\, \mu^{A0}_\alpha\, \mu^{B0}_\phi
\end{aligned}$$

$$\times \; \frac{\langle 0_B|\hat{\mu}_\beta^B|r_B\rangle\langle r_B|\hat{\mu}_\gamma^B|0_B\rangle\langle 0_A|\hat{\mu}_\epsilon^A|j_A\rangle\langle j_A|\hat{\mu}_\delta^A|0_A\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)}. \tag{212}$$

Also, adding terms 12 and 14 from Eqs. (210) and (211)) gives

$$\begin{aligned} &- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}_\alpha^A\, T_{\alpha\beta}\, \mu_\beta^{B0}\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle \\ &- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \mu_\alpha^{A0}\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle = \\ &- \sum_{j_A, r_B \neq 0} T_{\alpha\beta}\, T_{\delta\gamma}\, T_{\epsilon\phi}\, \mu_\alpha^{A0}\, \mu_\phi^{B0} \\ &\times \frac{\langle 0_A|\hat{\mu}_\delta^A|j_A\rangle\langle j_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_B|\hat{\mu}_\gamma^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)}. \end{aligned} \tag{213}$$

If we replace k_A and t_B with j_A and r_B in Eq. (199) and then use Eqs. (199), (206), (208), (212), and (213), we can replace the sum of terms 1, 4, 5, 7, 12, and 14 with

$$S_1 = -T_{\alpha\beta}\, T_{\delta\gamma}\, T_{\epsilon\phi}\, \mu_\alpha^{A0}\, \mu_\phi^{B0}\, \alpha_{\epsilon\delta}^A\, \alpha_{\gamma\beta}^B. \tag{214}$$

Physically, this sum represents a higher-order induction effect: The permanent dipole of molecule A sets up a field that polarizes molecule B, producing a reaction field that acts back on molecule A. Molecule A is polarized by the reaction field due to B; the polarization of A creates a field acting on B, which alters the energy of the pair due to the permanent dipole of B (and similarly, with the roles of A and B interchanged).

4.3 Hyperpolarization: Terms of Third-Order in μ^{B0} or μ^{A0}

The static hyperpolarizability $\beta_{\gamma\alpha\epsilon}$ of molecule A is

$$\begin{aligned} \beta_{\gamma\alpha\epsilon}^A \; = \; & \sum_{k_A, l_A \neq 0} \frac{1}{\left(E_{k_A}^{(0)} - E_{0_A}^{(0)}\right)\left(E_{l_A}^{(0)} - E_{0_A}^{(0)}\right)} \\ \times \; & \Big[\langle 0_A|\hat{\mu}_\gamma^A|k_A\rangle\langle k_A|\hat{\bar{\mu}}_\alpha^A|l_A\rangle\langle l_A|\hat{\mu}_\epsilon^A|0_A\rangle \\ + \; & \langle 0_A|\hat{\mu}_\alpha^A|k_A\rangle\langle k_A|\hat{\bar{\mu}}_\gamma^A|l_A\rangle\langle l_A|\hat{\mu}_\epsilon^A|0_A\rangle \\ + \; & \langle 0_A|\hat{\mu}_\alpha^A|k_A\rangle\langle k_A|\hat{\bar{\mu}}_\epsilon^A|l_A\rangle\langle l_A|\hat{\mu}_\gamma^A|0_A\rangle \\ + \; & \langle 0_A|\hat{\mu}_\gamma^A|k_A\rangle\langle k_A|\hat{\bar{\mu}}_\epsilon^A|l_A\rangle\langle l_A|\hat{\mu}_\alpha^A|0_A\rangle \end{aligned}$$

$$
\begin{aligned}
&+ \quad \langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\gamma|l_A\rangle\langle l_A|\hat{\mu}^A_\alpha|0_A\rangle \\
&+ \quad \langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|l_A\rangle\langle l_A|\hat{\mu}^A_\gamma|0_A\rangle\Big]\,,
\end{aligned}
\tag{215}
$$

where $|k_A\rangle$ and $|l_A\rangle$ are the k^{th} and l^{th} unperturbed excited states of molecule A, and $E^{(0)}_{k_A}$ and $E^{(0)}_{l_A}$ are the corresponding energies. Now, consider term 3 in Table 1. When we evaluate term 3, we have

$$
\begin{aligned}
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \mu^{B0}_\beta\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \quad T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_\beta\, \mu^{B0}_\delta\, \mu^{B0}_\phi \\
&\times \sum_{j_A, q_A \neq 0} \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)}.
\end{aligned}
\tag{216}
$$

If we convert α to γ, γ to α, β to δ , and δ to β in Eq. (216), we have

$$
\begin{aligned}
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\gamma\, T_{\gamma\delta}\, \mu^{B0}_\delta\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \quad T_{\gamma\delta}\, T_{\alpha\beta}\, T_{\epsilon\phi}\, \mu^{B0}_\delta\, \mu^{B0}_\beta\, \mu^{B0}_\phi \\
&\times \sum_{j_A, q_A \neq 0} \frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)}.
\end{aligned}
\tag{217}
$$

Converting γ to ϵ, ϵ to γ, δ to ϕ , and ϕ to δ in Eq. (217) gives

$$
\begin{aligned}
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \mu^{B0}_\beta\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \quad T_{\epsilon\phi}\, T_{\alpha\beta}\, T_{\gamma\delta}\, \mu^{B0}_\phi\, \mu^{B0}_\beta\, \mu^{B0}_\delta \\
&\times \sum_{j_A, q_A \neq 0} \frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)}.
\end{aligned}
\tag{218}
$$

If we convert α to γ, γ to α, β to δ , and δ to β in Eq. (218), we have

$$
\begin{aligned}
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\gamma\, T_{\gamma\delta}\, \mu^{B0}_\delta\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \quad T_{\epsilon\phi}\, T_{\gamma\delta}\, T_{\alpha\beta}\, \mu^{B0}_\phi\, \mu^{B0}_\delta\, \mu^{B0}_\beta \\
&\times \sum_{j_A, q_A \neq 0} \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)}.
\end{aligned}
\tag{219}
$$

Converting ϵ to γ, γ to ϵ, δ to ϕ , and ϕ to δ in Eq. (219) gives

$$\begin{aligned}
&- \quad \langle 0_A 0_B | \hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\epsilon\, T_{\epsilon\phi}\, \mu^{B0}_\phi\, G^A\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- \quad T_{\gamma\delta}\, T_{\epsilon\phi}\, T_{\alpha\beta}\, \mu^{B0}_\delta\, \mu^{B0}_\phi\, \mu^{B0}_\beta \\
&\times \sum_{j_A, q_A \neq 0} \frac{\langle 0_A | \hat{\mu}^A_\epsilon | j_A \rangle \langle j_A | \hat{\bar{\mu}}^A_\gamma | q_A \rangle \langle q_A | \hat{\mu}^A_\alpha | 0_A \rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)};
\end{aligned} \tag{220}$$

also, converting α to γ, γ to α, β to δ and δ to β in Eq. (220), we have

$$\begin{aligned}
&- \quad \langle 0_A 0_B | \hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\epsilon\, T_{\epsilon\phi}\, \mu^{B0}_\phi\, G^A\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- \quad T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu^{B0}_\beta\, \mu^{B0}_\phi\, \mu^{B0}_\delta \\
&\times \sum_{j_A, q_A \neq 0} \frac{\langle 0_A | \hat{\mu}^A_\epsilon | j_A \rangle \langle j_A | \hat{\bar{\mu}}^A_\alpha | q_A \rangle \langle q_A | \hat{\mu}^A_\gamma | 0_A \rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)}.
\end{aligned} \tag{221}$$

If we multiply Eqs. (216) - (221) by 1/6, sum the results, and use Eq. (215), the result is

$$\begin{aligned}
-\langle 0_A 0_B | \hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \mu^{B0}_\beta\, G^A\, \hat{V}^{AB} | 0_A 0_B \rangle = -\frac{1}{6} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \quad \times \\
\mu^{B0}_\beta\, \mu^{B0}_\delta\, \mu^{B0}_\phi\, \beta^A_{\gamma\alpha\epsilon},
\end{aligned} \tag{222}$$

where we have replaced $|k_A\rangle$, $|l_A\rangle$, $E^{(0)}_{k_A}$ and $E^{(0)}_{l_A}$ in (215) with $|j_A\rangle$, $|q_A\rangle$, $E^{(0)}_{j_A}$ and $E^{(0)}_{q_A}$. Physically, Eq. (222) represents the change in energy due to the hyperpolarization of molecule A by the field from the permanent dipole of molecule B. A similar analysis allows us to write term 8 in terms of the static hyperpolarizability $\beta^B_{\delta\beta\phi}$ of molecule B. The static hyperpolarizability $\beta^B_{\delta\beta\phi}$ of molecule B is

$$\begin{aligned}
\beta^B_{\delta\beta\phi} \;=\; & \sum_{t_B, u_B \neq 0} \frac{1}{\left(E^{(0)}_{t_B} - E^{(0)}_{0_B}\right)\left(E^{(0)}_{u_B} - E^{(0)}_{0_B}\right)} \\
\times \; & \Big[\langle 0_B | \hat{\mu}^B_\delta | t_B \rangle \langle t_B | \hat{\bar{\mu}}^B_\beta | u_B \rangle \langle u_B | \hat{\mu}^B_\phi | 0_B \rangle \\
+ \; & \langle 0_B | \hat{\mu}^B_\beta | t_B \rangle \langle t_B | \hat{\bar{\mu}}^B_\delta | u_B \rangle \langle u_B | \hat{\mu}^B_\phi | 0_B \rangle \\
+ \; & \langle 0_B | \hat{\mu}^B_\beta | t_B \rangle \langle t_B | \hat{\bar{\mu}}^B_\phi | u_B \rangle \langle u_B | \hat{\mu}^B_\delta | 0_B \rangle \\
+ \; & \langle 0_B | \hat{\mu}^B_\delta | t_B \rangle \langle t_B | \hat{\bar{\mu}}^B_\phi | u_B \rangle \langle u_B | \hat{\mu}^B_\beta | 0_B \rangle \\
+ \; & \langle 0_B | \hat{\mu}^B_\phi | t_B \rangle \langle t_B | \hat{\bar{\mu}}^B_\delta | u_B \rangle \langle u_B | \hat{\mu}^B_\beta | 0_B \rangle \\
+ \; & \langle 0_B | \hat{\mu}^B_\phi | t_B \rangle \langle t_B | \hat{\bar{\mu}}^B_\beta | u_B \rangle \langle u_B | \hat{\mu}^B_\delta | 0_B \rangle \Big].
\end{aligned} \tag{223}$$

In Eq. (223), $|t_B\rangle$ and $|u_B\rangle$ are the t^{th} and u^{th} unperturbed excited states of molecule B with energies $E^{(0)}_{t_B}$ and $E^{(0)}_{u_B}$. When term 8 is evaluated, the result is

$$\begin{aligned}
&- \ \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \mu^{A0}_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \ T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\mu^{A0}_\alpha\, \mu^{A0}_\gamma\, \mu^{A0}_\epsilon \\
&\times \sum_{r_B, s_B \neq 0} \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B}\right)}.
\end{aligned} \tag{224}$$

When we convert δ to β, β to δ, α to γ, and γ to α, Eq. (224) becomes

$$\begin{aligned}
&- \ \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \mu^{A0}_\gamma\, T_{\gamma\delta}\, \hat{\bar{\mu}}^B_\delta\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \ T_{\gamma\delta}\, T_{\alpha\beta}\, T_{\epsilon\phi}\, \mu^{A0}_\gamma\, \mu^{A0}_\alpha\, \mu^{A0}_\epsilon \\
&\times \sum_{r_B, s_B \neq 0} \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B}\right)}.
\end{aligned} \tag{225}$$

Converting ϕ to δ, δ to ϕ, ϵ to γ, and γ to ϵ in Eq. (225) gives

$$\begin{aligned}
&- \ \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \mu^{A0}_\epsilon\, T_{\epsilon\phi}\, \hat{\bar{\mu}}^B_\phi\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \ T_{\epsilon\phi}\, T_{\alpha\beta}\, T_{\gamma\delta}\, \mu^{A0}_\epsilon\, \mu^{A0}_\alpha\, \mu^{A0}_\gamma \\
&\times \sum_{r_B, s_B \neq 0} \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B}\right)}.
\end{aligned} \tag{226}$$

If we set β to δ, δ to β, α to γ, and γ to α in Eq. (226), we have

$$\begin{aligned}
&- \ \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \mu^{A0}_\epsilon\, T_{\epsilon\phi}\, \hat{\bar{\mu}}^B_\phi\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \ T_{\epsilon\phi}\, T_{\gamma\delta}\, T_{\alpha\beta}\, \mu^{A0}_\epsilon\, \mu^{A0}_\gamma\, \mu^{A0}_\alpha \\
&\times \sum_{r_B, s_B \neq 0} \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B}\right)},
\end{aligned} \tag{227}$$

and, converting ϕ to δ, δ to ϕ, ϵ to γ, and γ to ϵ in Eq. (227) gives

$$\begin{aligned}
&- \ \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \mu^{A0}_\gamma\, T_{\gamma\delta}\, \hat{\bar{\mu}}^B_\delta\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \ T_{\gamma\delta}\, T_{\epsilon\phi}\, T_{\alpha\beta}\, \mu^{A0}_\gamma\, \mu^{A0}_\epsilon\, \mu^{A0}_\alpha \\
&\times \sum_{r_B, s_B \neq 0} \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B}\right)}.
\end{aligned} \tag{228}$$

Finally, if we convert β to δ, δ to β, α to γ, and γ to α in Eq. (228), the result is

$$\begin{aligned} - &\ \langle 0_A 0_B | \hat{V}^{AB}\, G^B\, \mu_\alpha^{A0}\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^B\, \hat{V}^{AB} | 0_A 0_B \rangle = \\ - &\ T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu_\alpha^{A0}\, \mu_\epsilon^{A0}\, \mu_\gamma^{A0} \\ \times &\ \sum_{r_B, s_B \neq 0} \frac{\langle 0_B | \hat{\mu}_\phi^B | r_B \rangle \langle r_B | \hat{\bar{\mu}}_\beta^B | s_B \rangle \langle s_B | \hat{\mu}_\delta^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)}. \end{aligned} \tag{229}$$

If we multiply Eqs. (224) - (229) by 1/6 and sum, the result is

$$\begin{aligned} - &\ \langle 0_A 0_B | \hat{V}^{AB}\, G^B\, \mu_\alpha^{A0}\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^B\, \hat{V}^{AB} | 0_A 0_B \rangle = \\ - &\ \frac{1}{6} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \mu_\alpha^{A0}\, \mu_\gamma^{A0}\, \mu_\epsilon^{A0}\, \beta_{\delta\beta\phi}^B, \end{aligned} \tag{230}$$

where we have replaced t_B, u_B, $E_{t_B}^{(0)}$ and $E_{u_B}^{(0)}$ in Eq. (223) with r_B, s_B, $E_{r_B}^{(0)}$ and $E_{s_B}^{(0)}$. Eq. (230) gives the energy change due to the hyperpolarization of molecule B by the field from the permanent dipole of molecule A.

4.4 Induction-Dispersion: Terms of First-Order in μ^{A0} or μ^{B0}

We are now ready to determine the contribution to $\Delta E_{0_{AB}}^{(3)}$ from terms listed in Table 1. When term 2 in Table 1 is evaluated, the result is

$$\begin{aligned} - &\ \langle 0_A 0_B | \hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}_\alpha^A\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^{A \oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_\delta^{B0} \\ \times &\ \sum_{j_A, q_A, r_B \neq 0} \langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle \\ \times &\ \frac{\langle 0_B | \hat{\mu}_\beta^B | r_B \rangle \langle r_B | \hat{\mu}_\phi^B | 0_B \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right)\left[\left(E_{q_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\right]}. \end{aligned} \tag{231}$$

We can replace $1/\left[\left(E_{q_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\right]$ in Eq. (231) with an integral over frequencies,

$$\begin{aligned} &\frac{1}{\left[\left(E_{q_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\right]} = \left(\frac{\hbar}{4\pi}\right) \\ \times &\int_{-\infty}^{+\infty} d\omega \left[\frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)}\right. \end{aligned}$$

$$
\begin{aligned}
&+ \left.\frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)}\right] \left[\frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)}\right. \\
&+ \left.\frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}\right] ,
\end{aligned}
\tag{232}
$$

so that term 2 (as expressed in Eq. (231)) becomes

$$
\begin{aligned}
&- \langle 0_A 0_B | \hat{V}^{AB} \, G^A \, \hat{\bar{\mu}}_\alpha^A \, T_{\alpha\beta} \, \hat{\bar{\mu}}_\beta^B \, G^{A\oplus B} \, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- T_{\alpha\beta} \, T_{\gamma\delta} \, T_{\epsilon\phi} \, \mu_\delta^{B0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, q_A, r_B \neq 0} \\
&\left[\frac{\langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)}\right. \\
&+ \left.\frac{\langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)}\right] \\
&\times \left[\frac{\langle 0_B | \hat{\mu}_\beta^B | r_B \rangle \langle r_B | \hat{\mu}_\phi^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} + \frac{\langle 0_B | \hat{\mu}_\beta^B | r_B \rangle \langle r_B | \hat{\mu}_\phi^B | 0_B \rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}\right] .
\end{aligned}
\tag{233}
$$

When term 9 is evaluated, the result is

$$
\begin{aligned}
&- \langle 0_A 0_B | \hat{V}^{AB} \, G^{A\oplus B} \, \hat{\bar{\mu}}_\alpha^A \, T_{\alpha\beta} \, \hat{\bar{\mu}}_\beta^B \, G^A \, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- \sum_{j_A, q_A, r_B \neq 0} T_{\alpha\beta} \, T_{\gamma\delta} \, T_{\epsilon\phi} \, \mu_\phi^{B0} \\
&\times \frac{\langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle \langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\mu}_\beta^B | 0_B \rangle}{\left[\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\right] \left(E_{q_A}^{(0)} - E_{0_A}^{(0)}\right)} .
\end{aligned}
\tag{234}
$$

From Eqs. (232) and (234), we have

$$
\begin{aligned}
&- \langle 0_A 0_B | \hat{V}^{AB} \, G^{A\oplus B} \, \hat{\bar{\mu}}_\alpha^A \, T_{\alpha\beta} \, \hat{\bar{\mu}}_\beta^B \, G^A \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- T_{\alpha\beta} \, T_{\gamma\delta} \, T_{\epsilon\phi} \, \mu_\phi^{B0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, q_A, r_B \neq 0}
\end{aligned}
$$

$$
\begin{aligned}
& \left[\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)} \right. \\
+ & \left. \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)} \right] \\
\times & \left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} + \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \right],
\end{aligned}
\tag{235}
$$

where we have replaced q_A with j_A in Eq. (232). Term 13 is

$$
\begin{aligned}
- & \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\overline{\mu}}^A_\alpha\, T_{\alpha\beta}\, \mu^{B0}_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
- & \sum_{j_A, q_A, r_B \neq 0} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_\beta \\
\times & \langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\phi|0_B\rangle \\
\times & \frac{1}{\left[\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) + \left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\right]} \\
\times & \frac{1}{\left[\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right) + \left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\right]}.
\end{aligned}
\tag{236}
$$

We can use[59]

$$
\begin{aligned}
& 1/\left\{\left[\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) + \left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\right]\right. \\
\times & \left.\left[\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right) + \left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\right]\right\} = \\
& \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \left[\frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} + \frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \right] \\
\times & \left[\frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)} \right. \\
+ & \left. \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)} \right]
\end{aligned}
\tag{237}
$$

to write Eq. (236) as

$$
\begin{aligned}
- \quad & \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \mu^{B0}_\beta\, G^{A\ominus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
- \quad & T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_\beta \\
\times \quad & \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega \sum_{j_A, q_A, r_B \neq 0} \\
& \left[\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle \langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle \langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle \langle 0_B|\hat{\mu}^B_\delta|r_B\rangle \langle r_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)} \right. \\
+ \quad & \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle \langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle \langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle \langle 0_B|\hat{\mu}^B_\delta|r_B\rangle \langle r_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)} \\
+ \quad & \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle \langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle \langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle \langle 0_B|\hat{\mu}^B_\delta|r_B\rangle \langle r_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)} \\
+ \quad & \frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)} \\
\times \quad & \left. \langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle \langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle \langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle \langle 0_B|\hat{\mu}^B_\delta|r_B\rangle \langle r_B|\hat{\mu}^B_\phi|0_B\rangle \right]. \qquad (238)
\end{aligned}
$$

At this point, we will relabel Eqs. (233) and (238) so that the static dipole moment μ^{B0} has the same index in Eqs. (233), (235), and (238). Converting δ to ϕ, ϕ to δ, γ to ϵ, and ϵ to γ in Eq. (233) and expanding gives

$$
\begin{aligned}
- \quad & \langle 0_A 0_B | \hat{V}^{AB}\, G^{A}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
- \quad & T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu^{B0}_\phi \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega \sum_{j_A, q_A, r_B \neq 0} \\
\times \quad & \left[\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle \langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle \langle q_A|\hat{\mu}^A_\gamma|0_A\rangle \langle 0_B|\hat{\mu}^B_\beta|r_B\rangle \langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \right. \\
+ \quad & \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle \langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle \langle q_A|\hat{\mu}^A_\gamma|0_A\rangle \langle 0_B|\hat{\mu}^B_\beta|r_B\rangle \langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}
\end{aligned}
$$

$$
\begin{aligned}
&+ \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \\
&+ \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \\
&\times \left.\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle\right] .
\end{aligned}
\tag{239}
$$

If we convert ϕ to β, β to ϕ, α to ϵ and ϵ to α in Eq. (238), the result is

$$
\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\epsilon\, T_{\epsilon\phi}\, \mu^{B0}_\phi\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- T_{\epsilon\phi}\, T_{\gamma\delta}\, T_{\alpha\beta}\, \mu^{B0}_\phi \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, q_A, r_B \neq 0} \\
&\left[\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)} \right. \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)} \\
&+ \frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)} \\
&\times \left.\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle\right] .
\end{aligned}
\tag{240}
$$

Expanding Eq. (235) and adding this to Eqs. (239) and (240) gives

$$
\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{A}\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\epsilon\, T_{\epsilon\phi}\, \mu^{B0}_\phi\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_\phi \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, q_A, r_B \neq 0}
\end{aligned}
$$

$$\left[\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right.$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}$$

$$
\begin{aligned}
&+ \frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
&\times \left.\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\overline{\hat{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle\right] . \qquad (241)
\end{aligned}
$$

Now we will show that Eq. (241) is equal to the product of the frequency-dependent hyperpolarizability $\beta_{\alpha\gamma\epsilon}^A(-\imath\omega; \imath\omega, 0)$ for molecule A and the frequency-dependent polarizability $\alpha_{\delta\beta}^B(\imath\omega)$ for molecule B. We can use Eq. (187) from Chap. 3 with ϕ converted to β to write the frequency-dependent polarizability $\alpha_{\delta\beta}^B(\imath\omega)$ of molecule B as

$$
\begin{aligned}
\alpha_{\delta\beta}^B(\imath\omega) &= \sum_{r_B \neq 0} \left[\frac{\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega} \right. \\
&+ \left. \frac{\langle 0_B|\hat{\mu}_\beta^B|r_B\rangle\langle r_B|\hat{\mu}_\delta^B|0_B\rangle}{E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega} \right] . \qquad (242)
\end{aligned}
$$

Orr and Ward[61] have derived an expression for the second-order nonlinear polarization $\mathbf{P}^{\omega_\sigma}$ of an isolated molecule due to applied fields of frequencies ω_1 and ω_2,

$$
\begin{aligned}
\mathbf{P}^{\omega_\sigma} &= K(-\omega_\sigma; \omega_1, \omega_2)\, I_{1,2} \sum_{m,n \neq 0} \\
&\times \left[\frac{\langle 0|P|m\rangle\langle m|\overline{\hat{H}'}^{\omega_2}|n\rangle\langle n|\hat{H}'^{\omega_1}|0\rangle}{\left(E_m^{(0)} - E_0^{(0)} - \hbar\omega_\sigma\right)\left(E_n^{(0)} - E_0^{(0)} - \hbar\omega_1\right)} \right. \\
&+ \frac{\langle 0|\hat{H}'^{\omega_2}|m\rangle\langle m|\overline{\hat{H}'}^{\omega_1}|n\rangle\langle n|P|0\rangle}{\left(E_m^{(0)} - E_0^{(0)} + \hbar\omega_2\right)\left(E_n^{(0)} - E_0^{(0)} + \hbar\omega_\sigma\right)} \\
&+ \left. \frac{\langle 0|\hat{H}'^{\omega_2}|m\rangle\langle m|\overline{\hat{P}}|n\rangle\langle n|\hat{H}'^{\omega_1}|0\rangle}{\left(E_m^{(0)} - E_0^{(0)} + \hbar\omega_2\right)\left(E_n^{(0)} - E_0^{(0)} - \hbar\omega_1\right)} \right] \\
&= K(-\omega_\sigma; \omega_1, \omega_2)\,(-\hbar)^{-2} \sum_{m,n \neq 0} \\
&\times \left[\frac{\langle 0|P|m\rangle\langle m|\overline{\hat{H}'}^{\omega_2}|n\rangle\langle n|\hat{H}'^{\omega_1}|0\rangle}{\left(E_m^{(0)} - E_0^{(0)} - \hbar\omega_\sigma\right)\left(E_n^{(0)} - E_0^{(0)} - \hbar\omega_1\right)} \right.
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{\langle 0|P|m\rangle\langle m|\overline{\hat{H}'}^{\omega_1}|n\rangle\langle n|\hat{H}'^{\omega_2}|0\rangle}{\left(E_m^{(0)}-E_0^{(0)}-\hbar\omega_\sigma\right)\left(E_n^{(0)}-E_0^{(0)}-\hbar\omega_2\right)}\\
&+\frac{\langle 0|\hat{H}'^{\omega_2}|m\rangle\langle m|\overline{\hat{H}'}^{\omega_1}|n\rangle\langle n|P|0\rangle}{\left(E_m^{(0)}-E_0^{(0)}+\hbar\omega_2\right)\left(E_n^{(0)}-E_0^{(0)}+\hbar\omega_\sigma\right)}\\
&+\frac{\langle 0|\hat{H}'^{\omega_1}|m\rangle\langle m|\overline{\hat{H}'}^{\omega_2}|n\rangle\langle n|P|0\rangle}{\left(E_m^{(0)}-E_0^{(0)}+\hbar\omega_1\right)\left(E_n^{(0)}-E_0^{(0)}+\hbar\omega_\sigma\right)}\\
&+\frac{\langle 0|\hat{H}'^{\omega_2}|m\rangle\langle m|\overline{\hat{P}}|n\rangle\langle n|\hat{H}'^{\omega_1}|0\rangle}{\left(E_m^{(0)}-E_0^{(0)}+\hbar\omega_2\right)\left(E_n^{(0)}-E_0^{(0)}-\hbar\omega_1\right)}\\
&\left.+\frac{\langle 0|\hat{H}'^{\omega_1}|m\rangle\langle m|\overline{\hat{P}}|n\rangle\langle n|\hat{H}'^{\omega_2}|0\rangle}{\left(E_m^{(0)}-E_0^{(0)}+\hbar\omega_1\right)\left(E_n^{(0)}-E_0^{(0)}-\hbar\omega_2\right)}\right]. \qquad (243)
\end{aligned}
$$

where $\omega_\sigma = \omega_1 + \omega_2$, and $|m\rangle$ is an unperturbed excited state of the molecule with energy $E_m^{(0)}$. In Eq. (243), $K\left(-\omega_\sigma;\omega_1,\omega_2\right)$ is determined by

$$K\left(-\omega_\sigma;\omega_1,\omega_2\right) = 2^m \times D, \qquad (244)$$

where m is the difference between the number of polarization frequencies and field-frequency labels in the set of frequencies $\omega_1, \omega_2, \ldots$, excluding zero. Also, D is the number of times that the field-frequency labels can be arranged distinguishably, where $+\omega$ and $-\omega$ are distinguishable for all $\omega \neq 0$. In addition, $I_{1,2}$ indicates that a second term should be produced from each term in $\mathbf{P}^{\omega_\sigma}$ by permuting ω_1 and ω_2, and $\overline{\hat{P}}$ is defined by

$$\overline{\hat{P}} = \hat{P} - \langle 0|\hat{P}|0\rangle. \qquad (245)$$

The quantities $\hat{H}'^{\omega_1}$ and $\hat{H}'^{\omega_2}$ denote the perturbations due to the ω_1 and ω_2 frequency components of the applied field, and

$$\overline{\hat{H}'}^{\omega} = \hat{H}'^{\omega} - \langle 0|\hat{H}'^{\omega}|0\rangle. \qquad (246)$$

If we let $\hat{P} = \mu_\alpha^A$, $\omega_1 = \imath\omega$, $\omega_2 = 0$ (therefore, $\omega_\sigma = \imath\omega$, $-\omega_\sigma = -\imath\omega$), $\hat{H}'^{\omega_1} = \hat{H}'^{A,\imath\omega} = -\hat{\mu}_\gamma^A F_\gamma^{A,\imath\omega}$, $\hat{H}'^{\omega_2} = \hat{H}'^{A,0} = -\hat{\mu}_\epsilon^A F_\epsilon^{A,0}$, $\overline{\hat{H}}'^{\omega_1} = \overline{\hat{H}}'^{A,\imath\omega} = -\overline{\hat{\mu}}_\gamma^A F_\gamma^{A,\imath\omega}$, and $\overline{\hat{H}}'^{\omega_2} = \overline{\hat{H}}'^{A,0} = -\overline{\hat{\mu}}_\epsilon^A F_\epsilon^{A,0}$, where $\hat{H}'^{A,\imath\omega}$ is the perturbation when the field $F_\gamma^{A,\imath\omega}$ is applied to molecule A and $\hat{H}'^{A,0}$ is the perturbation when the field $F_\epsilon^{A,0}$ is applied to molecule A, then Eq. (243) becomes

$$\begin{aligned}
\langle \mu_\alpha^A \rangle^{\imath\omega} &= F_\epsilon^{A,0}\, F_\gamma^{A,\imath\omega} \sum_{j_A, q_A \neq 0} \left[\frac{\langle 0_A | \mu_\alpha^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\epsilon^A | q_A \rangle \langle q_A | \hat{\mu}_\gamma^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega \right)} \right. \\
&+ \frac{\langle 0_A | \mu_\alpha^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\gamma^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} \right)} \\
&+ \frac{\langle 0_A | \mu_\epsilon^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\gamma^A | q_A \rangle \langle q_A | \mu_\alpha^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega \right)} \\
&+ \frac{\langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\epsilon^A | q_A \rangle \langle q_A | \mu_\alpha^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega \right)} \\
&+ \frac{\langle 0_A | \hat{\mu}_\epsilon^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\gamma^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega \right)} \\
&+ \left. \frac{\langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} \right)} \right] \\
&= (\hbar)^{-2} F_\epsilon^{A,0}\, F_\gamma^{A,\imath\omega} \beta_{\alpha\gamma\epsilon}^A (-\imath\omega; \imath\omega, 0)\,. \qquad (247)
\end{aligned}$$

Therefore, from Eq. (247), the frequency-dependent hyperpolarizability of molecule A is

$$\begin{aligned}
\beta_{\alpha\gamma\epsilon}^A (-\imath\omega; \imath\omega, 0) &= \sum_{j_A, q_A \neq 0} \left[\frac{\langle 0_A | \mu_\alpha^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\epsilon^A | q_A \rangle \langle q_A | \hat{\mu}_\gamma^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega \right)} \right. \\
&+ \frac{\langle 0_A | \mu_\alpha^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\gamma^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} \right)} \\
&+ \frac{\langle 0_A | \mu_\epsilon^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\gamma^A | q_A \rangle \langle q_A | \mu_\alpha^A | 0_A \rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} \right) \left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega \right)}
\end{aligned}$$

$$+\frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\mu_\alpha^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}_\epsilon^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\alpha^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)}$$

$$\left.+\frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\alpha^A|q_A\rangle\langle q_A|\hat{\mu}_\epsilon^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}\right)}\right]. \tag{248}$$

Note that we have let $K\left(-\omega_\sigma;\omega_1,\omega_2\right)=1$, $|m\rangle=|j_A\rangle$, $|n\rangle=|q_A\rangle$, and $|0\rangle=|0_A\rangle$. Now, let us calculate the product of the frequency-dependent polarizability $\alpha_{\delta\beta}^B\left(\imath\omega\right)$ of molecule B with the frequency-dependent hyperpolarizability $\beta_{\alpha\gamma\epsilon}^A\left(-\imath\omega;\imath\omega,0\right)$ of molecule A. According to Eqs. (242) and (248), $\alpha_{\delta\beta}^B\left(\imath\omega\right)\beta_{\alpha\gamma\epsilon}^A\left(-\imath\omega;\imath\omega,0\right)$ is

$$\alpha_{\delta\beta}^B\left(\imath\omega\right)\beta_{\epsilon\alpha\gamma}^A\left(-\imath\omega;\imath\omega,0\right)=\sum_{j_A,q_A,r_B\neq 0}$$

$$\left[\frac{\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}-\imath\hbar\omega\right)}\right.$$

$$+\frac{\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\gamma^A|q_A\rangle\langle q_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}\right)\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}_\epsilon^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\gamma^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}_\epsilon^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\alpha^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\alpha^A|q_A\rangle\langle q_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}\right)\left(E_{r_B}^{(0)}-E_{0_B}^{(0)}-\imath\hbar\omega\right)}$$

$$+ \frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}$$

$$+ \frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}$$

$$+ \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}$$

$$+ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}$$

$$+ \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}$$

$$+ \left.\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}\right] . \qquad (249)$$

Let us return to Eq. (241). If we convert α to γ, β to δ, γ to α, and δ to β in the first, second, sixth, eighth, tenth and twelfth terms in Eq. (241), the result is

$$\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\epsilon\, T_{\epsilon\phi}\, \mu^{B0}_\phi\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle =
\end{aligned}$$

$$- \; T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_\phi \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega \sum_{j_A, q_A, r_B \neq 0}$$

$$\left[\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}\right.$$

$$+ \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}$$

$$
\begin{aligned}
&+ \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\mu}^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)} \\
&+ \frac{1}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)} \\
&\times \left.\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\overline{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\mu}^B_\delta|0_B\rangle\right] . \qquad (250)
\end{aligned}
$$

If we assume that the matrix elements of μ^B_β and μ^B_δ are real, then

$$
\begin{aligned}
\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle &= \langle r_B|\hat{\mu}^B_\delta|0_B\rangle \\
\langle r_B|\hat{\mu}^B_\beta|0_B\rangle &= \langle 0_B|\hat{\mu}^B_\beta|r_B\rangle . \qquad (251)
\end{aligned}
$$

Using these relationships in the first, fourth, fifth, eighth, ninth, and twelfth terms in Eq. (250) gives

$$
\begin{aligned}
&- \langle 0_A 0_B | \hat{V}^{AB}\, G^{A}\, \hat{\bar{\mu}}^{A}_{\alpha}\, T_{\alpha\beta}\, \hat{\bar{\mu}}^{B}_{\beta}\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle \\
&- \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^{A}_{\alpha}\, T_{\alpha\beta}\, \hat{\bar{\mu}}^{B}_{\beta}\, G^{A}\, \hat{V}^{AB} | 0_A 0_B \rangle \\
&- \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^{A}_{\epsilon}\, T_{\epsilon\phi}\, \mu^{B0}_{\phi}\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\phi} \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega \sum_{j_A, q_A, r_B \neq 0} \\
&\left[\frac{\langle 0_A | \hat{\mu}^{A}_{\epsilon} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\gamma} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\alpha} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\beta} | r_B \rangle \langle r_B | \hat{\mu}^{B}_{\delta} | 0_B \rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \right. \\
&+ \frac{\langle 0_A | \hat{\mu}^{A}_{\epsilon} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\gamma} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\alpha} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\delta} | r_B \rangle \langle r_B | \hat{\mu}^{B}_{\beta} | 0_B \rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A | \hat{\mu}^{A}_{\epsilon} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\alpha} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\gamma} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\beta} | r_B \rangle \langle r_B | \hat{\mu}^{B}_{\delta} | 0_B \rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A | \hat{\mu}^{A}_{\epsilon} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\alpha} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\gamma} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\delta} | r_B \rangle \langle r_B | \hat{\mu}^{B}_{\beta} | 0_B \rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A | \hat{\mu}^{A}_{\gamma} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\alpha} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\epsilon} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\beta} | r_B \rangle \langle r_B | \hat{\mu}^{B}_{\delta} | 0_B \rangle}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A | \hat{\mu}^{A}_{\alpha} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\gamma} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\epsilon} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\beta} | r_B \rangle \langle r_B | \hat{\mu}^{B}_{\delta} | 0_B \rangle}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A | \hat{\mu}^{A}_{\gamma} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\alpha} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\epsilon} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\delta} | r_B \rangle \langle r_B | \hat{\mu}^{B}_{\beta} | 0_B \rangle}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A | \hat{\mu}^{A}_{\alpha} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\gamma} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\epsilon} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\delta} | r_B \rangle \langle r_B | \hat{\mu}^{B}_{\beta} | 0_B \rangle}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right) \left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right) \left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}
\end{aligned}
$$

$$
\begin{aligned}
&+ \frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_B|\hat{\mu}_\beta^B|r_B\rangle\langle r_B|\hat{\mu}_\delta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_B|\hat{\mu}_\beta^B|r_B\rangle\langle r_B|\hat{\mu}_\delta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} \\
&+ \frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
&\times \left.\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\mu}_\beta^B|0_B\rangle\right] . \qquad (252)
\end{aligned}
$$

Each term in Eq. (252) is identical to a term in Eq. (249). Therefore, we can write the sum of the $(0,1)$ terms as

$$
\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^A\, \hat{\bar{\mu}}_\alpha^A\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}_\alpha^A\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^A\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}_\epsilon^A\, T_{\epsilon\phi}\, \mu_\phi^{B0}\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_\phi^{B0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega\, \alpha_{\delta\beta}^B(\imath\omega)\, \beta_{\alpha\gamma\epsilon}^A(-\imath\omega; \imath\omega, 0) . \qquad (253)
\end{aligned}
$$

Now that we have derived the final expression for the sum of the $(0,1)$ terms, let us consider the $(1,0)$ terms. When term 6 in Table 1 is evaluated, the result is

$$
\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \hat{\bar{\mu}}_\alpha^A\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_\gamma^{A0} \\
&\times \sum_{j_A, r_B, s_B \neq 0} \langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\beta^B|s_B\rangle\langle s_B|\hat{\mu}_\phi^B|0_B\rangle\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\mu}_\epsilon^A|0_A\rangle \\
&\times \frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left[\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\right]} . \qquad (254)
\end{aligned}
$$

Using Eq. (232) with q_A replaced by j_A and r_B replaced by s_B in Eq. (254) gives

$$
- \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \hat{\bar{\mu}}_\alpha^A\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle =
$$

$$
\begin{aligned}
&- \quad T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\gamma}^{A0} \left(\frac{\hbar}{4\pi}\right) \\
&\times \int_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0} \left[\frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \right. \\
&+ \quad \left. \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)} \right] \\
&\times \quad \left[\frac{\langle 0_A|\hat{\mu}_{\alpha}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} + \frac{\langle 0_A|\hat{\mu}_{\alpha}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \right] . \qquad (255)
\end{aligned}
$$

When term 10 in Table 1 is evaluated, the result is

$$
\begin{aligned}
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}_{\alpha}^{A}\, T_{\alpha\beta}\, \hat{\bar{\mu}}_{\beta}^{B}\, G^{B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \quad \sum_{j_A, r_B, s_B \neq 0} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\epsilon}^{A0} \\
&\times \quad \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left[\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\right]\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)} . \quad (256)
\end{aligned}
$$

From Eqs. (232) (with q_A replaced by j_A) and (256),

$$
\begin{aligned}
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}_{\alpha}^{A}\, T_{\alpha\beta}\, \hat{\bar{\mu}}_{\beta}^{B}\, G^{B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
&- \quad T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\epsilon}^{A0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0} \\
&\quad \left[\frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \right. \\
&+ \quad \left. \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)} \right] \\
&\times \quad \left[\frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} + \frac{\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \right]
\end{aligned}
$$

$$
\begin{aligned}
= \; - \; & T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\epsilon}^{A0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0} \\
& \left[\frac{\langle 0_B | \hat{\mu}_{\delta}^{B} | r_B \rangle \langle r_B | \hat{\bar{\mu}}_{\beta}^{B} | s_B \rangle \langle s_B | \hat{\mu}_{\phi}^{B} | 0_B \rangle \langle 0_A | \hat{\mu}_{\gamma}^{A} | j_A \rangle \langle j_A | \hat{\mu}_{\alpha}^{A} | 0_A \rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right) \left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right) \left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} \right. \\
+ & \frac{\langle 0_B | \hat{\mu}_{\delta}^{B} | r_B \rangle \langle r_B | \hat{\bar{\mu}}_{\beta}^{B} | s_B \rangle \langle s_B | \hat{\mu}_{\phi}^{B} | 0_B \rangle \langle 0_A | \hat{\mu}_{\gamma}^{A} | j_A \rangle \langle j_A | \hat{\mu}_{\alpha}^{A} | 0_A \rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right) \left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right) \left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
+ & \frac{\langle 0_B | \hat{\mu}_{\delta}^{B} | r_B \rangle \langle r_B | \hat{\bar{\mu}}_{\beta}^{B} | s_B \rangle \langle s_B | \hat{\mu}_{\phi}^{B} | 0_B \rangle \langle 0_A | \hat{\mu}_{\gamma}^{A} | j_A \rangle \langle j_A | \hat{\mu}_{\alpha}^{A} | 0_A \rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right) \left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right) \left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} \\
+ & \frac{1}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right) \left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right) \left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
\times & \left. \langle 0_B | \hat{\mu}_{\delta}^{B} | r_B \rangle \langle r_B | \hat{\bar{\mu}}_{\beta}^{B} | s_B \rangle \langle s_B | \hat{\mu}_{\phi}^{B} | 0_B \rangle \langle 0_A | \hat{\mu}_{\gamma}^{A} | j_A \rangle \langle j_A | \hat{\mu}_{\alpha}^{A} | 0_A \rangle \right] \qquad (257)
\end{aligned}
$$

Term 15 is

$$
\begin{aligned}
- \; & \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \mu_{\alpha}^{A0}\, T_{\alpha\beta}\, \hat{\bar{\mu}}_{\beta}^{B}\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
- \; & \sum_{j_A, r_B, s_B \neq 0} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu_{\alpha}^{A0} \\
\times \; & \frac{1}{\left[\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\right] \left[\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\right]} \\
\times \; & \langle 0_B | \hat{\mu}_{\delta}^{B} | r_B \rangle \langle r_B | \hat{\bar{\mu}}_{\beta}^{B} | s_B \rangle \langle s_B | \hat{\mu}_{\phi}^{B} | 0_B \rangle \langle 0_A | \hat{\mu}_{\gamma}^{A} | j_A \rangle \langle j_A | \hat{\mu}_{\epsilon}^{A} | 0_A \rangle. \qquad (258)
\end{aligned}
$$

Using[59]

$$
\begin{aligned}
& 1/\left\{ \left[\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\right] \right. \\
\times \; & \left. \left[\left(E_{j_A}^{(0)} - E_{0_A}^{(0)}\right) + \left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\right] \right\} = \\
& \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \left[\frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} + \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \right] \\
\times \; & \left[\frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right) \left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \right.
\end{aligned}
$$

$$+ \quad \frac{1}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}\Bigg], \qquad (259)$$

we can write term 15 as

$$\begin{aligned}
- & \quad \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \mu^{A0}_{\alpha}\, T_{\alpha\beta}\, \hat{\bar{\mu}}^{B}_{\beta}\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
- & \quad T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{A0}_{\alpha} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0} \\
& \Bigg[\frac{\langle 0_B|\hat{\mu}^B_{\delta}|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_{\beta}|s_B\rangle\langle s_B|\hat{\mu}^B_{\phi}|0_B\rangle\langle 0_A|\hat{\mu}^A_{\gamma}|j_A\rangle\langle j_A|\hat{\mu}^A_{\epsilon}|0_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \\
+ & \quad \frac{\langle 0_B|\hat{\mu}^B_{\delta}|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_{\beta}|s_B\rangle\langle s_B|\hat{\mu}^B_{\phi}|0_B\rangle\langle 0_A|\hat{\mu}^A_{\gamma}|j_A\rangle\langle j_A|\hat{\mu}^A_{\epsilon}|0_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \\
+ & \quad \frac{\langle 0_B|\hat{\mu}^B_{\delta}|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_{\beta}|s_B\rangle\langle s_B|\hat{\mu}^B_{\phi}|0_B\rangle\langle 0_A|\hat{\mu}^A_{\gamma}|j_A\rangle\langle j_A|\hat{\mu}^A_{\epsilon}|0_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \\
+ & \quad \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \\
\times & \quad \langle 0_B|\hat{\mu}^B_{\delta}|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_{\beta}|s_B\rangle\langle s_B|\hat{\mu}^B_{\phi}|0_B\rangle\langle 0_A|\hat{\mu}^A_{\gamma}|j_A\rangle\langle j_A|\hat{\mu}^A_{\epsilon}|0_A\rangle \Bigg] . \qquad (260)
\end{aligned}$$

Now, we will relabel the indices in Eqs. (255) and (260) so that the component of the static dipole moment of molecule A in Eqs. (255), (257), and (260) has the same index in all three equations. Converting γ to ϵ, ϵ to γ, ϕ to δ, andδ to ϕ in Eq. (255) and expanding gives

$$\begin{aligned}
- & \quad \langle 0_A 0_B | \hat{V}^{AB}\, G^{B}\, \hat{\bar{\mu}}^{A}_{\alpha}\, T_{\alpha\beta}\, \hat{\bar{\mu}}^{B}_{\beta}\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
- & \quad T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu^{A0}_{\epsilon} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0} \\
& \Bigg[\frac{\langle 0_B|\hat{\mu}^B_{\phi}|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_{\beta}|s_B\rangle\langle s_B|\hat{\mu}^B_{\delta}|0_B\rangle\langle 0_A|\hat{\mu}^A_{\alpha}|j_A\rangle\langle j_A|\hat{\mu}^A_{\gamma}|0_A\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)}
\end{aligned}$$

$$
\begin{aligned}
+ & \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)} \\
+ & \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)} \\
+ & \frac{1}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)} \\
\times & \left.\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle\right] . \qquad (261)
\end{aligned}
$$

Converting ϵ to α, α to ϵ, ϕ to β and β to ϕ in Eq. (260), we have

$$
\begin{aligned}
- & \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \mu^{A0}_\epsilon\, T_{\epsilon\phi}\, \hat{\bar{\mu}}^B_\phi\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle = \\
- & T_{\epsilon\phi}\, T_{\gamma\delta}\, T_{\alpha\beta}\, \mu^{A0}_\epsilon \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0} \\
& \left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right. \\
+ & \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)} \\
+ & \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)} \\
+ & \frac{1}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)} \\
\times & \left.\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle\right] . \qquad (262)
\end{aligned}
$$

Adding Eqs. (261), (257) and (262) produces

$$
\begin{aligned}
- & \langle 0_A 0_B|\hat{V}^{AB}\, G^{B}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle \\
- & \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{B}\, \hat{V}^{AB}|0_A 0_B\rangle \\
- & \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \mu^{A0}_\epsilon\, T_{\epsilon\phi}\, \hat{\bar{\mu}}^B_\phi\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle =
\end{aligned}
$$

$$
\begin{aligned}
- \; & T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu_{\epsilon}^{A0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0} \\
& \left[\frac{\langle 0_B|\hat{\mu}_{\phi}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\delta}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\alpha}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\gamma}^{A}|0_A\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} \right. \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\phi}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\delta}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\alpha}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\gamma}^{A}|0_A\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\phi}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\delta}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\alpha}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\gamma}^{A}|0_A\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\phi}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\delta}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\alpha}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\gamma}^{A}|0_A\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\beta}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\phi}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)} \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\phi}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\beta}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \\
+ \; & \frac{\langle 0_B|\hat{\mu}_{\delta}^{B}|r_B\rangle\langle r_B|\hat{\bar{\mu}}_{\phi}^{B}|s_B\rangle\langle s_B|\hat{\mu}_{\beta}^{B}|0_B\rangle\langle 0_A|\hat{\mu}_{\gamma}^{A}|j_A\rangle\langle j_A|\hat{\mu}_{\alpha}^{A}|0_A\rangle}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}
\end{aligned}
$$

$$
\begin{aligned}
&+ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \\
&+ \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)} \\
&\times \left.\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle\right] . \qquad (263)
\end{aligned}
$$

Now we will show that Eq. (263) is equal to the product of the frequency-dependent hyperpolarizability $\beta^B_{\beta\delta\phi}\left(-\imath\omega;\imath\omega,0\right)$ for molecule B and the frequency-dependent polarizability $\alpha^A_{\alpha\gamma}\left(\imath\omega\right)$ for molecule A. We can use Eq. (186) from Chap. 3 with γ converted to α and ϵ converted to γ to write the frequency-dependent polarizability $\alpha^A_{\alpha\gamma}\left(\imath\omega\right)$ of molecule A as

$$
\begin{aligned}
\alpha^A_{\alpha\gamma}\left(\imath\omega\right) &= \sum_{j_A\neq 0}\left[\frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega}\right. \\
&+ \left.\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega}\right] . \qquad (264)
\end{aligned}
$$

At this point, we will use Eq. (243) to derive the frequency-dependent hyperpolarizability $\beta^B_{\beta\delta\phi}\left(-\imath\omega;\imath\omega,0\right)$ of molecule B. If we let $\hat{P} = \mu^B_\beta$, $\omega_1 = \imath\omega$, $\omega_2 = 0$ (therefore, $\omega_\sigma = \imath\omega$, $-\omega_\sigma = -\imath\omega$), $\hat{H}'^{\omega_1} = \hat{H}'^{B,\imath\omega} = -\hat{\mu}^B_\delta\, F^{B,\imath\omega}_\delta$, $\hat{H}'^{\omega_2} = \hat{H}'^{B,0} = -\hat{\mu}^B_\phi\, F^{B,0}_\phi$, $\hat{\bar{H}}'^{\omega_1} = \hat{\bar{H}}'^{B,\imath\omega} = -\hat{\bar{\mu}}^B_\delta\, F^{B,\imath\omega}_\delta$, and $\hat{\bar{H}}'^{\omega_2} = \hat{\bar{H}}'^{B,0} = -\hat{\bar{\mu}}^B_\phi\, F^{B,0}_\phi$, where $\hat{H}'^{B,\imath\omega}$ is the perturbation when the field $F^{B,\imath\omega}_\delta$ is applied to molecule B and $\hat{H}'^{B,0}$ is the perturbation when the field $F^{B,0}_\phi$ is applied to molecule B, then Eq. (243) becomes

$$
\begin{aligned}
\langle\mu^B_\beta\rangle^{\imath\omega} &= F^{B,0}_\phi\, F^{B,\imath\omega}_\delta \sum_{r_B,s_B\neq 0}\left[\frac{\langle 0_B|\mu^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}\right. \\
&+ \frac{\langle 0_B|\mu^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B}\right)} \\
&+ \frac{\langle 0_B|\mu^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\mu^B_\beta|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)}
\end{aligned}
$$

$$
\begin{aligned}
&+ \frac{\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\phi^B|s_B\rangle\langle s_B|\mu_\beta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}_\phi^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\beta^B|s_B\rangle\langle s_B|\hat{\mu}_\delta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)} \\
&+ \left.\frac{\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\beta^B|s_B\rangle\langle s_B|\hat{\mu}_\phi^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)}\right] \\
&= F_\phi^{B,0}\, F_\delta^{B,\imath\omega} \beta_{\beta\delta\phi}^B\left(-\imath\omega; \imath\omega, 0\right). \qquad (265)
\end{aligned}
$$

Therefore, from Eq. (265), the frequency-dependent hyperpolarizability of molecule B is

$$
\begin{aligned}
\beta_{\beta\delta\phi}^B\left(-\imath\omega; \imath\omega, 0\right) = \sum_{r_B, s_B \neq 0} &\left[\frac{\langle 0_B|\mu_\beta^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\phi^B|s_B\rangle\langle s_B|\hat{\mu}_\delta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}\right. \\
&+ \frac{\langle 0_B|\mu_\beta^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\delta^B|s_B\rangle\langle s_B|\hat{\mu}_\phi^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)} \\
&+ \frac{\langle 0_B|\mu_\phi^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\delta^B|s_B\rangle\langle s_B|\mu_\beta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\phi^B|s_B\rangle\langle s_B|\mu_\beta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}_\phi^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\beta^B|s_B\rangle\langle s_B|\hat{\mu}_\delta^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)}\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)} \\
&+ \left.\frac{\langle 0_B|\hat{\mu}_\delta^B|r_B\rangle\langle r_B|\hat{\bar{\mu}}_\beta^B|s_B\rangle\langle s_B|\hat{\mu}_\phi^B|0_B\rangle}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)}\right)}\right]. \qquad (266)
\end{aligned}
$$

Note that we have let $|m\rangle = |r_B\rangle$, $|n\rangle = |s_B\rangle$, and $|0\rangle = |0_B\rangle$. Now, let us calculate the product of the frequency-dependent polarizability $\alpha_{\alpha\gamma}^A\left(\imath\omega\right)$ of molecule A with the frequency-dependent hyperpolarizability $\beta_{\beta\delta\phi}^B\left(-\imath\omega; \imath\omega, 0\right)$ of molecule B. According to Eqs. (264) and (266), $\alpha^{A}_{\alpha\gamma}(\imath\omega)\,\beta^{B}_{\beta\delta\phi}(-\imath\omega;\imath\omega,0)$ is

$$\alpha^{A}_{\alpha\gamma}(\imath\omega)\,\beta^{B}_{\beta\delta\phi}(-\imath\omega;\imath\omega,0) = \sum_{j_A,r_B,s_B\neq 0}$$

$$\Bigg[\frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}$$

$$+\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}$$

$$
\left. + \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)} \right.
$$

$$
\left. + \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}\right] . \qquad (267)
$$

Let us return to Eq. (263). If we convert α to γ, γ to α, β to δ, and δ to β in the first, second, seventh, eighth, tenth and twelfth terms in Eq. (263), the result is

$$
\begin{aligned}
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle \\
&- \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \mu^{A0}_\epsilon\, T_{\epsilon\phi}\, \hat{\bar{\mu}}^B_\phi\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle =
\end{aligned}
$$

$$
- \; T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\; \mu^{A0}_\epsilon \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0}
$$

$$
\left[\frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)} \right.
$$

$$
+ \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}
$$

$$
+ \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}
$$

$$
+ \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}
$$

$$
+ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}
$$

$$
+ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}
$$

$$+\quad \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}$$

$$+\quad \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)}$$

$$+\quad \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}$$

$$+\quad \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}$$

$$+\quad \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}$$

$$+\quad \frac{1}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}$$

$$\times\quad \langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle\Bigg]. \tag{268}$$

If we assume that the matrix elements of μ^A_α and μ^A_γ are real, then

$$\begin{aligned}\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle &= \langle j_A|\hat{\mu}^A_\gamma|0_A\rangle\\ \langle j_A|\hat{\mu}^A_\alpha|0_A\rangle &= \langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle.\end{aligned} \tag{269}$$

Using these relationships in the second, third, sixth, seventh, tenth, and eleventh terms of Eq. (268) gives

$$\begin{aligned}
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^B\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle\\
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^A_\alpha\, T_{\alpha\beta}\, \hat{\bar{\mu}}^B_\beta\, G^B\, \hat{V}^{AB}|0_A 0_B\rangle\\
&- \quad \langle 0_A 0_B|\hat{V}^{AB}\, G^{A\oplus B}\, \mu^{A0}_\epsilon\, T_{\epsilon\phi}\, \hat{\bar{\mu}}^B_\phi\, G^{A\oplus B}\, \hat{V}^{AB}|0_A 0_B\rangle =\\
&- \quad T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu^{A0}_\epsilon \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \sum_{j_A, r_B, s_B \neq 0}
\end{aligned}$$

$$\Bigg[\frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}$$

$$
\begin{aligned}
&+ \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\phi|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\delta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)} \\
&+ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\beta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)} \\
&+ \frac{1}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)} \\
&\times \langle 0_B|\hat{\mu}^B_\beta|r_B\rangle\langle r_B|\bar{\hat{\mu}}^B_\phi|s_B\rangle\langle s_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle\Big] . \qquad (270)
\end{aligned}
$$

Each term in Eq. (270) is identical to a term in Eq. (267). Therefore, we can write the sum of the $(1,0)$ terms as

$$
\begin{aligned}
&- \langle 0_A 0_B | \hat{V}^{AB}\, G^{B}\, \hat{\bar{\mu}}^{A}_{\alpha}\, T_{\alpha\beta}\, \hat{\bar{\mu}}^{B}_{\beta}\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle \\
&- \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^{A}_{\alpha}\, T_{\alpha\beta}\, \hat{\bar{\mu}}^{B}_{\beta}\, G^{B}\, \hat{V}^{AB} | 0_A 0_B \rangle \\
&- \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \mu^{A0}_{\epsilon}\, T_{\epsilon\phi}\, \hat{\bar{\mu}}^{B}_{\phi}\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu^{A0}_{\epsilon} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega\, \alpha^{A}_{\alpha\gamma}(\imath\omega)\, \beta^{B}_{\beta\delta\phi}(-\imath\omega; \imath\omega, 0)\,. \quad (271)
\end{aligned}
$$

4.5 Third-Order Dispersion: Terms of Order Zero in Both μ^{A0} and μ^{B0}

In this section, we derive a new expression for third-order dispersion energies as integrals of nonlinear response tensors over imaginary frequencies. When we evaluate term 11 in Table 1, the result is

$$
\begin{aligned}
&-\langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}^{A}_{\alpha}\, T_{\alpha\beta}\, \hat{\bar{\mu}}^{B}_{\beta}\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = \\
&- T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \sum_{j_A, q_A, r_B, s_B \neq 0} \\
&\frac{1}{\left[\left(E^{(0)}_{j_A} - E^{(0)}_{0_A}\right) + \left(E^{(0)}_{r_B} - E^{(0)}_{0_B}\right)\right] \left[\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right) + \left(E^{(0)}_{s_B} - E^{(0)}_{0_B}\right)\right]} \\
&\times \langle 0_A | \hat{\mu}^{A}_{\gamma} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\alpha} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\epsilon} | 0_A \rangle \\
&\times \langle 0_B | \hat{\mu}^{B}_{\delta} | r_B \rangle \langle r_B | \hat{\bar{\mu}}^{B}_{\beta} | s_B \rangle \langle s_B | \hat{\mu}^{B}_{\phi} | 0_B \rangle . \quad (272)
\end{aligned}
$$

Replacing q_A with j_A in Eq. (232) and using Eqs. (232) and (272), we have

$$
\begin{aligned}
&- \langle 0_A 0_B | \hat{V}^{AB} G^{A\oplus B} \hat{\bar{\mu}}^{A}_{\alpha} T_{\alpha\beta} \hat{\bar{\mu}}^{B}_{\beta} G^{A\oplus B} \hat{V}^{AB} | 0_A 0_B \rangle = -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \\
&\times \sum_{j_A, q_A, r_B, s_B \neq 0} \frac{1}{\left[\left(E^{(0)}_{q_A} - E^{(0)}_{0_A}\right) + \left(E^{(0)}_{s_B} - E^{(0)}_{0_B}\right)\right]} \\
&\times \langle 0_A | \hat{\mu}^{A}_{\gamma} | j_A \rangle \langle j_A | \hat{\bar{\mu}}^{A}_{\alpha} | q_A \rangle \langle q_A | \hat{\mu}^{A}_{\epsilon} | 0_A \rangle \langle 0_B | \hat{\mu}^{B}_{\delta} | r_B \rangle \langle r_B | \hat{\bar{\mu}}^{B}_{\beta} | s_B \rangle \langle s_B | \hat{\mu}^{B}_{\phi} | 0_B \rangle \\
&\times \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \left[\frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)} + \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)}\right]
\end{aligned}
$$

$$\times \left[\frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} + \frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}\right]. \tag{273}$$

Replacing r_B with s_B in Eq. (232) and using Eq. (232) in Eq. (273) gives

$$\begin{aligned}
- & \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}_\alpha^A\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \\
\times & \sum_{j_A, q_A, r_B, s_B \neq 0} \langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle \\
\times & \langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\bar{\mu}}_\beta^B | s_B \rangle \langle s_B | \hat{\mu}_\phi^B | 0_B \rangle \\
\times & \left(\frac{\hbar^2}{16\pi^2}\right) \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega' \\
\times & \left[\frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)} + \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)}\right] \\
\times & \left[\frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} + \frac{1}{\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}\right] \\
\times & \left[\frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega'\right)} + \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega'\right)}\right] \\
\times & \left[\frac{1}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega'\right)} + \frac{1}{\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega'\right)}\right] \\
= & -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \\
& \sum_{j_A, q_A, r_B, s_B \neq 0} \langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle \\
\times & \langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\bar{\mu}}_\beta^B | s_B \rangle \langle s_B | \hat{\mu}_\phi^B | 0_B \rangle \\
\times & \left(\frac{\hbar^2}{16\pi^2}\right) \left[\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)}\right. \\
+ & \int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}
\end{aligned}$$

$$
\begin{aligned}
&+\int\limits_{-\infty}^{+\infty} d\omega \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} \\
&+\left.\int\limits_{-\infty}^{+\infty} d\omega \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}\right] \\
&\times\left[\int\limits_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega'\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega'\right)}\right. \\
&+\int\limits_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega'\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega'\right)} \\
&+\int\limits_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega'\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega'\right)} \\
&+\left.\int\limits_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} - \imath\hbar\omega'\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega'\right)}\right].
\end{aligned}
\tag{274}
$$

We can use the properties of the integrals in Eq. (274) to reduce the number of terms. In the integral $\int\limits_{-\infty}^{+\infty} d\omega 1/\left[\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)\right]$, let $\omega = -\eta$ and $d\omega = -d\eta$,

$$
\begin{aligned}
&\int\limits_{-\infty}^{+\infty} d\omega \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)} = \\
-&\int\limits_{+\infty}^{-\infty} d\eta \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\eta\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\eta\right)} = \\
&\int\limits_{-\infty}^{+\infty} d\omega \frac{1}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} - \imath\hbar\omega\right)\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}.
\end{aligned}
\tag{275}
$$

Similarly

$$\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)} =$$

$$\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)}. \tag{276}$$

This means that we can write the ω-integrals in Eq. (274) as

$$\begin{aligned}
&\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \\
+ &\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)} \\
+ &\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \\
+ &\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)} \\
= &\; 2\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \\
+ &\; 2\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)}.
\end{aligned} \tag{277}$$

Similarly, we can write the sum of the ω' integrals as

$$\begin{aligned}
&\int_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega'\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega'\right)} \\
+ &\int_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega'\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega'\right)}
\end{aligned}$$

$$
\begin{aligned}
&+ \int_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega'\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega'\right)} \\
&+ \int_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} - \imath\hbar\omega'\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega'\right)} \\
&= 2\int_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega'\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega'\right)} \\
&+ 2\int_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega'\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega'\right)}. \qquad (278)
\end{aligned}
$$

Using Eqs. (274), (277), and (278), term 11 becomes

$$
\begin{aligned}
&- \langle 0_A 0_B | \hat{V}^{AB}\, G^{A\oplus B}\, \hat{\bar{\mu}}_\alpha^A\, T_{\alpha\beta}\, \hat{\bar{\mu}}_\beta^B\, G^{A\oplus B}\, \hat{V}^{AB} | 0_A 0_B \rangle = -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \\
&\times \sum_{j_A, q_A, r_B, s_B \neq 0} \langle 0_A | \hat{\mu}_\gamma^A | j_A \rangle \langle j_A | \hat{\bar{\mu}}_\alpha^A | q_A \rangle \langle q_A | \hat{\mu}_\epsilon^A | 0_A \rangle \\
&\times \langle 0_B | \hat{\mu}_\delta^B | r_B \rangle \langle r_B | \hat{\bar{\mu}}_\beta^B | s_B \rangle \langle s_B | \hat{\mu}_\phi^B | 0_B \rangle \\
&\times \left(\frac{\hbar^2}{4\pi^2}\right) \left[\int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega\right)} \right. \\
&+ \left. \int_{-\infty}^{+\infty} d\omega \frac{1}{\left(E_{j_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega\right)\left(E_{r_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega\right)} \right] \\
&\times \left[\int_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega'\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} + \imath\hbar\omega'\right)} \right. \\
&+ \left. \int_{-\infty}^{+\infty} d\omega' \frac{1}{\left(E_{q_A}^{(0)} - E_{0_A}^{(0)} + \imath\hbar\omega'\right)\left(E_{s_B}^{(0)} - E_{0_B}^{(0)} - \imath\hbar\omega'\right)} \right] \\
&= -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \left(\frac{\hbar^2}{4\pi^2}\right) \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega' \sum_{j_A, q_A, r_B, s_B \neq 0}
\end{aligned}
$$

$$
\begin{aligned}
&\left[\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right.\\
&\times\ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega'\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega'\right)}\\
&+\ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\\
&\times\ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega'\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega'\right)}\\
&+\ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}\\
&\times\ \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega'\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega'\right)}\\
&+\ \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)}\\
&\times\ \left.\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega'\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega'\right)}\right]. \qquad (279)
\end{aligned}
$$

When factored, Eq. (279) is

$$
\begin{aligned}
&-\ \langle 0_A 0_B|\hat{V}^{AB}\,G^{A\oplus B}\,\hat{\bar{\mu}}^A_\alpha\,T_{\alpha\beta}\,\hat{\bar{\mu}}^B_\beta\,G^{A\oplus B}\,\hat{V}^{AB}|0_A 0_B\rangle\\
&=\ -T_{\alpha\beta}\,T_{\gamma\delta}\,T_{\epsilon\phi}\left(\frac{\hbar^2}{4\pi^2}\right)\int\limits_{-\infty}^{+\infty}d\omega\int\limits_{-\infty}^{+\infty}d\omega'\sum_{j_A,q_A\neq 0}\\
&\qquad\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega'\right)}
\end{aligned}
$$

$$
\begin{aligned}
\times & \left[\sum_{r_B,s_B\neq 0}\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega'\right)}\right.\\
+ & \sum_{r_B,s_B\neq 0}\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega'\right)}\\
+ & \sum_{r_B,s_B\neq 0}\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega'\right)}\\
+ & \left.\sum_{r_B,s_B\neq 0}\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}-\imath\hbar\omega\right)\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}-\imath\hbar\omega'\right)}\right].
\end{aligned}
\tag{280}
$$

We define

$$
\begin{aligned}
b^A_{\epsilon\gamma\alpha}(-\omega_\sigma;\omega_2,\omega_1) &= \sum_{j_A,q_A\neq 0}\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\hbar\omega_\sigma\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\hbar\omega_1\right)}\\
b^A_{\epsilon\alpha\gamma}(-\omega_\sigma;\omega_1,\omega_2) &= \sum_{j_A,q_A\neq 0}\frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}-\hbar\omega_\sigma\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\hbar\omega_2\right)}\\
b^A_{\alpha\epsilon\gamma}(\omega_1;-\omega_\sigma,\omega_2) &= \sum_{j_A,q_A\neq 0}\frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\gamma|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\hbar\omega_1\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\hbar\omega_2\right)}\\
b^A_{\alpha\gamma\epsilon}(\omega_1;\omega_2,-\omega_\sigma) &= \sum_{j_A,q_A\neq 0}\frac{\langle 0_A|\hat{\mu}^A_\alpha|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\gamma|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\hbar\omega_1\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\hbar\omega_\sigma\right)}\\
b^A_{\gamma\epsilon\alpha}(\omega_2;-\omega_\sigma,\omega_1) &= \sum_{j_A,q_A\neq 0}\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\epsilon|q_A\rangle\langle q_A|\hat{\mu}^A_\alpha|0_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\hbar\omega_2\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}-\hbar\omega_1\right)}\\
b^A_{\gamma\alpha\epsilon}(\omega_2;\omega_1,-\omega_\sigma) &= \sum_{j_A,q_A\neq 0}\frac{1}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\hbar\omega_2\right)\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\hbar\omega_\sigma\right)}\\
&\times\ \langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle.
\end{aligned}
\tag{281}
$$

Then

$$
\beta^A_{\epsilon\alpha\gamma}(-\omega_\sigma;\omega_1,\omega_2) = b^A_{\epsilon\alpha\gamma}(-\omega_\sigma;\omega_1,\omega_2)+b^A_{\epsilon\gamma\alpha}(-\omega_\sigma;\omega_2,\omega_1)
$$

$$\begin{aligned} &+ \; b^A_{\alpha\epsilon\gamma}\left(\omega_1;-\omega_\sigma,\omega_2\right)+b^A_{\alpha\gamma\epsilon}\left(\omega_1;\omega_2,-\omega_\sigma\right) \\ &+ \; b^A_{\gamma\epsilon\alpha}\left(\omega_2;-\omega_\sigma,\omega_1\right)+b^A_{\gamma\alpha\epsilon}\left(\omega_2;\omega_1,-\omega_\sigma\right), \end{aligned} \quad (282)$$

Similarly

$$\begin{aligned} \beta^B_{\phi\beta\delta}\left(-\omega_\sigma;\omega_1,\omega_2\right) &= b^B_{\phi\beta\delta}\left(-\omega_\sigma;\omega_1,\omega_2\right)+b^B_{\phi\delta\beta}\left(-\omega_\sigma;\omega_2,\omega_1\right) \\ &+ \; b^B_{\beta\phi\delta}\left(\omega_1;-\omega_\sigma,\omega_2\right)+b^B_{\beta\delta\phi}\left(\omega_1;\omega_2,-\omega_\sigma\right) \\ &+ \; b^B_{\delta\phi\beta}\left(\omega_2;-\omega_\sigma,\omega_1\right)+b^B_{\delta\beta\phi}\left(\omega_2;\omega_1,-\omega_\sigma\right). \end{aligned} \quad (283)$$

If we let $\omega_1 = \imath\omega' - \imath\omega$ and $\omega_2 = \imath\omega$ in Eq. (282), then $\omega_\sigma = \omega_1 + \omega_2 = \imath\omega'$, and

$$\begin{aligned} b^A_{\gamma\alpha\epsilon}\left(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega'\right) &= \sum_{j_A,q_A\neq 0}\left[\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle}{\left(E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega\right)}\right. \\ &\times \left.\frac{\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{q_A}-E^{(0)}_{0_A}+\imath\hbar\omega'\right)}\right]. \end{aligned} \quad (284)$$

Similarly, when we let $\omega_1 = \imath\omega' - \imath\omega$ and $\omega_2 = \imath\omega$ for molecule B then $\omega_\sigma = \omega_1 + \omega_2 = \imath\omega'$, and

$$\begin{aligned} b^B_{\delta\beta\phi}\left(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega'\right) &= \sum_{r_B,s_B\neq 0}\left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right. \\ &\times \left.\frac{\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{s_B}-E^{(0)}_{0_B}+\imath\hbar\omega'\right)}\right]. \end{aligned} \quad (285)$$

Comparison of $b^A_{\gamma\alpha\epsilon}\left(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega'\right)$ with the A term in Eq. (280) indicates that the $(0,0)$ term, as specified by Eq. (280), contains $b^A_{\gamma\alpha\epsilon}\left(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega'\right)$. Also, examination of $b^B_{\delta\beta\phi}\left(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega'\right)$ in Eq. (285) and the first B term in Eq. (280) indicates that the $(0,0)$ term contains $b^B_{\delta\beta\phi}\left(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega'\right)$. If we let $\omega_1 = -\imath\omega' - \imath\omega$ and $\omega_2 = \imath\omega$ in $b^B_{\delta\beta\phi}\left(\omega_2;\omega_1,-\omega_\sigma\right)$, then $\omega_\sigma = -\imath\omega'$ and

$$b^B_{\delta\beta\phi}\left(\imath\omega;-\imath\omega'-\imath\omega,\imath\omega'\right) = \sum_{r_B,s_B\neq 0}\left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle}{\left(E^{(0)}_{r_B}-E^{(0)}_{0_B}+\imath\hbar\omega\right)}\right.$$

$$\times \left.\frac{\langle s_B|\hat{\mu}^B_\phi|0\rangle}{\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega'\right)}\right] . \tag{286}$$

Inspection of Eqs. (280) and (286) indicates that $b^B_{\delta\beta\phi}\left(\imath\omega; -\imath\omega' - \imath\omega, \imath\omega'\right)$ is the second B term in Eq. (280). When we let $\omega_1 = \imath\omega' + \imath\omega$ and $\omega_2 = -\imath\omega$ in $b^B_{\delta\beta\phi}\left(\omega_2; \omega_1, -\omega_\sigma\right)$, then $\omega_\sigma = \imath\omega'$ and

$$b^B_{\delta\beta\phi}\left(-\imath\omega; \imath\omega' + \imath\omega, -\imath\omega'\right) = \sum_{r_B, s_B \neq 0} \left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}\right.$$

$$\times \left.\frac{\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega'\right)}\right] . \tag{287}$$

Examination of Eqs. (280) and (287) indicates that $b^B_{\delta\beta\phi}\left(-\imath\omega; \imath\omega' + \imath\omega, -\imath\omega'\right)$ is the third B term in Eq. (280). When we let $\omega_1 = \imath\omega - \imath\omega'$ and $\omega_2 = -\imath\omega$ in $b^B_{\delta\beta\phi}\left(\omega_2; \omega_1, -\omega_\sigma\right)$, then $\omega_\sigma = -\imath\omega'$ and

$$b^B_{\delta\beta\phi}\left(-\imath\omega; \imath\omega - \imath\omega', \imath\omega'\right) = \sum_{r_B, s_B \neq 0} \left[\frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} - \imath\hbar\omega\right)}\right.$$

$$\times \left.\frac{\langle s_B|\hat{\mu}^B_\phi|0\rangle}{\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} - \imath\hbar\omega'\right)}\right] , \tag{288}$$

which is the last B term in Eq. (280). Therefore, from Eq. (280),

$$\begin{aligned}
- & \langle 0_A 0_B|\hat{V}^{AB} G^{A\oplus B} \hat{\bar{\mu}}^A_\alpha T_{\alpha\beta} \hat{\bar{\mu}}^B_\beta G^{A\oplus B} \hat{V}^{AB}|0_A 0_B\rangle = \\
- & T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \left(\frac{\hbar^2}{4\pi^2}\right) \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega'\, b^A_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) \\
\times & \left[b^B_{\delta\beta\phi}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right)\right. \\
+ & b^B_{\delta\beta\phi}\left(\imath\omega; -\imath\omega' - \imath\omega, \imath\omega'\right) \\
+ & b^B_{\delta\beta\phi}\left(-\imath\omega; \imath\omega' + \imath\omega, -\imath\omega'\right) \\
+ & \left. b^B_{\delta\beta\phi}\left(-\imath\omega; \imath\omega - \imath\omega', \imath\omega'\right)\right] .
\end{aligned} \tag{289}$$

Consequently, using Eqs. (214), (222), (230), (253), (271), and (289), we have

$$
\begin{aligned}
\Delta E^{(3)}_{0_{AB}} = & - T_{\alpha\beta}\, T_{\delta\gamma}\, T_{\epsilon\phi}\, \mu^{A0}_{\alpha}\, \mu^{B0}_{\phi}\, \alpha^{A}_{\epsilon\delta}\, \alpha^{B}_{\gamma\beta} \\
& - \frac{1}{6} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\beta}\, \mu^{B0}_{\delta}\, \mu^{B0}_{\phi}\, \beta^{A}_{\gamma\alpha\epsilon} \\
& - \frac{1}{6} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{A0}_{\alpha} \mu^{A0}_{\gamma} \mu^{A0}_{\epsilon}\, \beta^{B}_{\delta\beta\phi} \\
& - T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\phi} \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega\, \alpha^{B}_{\delta\beta}(\imath\omega)\, \beta^{A}_{\epsilon\alpha\gamma}(-\imath\omega; \imath\omega, 0) \\
& - T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu^{A0}_{\epsilon} \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega\, \alpha^{A}_{\alpha\gamma}(\imath\omega)\, \beta^{B}_{\beta\delta\phi}(-\imath\omega; \imath\omega, 0) \\
& - T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \left(\frac{\hbar^{2}}{4\pi^{2}}\right) \int\limits_{-\infty}^{+\infty} d\omega \int\limits_{-\infty}^{+\infty} d\omega' b^{A}_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) \\
& \times \left[b^{B}_{\delta\beta\phi}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right)\right. \\
& + b^{B}_{\delta\beta\phi}\left(\imath\omega; -\imath\omega' - \imath\omega, \imath\omega'\right) \\
& + b^{B}_{\delta\beta\phi}\left(-\imath\omega; \imath\omega' + \imath\omega, -\imath\omega'\right) \\
& + \left. b^{B}_{\delta\beta\phi}\left(-\imath\omega; \imath\omega - \imath\omega', \imath\omega'\right)\right]. \qquad (290)
\end{aligned}
$$

5 Numerical Estimates of the Second- and Third-Order Corrections to the Interaction Energy of Two or Three Hydrogen Fluoride (HF) Molecules for Various Geometries

5.1 Leading Contribution to the Second-Order Correction to the Interaction Energy of Two Molecules

According to Eq. (189) in Chap. 3, the second-order correction to the energy of interaction $\Delta E^{(2)}_{0_{AB}}$ of molecules A and B is

$$\begin{aligned} \Delta E^{(2)}_{0_{AB}} = & - T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\delta}\, \mu^{B0}_{\phi} \left(\frac{1}{2}\right) \alpha^{A}_{\gamma\epsilon} \\ & - T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{A0}_{\gamma}\, \mu^{A0}_{\epsilon} \left(\frac{1}{2}\right) \alpha^{B}_{\delta\phi} \\ & - T_{\gamma\delta}\, T_{\epsilon\phi} \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega\, \alpha^{A}_{\gamma\epsilon}(\imath\omega)\, \alpha^{B}_{\delta\phi}(\imath\omega)\,. \end{aligned} \tag{291}$$

Let us write Eq. (291) as

$$\Delta E^{(2)}_{0_{AB}} = \Delta E^{(2)}_{0_{AB}}(0,2) + \Delta E^{(2)}_{0_{AB}}(2,0) + \Delta E^{(2)}_{0_{AB}}(0,0)\,, \tag{292}$$

where

$$\begin{aligned} \Delta E^{(2)}_{0_{AB}}(0,2) &= -T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\delta}\, \mu^{B0}_{\phi} \left(\frac{1}{2}\right) \alpha^{A}_{\gamma\epsilon} \\ \Delta E^{(2)}_{0_{AB}}(2,0) &= -T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{A0}_{\gamma}\, \mu^{A0}_{\epsilon} \left(\frac{1}{2}\right) \alpha^{B}_{\delta\phi} \\ \Delta E^{(2)}_{0_{AB}}(0,0) &= -T_{\gamma\delta}\, T_{\epsilon\phi} \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega\, \alpha^{A}_{\gamma\epsilon}(\imath\omega)\, \alpha^{B}_{\delta\phi}(\imath\omega)\,. \end{aligned} \tag{293}$$

Eq. (291) (or Eqs. (292) and (293)) can be used to compute $\Delta E^{(2)}_{0_{AB}}$ for any choice of A and B and corresponding geometry.

5.1.1 The Second-Order Correction to the Interaction Energy of Two Colinear Molecules

Let us derive $\Delta E^{(2)}_{0_{AB}}$ for a pair of colinear molecules whose internuclear axes are oriented along the z axis of the x, y, z laboratory frame, as shown in Fig. 12. In Fig. 12 x, y and z denote the axes of the the laboratory frame, and x', y' and z' denote the axes of the molecular frames. The centers of mass of A and B are COM_A and COM_B, respectively. Also, the nuclei of A are A_1 and A_2, and the nuclei of B are B_1 and B_2. Finally, $\mathbf{R}_{AB}$, is the center-of-mass to center-of-mass distance between A and B.

It is important to mention that when we use the general formula for $\Delta E^{(2)}_{0_{AB}}$ from Sect. 5.1 to derive $\Delta E^{(2)}_{0_{AB}}$ for a specific $A - B$ geometry, we carry out the derivation in the laboratory frame. The non-zero components of the dipole moments and polarizabilities of A and B, however, are given in terms of the coordinates of the molecular frame. Therefore, if the laboratory and molecular frames are not the same, we need to transform the non-zero components of the dipole moments and polarizabilities of A and B from the molecular frame to the laboratory frame. In Fig. 12, x', y', and z' of the molecular frame are aligned with x, y, and z of the laboratory frame, so that the two coordinate systems are the same. Consequently, there is no need to transform the non-zero components of the relevant properties of A and B to the laboratory frame, and we can complete the derivation of $\Delta E^{(2)}_{0_{AB}}$ for this particular geometry in the laboratory frame. All quantities and equations in the remainder of this section will be given in terms of the coordinates of the laboratory frame.

The center-of-mass to center-of-mass distance between molecules A and B in Fig. 12 is defined as $\mathbf{R}_{AB} = R_{AB_x}\hat{\mathbf{x}} + R_{AB_y}\hat{\mathbf{y}} + R_{AB_z}\hat{\mathbf{z}}$, where R_{AB_x}, R_{AB_y} and R_{AB_z} are the x, y and z components of $\mathbf{R}_{AB}$. For this geometry, $R_{AB_x} = R_{AB_y} = 0$, so that $\mathbf{R}_{AB} = R_{AB_z}\hat{\mathbf{z}}$. To begin our derivation of $\Delta E^{(2)}_{0_{AB}}$ for A and B arranged colinearly, we will determine the contributions of $\Delta E^{(2)}_{0_{AB}}(0,2)$ and $\Delta E^{(2)}_{0_{AB}}(2,0)$

to $\Delta E^{(2)}_{0_{AB}}$. Recall Eq. (149) in Chap. 3,

$$T_{\alpha\beta} = \nabla_\alpha \nabla_\beta \frac{1}{\mathbf{R}} = \frac{3\, R_\alpha\, R_\beta - \delta_{\alpha\beta}\, \mathbf{R}^2}{\mathbf{R}^5}, \tag{294}$$

When we use Eq. (294) with $\mathbf{R} = \mathbf{R}_{AB}$ to evaluate $T_{\alpha\beta}$ for all possible α and β where α and β can be x, y, or z, we find that

$$\begin{aligned} T_{xx} &= T_{yy} = \frac{-1}{(\mathbf{R}_{AB})^3} \\ T_{zz} &= \frac{2}{(\mathbf{R}_{AB})^3}, \end{aligned} \tag{295}$$

and $T_{\alpha\beta} = 0$ when $\alpha \neq \beta$. The expression for $\Delta E^{(2)}_{0_{AB}}\,(0,2)$ given in Eq. (293) simplifies to

$$\begin{aligned} \Delta E^{(2)}_{0_{AB}}\,(0,2) = &- \left(\frac{1}{2}\right) T_{xx}\, T_{xx}\, \mu_x^{B0}\, \mu_x^{B0} \alpha_{xx}^A \\ &- \left(\frac{1}{2}\right) T_{xx}\, T_{yy}\, \mu_x^{B0}\, \mu_y^{B0} \alpha_{xy}^A \\ &- \left(\frac{1}{2}\right) T_{xx}\, T_{zz}\, \mu_x^{B0}\, \mu_z^{B0} \alpha_{xz}^A \\ &- \left(\frac{1}{2}\right) T_{yy}\, T_{xx}\, \mu_y^{B0}\, \mu_x^{B0} \alpha_{yx}^A \\ &- \left(\frac{1}{2}\right) T_{yy}\, T_{yy}\, \mu_y^{B0}\, \mu_y^{B0} \alpha_{yy}^A \\ &- \left(\frac{1}{2}\right) T_{yy}\, T_{zz}\, \mu_y^{B0}\, \mu_z^{B0} \alpha_{yz}^A \\ &- \left(\frac{1}{2}\right) T_{zz}\, T_{xx}\, \mu_z^{B0}\, \mu_x^{B0} \alpha_{zx}^A \\ &- \left(\frac{1}{2}\right) T_{zz}\, T_{yy}\, \mu_z^{B0}\, \mu_y^{B0} \alpha_{zy}^A \\ &- \left(\frac{1}{2}\right) T_{zz}\, T_{zz}\, \mu_z^{B0}\, \mu_z^{B0} \alpha_{zz}^A. \end{aligned} \tag{296}$$

In Eq. (296), we have omitted those terms that vanish because they contain $T_{\alpha\beta}$ with $\alpha \neq \beta$. Recall from Chap. 4 (Eq. (195)) that the permanent dipole moments

μ^{A0} and μ^{B0} of molecules A and B are

$$\begin{aligned}\mu^{A0} &= \mu_x^{A0}\hat{\mathbf{x}} + \mu_y^{A0}\hat{\mathbf{y}} + \mu_z^{A0}\hat{\mathbf{z}} \\ \mu^{B0} &= \mu_x^{B0}\hat{\mathbf{x}} + \mu_y^{B0}\hat{\mathbf{y}} + \mu_z^{B0}\hat{\mathbf{z}}\end{aligned} \tag{297}$$

For the colinear geometry of the dimer shown in Fig. 12, $\mu_x^{A0} = \mu_y^{A0} = 0$ and $\mu_x^{B0} = \mu_y^{B0} = 0$, so that $\mu^{A0} = \mu_z^{A0}\hat{\mathbf{z}}$ and $\mu^{B0} = \mu_z^{B0}\hat{\mathbf{z}}$. Therefore, Eq. (296) reduces to

$$\Delta E_{0_{AB}}^{(2)}(0,2) = -\left(\frac{1}{2}\right) T_{zz}\, T_{zz}\, \mu_z^{B0}\, \mu_z^{B0} \alpha_{zz}^{A}, \tag{298}$$

and similarly $\Delta E_{0_{AB}}^{(2)}(2,0)$ reduces to

$$\Delta E_{0_{AB}}^{(2)}(2,0) = -\left(\frac{1}{2}\right) T_{zz}\, T_{zz}\, \mu_z^{A0}\, \mu_z^{A0} \alpha_{zz}^{B}. \tag{299}$$

When we substitute $T_{zz} = \frac{2}{(\mathbf{R}_{AB})^3}$ into Eq. (298), the result is

$$\Delta E_{0_{AB}}^{(2)}(0,2) = -\left(\frac{2}{\mathbf{R}_{AB}{}^6}\right) \mu_z^{B0}\, \mu_z^{B0} \alpha_{zz}^{A}, \tag{300}$$

and substituting into (299) gives

$$\Delta E_{0_{AB}}^{(2)}(2,0) = -\left(\frac{2}{\mathbf{R}_{AB}{}^6}\right) \mu_z^{A0}\, \mu_z^{A0} \alpha_{zz}^{B}. \tag{301}$$

Now, we need to derive an equation for $\Delta E_{0_{AB}}^{(2)}(0,0)$ in terms of $\mathbf{R}_{AB}$. From Eq. (293),

$$\begin{aligned}\Delta E_{0_{AB}}^{(2)}(0,0) &= -\left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \left[T_{xx}\, T_{xx}\, \alpha_{xx}^{A}(\imath\omega)\, \alpha_{xx}^{B}(\imath\omega)\right. \\ &+ T_{xx}\, T_{yy}\, \alpha_{xy}^{A}(\imath\omega)\, \alpha_{xy}^{B}(\imath\omega) + T_{xx}\, T_{zz}\, \alpha_{xz}^{A}(\imath\omega)\, \alpha_{xz}^{B}(\imath\omega) \\ &+ T_{yy}\, T_{xx}\, \alpha_{yx}^{A}(\imath\omega)\, \alpha_{yx}^{B}(\imath\omega) + T_{yy}\, T_{yy}\, \alpha_{yy}^{A}(\imath\omega)\, \alpha_{yy}^{B}(\imath\omega) \\ &+ T_{yy}\, T_{zz}\, \alpha_{yz}^{A}(\imath\omega)\, \alpha_{yz}^{B}(\imath\omega) + T_{zz}\, T_{xx}\, \alpha_{zx}^{A}(\imath\omega)\, \alpha_{zx}^{B}(\imath\omega) \\ &+ T_{zz}\, T_{yy}\, \alpha_{zy}^{A}(\imath\omega)\, \alpha_{zy}^{B}(\imath\omega) \\ &+ \left. T_{zz}\, T_{zz}\, \alpha_{zz}^{A}(\imath\omega)\, \alpha_{zz}^{B}(\imath\omega)\right].\end{aligned} \tag{302}$$

Let us consider the imaginary-frequency polarizability $\alpha^A_{\gamma\epsilon}(\imath\omega)$ of molecule A, which is given in Eq. (186) of Chap. 3.

$$\alpha^A_{\gamma\epsilon}(\imath\omega) = \sum_{j_A\neq 0}\left[\frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle}{E^{(0)}_{j_A}-E^{(0)}_{0_A}-\imath\hbar\omega} + \frac{\langle 0_A|\hat{\mu}^A_\epsilon|j_A\rangle\langle j_A|\hat{\mu}^A_\gamma|0_A\rangle}{E^{(0)}_{j_A}-E^{(0)}_{0_A}+\imath\hbar\omega}\right]. \tag{303}$$

In general, $\alpha^A_{\gamma\epsilon}(\imath\omega)$ has nine components: $\alpha^A_{xx}(\imath\omega)$, $\alpha^A_{xy}(\imath\omega)$, $\alpha^A_{xz}(\imath\omega)$, $\alpha^A_{yx}(\imath\omega)$, $\alpha^A_{yy}(\imath\omega)$, $\alpha^A_{yz}(\imath\omega)$, $\alpha^A_{zx}(\imath\omega)$, $\alpha^A_{zy}(\imath\omega)$, and $\alpha^A_{zz}(\imath\omega)$. For any particular molecule, however, some of these components may vanish, depending on the symmetry of the molecule. Let us determine which components of the imaginary-frequency polarizibility vanish for molecule A, where A belongs to the $C_{\infty v}$ point group. Note that the components of the imaginary-frequency polarizability that vanish for molecule A will also vanish for any other molecule with the same symmetry as A, and that the static and frequency-dependent polarizabilities have the same symmetry properties.

Consider the product of matrix elements $\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle$ contained in Eq. (303). Using the fact that $\hat{\mu}^A_\alpha = \sum_{i=1}^{N^A} e_i r_{i\alpha} + \sum_{v=1}^{M^A} Z^v R_{v\alpha}$, we can write the product of matrix elements as

$$\begin{aligned}\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\mu}^A_\epsilon|0_A\rangle &= \sum_{m=1}^{N^A}\sum_{n=1}^{N^A} e_m e_n \langle 0_A|r_{m\gamma}|j_A\rangle\langle j_A|r_{n\epsilon}|0_A\rangle \\ &+ \sum_{m=1}^{N^A}\sum_{n=1}^{M^A} e_m Z^n \langle 0_A|r_{m\gamma}|j_A\rangle\langle j_A|R_{n\epsilon}|0_A\rangle \\ &+ \sum_{m=1}^{M^A}\sum_{n=1}^{N^A} Z^m e_n \langle 0_A|R_{m\gamma}|j_A\rangle\langle j_A|r_{n\epsilon}|0_A\rangle \\ &+ \sum_{m=1}^{M^A}\sum_{n=1}^{M^A} Z^m Z^n \\ &\times \langle 0_A|R_{m\gamma}|j_A\rangle\langle j_A|R_{n\epsilon}|0_A\rangle. \end{aligned} \tag{304}$$

The matrix elements of $R_{v\alpha}$ vanish between orthogonal electronic states. The polarizability components $\alpha^{A}_{xy}(\imath\omega)$, $\alpha^{A}_{xz}(\imath\omega)$, $\alpha^{A}_{yx}(\imath\omega)$, $\alpha^{A}_{yz}(\imath\omega)$, $\alpha^{A}_{zx}(\imath\omega)$, and $\alpha^{A}_{zy}(\imath\omega)$ vanish by inversion symmetry with respect to the x and y axes, but $\alpha^{A}_{xx}(\imath\omega)$, $\alpha^{A}_{yy}(\imath\omega)$, and $\alpha^{A}_{zz}(\imath\omega)$ are nonzero, and $\alpha^{A}_{xx}(\imath\omega) = \alpha^{A}_{yy}(\imath\omega)$. If molecule B also has $C_{\infty v}$ symmetry, then $\alpha^{B}_{xx}(\imath\omega)$, $\alpha^{B}_{yy}(\imath\omega)$, and $\alpha^{B}_{zz}(\imath\omega)$ are also nonzero, and $\alpha^{B}_{\delta\phi} = 0$ if $\delta \neq \phi$. In this case, Eq. (302) reduces to

$$\begin{aligned}\Delta E^{(2)}_{0_{AB}}(0,0) &= -\left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega \left[T_{xx}\,T_{xx}\,\alpha^{A}_{xx}(\imath\omega)\,\alpha^{B}_{xx}(\imath\omega)\right.\\ &+ T_{yy}\,T_{yy}\,\alpha^{A}_{yy}(\imath\omega)\,\alpha^{B}_{yy}(\imath\omega)\\ &+ \left.T_{zz}\,T_{zz}\,\alpha^{A}_{zz}(\imath\omega)\,\alpha^{B}_{zz}(\imath\omega)\right]. \qquad (305)\end{aligned}$$

Finally, because $\alpha^{A}_{xx}(\imath\omega) = \alpha^{A}_{yy}(\imath\omega)$, $\alpha^{B}_{xx}(\imath\omega) = \alpha^{B}_{yy}(\imath\omega)$, with (295), the total second-order correction to the energy of molecules A and B when they are aligned colinearly is

$$\begin{aligned}&\Delta E^{(2)}_{0_{AB}}(0,2) + \Delta E^{(2)}_{0_{AB}}(2,0) + \Delta E^{(2)}_{0_{AB}}(0,0) =\\ &-\left(\frac{2}{\mathbf{R}_{AB}{}^{6}}\right)\mu^{B0}_{z}\,\mu^{B0}_{z}\alpha^{A}_{zz}\\ &-\left(\frac{2}{\mathbf{R}_{AB}{}^{6}}\right)\mu^{A0}_{z}\,\mu^{A0}_{z}\alpha^{B}_{zz} - \left(\frac{\hbar}{4\pi}\right)\int\limits_{-\infty}^{+\infty} d\omega\left[\frac{2\alpha^{A}_{xx}(\imath\omega)\,\alpha^{B}_{xx}(\imath\omega)}{\mathbf{R}_{AB}{}^{6}}\right.\\ &+ \left.\frac{4\alpha^{A}_{zz}(\imath\omega)\,\alpha^{B}_{zz}(\imath\omega)}{\mathbf{R}_{AB}{}^{6}}\right]. \qquad (306)\end{aligned}$$

5.1.2 The Second-Order Correction to the Interaction Energy of Two Colinear HF Molecules

Now, we will use the information in Sect. 5.1.1 to derive the second-order correction to the energy of two interacting HF molecules. If we assume that $A = B =$HF in Eqs. (300), (301), and (305) then we have

$$\Delta E^{(2)}_{0_{HF-HF}}(0,2) = -\left(\frac{2}{\mathbf{R}_{HF-HF}{}^{6}}\right)\mu^{HF,0}_{z}\,\mu^{HF,0}_{z}\alpha^{HF}_{zz}, \qquad (307)$$

$$\Delta E^{(2)}_{0_{HF-HF}}(2,0) = -\left(\frac{2}{\mathbf{R}_{HF-HF}{}^{6}}\right)\mu^{HF,0}_{z}\,\mu^{HF,0}_{z}\alpha^{HF}_{zz}, \qquad (308)$$

and

$$\Delta E^{(2)}_{0_{HF-HF}}(0,0) = -\left(\frac{\hbar}{4\pi}\right)\int_{-\infty}^{+\infty} d\omega \left[\frac{2\alpha^{HF}_{xx}(\imath\omega)\,\alpha^{HF}_{xx}(\imath\omega)}{\mathbf{R}_{HF-HF}{}^{6}} + \frac{4\alpha^{HF}_{zz}(\imath\omega)\,\alpha^{HF}_{zz}(\imath\omega)}{\mathbf{R}_{HF-HF}{}^{6}}\right]. \tag{309}$$

Maroulis[62] has recently used coupled cluster theory at the CCSD(T) level and finite-field perturbation theory to calculate the electric properties as well as the property derivatives of the $X^1\Sigma^+$ state of HF as a function of bond length. According to Maroulis, the most accurate values of these properties have been obtained using CCSD(T) theory and a $(16s\,11p\,8d\,4f/10s\,6p\,3d\,2f)$ basis set. At the experimentally measured value of the equilibrium bond length of HF, $r_{(HF)_e} = 1.7328$ a.u., the CCSD(T) value of the permanent dipole moment $\mu^{HF,0}$ in the $(16s11p8d4f/10s6p3d2f)$ basis is $\mu^{HF,0} = 0.7043$ a.u., and the corresponding value of the zz component of the static polarizability of HF is $\alpha^{HF}_{zz} = 6.36$ a.u. Recall that for the geometry shown in Fig. 12, $\mu^{A0} = \mu^{A0}_z\hat{\mathbf{z}}$ and $\mu^{B0} = \mu^{B0}_z\hat{\mathbf{z}}$, so $\mu^{HF,0} = \mu^{HF,0}_z\hat{\mathbf{z}}$. Substituting $\mu^{HF,0} = 0.7043$ a.u. for $\mu^{HF,0}_z$ and $\alpha^{HF}_{zz} = 6.36$ a.u. for α^{HF}_{zz} into Eqs. (307) and (308), we obtain

$$\Delta E^{(2)}_{0_{HF-HF}}(0,2) = \Delta E^{(2)}_{0_{HF-HF}}(2,0) = -\left(\frac{6.31}{\mathbf{R}_{HF-HF}{}^{6}}\right). \tag{310}$$

In order to obtain numerical estimates of $\Delta E^{(2)}_{0_{HF-HF}}(0,0)$, we use the Unsöld approximation with the average excitation energy approximated by the ionization potential E^{HF}_{IP} of HF. Let us begin by considering the static polarizability of HF, as specified by Eq. (303), with $\omega = 0$ and $A =$HF. If we assume that the matrix elements in Eq. (303) are real, then $\langle 0_{HF}|\hat{\mu}^{HF}_{\gamma}|j_{HF}\rangle = \langle j_{HF}|\hat{\mu}^{HF}_{\gamma}|0_{HF}\rangle$ and $\langle 0_{HF}|\hat{\mu}^{HF}_{\epsilon}|j_{HF}\rangle = \langle j_{HF}|\hat{\mu}^{HF}_{\epsilon}|0_{HF}\rangle$, and Eq. (303) reduces to

$$\alpha^{HF}_{\gamma\epsilon}(0) = 2\sum_{j_{HF}\neq 0}\frac{\langle 0_{HF}|\hat{\mu}^{HF}_{\gamma}|j_{HF}\rangle\langle j_{HF}|\hat{\mu}^{HF}_{\epsilon}|0_{HF}\rangle}{E^{(0)}_{j_{HF}} - E^{(0)}_{0_{HF}}}. \tag{311}$$

We simplify Eq. (311) by using the Unsöld approximation. This approximation is suitable for numerical calculations if the transition energy from the ground electronic state to the first excited state is similar in magnitude to the ionization energy, and if high-lying continuum states do not contribute significantly to $\alpha_{\gamma\epsilon}(\imath\omega)$. Then we approximate

$$\frac{1}{E^{(0)}_{j_{HF}} - E^{(0)}_{0_{HF}}} \cong \frac{1}{E^{HF}_{IP}}. \tag{312}$$

Using Eq. (312) in Eq. (311) gives

$$\alpha^{HF}_{\gamma\epsilon} \cong 2 \sum_{j_{HF}\neq 0} \frac{\langle 0_{HF}|\hat{\mu}^{HF}_{\gamma}|j_{HF}\rangle\langle j_{HF}|\hat{\mu}^{HF}_{\epsilon}|0_{HF}\rangle}{E^{HF}_{IP}}. \tag{313}$$

When we solve Eq. (313) for the sum of the matrix elements of the polarizability $\alpha^{HF}_{\gamma\epsilon}$ of molecule HF, the result is

$$\sum_{j_{HF}\neq 0} \langle 0_{HF}|\hat{\mu}^{HF}_{\gamma}|j_{HF}\rangle\langle j_{HF}|\hat{\mu}^{HF}_{\epsilon}|0_{HF}\rangle = \frac{\alpha^{HF}_{\gamma\epsilon} E^{HF}_{IP}}{2}. \tag{314}$$

We get the frequency-dependent polarizability of HF by letting A = HF in Eq. (303),

$$\begin{aligned} \alpha^{HF}_{\gamma\epsilon}(\imath\omega) &= \sum_{j_{HF}\neq 0} \left[\frac{\langle 0_{HF}|\hat{\mu}^{HF}_{\gamma}|j_{HF}\rangle\langle j_{HF}|\hat{\mu}^{HF}_{\epsilon}|0_{HF}\rangle}{E^{(0)}_{j_{HF}} - E^{(0)}_{0_{HF}} - \imath\hbar\omega} \right. \\ &+ \left. \frac{\langle 0_{HF}|\hat{\mu}^{HF}_{\epsilon}|j_{HF}\rangle\langle j_{HF}|\hat{\mu}^{HF}_{\gamma}|0_{HF}\rangle}{E^{(0)}_{j_{HF}} - E^{(0)}_{0_{HF}} + \imath\hbar\omega} \right]. \end{aligned} \tag{315}$$

Setting $\left(E^{(0)}_{j_{HF}} - E^{(0)}_{0_{HF}}\right) \cong E^{HF}_{IP}$ and using Eqs. (314) and (315) gives

$$\alpha^{HF}_{\gamma\epsilon}(\imath\omega) = \frac{\left(E^{HF}_{IP}\right)^2 \alpha^{HF}_{\gamma\epsilon}}{\left[\left(E^{HF}_{IP}\right)^2 + \hbar^2\omega^2\right]}. \tag{316}$$

Therefore, from Eq. (316) with $\gamma = \epsilon = x$, $\gamma = \epsilon = y$, and $\gamma = \epsilon = z$, we have

$$\begin{aligned} \alpha^{HF}_{xx}(\imath\omega) &= \frac{\left(E^{HF}_{IP}\right)^2 \alpha^{HF}_{xx}}{\left[\left(E^{HF}_{IP}\right)^2 + \hbar^2\omega^2\right]} \\ \alpha^{HF}_{yy}(\imath\omega) &= \frac{\left(E^{HF}_{IP}\right)^2 \alpha^{HF}_{yy}}{\left[\left(E^{HF}_{IP}\right)^2 + \hbar^2\omega^2\right]} \\ \alpha^{HF}_{zz}(\imath\omega) &= \frac{\left(E^{HF}_{IP}\right)^2 \alpha^{HF}_{zz}}{\left[\left(E^{HF}_{IP}\right)^2 + \hbar^2\omega^2\right]}. \end{aligned} \tag{317}$$

Using $\alpha_{xx}^{HF} = \alpha_{yy}^{HF}$, Eq. (317), and Eq. (295) in Eq. (309) gives

$$\Delta E^{(2)}_{0_{HF-HF}}(0,0) = -\frac{2\left(E_{IP}^{HF}\right)^4\left(\alpha_{xx}^{HF}\right)^2}{\mathbf{R}_{HF-HF}{}^6}\left(\frac{\hbar}{4\pi}\right)$$

$$\times \int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]^2}$$

$$-\frac{4\left(E_{IP}^{HF}\right)^4\left(\alpha_{zz}^{HF}\right)^2}{\mathbf{R}_{HF-HF}{}^6}\left(\frac{\hbar}{4\pi}\right)\int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]^2}. \qquad (318)$$

In order to simplify Eq. (318), we need to evaluate the integral in this equation. If we let $E_{IP}^{HF} = a$ and $\hbar\omega = x$, then $d\omega = dx/\hbar$ and the integral is

$$\int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]^2} = \left(\frac{1}{\hbar}\right)\int_{-\infty}^{+\infty} dx \frac{1}{\left(a^2 + x^2\right)^2}. \qquad (319)$$

Since the integrand on the right-hand side of Eq. (319) is integrable from $-\infty$ to $+\infty$ and it is an even function,

$$\left(\frac{1}{\hbar}\right)\int_{-\infty}^{+\infty} dx \frac{1}{\left(a^2 + x^2\right)^2} = \left(\frac{2}{\hbar}\right)\int_{0}^{+\infty} dx \frac{1}{\left(a^2 + x^2\right)^2}. \qquad (320)$$

According to the integral tables of Gradshteyn and Ryzhik,[67]

$$\int_{0}^{+\infty} dx \frac{1}{\left(a^2 + x^2\right)^n} = \frac{(2n-3)!!}{(2n-2)!!}\frac{\pi}{a^{2n-1}}, \qquad (321)$$

where $(2n+1)!! = 1 \cdot 3 \cdots (2n+1)$ and $(2n)!! = 2 \cdot 4 \cdots (2n)$. For $n = 2$,

$$\int_{0}^{+\infty} dx \frac{1}{\left(a^2 + x^2\right)^2} = \frac{\pi}{2a^3}. \qquad (322)$$

From Eqs. (320) and (322),

$$\left(\frac{1}{\hbar}\right)\int_{-\infty}^{+\infty} dx \frac{1}{\left(a^2 + x^2\right)^2} = \frac{\pi}{a^3\hbar}, \qquad (323)$$

and

$$\int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]^2} = \frac{\pi}{E_{IP}^{HF^3}\hbar}. \tag{324}$$

Using Eq. (324) in Eq. (318),

$$\Delta E_{0_{HF-HF}}^{(2)}(0,0) = -\frac{E_{IP}^{HF}\left(\alpha_{xx}^{HF}\right)^2}{2(\mathbf{R}_{HF-HF})^6} - \frac{E_{IP}^{HF}\left(\alpha_{zz}^{HF}\right)^2}{(\mathbf{R}_{HF-HF})^6}. \tag{325}$$

When we let $\alpha_{zz}^{HF} = 6.36$ a.u., $\alpha_{xx}^{HF} = \alpha_{yy}^{HF} = 5.22$ a.u. (as calculated by Maroulis[62]) and $E_{IP}^{HF} = 0.5896$ a.u. in Eq. (325), the result is[68]

$$\Delta E_{0_{HF-HF}}^{(2)}(0,0) = -\frac{31.9\,a.u.}{(\mathbf{R}_{HF-HF})^6}. \tag{326}$$

Adding $\Delta E_{0_{HF-HF}}^{(2)}(2,0)$, $\Delta E_{0_{HF-HF}}^{(2)}(0,2)$, and $\Delta E_{0_{HF-HF}}^{(2)}(0,0)$ gives the total second-order correction to the interaction energy of two colinear HF molecules,

$$\Delta E_{0_{HF-HF}}^{(2)} = -\frac{44.5\,a.u.}{(\mathbf{R}_{HF-HF})^6}. \tag{327}$$

5.1.3 The Second-Order Correction to the Interaction Energy of Two Parallel Molecules

At this point, we will derive an expression for the second-order correction to the energy $\Delta E_{0_{AB}}^{(2)}$ of two interacting molecules A and B whose internuclear axes are parallel to each other and to the x axis of the x, y, z laboratory frame. This particular arrangement of molecules A and B is shown in Fig. 13. In Fig. 13, x', y', and z' are the axes for the molecular frame (A and B have the same molecular frame), A_1 and A_2 are the nuclei of molecule A, and B_1 and B_2 are the nuclei of molecule B. Also, COM$_A$ and COM$_B$ are the centers-of-mass of molecules A and B, respectively. We have denoted the vector extending from the center of mass of A to the center of mass of B by $\mathbf{R}_{AB}$.

Let us compare the geometry of A and B in Fig. 12 with the geometry of A and B in Fig. 13. The internuclear axes of A and B are designated as the z' axis of the x', y', z' molecular frames. Whereas the x', y', z' molecular and x, y, z laboratory frames are the same in Fig. 12, these frames are not the same in Fig. 13. Rather, the x', y', z' molecular frame in Fig. 13 is rotated 90° counterclockwise from its position in Fig. 12. Consequently, we need to rotate the non-zero components of the relevent properties of A and B for the geometry shown in Fig. 13 from the molecular frame to the laboratory frame.

While deriving $\Delta E^{(2)}_{0_{AB}}$ for the colinear arrangement of A and B shown in Fig. 12 (see Sect. 5.1.1), we determined that the non-zero components of the dipole moments and the static polarizabilities of A and B in the molecular frame are μ_z^{A0}, μ_z^{B0}, α^A_{xx}, α^A_{yy}, α^A_{zz}, α^B_{xx}, α^B_{yy}, and α^B_{zz}. These components have the same values in the molecular frames of Fig. 13. We can rotate these components from the molecular frame of Fig. 13 to the corresponding laboratory frame by interchanging the roles of x and z. Therefore, we have $\mu_{z'}^{A0} = \mu_x^{A0}$, $\mu_{z'}^{B0} = \mu_x^{B0}$, $\alpha^A_{x'x'} = \alpha^A_{zz}$, $\alpha^A_{z'z'} = \alpha^A_{xx}$, $\alpha^B_{x'x'} = \alpha^B_{zz}$, and $\alpha^B_{z'z'} = \alpha^B_{xx}$.

Recall Eq. (296) from Sect. 5.1.1. Because $\mu^{B0} = \mu_x^{B0}$ for the current geometry, Eq. (296) reduces to

$$\Delta E^{(2)}_{0_{AB}}(0,2) = -\left(\frac{1}{2}\right) T_{xx}\, T_{xx}\, \mu_x^{B0}\, \mu_x^{B0} \alpha^A_{xx}. \tag{328}$$

Similarly

$$\Delta E^{(2)}_{0_{AB}}(2,0) = -\left(\frac{1}{2}\right) T_{xx}\, T_{xx}\, \mu_x^{A0}\, \mu_x^{A0} \alpha^B_{xx}. \tag{329}$$

In Sect. 5.1.1, $\Delta E^{(2)}_{0_{AB}}(0,0)$ is given by Eq. (305). Since we have $\alpha^A_{xx} = \alpha^A_{z'z'}$, $\alpha^A_{zz} = \alpha^A_{x'x'}$, $\alpha^B_{xx} = \alpha^B_{z'z'}$, and $\alpha^B_{zz} = \alpha^B_{x'x'}$ for the current geometry, we can also use Eq. (305) to write $\Delta E^{(2)}_{0_{AB}}(0,0)$ for the geometry of A and B in Fig. 13. When A and B are parallel to each other and to the x axis of the laboratory frame, the total second-order correction to the interaction energy energy of A and B is

$$\begin{aligned}\Delta E^{(2)}_{0_{AB}} &= \Delta E^{(2)}_{0_{AB}}(0,2) + \Delta E^{(2)}_{0_{AB}}(2,0) + \Delta E^{(2)}_{0_{AB}}(0,0) \\ &= -\left(\frac{1}{2}\right) T_{xx}\, T_{xx}\, \mu_x^{B0}\, \mu_x^{B0} \alpha^A_{xx} - \left(\frac{1}{2}\right) T_{xx}\, T_{xx}\, \mu_x^{A0}\, \mu_x^{A0} \alpha^B_{xx}\end{aligned}$$

$$
\begin{aligned}
& - \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega \left[T_{xx}\, T_{xx}\, \alpha^{A}_{z'z'}(\imath\omega)\, \alpha^{B}_{z'z'}(\imath\omega) \right. \\
& - T_{yy}\, T_{yy}\, \alpha^{A}_{yy}(\imath\omega)\, \alpha^{B}_{yy}(\imath\omega) \\
& \left. - T_{zz}\, T_{zz}\, \alpha^{A}_{x'x'}(\imath\omega)\, \alpha^{B}_{x'x'}(\imath\omega) \right] .
\end{aligned} \tag{330}
$$

5.1.4 The Second-Order Correction to the Interaction Energy of Two Parallel HF molecules

Now, we will use the information in Sects. 5.1.1 - 5.1.3 to derive the second-order correction to the energy of two parallel interacting HF molecules. If we assume that $A = B =$HF in Eq. (330), the result is

$$
\begin{aligned}
\Delta E^{(2)}_{0_{HF-HF}} &= \Delta E^{(2)}_{0_{HF-HF}}(0,2) + \Delta E^{(2)}_{0_{HF-HF}}(2,0) + \Delta E^{(2)}_{0_{HF-HF}}(0,0) \\
&= -T_{xx}\, T_{xx} \left(\mu^{HF}_{x}\right)^2 \alpha^{HF}_{xx} \\
&- \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega \left\{ T_{xx}\, T_{xx} \left[\alpha^{HF}_{xx}(\imath\omega)\right]^2 \right. \\
&- T_{yy}\, T_{yy} \left[\alpha^{HF}_{yy}(\imath\omega)\right]^2 \\
&\left. - T_{zz}\, T_{zz} \left[\alpha^{HF}_{zz}(\imath\omega)\right]^2 \right\} .
\end{aligned} \tag{331}
$$

According to Eq. (295), T_{xx}, T_{yy} and T_{zz} for the colinear arrangement of A and B are

$$
\begin{aligned}
T_{xx} &= T_{yy} = \frac{-1}{(\mathbf{R}_{AB})^3} \\
T_{zz} &= \frac{2}{(\mathbf{R}_{AB})^3},
\end{aligned} \tag{332}
$$

Using these equations with $A = B =$HF in Eq. (330), we have

$$
\begin{aligned}
\Delta E^{(2)}_{0_{HF-HF}} &= \Delta E^{(2)}_{0_{HF-HF}}(0,2) + \Delta E^{(2)}_{0_{HF-HF}}(2,0) + \Delta E^{(2)}_{0_{HF-HF}}(0,0) \\
&= - \frac{1}{(\mathbf{R}_{HF-HF})^6} \left(\mu^{HF}_{x}\right)^2 \alpha^{HF}_{xx} \\
&- \left(\frac{\hbar}{4\pi}\right) \frac{1}{(\mathbf{R}_{HF-HF})^6} \int\limits_{-\infty}^{+\infty} d\omega \left[\alpha^{HF}_{xx}(\imath\omega)\right]^2
\end{aligned}
$$

$$
\begin{aligned}
&- \left(\frac{\hbar}{4\pi}\right) \frac{1}{(\mathbf{R}_{HF-HF})^6} \int_{-\infty}^{+\infty} d\omega \left[\alpha_{yy}^{HF}(\imath\omega)\right]^2 \\
&- \left(\frac{\hbar}{\pi}\right) \frac{1}{(\mathbf{R}_{HF-HF})^6} \int_{-\infty}^{+\infty} d\omega \left[\alpha_{zz}^{HF}(\imath\omega)\right]^2, \qquad (333)
\end{aligned}
$$

where we have also distributed the integral over ω. According to Eq. (317) in Sect. 5.1.2, the frequency-dependent polarizabilities $\alpha_{xx}^{HF}(\imath\omega)$, $\alpha_{yy}^{HF}(\imath\omega)$, and $\alpha_{zz}^{HF}(\imath\omega)$ can be approximated by

$$
\begin{aligned}
\alpha_{xx}^{HF}(\imath\omega) &= \frac{\left(E_{IP}^{HF}\right)^2 \alpha_{xx}^{HF}}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]} \\
\alpha_{yy}^{HF}(\imath\omega) &= \frac{\left(E_{IP}^{HF}\right)^2 \alpha_{yy}^{HF}}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]} \\
\alpha_{zz}^{HF}(\imath\omega) &= \frac{\left(E_{IP}^{HF}\right)^2 \alpha_{zz}^{HF}}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]}, \qquad (334)
\end{aligned}
$$

From Eqs. (333) and (334), we have

$$
\begin{aligned}
\Delta E_{0_{HF-HF}}^{(2)} &= \Delta E_{0_{HF-HF}}^{(2)}(0,2) + \Delta E_{0_{HF-HF}}^{(2)}(2,0) + \Delta E_{0_{HF-HF}}^{(2)}(0,0) \\
&= - \frac{1}{(\mathbf{R}_{HF-HF})^6} \left(\mu_x^{HF}\right)^2 \alpha_{xx}^{HF} \\
&- \left(\frac{\hbar}{4\pi}\right) \frac{\left(E_{IP}^{HF}\right)^4 \left(\alpha_{xx}^{HF}\right)^2}{(\mathbf{R}_{HF-HF})^6} \int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]^2} \\
&- \left(\frac{\hbar}{4\pi}\right) \frac{\left(E_{IP}^{HF}\right)^4 \left(\alpha_{yy}^{HF}\right)^2}{(\mathbf{R}_{HF-HF})^6} \int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]^2} \\
&- \left(\frac{\hbar}{\pi}\right) \frac{\left(E_{IP}^{HF}\right)^4 \left(\alpha_{zz}^{HF}\right)^2}{(\mathbf{R}_{HF-HF})^6} \int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]^2}. \qquad (335)
\end{aligned}
$$

The integrals in Eq. (335) were evaluated in Sect. 5.1.2. According to Eq. (324) in Sect. 5.1.2,

$$\int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{HF}\right)^2 + \hbar^2\omega^2\right]^2} = \frac{\pi}{E_{IP}^{HF^3}\hbar}. \tag{336}$$

From Eqs. (336) and (335),

$$\begin{aligned} \Delta E_{0_{HF-HF}}^{(2)} &= \Delta E_{0_{HF-HF}}^{(2)}(0,2) + \Delta E_{0_{HF-HF}}^{(2)}(2,0) + \Delta E_{0_{HF-HF}}^{(2)}(0,0) \\ &= -\frac{\left(\mu_x^{HF}\right)^2 \alpha_{xx}^{HF}}{\left(\mathbf{R}_{HF-HF}\right)^6} - \frac{\left(E_{IP}^{HF}\right)\left(\alpha_{xx}^{HF}\right)^2}{4\left(\mathbf{R}_{HF-HF}\right)^6} \\ &- \frac{\left(E_{IP}^{HF}\right)\left(\alpha_{yy}^{HF}\right)^2}{4\left(\mathbf{R}_{HF-HF}\right)^6} - \frac{\left(E_{IP}^{HF}\right)\left(\alpha_{zz}^{HF}\right)^2}{\left(\mathbf{R}_{HF-HF}\right)^6}. \end{aligned} \tag{337}$$

Recall that in the calculation of $\Delta E_{0_{HF-HF}}^{(2)}$ for two colinear HF molecules that we took $\mu_z^{HF} = 0.7043$ a.u., $E_{IP}^{HF} = 0.5896$ a.u., $\alpha_{xx}^{HF} = \alpha_{yy}^{HF} = 5.22$ a.u., and $\alpha_{zz}^{HF} = 6.36$ a.u. Because we have interchanged x and z for the current geometry, we have $\mu_x^{HF} = 0.7043$ a.u., $\alpha_{zz}^{HF} = \alpha_{yy}^{HF} = 5.22$ a.u., and $\alpha_{xx}^{HF} = 6.36$ a.u.. Using these values in Eq. (337), we obtain

$$\begin{aligned} \Delta E_{0_{HF-HF}}^{(2)} &= \Delta E_{0_{HF-HF}}^{(2)}(0,2) + \Delta E_{0_{HF-HF}}^{(2)}(2,0) + \Delta E_{0_{HF-HF}}^{(2)}(0,0) \\ &= -\frac{29.2\, a.u.}{\left(\mathbf{R}_{HF-HF}\right)^6}. \end{aligned} \tag{338}$$

5.1.5 The Second-Order Correction to the Interaction Energy of Two Perpendicular Molecules

In Fig. 14, the internuclear axis of molecule A lies along the z axis of the x, y, z laboratory frame, and the internuclear axis of molecule B lies along the x axis of the x, y, z laboratory frame, making these two molecules perpendicular to one another. The nuclei of molecules A and B in Fig. 14 are labeled A_1, A_2 and B_1, B_2, respectively, and the centers-of-mass of A and B are COM$_A$ and COM$_B$. Also, $\mathbf{R}_{AB}$ denotes the vector extending from COM$_A$ to COM$_B$.

Let us call the molecular frame of molecule A in Fig. 14 the x', y', z' frame, and the molecular frame of molecule B the x'', y'', z'' frame. The internuclear axis of molecule A lies along the z' axis of its molecular frame, and the internuclear axis of molecule B lies along the z'' axis of its molecular frame. Because the internuclear axis of A lies along z and z', the molecular frame of A is the same as the laboratory frame. Therefore, we do not have to rotate the non-zero components of the relevant properties of A, and we can specify these properties in the laboratory frame. However, because the internuclear axis of molecule B lies along z'' and x, we need to rotate the non-zero components of the relevant properties of B. The x'', y'', z'' frame is rotated 90° from the x, y, z frame. Thus $\mu_x^{B0} = \mu_{z''}^{B0}$, $\alpha_{xx}^B = \alpha_{z''z''}^B$, and $\alpha_{yy}^B = \alpha_{zz}^B = \alpha_{x''x''}^B$. From the properties of A and B and Eq. (293), we have

$$\Delta E^{(2)}_{0_{AB}}(0,2) = -\left(\frac{1}{2}\right) T_{xx}\, T_{xx} \left(\mu_{z''}^{B0}\right)^2 \alpha_{xx}^A, \tag{339}$$

$$\Delta E^{(2)}_{0_{AB}}(2,0) = -\left(\frac{1}{2}\right) T_{zz}\, T_{zz} \left(\mu_{z}^{A0}\right)^2 \alpha_{x''x''}^B, \tag{340}$$

and

$$\begin{aligned}\Delta E^{(2)}_{0_{AB}}(0,0) = & - T_{xx}\, T_{xx} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega\, \alpha_{xx}^A(\imath\omega)\, \alpha_{z''z''}^B(\imath\omega) \\ & - T_{yy}\, T_{yy} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega\, \alpha_{yy}^A(\imath\omega)\, \alpha_{y''y''}^B(\imath\omega) \\ & - T_{zz}\, T_{zz} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega\, \alpha_{zz}^A(\imath\omega)\, \alpha_{x''x''}^B(\imath\omega)\,. \end{aligned} \tag{341}$$

Letting $A = B =$HF in Eqs. (339), (340), and (341) gives

$$\Delta E^{(2)}_{0_{HF-HF}}(0,2) = -\left(\frac{1}{2}\right) T_{xx}\, T_{xx} \left(\mu_{z''}^{HF,0}\right)^2 \alpha_{xx}^{HF}, \tag{342}$$

$$\Delta E^{(2)}_{0_{HF-HF}}(2,0) = -\left(\frac{1}{2}\right) T_{zz}\, T_{zz} \left(\mu_{z}^{HF,0}\right)^2 \alpha_{x''x''}^{HF}, \tag{343}$$

and

$$
\begin{aligned}
\Delta E^{(2)}_{0_{HF-HF}}(0,0) = & - T_{xx}\,T_{xx}\left(\frac{\hbar}{4\pi}\right)\int_{-\infty}^{+\infty} d\omega\,\alpha^{HF}_{xx}(\imath\omega)\,\alpha^{HF}_{z''z''}(\imath\omega) \\
& - T_{yy}\,T_{yy}\left(\frac{\hbar}{4\pi}\right)\int_{-\infty}^{+\infty} d\omega\,\alpha^{HF}_{yy}(\imath\omega)\,\alpha^{HF}_{y''y''}(\imath\omega) \\
& - T_{zz}\,T_{zz}\left(\frac{\hbar}{4\pi}\right) \\
& \times \int_{-\infty}^{+\infty} d\omega\,\alpha^{HF}_{zz}(\imath\omega)\,\alpha^{HF}_{x''x''}(\imath\omega)\,. \qquad (344)
\end{aligned}
$$

5.2 The 2^{nd} -Order Correction to the Interaction Energy of Three Molecules

In Sect. 5.1, we wrote the second-order correction $\Delta E^{(2)}_{0_{AB}}$ to the interaction energy of molecules A and B (see Eq. 292) as

$$\Delta E^{(2)}_{0_{AB}} = \Delta E^{(2)}_{0_{AB}}(0,2) + \Delta E^{(2)}_{0_{AB}}(2,0) + \Delta E^{(2)}_{0_{AB}}(0,0)\,. \qquad (345)$$

If we have three molecules, which we will denote A, B, and C, we can write the total second-order correction to the energy of interaction $\Delta E^{(2)}_{0_{ABC}}$ of these molecules as the sum of the second-order, two-body corrections due to the interactions of A and B, A and C, and B and C,

$$\Delta E^{(2,2)}_{0_{ABC}} = \Delta E^{(2)}_{0_{AB}} + \Delta E^{(2)}_{0_{AC}} + \Delta E^{(2)}_{0_{BC}}, \qquad (346)$$

and an irreducible three-body energy of second-order, $\Delta E^{(2,3)}_{0_{ABC}}$. The second-order, two-body energy of interaction $\Delta E^{(2)}_{0_{AB}}$ of A and B is given in Eq. (345), $\Delta E^{(2)}_{0_{AC}}$ is given by Eq. (345) with B replaced by C,

$$\Delta E^{(2)}_{0_{AC}} = \Delta E^{(2)}_{0_{AC}}(0,2) + \Delta E^{(2)}_{0_{AC}}(2,0) + \Delta E^{(2)}_{0_{AC}}(0,0)\,, \qquad (347)$$

and $\Delta E^{(2)}_{0_{BC}}$ is given by Eq. (347) with A replaced by B,

$$\Delta E^{(2)}_{0_{BC}} = \Delta E^{(2)}_{0_{BC}}(0,2) + \Delta E^{(2)}_{0_{BC}}(2,0) + \Delta E^{(2)}_{0_{BC}}(0,0)\,. \qquad (348)$$

The irreducible three-body energy $\Delta E^{(2,3)}_{0_{ABC}}$ is a sum of three contributions, $\Delta E^{(2,3)}_{0_A}$, $\Delta E^{(2,3)}_{0_B}$, and $\Delta E^{(2,3)}_{0_C}$, where

$$\Delta E^{(2,3)}_{0_A} = -\alpha^A_{\alpha\beta}\, T_{\alpha\gamma}(\mathbf{R}_{AB})\, \mu^{B0}_\gamma\, T_{\beta\delta}(\mathbf{R}_{AC})\, \mu^{C0}_\delta. \tag{349}$$

The full nonadditive second-order correction to the energy $\Delta E^{(2,3)}_{0_{ABC}}$ is

$$\begin{aligned}\Delta E^{(2,3)}_{0_{ABC}} = & - \alpha^A_{\alpha\beta}\, T_{\alpha\gamma}(\mathbf{R}_{AB})\, \mu^{B0}_\gamma\, T_{\beta\delta}(\mathbf{R}_{AC})\, \mu^{C0}_\delta \\ & - \alpha^B_{\alpha\beta}\, T_{\alpha\gamma}(\mathbf{R}_{AB})\, \mu^{A0}_\gamma\, T_{\beta\delta}(\mathbf{R}_{BC})\, \mu^{C0}_\delta \\ & - \alpha^C_{\alpha\beta}\, T_{\alpha\gamma}(\mathbf{R}_{AC})\, \mu^{A0}_\gamma\, T_{\beta\delta}(\mathbf{R}_{BC})\, \mu^{B0}_\delta.\end{aligned} \tag{350}$$

Therefore, using Eqs. (346), (345), (347), and (348), we obtain an equation for $\Delta E^{(2)}_{0_{ABC}}$,

$$\begin{aligned}\Delta E^{(2)}_{0_{ABC}} = & \Delta E^{(2)}_{0_{AB}}(0,2) + \Delta E^{(2)}_{0_{AB}}(2,0) \\ + & \Delta E^{(2)}_{0_{AB}}(0,0) + \Delta E^{(2)}_{0_{AC}}(0,2) \\ + & \Delta E^{(2)}_{0_{AC}}(2,0) + \Delta E^{(2)}_{0_{AC}}(0,0) \\ + & \Delta E^{(2)}_{0_{BC}}(0,2) + \Delta E^{(2)}_{0_{BC}}(2,0) \\ + & \Delta E^{(2)}_{0_{BC}}(0,0) + \Delta E^{(2,3)}_{0_{ABC}}.\end{aligned} \tag{351}$$

We will use Eq. (351) and the results of the derivation of $\Delta E^{(2)}_{0_{HF-HF}}$ in Sect. 5.1.2 to derive and equation for $\Delta E^{(2)}_{0_{HF-HF-HF}}$.

5.2.1 The Second-Order Correction to the Interaction Energy of Three HF molecules, Arranged Colinearly

Fig. 15 shows three colinear HF molecules which have their internuclear axes on the z' axis of the x', y', z' molecular frame. Their internuclear axes are also aligned with the x, y, z laboratory frame. Note that the molecular and laboratory coordinate systems are the same, as in Fig. 12. In Fig. 15, we have labeled the HF molecules HF_1, HF_2, and HF_3. Also, H_1, H_2 and H_3 denote the hydrogen atoms in HF_1, HF_2, and HF_3; and F_1, F_2 and F_3 denote the fluorine atoms in HF_1, HF_2, and HF_3, respectively. The HF_1, HF_2, and HF_3 molecules have centers-of-mass COM_{HF_1}, COM_{HF_2}, and COM_{HF_3}, respectively. We have let $\mathbf{R}_{HF_1-HF_2}$, $\mathbf{R}_{HF_1-HF_3}$, and $\mathbf{R}_{HF_2-HF_3}$ be the vectors between HF_1 and HF_2, HF_1 and HF_3, and HF_2 and HF_3. If we let $A =$

HF_1, $B = HF_2$, and $C = HF_3$ in Eq. (351), we have

$$\begin{aligned}\Delta E^{(2)}_{0_{HF_1-HF_2-HF_3}} &= \Delta E^{(2)}_{0_{HF_1-HF_2}}(0,2) + \Delta E^{(2)}_{0_{HF_1-HF_2}}(2,0)\\ &+ \Delta E^{(2)}_{0_{HF_1-HF_2}}(0,0) + \Delta E^{(2)}_{0_{HF_1-HF_3}}(0,2)\\ &+ \Delta E^{(2)}_{0_{HF_1-HF_3}}(2,0) + \Delta E^{(2)}_{0_{HF_1-HF_3}}(0,0)\\ &+ \Delta E^{(2)}_{0_{HF_2-HF_3}}(0,2) + \Delta E^{(2)}_{0_{HF_2-HF_3}}(2,0)\\ &+ \Delta E^{(2)}_{0_{HF_2-HF_3}}(0,0) + \Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}\\ &= \Delta E^{(2)}_{0_{HF_1-HF_2}} + \Delta E^{(2)}_{0_{HF_1-HF_3}} + \Delta E^{(2)}_{0_{HF_2-HF_3}}\\ &+ \Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}. \end{aligned} \tag{352}$$

Recall Eq. (327) from Sect. 5.1.2, which gives $\Delta E^{(2)}_{0_{HF-HF}}$ for two colinear HF molecules

$$\Delta E^{(2)}_{0_{HF-HF}} = -\frac{44.5\,a.u.}{(\mathbf{R}_{HF-HF})^6}. \tag{353}$$

Using Eqs. (352) and (353), we have

$$\begin{aligned}\Delta E^{(2)}_{0_{HF_1-HF_2-HF_3}} &= -\frac{44.5\,a.u.}{(\mathbf{R}_{HF_1-HF_2})^6} - \frac{44.5\,a.u.}{(\mathbf{R}_{HF_1-HF_3})^6} - \frac{44.5\,a.u.}{(\mathbf{R}_{HF_2-HF_3})^6}\\ &+ \Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}. \end{aligned} \tag{354}$$

From Eq. (350), the irreducible three-body energy for this geometry is

$$\begin{aligned}\Delta E^{(2,3)}_{0_{ABC}} &= -\ \alpha^A_{zz}\, T_{zz}(\mathbf{R}_{AB})\, \mu^B_z\, T_{zz}(\mathbf{R}_{AC})\, \mu^C_z\\ &-\ \alpha^B_{zz}\, T_{zz}(\mathbf{R}_{AB})\, \mu^A_z\, T_{zz}(\mathbf{R}_{BC})\, \mu^C_z\\ &-\ \alpha^C_{zz}\, T_{zz}(\mathbf{R}_{AC})\, \mu^A_z\, T_{zz}(\mathbf{R}_{BC})\, \mu^B_z. \end{aligned} \tag{355}$$

and, letting $A = HF_1$, $B = HF_2$, and $C = HF_3$ in Eq. (355), we have

$$\begin{aligned}\Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}} &= -\ \alpha^{HF_1}_{zz}\, T_{zz}(\mathbf{R}_{HF_1-HF_2})\, \mu^{HF_2}_z\, T_{zz}(\mathbf{R}_{HF_1-HF_3})\, \mu^{HF_3}_z\\ &-\ \alpha^{HF_2}_{zz}\, T_{zz}(\mathbf{R}_{HF_1-HF_2})\, \mu^{HF_1}_z\, T_{zz}(\mathbf{R}_{HF_2-HF_3})\, \mu^{HF_3}_z\\ &-\ \alpha^{HF_3}_{zz}\, T_{zz}(\mathbf{R}_{HF_1-HF_3})\, \mu^{HF_1}_z\\ &\times\ T_{zz}(\mathbf{R}_{HF_2-HF_3})\, \mu^{HF_2}_z. \end{aligned} \tag{356}$$

5.2.2 The Second-Order Correction to the Interaction Energy of Three Parallel HF molecules

Fig. 16 shows three parallel HF molecules which have their internuclear axes aligned with the z' axis of the x', y', z' molecular frame, and with the x axis of the x, y, z laboratory frame. In Fig. 16, we have labeled the HF molecules HF_1, HF_2, and HF_3. Also, H_1, H_2 and H_3 denote the hydrogen atoms in HF_1, HF_2, and HF_3; and F_1, F_2 and F_3 denote the fluorine atoms in HF_1, HF_2, and HF_3, respectively. The HF_1, HF_2, and HF_3 molecules have centers-of-mass COM_{HF_1}, COM_{HF_2}, and COM_{HF_3}, respectively. We have let $\mathbf{R}_{HF_1-HF_2}$, $\mathbf{R}_{HF_1-HF_3}$, and $\mathbf{R}_{HF_2-HF_3}$ be the vectors between HF_1 and HF_2, HF_1 and HF_3, and HF_2 and HF_3.

The relationship between the molecular and laboratory frames in Fig. 16 is identical to the relationship between these two coordinate systems in Fig. 13. Therefore, we can use the equation for $\Delta E^{(2)}_{0_{HF-HF}}$ derived for two parallel HF molecules in Sect. 5.1.4 to write $\Delta E^{(2)}_{0_{HF-HF}}$ for each pair of molecules in Fig. 16. According to Eq. (352) in Sect. 5.2.1, $\Delta E^{(2)}_{0_{HF_1-HF_2-HF_3}}$ is

$$\begin{aligned}
\Delta E^{(2)}_{0_{HF_1-HF_2-HF_3}} &= \Delta E^{(2)}_{0_{HF_1-HF_2}}(0,2) + \Delta E^{(2)}_{0_{HF_1-HF_2}}(2,0) \\
&+ \Delta E^{(2)}_{0_{HF_1-HF_2}}(0,0) + \Delta E^{(2)}_{0_{HF_1-HF_3}}(0,2) \\
&+ \Delta E^{(2)}_{0_{HF_1-HF_3}}(2,0) + \Delta E^{(2)}_{0_{HF_1-HF_3}}(0,0) \\
&+ \Delta E^{(2)}_{0_{HF_2-HF_3}}(0,2) + \Delta E^{(2)}_{0_{HF_2-HF_3}}(2,0) \\
&+ \Delta E^{(2)}_{0_{HF_2-HF_3}}(0,0) + \Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}} \\
&= \Delta E^{(2)}_{0_{HF_1-HF_2}} + \Delta E^{(2)}_{0_{HF_1-HF_3}} + \Delta E^{(2)}_{0_{HF_2-HF_3}} \\
&+ \Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}. \qquad (357)
\end{aligned}$$

Recall Eq. (338) from Sect. 5.1.4, which gives $\Delta E^{(2)}_{0_{HF-HF}}$ for two HF molecules that are parallel to each other and to the x axis,

$$\Delta E^{(2)}_{0_{HF-HF}} = -\frac{29.2\,a.u.}{(\mathbf{R}_{HF-HF})^6}. \qquad (358)$$

Using Eqs. (357) and (358), we have

$$\begin{aligned}\Delta E^{(2)}_{0_{HF_1-HF_2-HF_3}} = & - \frac{29.2\,a.u.}{(\mathbf{R}_{HF_1-HF_2})^6} - \frac{29.2\,a.u.}{(\mathbf{R}_{HF_1-HF_3})^6} - \frac{29.2\,a.u.}{(\mathbf{R}_{HF_2-HF_3})^6} \\ & + \Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}. \end{aligned} \tag{359}$$

From Eq. (350), the irreducible three-body energy for this geometry is

$$\begin{aligned}\Delta E^{(2,3)}_{0_{ABC}} = & - \alpha^A_{z'z'}\, T_{xx}(\mathbf{R}_{AB})\, \mu^A_{z'}\, T_{xx}(\mathbf{R}_{AC})\, \mu^C_{z'} \\ & - \alpha^B_{z'z'}\, T_{xx}(\mathbf{R}_{AB})\, \mu^A_{z'}\, T_{xx}(\mathbf{R}_{BC})\, \mu^C_{z'} \\ & - \alpha^C_{z'z'}\, T_{xx}(\mathbf{R}_{AC})\, \mu^A_{z'}\, T_{xx}(\mathbf{R}_{BC})\, \mu^B_{z'}. \end{aligned} \tag{360}$$

and, letting $A = \mathrm{HF}_1$, $B = \mathrm{HF}_2$, and $C = \mathrm{HF}_3$ in Eq. (360), we have

$$\begin{aligned}\Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}} = & - \alpha^{HF_1}_{z'z'}\, T_{xx}(\mathbf{R}_{HF_1-HF_2})\, \mu^{HF_1}_{z'}\, T_{xx}(\mathbf{R}_{HF_1-HF_3})\, \mu^{HF_3}_{z'} \\ & - \alpha^{HF_2}_{z'z'}\, T_{xx}(\mathbf{R}_{HF_1-HF_2})\, \mu^{HF_1}_{z'}\, T_{xx}(\mathbf{R}_{HF_2-HF_3})\, \mu^{HF_3}_{z'} \\ & - \alpha^{HF_3}_{z'z'}\, T_{xx}(\mathbf{R}_{HF_1-HF_3})\, \mu^{HF_1}_{z'} \\ & \times\, T_{xx}(\mathbf{R}_{HF_2-HF_3})\, \mu^{HF_2}_{z'}. \end{aligned} \tag{361}$$

5.3 The Third-Order Correction to the Energy of Interaction of A and B

According to Eq. (290) in Chap. 4, the third-order correction $\Delta E^{(3)}_{0_{AB}}$ to the energy of two interacting molecules A and B is

$$\begin{aligned}\Delta E^{(3)}_{0_{AB}} = & - T_{\alpha\beta}\, T_{\delta\gamma}\, T_{\epsilon\phi}\, \mu^{A0}_{\alpha}\, \mu^{B0}_{\phi}\, \alpha^A_{\epsilon\delta}\, \alpha^B_{\gamma\beta} \\ & - \frac{1}{6} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\beta}\, \mu^{B0}_{\delta}\, \mu^{B0}_{\phi}\, \beta^A_{\gamma\alpha\epsilon} \\ & - \frac{1}{6} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{A0}_{\alpha}\mu^{A0}_{\gamma}\mu^{A0}_{\epsilon}\, \beta^B_{\delta\beta\phi} \\ & - T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\phi} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega\, \alpha^B_{\delta\beta}(\imath\omega)\, \beta^A_{\epsilon\alpha\gamma}(-\imath\omega; \imath\omega, 0) \\ & - T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu^{A0}_{\epsilon} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega\, \alpha^A_{\alpha\gamma}(\imath\omega)\, \beta^B_{\beta\delta\phi}(-\imath\omega; \imath\omega, 0) \end{aligned}$$

$$
\begin{aligned}
- &\; T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \left(\frac{\hbar^2}{4\pi^2}\right) \int\limits_{-\infty}^{+\infty} d\omega \int\limits_{-\infty}^{+\infty} d\omega'\, b^{A}_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) \\
\times &\; \Big[b^{B}_{\delta\beta\phi}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) \\
+ &\; b^{B}_{\delta\beta\phi}\left(\imath\omega; -\imath\omega' - \imath\omega, \imath\omega'\right) \\
+ &\; b^{B}_{\delta\beta\phi}\left(-\imath\omega; \imath\omega' + \imath\omega, -\imath\omega'\right) \\
+ &\; b^{B}_{\delta\beta\phi}\left(-\imath\omega; \imath\omega - \imath\omega', \imath\omega'\right) \Big] .
\end{aligned}
\tag{362}
$$

The individual terms in $\Delta E^{(3)}_{0_{AB}}$ are

$$
\begin{aligned}
\Delta E^{(3)}_{0_{AB}}(1,1) &= -T_{\alpha\beta}\, T_{\delta\gamma}\, T_{\epsilon\phi}\, \mu^{A0}_{\alpha}\, \mu^{B0}_{\phi}\, \alpha^{A}_{\epsilon\delta}\, \alpha^{B}_{\gamma\beta} \\
\Delta E^{(3)}_{0_{AB}}(3,0) &= -\frac{1}{6} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{A0}_{\alpha}\, \mu^{A0}_{\gamma} \mu^{A0}_{\epsilon}\, \beta^{B}_{\delta\beta\phi} \\
\Delta E^{(3)}_{0_{AB}}(0,3) &= -\frac{1}{6} T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\beta}\, \mu^{B0}_{\delta}\, \mu^{B0}_{\phi}\, \beta^{A}_{\gamma\alpha\epsilon} \\
\Delta E^{(3)}_{0_{AB}}(0,1) &= -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\, \mu^{B0}_{\phi} \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega\, \alpha^{B}_{\delta\beta}(\imath\omega) \\
&\times\; \beta^{A}_{\epsilon\alpha\gamma}(-\imath\omega; \imath\omega, 0) \\
\Delta E^{(3)}_{0_{AB}}(1,0) &= -T_{\alpha\beta}\, T_{\epsilon\phi}\, T_{\gamma\delta}\, \mu^{A0}_{\epsilon} \left(\frac{\hbar}{4\pi}\right) \int\limits_{-\infty}^{+\infty} d\omega\, \alpha^{A}_{\alpha\gamma}(\imath\omega) \\
&\times\; \beta^{B}_{\beta\delta\phi}(-\imath\omega; \imath\omega, 0) \\
\Delta E^{(3)}_{0_{AB}}(0,0) &= -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi} \left(\frac{\hbar^2}{4\pi^2}\right) \int\limits_{-\infty}^{+\infty} d\omega \int\limits_{-\infty}^{+\infty} d\omega' \\
&\times\; b^{A}_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) \\
&\times\; \Big[b^{B}_{\delta\beta\phi}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) \\
&+\; b^{B}_{\delta\beta\phi}\left(\imath\omega; -\imath\omega' - \imath\omega, \imath\omega'\right) \\
&+\; b^{B}_{\delta\beta\phi}\left(-\imath\omega; \imath\omega' + \imath\omega, -\imath\omega'\right)
\end{aligned}
$$

$$+ \quad b^{B}_{\delta\beta\phi}\left(-\imath\omega; \imath\omega - \imath\omega', \imath\omega'\right)\Big] . \tag{363}$$

We can use Eq. (362) or (363) to derive expressions for $\Delta E^{(3)}_{0_{AB}}$ as a function of $\mathbf{R}_{AB}$ for various geometries of A and B.

5.3.1 The Third-Order Correction to the Interaction Energy of Two Colinear Molecules

Let us derive an expression for $\Delta E^{(3)}_{0_{AB}}$ as a function of $\mathbf{R}_{AB}$ for the colinear geometry of A and B in Fig. 12. To begin, let us derive an expression for the $\Delta E^{(3)}_{0_{AB}}(1,1)$ term in Eq. (363) as a function of $\mathbf{R}_{AB}$. Recall from the derivation of $\Delta E^{(2)}_{0_{AB}}$ as a function of $\mathbf{R}_{AB}$ for this geometry that the molecular and laboratory axes are the same, so there is no need to rotate the non-zero components of the properties of A and B before deriving $\Delta E^{(3)}_{0_{AB}}$ in terms of the laboratory coordinates. While deriving $\Delta E^{(2)}_{0_{AB}}$ for this geometry, we also determined that $T_{xx} = T_{yy} \neq 0$, $T_{zz} \neq 0$, and $T_{\alpha\beta} = 0$ when $\alpha \neq \beta$. In the colinear configuration of A and B shown in Fig. 12, $\mu^{A0}_x = \mu^{A0}_y = 0$ and $\mu^{B0}_x = \mu^{B0}_y = 0$. Therefore,

$$\begin{aligned}\Delta E^{(3)}_{0_{AB}}(1,1) = & - T_{zz}\, T_{xx}\, T_{zz}\, \mu^{A0}_z\, \mu^{B0}_z\, \alpha^{A}_{zx}\, \alpha^{B}_{xz} \\ & - T_{zz}\, T_{yy}\, T_{zz}\, \mu^{A0}_z\, \mu^{B0}_z\, \alpha^{A}_{zy}\, \alpha^{B}_{yz} \\ & - T_{zz}\, T_{zz}\, T_{zz}\, \mu^{A0}_z\, \mu^{B0}_z\, \alpha^{A}_{zz}\, \alpha^{B}_{zz}.\end{aligned} \tag{364}$$

Finally, since $\alpha_{\alpha\beta} = 0$ if $\alpha \neq \beta$,

$$\Delta E^{(3)}_{0_{AB}}(1,1) = -T_{zz}\, T_{zz}\, T_{zz}\, \mu^{A0}_z\, \mu^{B0}_z\, \alpha^{A}_{zz}\, \alpha^{B}_{zz}. \tag{365}$$

Recall Eq. (295) from Sect. 5.1.1,

$$\begin{aligned} T_{xx} &= T_{yy} = \frac{-1}{(\mathbf{R}_{AB})^3} \\ T_{zz} &= \frac{2}{(\mathbf{R}_{AB})^3}. \end{aligned} \tag{366}$$

Using Eq. (366) in Eq. (365) gives

$$\Delta E^{(3)}_{0_{AB}}(1,1) = \frac{8\, \mu^{A0}_z\, \mu^{B0}_z\, \alpha^{A}_{zz}\, \alpha^{B}_{zz}}{(\mathbf{R}_{AB})^9}. \tag{367}$$

Now, let us derive an equation for $\Delta E^{(3)}_{0_{AB}}(0,3)$ for this geometry. According to Eq. (363), $\Delta E^{(3)}_{0_{AB}}(0,3)$ is

$$\Delta E^{(3)}_{0_{AB}}(0,3) \;=\; -\frac{1}{6}T_{\alpha\beta}\,T_{\gamma\delta}\,T_{\epsilon\phi}\,\mu^{B0}_{\beta}\mu^{B0}_{\delta}\mu^{B0}_{\phi}\,\beta^{A}_{\gamma\alpha\epsilon}. \tag{368}$$

Since $T_{xx} = T_{yy} \neq 0$, $T_{zz} \neq 0$, and $T_{\alpha\beta} = 0$ when $\alpha \neq \beta$, and $\mu^{B0}_{x} = \mu^{B0}_{y} = 0$,

$$\Delta E^{(3)}_{0_{AB}}(0,3) = -\frac{1}{6}T_{zz}\,T_{zz}\,T_{zz}\,\mu^{B0}_{z}\mu^{B0}_{z}\mu^{B0}_{z}\,\beta^{A}_{zzz}. \tag{369}$$

Using Eq. (366) in Eq. (369) gives

$$\Delta E^{(3)}_{0_{AB}}(0,3) = -\frac{4\left(\mu^{B0}_{z}\right)^{3}\beta^{A}_{zzz}}{3(\mathbf{R}_{AB})^{9}}. \tag{370}$$

Similarly, according to Eq. (363), $\Delta E^{(3)}_{0_{AB}}(3,0)$ for A and B as arranged in Fig. 12 is

$$\Delta E^{(3)}_{0_{AB}}(3,0) \;=\; -\frac{1}{6}T_{\alpha\beta}\,T_{\gamma\delta}\,T_{\epsilon\phi}\,\mu^{A0}_{\alpha}\mu^{A0}_{\gamma}\mu^{A0}_{\epsilon}\,\beta^{B}_{\delta\beta\phi}. \tag{371}$$

and

$$\Delta E^{(3)}_{0_{AB}}(3,0) = -\frac{1}{6}T_{zz}\,T_{zz}\,T_{zz}\left(\mu^{A0}_{z}\right)^{3}\beta^{B}_{zzz}. \tag{372}$$

Using Eq. (366) in Eq. (372) gives

$$\Delta E^{(3)}_{0_{AB}}(3,0) = -\frac{4\left(\mu^{A0}_{z}\right)^{3}\beta^{B}_{zzz}}{3(\mathbf{R}_{AB})^{9}}. \tag{373}$$

At this point, we are ready to calculate $\Delta E^{(3)}_{0_{AB}}(0,1)$ and $\Delta E^{(3)}_{0_{AB}}(1,0)$ for A and B as arranged in Fig. 12. According to Eq. (363) in Sect. 5.3, $\Delta E^{(3)}_{0_{AB}}(0,1)$ is

$$\begin{aligned}\Delta E^{(3)}_{0_{AB}}(0,1) \;=\; & -T_{\alpha\beta}\,T_{\gamma\delta}\,T_{\epsilon\phi}\,\mu^{B0}_{\phi}\left(\frac{\hbar}{4\pi}\right)\int_{-\infty}^{+\infty} d\omega\,\beta^{A}_{\epsilon\alpha\gamma}(-\imath\omega;\imath\omega,0)\\ & \times\;\alpha^{B}_{\delta\beta}(\imath\omega)\,.\end{aligned} \tag{374}$$

Since a) $T_{xx} = T_{yy} \neq 0$, $T_{zz} \neq 0$, and $T_{\alpha\beta} = 0$ when $\alpha \neq \beta$, b) $\mu_x^{A0} = \mu_y^{A0} = 0$ and c) $\alpha_{\alpha\beta} = 0$ when $\alpha \neq \beta$ (for HF),

$$\begin{aligned} \Delta E^{(3)}_{0_{AB}}(0,1) = & - \; T_{xx}\, T_{xx}\, T_{zz}\, \mu_z^{B0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \, \beta^{A}_{zxx}(-\imath\omega; \imath\omega, 0) \\ & \times \; \alpha^{A}_{xx}(\imath\omega) \\ & - \; T_{yy}\, T_{yy}\, T_{zz}\, \mu_z^{B0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \, \beta^{A}_{zyy}(-\imath\omega; \imath\omega, 0) \\ & \times \; \alpha^{A}_{yy}(\imath\omega) \\ & - \; T_{zz}\, T_{zz}\, T_{zz}\, \mu_z^{B0} \left(\frac{\hbar}{4\pi}\right) \int_{-\infty}^{+\infty} d\omega \, \beta^{A}_{zzz}(-\imath\omega; \imath\omega, 0) \\ & \times \; \alpha^{A}_{zz}(\imath\omega) \, . \end{aligned} \tag{375}$$

In order to simplify Eq. (375), we need to determine which elements of the hyperpolarizability $\beta^{A}_{\epsilon\alpha\gamma}$ are nonzero. For a $C_{\infty v}$ molecule with its axis in the x direction by reflection symmetry in the xz and yz planes components of the β hyperpolarizability tensor that are odd in either subscript x or subscript y vanish. By rotational symmetry around the z axis, the non-zero components of the hyperpolarizability $\beta^{A}_{\epsilon\alpha\gamma}$ of molecule A (with $C_{\infty v}$ symmetry) are $\beta^{A}_{xxz} = \beta^{A}_{xzx} = \beta^{A}_{zxx} = \beta^{A}_{yyz} = \beta^{A}_{yzy} = \beta^{A}_{zyy}$, and β^{A}_{zzz}. If we assume that molecule B also has $C_{\infty v}$ symmetry, then the non-zero components of the hyperpolarizability of molecule B are $\beta^{B}_{xxz} = \beta^{B}_{xzx} = \beta^{B}_{zxx} = \beta^{B}_{yyz} = \beta^{B}_{yzy} = \beta^{B}_{zyy}$, and β^{B}_{zzz}. Note that the non-zero matrix elements of the static and frequency-dependent hyperpolarizabilities of molecules A and B will be the same.

When we inspect Eq. (375), we see that it contains only non-zero matrix elements of the hyperpolarizability of molecule A. Therefore, we cannot eliminate any more terms from this equation for $\Delta E^{(3)}_{0_{AB}}(0,1)$. However, we can simplify the expression for $\Delta E^{(3)}_{0_{AB}}(0,1)$ by simplifying the expressions for the frequency-dependent hyperpolarizabilities contained in Eq. (375). Eq. (215) in Chap. 4 gives the static hyperpolarizability $\beta_{\gamma\alpha\epsilon}$ of molecule A. From Eq. (215) with γ and ϵ interchanged, we have

$$\begin{aligned}
\beta^A_{\epsilon\alpha\gamma} &= \sum_{k_A, l_A \neq 0} \frac{1}{\left(E^{(0)}_{k_A} - E^{(0)}_{0_A}\right)\left(E^{(0)}_{l_A} - E^{(0)}_{0_A}\right)} \\
&\times \Big[\langle 0_A | \hat{\mu}^A_\epsilon | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\alpha | l_A \rangle \langle l_A | \hat{\mu}^A_\gamma | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\alpha | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\epsilon | l_A \rangle \langle l_A | \hat{\mu}^A_\gamma | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\alpha | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\gamma | l_A \rangle \langle l_A | \hat{\mu}^A_\epsilon | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\epsilon | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\gamma | l_A \rangle \langle l_A | \hat{\mu}^A_\alpha | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\gamma | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\epsilon | l_A \rangle \langle l_A | \hat{\mu}^A_\alpha | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\gamma | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\alpha | l_A \rangle \langle l_A | \hat{\mu}^A_\epsilon | 0_A \rangle \Big] . \qquad (376)
\end{aligned}$$

As discussed in Sect. 5.1.2, we can use the Unsöld approximation to write

$$\frac{1}{E^{(0)}_{k_A} - E^{(0)}_{0_A}} \cong \frac{1}{E^A_{IP}}, \qquad (377)$$

and

$$\frac{1}{E^{(0)}_{l_A} - E^{(0)}_{0_A}} \cong \frac{1}{E^A_{IP}}. \qquad (378)$$

When we use Eqs. (377) and (378) in Eq. (376), the result is

$$\begin{aligned}
\beta^A_{\epsilon\alpha\gamma} &\cong \frac{1}{\left(E^A_{IP}\right)^2} \sum_{k_A, l_A \neq 0} \Big[\langle 0_A | \hat{\mu}^A_\epsilon | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\alpha | l_A \rangle \langle l_A | \hat{\mu}^A_\gamma | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\alpha | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\epsilon | l_A \rangle \langle l_A | \hat{\mu}^A_\gamma | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\alpha | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\gamma | l_A \rangle \langle l_A | \hat{\mu}^A_\epsilon | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\epsilon | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\gamma | l_A \rangle \langle l_A | \hat{\mu}^A_\alpha | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\gamma | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\epsilon | l_A \rangle \langle l_A | \hat{\mu}^A_\alpha | 0_A \rangle \\
&+ \langle 0_A | \hat{\mu}^A_\gamma | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\alpha | l_A \rangle \langle l_A | \hat{\mu}^A_\epsilon | 0_A \rangle \Big] . \qquad (379)
\end{aligned}$$

Let us consider the sum over k_A and l_A of $\langle 0_A | \hat{\mu}^A_\epsilon | k_A \rangle \; \langle k_A | \hat{\bar{\mu}}^A_\alpha | l_A \rangle \; \langle l_A | \hat{\mu}^A_\gamma | 0_A \rangle$. We can write this sum as

$$\sum_{k_A, l_A \neq 0} \langle 0_A | \hat{\mu}^A_\epsilon | k_A \rangle \langle k_A | \hat{\bar{\mu}}^A_\alpha | l_A \rangle \langle l_A | \hat{\mu}^A_\gamma | 0_A \rangle =$$

$$\begin{aligned}&\sum_{k_A\neq0}\sum_{l_A}\Big[\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|l_A\rangle\langle l_A|\hat{\mu}^A_\gamma|0_A\rangle\\&-\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\Big]\,.\end{aligned}\tag{380}$$

Because $\sum_{l_A}|l_A\rangle\langle l_A| = 1$, we can write Eq. (380) as

$$\begin{aligned}&\sum_{k_A,l_A\neq0}\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|l_A\rangle\langle l_A|\hat{\mu}^A_\gamma|0_A\rangle =\\&\sum_{k_A\neq0}\Big[\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle\\-\;&\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\Big]\\=\;&\sum_{k_A}\Big[\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle\\-\;&\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle\\-\;&\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\\+\;&\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha|0_A\rangle\\\times\;&\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\Big]\,.\end{aligned}\tag{381}$$

Similarly, since $\sum_{k_A}|k_A\rangle\langle k_A| = 1$,

$$\begin{aligned}&\sum_{k_A,l_A\neq0}\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|l_A\rangle\langle l_A|\hat{\mu}^A_\gamma|0_A\rangle =\\&\langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle\\-\;&\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle\\-\;&\langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\\+\;&\Big(\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\\\times\;&\langle 0_A|\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\Big)\,.\end{aligned}\tag{382}$$

Recall from Sect. 4.1 that $\hat{\bar{\mu}}^A_\alpha = \hat{\mu}^A_\alpha - \mu^{A0}_\alpha$. When we use this equation in Eq. (382), the result is

$$\sum_{k_A,l_A\neq0}\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|l_A\rangle\langle l_A|\hat{\mu}^A_\gamma|0_A\rangle =$$

$$
\begin{aligned}
& \langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle \\
+ & \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\mu_\alpha^{A0}\langle 0_A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle \\
= & \langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle \\
+ & \mu_\epsilon^{A0}\mu_\alpha^{A0}\mu_\gamma^{A0} - \mu_\epsilon^{A0}\mu_\alpha^{A0}\mu_\gamma^{A0} \\
= & \langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle .
\end{aligned}
\tag{383}
$$

Now, consider the sum over k_A and l_A of $\langle 0_A|\hat{\mu}_\alpha^A|k_A\rangle$ $\langle k_A|\hat{\bar{\mu}}_\epsilon^A|l_A\rangle$ $\langle l_A|\hat{\mu}_\gamma^A|0_A\rangle$ in Eq. (379). We can use Eq. (383) with ϵ and α interchanged to write this quantity as

$$
\begin{aligned}
& \sum_{k_A,l_A\neq 0}\langle 0_A|\hat{\mu}_\alpha^A|k_A\rangle\langle k_A|\hat{\bar{\mu}}_\epsilon^A|l_A\rangle\langle l_A|\hat{\mu}_\gamma^A|0_A\rangle = \\
& \langle 0_A|\hat{\mu}_\alpha^A\hat{\bar{\mu}}_\epsilon^A\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\epsilon^A\hat{\mu}_\gamma^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\alpha^A\hat{\bar{\mu}}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle .
\end{aligned}
\tag{384}
$$

Again, using Eq. (383) with ϵ replaced by α, α replaced by γ, and γ replaced by ϵ in the sum over k_A and l_A of $\langle 0_A|\hat{\mu}_\alpha^A|k_A\rangle$ $\langle k_A|\hat{\bar{\mu}}_\gamma^A|l_A\rangle$ $\langle l_A|\hat{\mu}_\epsilon^A|0_A\rangle$ gives

$$
\begin{aligned}
& \sum_{k_A,l_A\neq 0}\langle 0_A|\hat{\mu}_\alpha^A|k_A\rangle\langle k_A|\hat{\bar{\mu}}_\gamma^A|l_A\rangle\langle l_A|\hat{\mu}_\epsilon^A|0_A\rangle = \\
& \langle 0_A|\hat{\mu}_\alpha^A\hat{\bar{\mu}}_\gamma^A\hat{\mu}_\epsilon^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\gamma^A\hat{\mu}_\epsilon^A|0_A\rangle \\
- & \langle 0_A|\hat{\mu}_\alpha^A\hat{\bar{\mu}}_\gamma^A|0_A\rangle\langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle .
\end{aligned}
\tag{385}
$$

Using Eq. (383) with γ and α interchanged in the sum over k_A and l_A of $\langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\ \langle k_A|\hat{\bar{\mu}}^A_\gamma|l_A\rangle\ \langle l_A|\hat{\mu}^A_\alpha|0_A\rangle$ yields

$$
\begin{aligned}
&\sum_{k_A,l_A\neq 0} \langle 0_A|\hat{\mu}^A_\epsilon|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\gamma|l_A\rangle\langle l_A|\hat{\mu}^A_\alpha|0_A = \\
&\langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\alpha|0_A\rangle \\
- \ &\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\alpha|0_A\rangle \\
- \ &\langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\gamma|0_A\rangle\langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle. \qquad (386)
\end{aligned}
$$

We can also use Eq. (383) with ϵ replaced by γ, γ replaced by α, and α replaced by ϵ to write

$$
\begin{aligned}
&\sum_{k_A,l_A\neq 0} \langle 0_A|\hat{\mu}^A_\gamma|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\epsilon|l_A\rangle\langle l_A|\hat{\mu}^A_\alpha|0_A\rangle = \\
&\langle 0_A|\hat{\mu}^A_\gamma\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\alpha|0_A\rangle \\
- \ &\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\alpha|0_A\rangle \\
- \ &\langle 0_A|\hat{\mu}^A_\gamma\hat{\bar{\mu}}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle. \qquad (387)
\end{aligned}
$$

Finally, interchanging γ and ϵ in Eq. (383) allows us to write the last product of matrix elements (summed over all $k_A, l_A \neq 0$) in Eq. (379) as

$$
\begin{aligned}
&\sum_{k_A,l_A\neq 0} \langle 0_A|\hat{\mu}^A_\gamma|k_A\rangle\langle k_A|\hat{\bar{\mu}}^A_\alpha|l_A\rangle\langle l_A|\hat{\mu}^A_\epsilon|0_A\rangle = \\
&\langle 0_A|\hat{\mu}^A_\gamma\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\epsilon|0_A\rangle \\
- \ &\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\epsilon|0_A\rangle \\
- \ &\langle 0_A|\hat{\mu}^A_\gamma\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle. \qquad (388)
\end{aligned}
$$

Therefore, we can use Eqs. (379), (383), (384), (385), (386), (387), and (388) to write

$$
\begin{aligned}
\beta^A_{\epsilon\alpha\gamma} \ &\cong \ \frac{1}{\left(E^A_{IP}\right)^2}\Big[\langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle - \langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle \\
&- \ \langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle + \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\gamma|0_A\rangle \\
&- \ \langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\gamma|0_A\rangle - \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle
\end{aligned}
$$

$$\begin{aligned}
&+ \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\epsilon|0_A\rangle - \langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\epsilon|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\gamma|0_A\rangle\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle + \langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\alpha|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\alpha|0_A\rangle - \langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\gamma|0_A\rangle\langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle \\
&+ \langle 0_A|\hat{\mu}^A_\gamma\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\alpha|0_A\rangle - \langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\alpha|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\gamma\hat{\bar{\mu}}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle + \langle 0_A|\hat{\mu}^A_\gamma\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\epsilon|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\epsilon|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\gamma\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\Big] . \qquad (389)
\end{aligned}$$

Since the matrix elements in Eq. (389) are real, we can write Eq. (389) as

$$\begin{aligned}
\beta^A_{\epsilon\alpha\gamma} &\cong \frac{2}{\left(E^A_{IP}\right)^2}\Big[\langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle - \langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle + \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\gamma|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\gamma|0_A\rangle - \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle \\
&+ \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\epsilon|0_A\rangle - \langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\epsilon|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\gamma|0_A\rangle\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\Big] . \qquad (390)
\end{aligned}$$

Solving for the matrix elements in (390) gives

$$\begin{aligned}
&\frac{\left(E^A_{IP}\right)^2\beta^A_{\epsilon\alpha\gamma}}{2} \\
&= \Big[\langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle - \langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle + \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\gamma|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\epsilon\hat{\mu}^A_\gamma|0_A\rangle - \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle \\
&+ \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\epsilon|0_A\rangle - \langle 0_A|\hat{\mu}^A_\alpha|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\gamma\hat{\mu}^A_\epsilon|0_A\rangle \\
&- \langle 0_A|\hat{\mu}^A_\alpha\hat{\bar{\mu}}^A_\gamma|0_A\rangle\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\Big] . \qquad (391)
\end{aligned}$$

Expansion of the matrix elements in Eq. (391) using $\hat{\bar{\mu}}^A_\alpha = \hat{\mu}^A_\alpha - \mu^A_\alpha$ (and similarly for $\hat{\bar{\mu}}^A_\gamma$ and $\hat{\bar{\mu}}^A_\epsilon$) followed by comparison of terms shows that

$$\langle 0_A|\hat{\mu}^A_\epsilon\hat{\bar{\mu}}^A_\alpha\hat{\mu}^A_\gamma|0_A\rangle$$

$$
\begin{aligned}
& -\langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle\langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle \\
= & \ \langle 0_A|\hat{\mu}_\alpha^A\hat{\bar{\mu}}_\epsilon^A\hat{\mu}_\gamma^A|0_A\rangle - \langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\epsilon^A\hat{\mu}_\gamma^A|0_A\rangle \\
& -\langle 0_A|\hat{\mu}_\alpha^A\hat{\bar{\mu}}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle \\
= & \ \langle 0_A|\hat{\mu}_\alpha^A\hat{\bar{\mu}}_\gamma^A\hat{\mu}_\epsilon^A|0_A\rangle - \langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\gamma^A\hat{\mu}_\epsilon^A|0_A\rangle \\
- & \ \langle 0_A|\hat{\mu}_\alpha^A\hat{\bar{\mu}}_\gamma^A|0_A\rangle\langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle,
\end{aligned}
\tag{392}
$$

and therefore

$$
\begin{aligned}
\frac{\beta_{\epsilon\alpha\gamma}^A\left(E_{IP}^A\right)^2}{6} = & \left[\langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle - \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle\right. \\
- & \left.\langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle\right].
\end{aligned}
\tag{393}
$$

We can use Eq. (393) to rewrite the frequency-dependent hyperpolarizabilities of A and B. We can use Eq. (248) with α replaced by ϵ, γ replaced by α, and ϵ replaced by γ to write the frequency-dependent polarizability $\beta_{\epsilon\alpha\gamma}^A(-\imath\omega;\imath\omega,0)$ of molecule A as

$$
\begin{aligned}
\beta_{\epsilon\alpha\gamma}^A(-\imath\omega;\imath\omega,0) \cong & \sum_{j_A,q_A\neq 0}\left[\frac{\langle 0_A|\mu_\epsilon^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\gamma^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)}\right. \\
+ & \ \frac{\langle 0_A|\mu_\epsilon^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\alpha^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}\right)} \\
+ & \ \frac{\langle 0_A|\mu_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\alpha^A|q_A\rangle\langle q_A|\mu_\epsilon^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)} \\
+ & \ \frac{\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\gamma^A|q_A\rangle\langle q_A|\mu_\epsilon^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)} \\
+ & \ \frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}-\imath\hbar\omega\right)} \\
+ & \left.\ \frac{\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{j_A}^{(0)}-E_{0_A}^{(0)}+\imath\hbar\omega\right)\left(E_{q_A}^{(0)}-E_{0_A}^{(0)}\right)}\right].
\end{aligned}
\tag{394}
$$

In one version of the Unsöld approximation,

$$E_{j_A}^{(0)} - E_{0_A}^{(0)} = E_{q_A}^{(0)} - E_{0_A}^{(0)} = E_{IP}^A, \tag{395}$$

so that Eq. (394) is

$$\begin{aligned}
\beta_{\epsilon\alpha\gamma}^A(-\imath\omega;\imath\omega,0) \cong \sum_{j_A,q_A\neq 0} \Bigg[& \frac{\langle 0_A|\mu_\epsilon^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\gamma^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle}{\left(E_{IP}^A - \imath\hbar\omega\right)\left(E_{IP}^A - \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\mu_\epsilon^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\alpha^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{IP}^A - \imath\hbar\omega\right)E_{IP}^A} \\
&+ \frac{\langle 0_A|\mu_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\alpha^A|q_A\rangle\langle q_A|\mu_\epsilon^A|0_A\rangle}{E_{IP}^A\left(E_{IP}^A + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\gamma^A|q_A\rangle\langle q_A|\mu_\epsilon^A|0_A\rangle}{\left(E_{IP}^A + \imath\hbar\omega\right)\left(E_{IP}^A + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}_\gamma^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\alpha^A|0_A\rangle}{E_{IP}^A\left(E_{IP}^A - \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}_\alpha^A|j_A\rangle\langle j_A|\hat{\bar{\mu}}_\epsilon^A|q_A\rangle\langle q_A|\hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{IP}^A + \imath\hbar\omega\right)E_{IP}^A} \Bigg].
\end{aligned} \tag{396}$$

Using Eqs. (383) - (388) with $k_A = j_A$ and $l_A = q_A$ in Eq. (396) gives

$$\begin{aligned}
& \beta_{\epsilon\alpha\gamma}^A(-\imath\omega;\imath\omega,0) \\
\cong & \Bigg[\frac{\langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\gamma^A\hat{\mu}_\alpha^A|0_A\rangle - \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\gamma^A\hat{\mu}_\alpha^A|0_A\rangle}{\left(E_{IP}^A - \imath\hbar\omega\right)\left(E_{IP}^A - \imath\hbar\omega\right)} \\
- & \frac{\langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\gamma^A|0_A\rangle\langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle}{\left(E_{IP}^A - \imath\hbar\omega\right)\left(E_{IP}^A - \imath\hbar\omega\right)} \\
+ & \frac{\langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle - \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{IP}^A - \imath\hbar\omega\right)E_{IP}^A} \\
- & \frac{\langle 0_A|\hat{\mu}_\epsilon^A\hat{\bar{\mu}}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{IP}^A - \imath\hbar\omega\right)E_{IP}^A} \\
+ & \frac{\langle 0_A|\hat{\mu}_\gamma^A\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\epsilon^A|0_A\rangle - \langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_A|\hat{\bar{\mu}}_\alpha^A\hat{\mu}_\epsilon^A|0_A\rangle}{E_{IP}^A\left(E_{IP}^A + \imath\hbar\omega\right)}
\end{aligned}$$

$$\begin{aligned}
&- \frac{\langle 0_A|\hat{\mu}_\gamma^A \hat{\overline{\mu}}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle}{E_{IP}^A\left(E_{IP}^A + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}_\alpha^A \hat{\overline{\mu}}_\gamma^A \hat{\mu}_\epsilon^A|0_A\rangle - \langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\overline{\mu}}_\gamma^A \hat{\mu}_\epsilon^A|0_A\rangle}{\left(E_{IP}^A + \imath\hbar\omega\right)\left(E_{IP}^A + \imath\hbar\omega\right)} \\
&- \frac{\langle 0_A|\hat{\mu}_\alpha^A \hat{\overline{\mu}}_\gamma^A|0_A\rangle\langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle}{\left(E_{IP}^A + \imath\hbar\omega\right)\left(E_{IP}^A + \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}_\gamma^A \hat{\overline{\mu}}_\epsilon^A \hat{\mu}_\alpha^A|0_A\rangle - \langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_A|\hat{\overline{\mu}}_\epsilon^A \hat{\mu}_\alpha^A|0_A\rangle}{E_{IP}^A\left(E_{IP}^A - \imath\hbar\omega\right)} \\
&- \frac{\langle 0_A|\hat{\mu}_\gamma^A \hat{\overline{\mu}}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle}{E_{IP}^A\left(E_{IP}^A - \imath\hbar\omega\right)} \\
&+ \frac{\langle 0_A|\hat{\mu}_\alpha^A \hat{\overline{\mu}}_\epsilon^A \hat{\mu}_\gamma^A|0_A\rangle - \langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\overline{\mu}}_\epsilon^A \hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{IP}^A + \imath\hbar\omega\right)E_{IP}^A} \\
&- \left.\frac{\langle 0_A|\hat{\mu}_\alpha^A \hat{\overline{\mu}}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle}{\left(E_{IP}^A + \imath\hbar\omega\right)E_{IP}^A}\right] .
\end{aligned} \tag{397}$$

Since the matrix elements in Eq. (397) are real, we obtain

$$\begin{aligned}
&\beta_{\epsilon\alpha\gamma}^A\left(-\imath\omega; \imath\omega, 0\right) \\
\cong\; &\Big[\langle 0_A|\hat{\mu}_\alpha^A \hat{\overline{\mu}}_\gamma^A \hat{\mu}_\epsilon^A|0_A\rangle - \langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\overline{\mu}}_\gamma^A \hat{\mu}_\epsilon^A|0_A\rangle \\
-\; &\langle 0_A|\hat{\mu}_\alpha^A \hat{\overline{\mu}}_\gamma^A|0_A\rangle\langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\Big] \\
\times\; &\left[\frac{1}{\left(E_{IP}^A + \imath\hbar\omega\right)\left(E_{IP}^A + \imath\hbar\omega\right)} + \frac{1}{\left(E_{IP}^A - \imath\hbar\omega\right)\left(E_{IP}^A - \imath\hbar\omega\right)}\right] \\
+\; &\Big[\langle 0_A|\hat{\mu}_\epsilon^A \hat{\overline{\mu}}_\alpha^A \hat{\mu}_\gamma^A|0_A\rangle - \langle 0_A|\hat{\mu}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\overline{\mu}}_\alpha^A \hat{\mu}_\gamma^A|0_A\rangle \\
-\; &\langle 0_A|\hat{\mu}_\epsilon^A \hat{\overline{\mu}}_\alpha^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle\Big] \\
\times\; &\left[\frac{1}{\left(E_{IP}^A - \imath\hbar\omega\right)E_{IP}^A} + \frac{1}{E_{IP}^A\left(E_{IP}^A + \imath\hbar\omega\right)}\right] \\
+\; &\Big[\langle 0_A|\hat{\mu}_\alpha^A \hat{\overline{\mu}}_\epsilon^A \hat{\mu}_\gamma^A|0_A\rangle \\
-\; &\langle 0_A|\hat{\mu}_\alpha^A|0_A\rangle\langle 0_A|\hat{\overline{\mu}}_\epsilon^A \hat{\mu}_\gamma^A|0_A\rangle - \langle 0_A|\hat{\mu}_\alpha^A \hat{\overline{\mu}}_\epsilon^A|0_A\rangle\langle 0_A|\hat{\mu}_\gamma^A|0_A\rangle\Big]
\end{aligned}$$

$$\times \quad \left[\frac{1}{E_{IP}^{A}\left(E_{IP}^{A}-\imath\hbar\omega\right)}+\frac{1}{\left(E_{IP}^{A}+\imath\hbar\omega\right)E_{IP}^{A}}\right]. \tag{398}$$

Then, from Eqs. (392) and (398),

$$\begin{aligned}
\beta_{\epsilon\alpha\gamma}^{A}\left(-\imath\omega;\imath\omega,0\right) &\cong \Big[\langle 0_A|\hat{\mu}_{\epsilon}^{A}\hat{\overline{\mu}}_{\alpha}^{A}\hat{\mu}_{\gamma}^{A}|0_A\rangle - \langle 0_A|\hat{\mu}_{\epsilon}^{A}|0_A\rangle\langle 0_A|\hat{\overline{\mu}}_{\alpha}^{A}\hat{\mu}_{\gamma}^{A}|0_A\rangle \\
&- \langle 0_A|\hat{\mu}_{\epsilon}^{A}\hat{\overline{\mu}}_{\alpha}^{A}|0_A\rangle\langle 0_A|\hat{\mu}_{\gamma}^{A}|0_A\rangle\Big] \\
&\times \left[\frac{2}{E_{IP}^{A}\left(E_{IP}^{A}+\imath\hbar\omega\right)}+\frac{2}{E_{IP}^{A}\left(E_{IP}^{A}-\imath\hbar\omega\right)}\right. \\
&+ \left.\frac{1}{\left(E_{IP}^{A}+\imath\hbar\omega\right)\left(E_{IP}^{A}+\imath\hbar\omega\right)}+\frac{1}{\left(E_{IP}^{A}-\imath\hbar\omega\right)\left(E_{IP}^{A}-\imath\hbar\omega\right)}\right].
\end{aligned} \tag{399}$$

Using Eq. (393) in Eq. (399) and combining the frequency-dependent denominators in Eq. (399),

$$\beta_{\epsilon\alpha\gamma}^{A}\left(-\imath\omega;\imath\omega,0\right) \cong \frac{\beta_{\epsilon\alpha\gamma}^{A}\left[3\left(E_{IP}^{A}\right)^{4}+\left(E_{IP}^{A}\right)^{2}\hbar^{2}\omega^{2}\right]}{3\left(E_{IP}^{A}+\imath\hbar\omega\right)^{2}\left(E_{IP}^{A}-\imath\hbar\omega\right)^{2}}. \tag{400}$$

Let us return to the calculation of $\Delta E_{0_{AB}}^{(3)}\left(0,1\right)$. We will use Eq. (400) with $\epsilon = z$, $\alpha = x$ and $\gamma = x$; with $\epsilon = z$, $\alpha = y$ and $\gamma = y$; and with $\epsilon = \alpha = \gamma = z$ in Eq. (375)

$$\begin{aligned}
\Delta E_{0_{AB}}^{(3)}\left(0,1\right) &\cong -T_{xx}\,T_{xx}\,T_{zz}\,\mu_{z}^{B0}\left(\frac{\hbar}{2\pi}\right) \\
&\times \int_{-\infty}^{+\infty} d\omega \frac{\beta_{zxx}^{A}\left[3\left(E_{IP}^{A}\right)^{4}+\left(E_{IP}^{A}\right)^{2}\hbar^{2}\omega^{2}\right]}{3\left(E_{IP}^{A}+\imath\hbar\omega\right)^{2}\left(E_{IP}^{A}-\imath\hbar\omega\right)^{2}}\alpha_{xx}^{B}\left(\imath\omega\right) \\
&- T_{zz}\,T_{zz}\,T_{zz}\,\mu_{z}^{B0}\left(\frac{\hbar}{4\pi}\right) \\
&\times \int_{-\infty}^{+\infty} d\omega \frac{\beta_{zzz}^{A}\left[3\left(E_{IP}^{A}\right)^{4}+\left(E_{IP}^{A}\right)^{2}\hbar^{2}\omega^{2}\right]}{3\left(E_{IP}^{A}+\imath\hbar\omega\right)^{2}\left(E_{IP}^{A}-\imath\hbar\omega\right)^{2}}\alpha_{zz}^{B}\left(\imath\omega\right).
\end{aligned} \tag{401}$$

Then, using Eq. (317) from Sect. 5.1.2 (with HF replaced by B) in Eq. (401), we find

$$\Delta E_{0_{AB}}^{(3)}\left(0,1\right) \cong -T_{xx}\,T_{xx}\,T_{zz}\mu_{z}^{B0}\left(\frac{\hbar}{2\pi}\right)$$

$$\times \int_{-\infty}^{+\infty} d\omega \frac{\beta^{A}_{zxx}\left[3\left(E^{A}_{IP}\right)^{4} + \left(E^{A}_{IP}\right)^{2}\hbar^{2}\omega^{2}\right]}{3\left(E^{A}_{IP} + \imath\hbar\omega\right)^{2}\left(E^{A}_{IP} - \imath\hbar\omega\right)^{2}} \frac{\left(E^{B}_{IP}\right)^{2}\alpha^{B}_{xx}}{\left[\left(E^{B}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]}$$

$$- \; T_{zz}\, T_{zz}\, T_{zz}\, \mu^{B0}_{z} \left(\frac{\hbar}{4\pi}\right)$$

$$\times \int_{-\infty}^{+\infty} d\omega \frac{\beta^{A}_{zzz}\left[3\left(E^{A}_{IP}\right)^{4} + \left(E^{A}_{IP}\right)^{2}\hbar^{2}\omega^{2}\right]}{3\left(E^{A}_{IP} + \imath\hbar\omega\right)^{2}\left(E^{A}_{IP} - \imath\hbar\omega\right)^{2}} \frac{\left(E^{B}_{IP}\right)^{2}\alpha^{B}_{zz}}{\left[\left(E^{B}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]}$$

$$\cong \; -T_{xx}\, T_{xx}\, T_{zz}\, \mu^{B0}_{z} \left(\frac{\hbar}{6\pi}\right) \beta^{A}_{zxx}\left(E^{A}_{IP}\right)^{2}\left(E^{B}_{IP}\right)^{2}\alpha^{B}_{xx}$$

$$\times \int_{-\infty}^{+\infty} d\omega \frac{\left[3\left(E^{A}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]}{\left[\left(E^{A}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]^{2}\left[\left(E^{B}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]}$$

$$- \; T_{zz}\, T_{zz}\, T_{zz}\, \mu^{B0}_{z} \left(\frac{\hbar}{12\pi}\right) \beta^{A}_{zzz}\left(E^{A}_{IP}\right)^{2}\left(E^{B}_{IP}\right)^{2}\alpha^{B}_{zz}$$

$$\times \int_{-\infty}^{+\infty} d\omega \frac{\left[3\left(E^{A}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]}{\left[\left(E^{A}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]^{2}\left[\left(E^{B}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]}$$

$$\cong \; -T_{xx}\, T_{xx}\, T_{zz}\, \mu^{B0}_{z} \left(\frac{\hbar}{2\pi}\right) \beta^{A}_{zxx}\left(E^{A}_{IP}\right)^{4}\left(E^{B}_{IP}\right)^{2}\alpha^{B}_{xx}$$

$$\times \int_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E^{A}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]^{2}\left[\left(E^{B}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]}$$

$$- \; T_{xx}\, T_{xx}\, T_{zz}\, \mu^{B0}_{z} \left(\frac{\hbar^{3}}{6\pi}\right) \beta^{A}_{zxx}\left(E^{A}_{IP}\right)^{2}\left(E^{B}_{IP}\right)^{2}\alpha^{B}_{xx}$$

$$\times \int_{-\infty}^{+\infty} d\omega \frac{\omega^{2}}{\left[\left(E^{A}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]^{2}\left[\left(E^{B}_{IP}\right)^{2} + \hbar^{2}\omega^{2}\right]}$$

$$- \; T_{zz}\, T_{zz}\, T_{zz}\, \mu^{B0}_{z} \left(\frac{\hbar}{4\pi}\right) \beta^{A}_{zzz}\left(E^{A}_{IP}\right)^{4}\left(E^{B}_{IP}\right)^{2}\alpha^{B}_{zz}$$

$$
\begin{aligned}
&\times \int\limits_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{A}\right)^{2}+\hbar^{2}\omega^{2}\right]^{2}\left[\left(E_{IP}^{B}\right)^{2}+\hbar^{2}\omega^{2}\right]} \\
&- \; T_{zz}T_{zz}T_{zz}\,\mu_{z}^{B0}\left(\frac{\hbar^{3}}{12\pi}\right)\beta_{zzz}^{A}\left(E_{IP}^{A}\right)^{2}\left(E_{IP}^{B}\right)^{2}\alpha_{zz}^{B} \\
&\times \int\limits_{-\infty}^{+\infty} d\omega \frac{\omega^{2}}{\left[\left(E_{IP}^{A}\right)^{2}+\hbar^{2}\omega^{2}\right]^{2}\left[\left(E_{IP}^{B}\right)^{2}+\hbar^{2}\omega^{2}\right]}. \qquad (402)
\end{aligned}
$$

In order to simplify Eq. (402), we need to evaluate the integrals contained within this equation. From the Mathematica software package,

$$
\begin{aligned}
&\hbar \int\limits_{-\infty}^{+\infty} d\omega \frac{1}{\left[\left(E_{IP}^{A}\right)^{2}+\hbar^{2}\omega^{2}\right]^{2}\left[\left(E_{IP}^{B}\right)^{2}+\hbar^{2}\omega^{2}\right]} = \\
&\imath\hbar\left\{\left[-3\left(E_{IP}^{A}\right)^{2}E_{IP}^{B}+\left(E_{IP}^{B}\right)^{3}\right]\right. \\
&\times \; \log\left(-\frac{\imath}{E_{IP}^{A}}\right) \\
&+ \; \left[3\left(E_{IP}^{A}\right)^{2}E_{IP}^{B}-\left(E_{IP}^{B}\right)^{3}\right]\log\left(\frac{\imath}{E_{IP}^{A}}\right) \\
&+ \; 2\left(E_{IP}^{A}\right)^{3} \\
&\times \; \left.\left[\log\left(-\frac{\imath}{E_{IP}^{B}}\right)-\log\left(\frac{\imath}{E_{IP}^{B}}\right)\right]\right\} \\
&\times \; \frac{1}{4\left(E_{IP}^{A}\right)^{3}E_{IP}^{B}\left[\left(E_{IP}^{A}\right)^{2}-\left(E_{IP}^{B}\right)^{2}\right]^{2}} \\
&= \; D\left(E_{IP}^{A},E_{IP}^{B}\right), \qquad (403)
\end{aligned}
$$

where we have designated the result in Eq. (403) $D\left(E_{IP}^{A},E_{IP}^{B}\right)$. At this point, we will simplify the other integrals in Eq. (402), that is, those that have ω^2 in their numerators. According to Gradshteyn and Ryzhik,[67]

$$
\int\limits_{0}^{+\infty} dx \frac{x^{2}}{\left(x^{2}+a^{2}\right)\left(x^{2}+b^{2}\right)\left(x^{2}+c^{2}\right)} = \frac{\pi}{2\left(a+b\right)\left(a+c\right)\left(b+c\right)}. \qquad (404)
$$

If we let $x = \hbar\omega$, $dx = \hbar d\omega$, $a = b = E_{IP}^{A}$, and $c = E_{IP}^{B}$ in Eq. (404), then we have

$$(\hbar)^3 \int_{0}^{+\infty} d\omega \frac{\omega^2}{\left[\hbar^2\omega^2 + \left(E_{IP}^{A}\right)^2\right]^2 \left[\hbar^2\omega^2 + \left(E_{IP}^{B}\right)^2\right]} = \frac{\pi}{4E_{IP}^{A}\left(E_{IP}^{A} + E_{IP}^{B}\right)^2}. \tag{405}$$

The integrand in Eq. (405) is integrable from $-\infty$ to $+\infty$, and it is an even function. Therefore,

$$2(\hbar)^3 \int_{0}^{+\infty} d\omega \frac{\omega^2}{\left[\hbar^2\omega^2 + \left(E_{IP}^{A}\right)^2\right]^2 \left[\hbar^2\omega^2 + \left(E_{IP}^{B}\right)^2\right]} = (\hbar)^3 \int_{-\infty}^{+\infty} d\omega \frac{\omega^2}{\left[\hbar^2\omega^2 + \left(E_{IP}^{A}\right)^2\right]^2 \left[\hbar^2\omega^2 + \left(E_{IP}^{B}\right)^2\right]} = \frac{\pi}{E_{IP}^{A}\left(E_{IP}^{A} + E_{IP}^{B}\right)^2}. \tag{406}$$

When we use Eqs. (403) and (406) in Eq. (402), the result is

$$\begin{aligned} \Delta E_{0_{AB}}^{(3)}(0,1) \cong & -T_{xx}\,T_{xx}\,T_{zz}\,\mu_z^{B0}\left(\frac{\hbar}{2\pi}\right)\beta_{zxx}^{A} {E_{IP}^{A}}^{4} {E_{IP}^{B}}^{2} \alpha_{xx}^{B} D\left(E_{IP}^{A}, E_{IP}^{B}\right) \\ & - \frac{T_{xx}\,T_{xx}\,T_{zz}\,\mu_z^{B0}\beta_{zxx}^{A}\alpha_{xx}^{B}E_{IP}^{A}{E_{IP}^{B}}^{2}}{12\left(E_{IP}^{A} + E_{IP}^{B}\right)^2} \\ & - T_{zz}\,T_{zz}\,T_{zz}\,\mu_z^{B0}\left(\frac{\hbar}{4\pi}\right)\beta_{zzz}^{A} {E_{IP}^{A}}^{4} {E_{IP}^{B}}^{2} \alpha_{zz}^{B} D\left(E_{IP}^{A}, E_{IP}^{B}\right) \\ & - \frac{T_{zz}\,T_{zz}\,T_{zz}\,\mu_z^{B0}\beta_{zzz}^{A}\alpha_{zz}^{B}E_{IP}^{A}{E_{IP}^{B}}^{2}}{24\left(E_{IP}^{A} + E_{IP}^{B}\right)^2}. \end{aligned} \tag{407}$$

Now that we have derived $\Delta E_{0_{AB}}^{(3)}(0,1)$ for the colinear geometry A and B, let us derive $\Delta E_{0_{AB}}^{(3)}(1,0)$ for this geometry. We can obtain $\Delta E_{0_{AB}}^{(3)}(1,0)$ by interchanging B and A in Eq. (407),

$$\Delta E_{0_{AB}}^{(3)}(1,0) \cong - T_{xx}\,T_{xx}\,T_{zz}\,\mu_z^{A0}\left(\frac{3\hbar}{16}\right)\beta_{zxx}^{B}E_{IP}^{B}\alpha_{xx}^{A}D\left(E_{IP}^{B}, E_{IP}^{A}\right)$$

$$
\begin{aligned}
&- \frac{T_{xx}\, T_{xx}\, T_{zz}\mu_z^{A0}\beta^B_{zxx}\alpha^A_{xx}E^B_{IP}\left(E^A_{IP}\right)^2}{12\left(E^B_{IP}+E^A_{IP}\right)^2} \\
&- T_{zz}\, T_{zz}\, T_{zz}\, \mu_z^{A0}\left(\frac{3\hbar}{16}\right)\beta^B_{zzz}E^B_{IP}\alpha^A_{zz}D\left(E^B_{IP}, E^A_{IP}\right) \\
&- \frac{T_{zz}\, T_{zz}\, T_{zz}\, \mu_z^{A0}\beta^B_{zzz}\alpha^A_{zz}E^B_{IP}\left(E^A_{IP}\right)^2}{12\left(E^B_{IP}+E^A_{IP}\right)^2}. \qquad (408)
\end{aligned}
$$

These results are equivalent to those obtained by Piecuch at the level of the Unsöld approximation.[63–66]

We are now ready to derive the expression for $\Delta E^{(3)}_{0_{AB}}(0,0)$ for the colinear geometry of A and B. According to Eq. (363), $\Delta E^{(3)}_{0_{AB}}(0,0)$ is

$$
\begin{aligned}
\Delta E^{(3)}_{0_{AB}}(0,0) &= -T_{\alpha\beta}\, T_{\gamma\delta}\, T_{\epsilon\phi}\left(\frac{\hbar^2}{4\pi^2}\right) \\
&\times \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega'\, b^A_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) \\
&\times \left[b^B_{\delta\beta\phi}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right)\right. \\
&+ b^B_{\delta\beta\phi}\left(\imath\omega; -\imath\omega' - \imath\omega, \imath\omega'\right) \\
&+ b^B_{\delta\beta\phi}\left(-\imath\omega; \imath\omega' + \imath\omega, -\imath\omega'\right) \\
&+ \left. b^B_{\delta\beta\phi}\left(-\imath\omega; \imath\omega - \imath\omega', \imath\omega'\right)\right]. \qquad (409)
\end{aligned}
$$

Recall from Eq. (284) that $b^A_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right)$ is

$$
\begin{aligned}
b^A_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) &= \sum_{j_A, q_A \neq 0} \frac{\langle 0_A|\hat{\mu}^A_\gamma|j_A\rangle\langle j_A|\hat{\bar{\mu}}^A_\alpha|q_A\rangle}{\left(E^{(0)}_{j_A} - E^{(0)}_{0_A} + \imath\hbar\omega\right)} \\
&\times \frac{\langle q_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^{(0)}_{q_A} - E^{(0)}_{0_A} + \imath\hbar\omega'\right)}. \qquad (410)
\end{aligned}
$$

We can use the Unsöld approximation to simplify Eq. (410). From Eq. (395) and (410),

$$
b^A_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) =
$$

$$\frac{\langle 0_A|\hat{\mu}^A_\gamma \hat{\bar{\mu}}^A_\alpha \hat{\mu}^A_\epsilon|0_A\rangle - \langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha \hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^A_{IP} + \imath\hbar\omega\right)\left(E^A_{IP} + \imath\hbar\omega'\right)}$$

$$- \quad \frac{\langle 0_A|\hat{\mu}^A_\gamma \hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle}{\left(E^A_{IP} + \imath\hbar\omega\right)\left(E^A_{IP} + \imath\hbar\omega'\right)}. \tag{411}$$

Recall Eq. (393),

$$\frac{\beta^A_{\epsilon\alpha\gamma}\left(E^A_{IP}\right)^2}{6} = \langle 0_A|\hat{\mu}^A_\epsilon \hat{\bar{\mu}}^A_\alpha \hat{\mu}^A_\gamma|0_A\rangle - \langle 0_A|\hat{\mu}^A_\epsilon|0_A\rangle\langle 0_A|\hat{\bar{\mu}}^A_\alpha \hat{\mu}^A_\gamma|0_A\rangle$$

$$- \quad \langle 0_A|\hat{\mu}^A_\epsilon \hat{\bar{\mu}}^A_\alpha|0_A\rangle\langle 0_A|\hat{\mu}^A_\gamma|0_A\rangle. \tag{412}$$

Using Eq. (412) with γ and ϵ interchanged in Eq. (411) gives

$$b^A_{\gamma\alpha\epsilon}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right)$$

$$= \frac{\beta^A_{\gamma\alpha\epsilon}\left(E^A_{IP}\right)^2}{6\left(E^A_{IP} + \imath\hbar\omega\right)\left(E^A_{IP} + \imath\hbar\omega'\right)}. \tag{413}$$

At this point, let us simplify the terms associated with molecule B in Eq. (409). Recall from Sect. 4.5 that $b^B_{\delta\beta\phi}\left(\omega_2; \omega_1, -\omega_\sigma\right)$ is

$$b^B_{\delta\beta\phi}\left(\omega_2; \omega_1, -\omega_\sigma\right) =$$

$$\sum_{r_B, s_B \neq 0} \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \hbar\omega_2\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \hbar\omega_\sigma\right)}. \tag{414}$$

If we let $\omega_2 = \imath\omega$, $\omega_1 = \imath\omega' - \imath\omega$, and $\omega_\sigma = \imath\omega'$ in Eq. (414), the result is

$$b^B_{\delta\beta\phi}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) =$$

$$\sum_{r_B, s_B \neq 0} \frac{\langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^{(0)}_{r_B} - E^{(0)}_{0_B} + \imath\hbar\omega\right)\left(E^{(0)}_{s_B} - E^{(0)}_{0_B} + \imath\hbar\omega'\right)}. \tag{415}$$

In order to simplify Eq. (415), we need an expression for molecule B which is analagous to Eq. (388) for molecule A, specifically

$$\sum_{r_B, s_B \neq 0} \langle 0_B|\hat{\mu}^B_\delta|r_B\rangle\langle r_B|\hat{\bar{\mu}}^B_\beta|s_B\rangle\langle s_B|\hat{\mu}^B_\phi|0_B\rangle = \langle 0_B|\hat{\mu}^B_\delta \hat{\bar{\mu}}^B_\beta \hat{\mu}^B_\phi|0_B\rangle$$

$$- \quad \langle 0_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_B|\hat{\bar{\mu}}^B_\beta \hat{\mu}^B_\phi|0_B\rangle - \langle 0_B|\hat{\mu}^B_\delta \hat{\bar{\mu}}^B_\beta|0_B\rangle\langle 0_B|\hat{\mu}^B_\phi|0_B\rangle. \tag{416}$$

We also need to write the Unsöld approximation to b for molecule B. Using Eq. (416) and the Unsöld approximation for molecule B in Eq. (415) gives

$$\begin{aligned} & b^B_{\delta\beta\phi}\left(\imath\omega; \imath\omega' - \imath\omega, -\imath\omega'\right) = \\ & \frac{\langle 0_B|\hat{\mu}^B_\delta \hat{\bar{\mu}}^B_\beta \hat{\mu}^B_\phi|0_B\rangle - \langle 0_B|\hat{\mu}^B_\delta|0_B\rangle\langle 0_B|\hat{\bar{\mu}}^B_\beta \hat{\mu}^B_\phi|0_B\rangle}{\left(E^B_{IP} + \imath\hbar\omega\right)\left(E^B_{IP} + \imath\hbar\omega'\right)} \\ & -\frac{\langle 0_B|\hat{\mu}^B_\delta \hat{\bar{\mu}}^B_\beta|0_B\rangle\langle 0_B|\hat{\mu}^B_\phi|0_B\rangle}{\left(E^B_{IP} + \imath\hbar\omega\right)\left(E^B_{IP} + \imath\hbar\omega'\right)}. \end{aligned} \tag{417}$$

Thus the results are equivalent to those obtained by Piecuch, in the Unsöld approximation.[63–66]

6 Summary, Concluding Remarks, and Future Perspectives

The charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$ of a molecule is defined as the change in the ω-frequency component $\delta\rho^e(\mathbf{r},\omega)$ of the electronic charge density at a point $\mathbf{r}$ within a molecule, due to a perturbing potential $v_e(\mathbf{r}',\omega)$ of frequency ω applied at $\mathbf{r}'$ (within linear response), as given by Eq. (1). Several molecular properties, including dipole- and higher-order polarizabilities, dielectric functions, and other properties mentioned in Chap. 1, depend on the charge-density susceptibility. We have derived an *ab initio* expression for the charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$ in CISD theory, developed an algorithm for calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ which is based on this expression, and written a program which is based on this algorithm. Finally, we have used our program to calculate $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 as a function of $\mathbf{r}$, $\mathbf{r}'$, and ω in the aug-cc-pVDZ basis set and at the equilibrium bond length of the molecule. Since CISD is equivalent to full CI in a two-electron case, our results are exact within the aug-cc-pVDZ basis.

The charge-density susceptibility can be calculated using the method described here, or it can be calculated using several other methods mentioned in Chap. 1. The advantage of the method presented in this work is that one can easily obtain the exact value of $\chi(\mathbf{r},\mathbf{r}';\omega)$ for a molecule (in a given basis) at any frequency ω. However, using one of the methods mentioned in Chap. 1, one can only obtain the exact value of $\chi(\mathbf{r},\mathbf{r}';\omega)$ for a given molecule at limited number of frequencies.

According to Eq. (20), the charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 is finite at all energies $\hbar\omega \neq (E_K - E_0)$. This is demonstrated in Fig. 1, which shows $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 as a function of y and z with $x = 0$, $\omega = 0$, and $\mathbf{r}' = (0,0,0)$. In this case, $\hbar\omega = 0$, and $\chi(\mathbf{r},\mathbf{r}';\omega)$ is small at all $\mathbf{r}$ and $\mathbf{r}'$.

Eq. (20) suggests that $\chi(\mathbf{r},\mathbf{r}';\omega)$ is singular at energies $\hbar\omega = (E_K - E_0)$. However, this is the case only for specific excited states Ψ_K. For example, triplet excited states Ψ_K do not cause singularities in $\chi(\mathbf{r},\mathbf{r}';\omega)$ at $\hbar\omega = (E_K - E_0)$. This is because Ψ_0 for H_2 is a $^1\Sigma_g$ state (recall the H_2 has $D_{\infty h}$ symmetry), and $\hat{\rho}^e(\mathbf{r})$ $(\hat{\rho}^e(\mathbf{r}'))$ is spin-independent, so that matrix elements $\langle\Psi_0|\hat{\rho}_e(\mathbf{r})|\Psi_K\rangle$ and $\langle\Psi_K|\hat{\rho}_e(\mathbf{r})|\Psi_0\rangle$ (and the corresponding matrix elements of $\hat{\rho}_e(\mathbf{r}')$) are nonzero only for singlet excited states Ψ_K . This is demonstrated, for example, by Fig. 2, which shows $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 as a function of y and z with $x = 0$, $\hbar\omega \sim (E_1 - E_0)$, and $\mathbf{r}' = (0,0,0)$. Although $\hbar\omega \sim (E_1 - E_0)$, $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 is small because Ψ_1 is a triplet state.

In addition to the fact that $\chi(\mathbf{r},\mathbf{r}';\omega)$ vanishes for triplet states, $\chi(\mathbf{r},\mathbf{r}';\omega)$ also vanishes for many singlet states when $\mathbf{r}$ and $\mathbf{r}'$ take specific values. We have determined which particular types of singlet states contribute to $\chi(\mathbf{r},\mathbf{r}';\omega)$ for the H_2 molecule. We did this by writing $\chi(\mathbf{r},\mathbf{r}';\omega)$ as a sum of products of orbitals evaluated at $\mathbf{r}$ and $\mathbf{r}'$, and determining which types of orbitals are nonzero when evaluated at various $\mathbf{r}$ and $\mathbf{r}'$ values. The states that contribute to $\chi(\mathbf{r},\mathbf{r}';\omega)$ for particular $\mathbf{r}$ and $\mathbf{r}'$ values are determined by the orbitals which are nonzero at those $\mathbf{r}$ and $\mathbf{r}'$. When $\mathbf{r} = (0,0,0)$ or $\mathbf{r}' = (0,0,0)$, only σ_g -type orbitals and Ψ_K states with $^1\Sigma_g$ symmetry contribute to $\chi(\mathbf{r},\mathbf{r}';\omega)$. This is because σ_g orbitals are the only molecular orbitals of H_2 that are nonzero at $\mathbf{r} = (0,0,0)$ or at $\mathbf{r}' = (0,0,0)$. For example, this is demonstrated in Fig. 3, which shows $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 as a function of y and z with $x = 0$, $\mathbf{r}' = (0,0,0)$, and $\hbar\omega \sim (E_4 - E_0)$. The charge-density susceptibility of H_2 is singular here because Ψ_4 is a $^1\Sigma_g$ state; $\chi(\mathbf{r},\mathbf{r}';\omega)$ has the shape of a σ_g orbital because σ_g orbitals are the only nonzero orbitals at $\mathbf{r} = (0,0,0)$ or $\mathbf{r}' = (0,0,0)$. If $\mathbf{r}$ or $\mathbf{r}'$ lies along the molecular axis, σ_g- and σ_u-type orbitals and excited states Ψ_K with $^1\Sigma_g$ and $^1\Sigma_u$ symmetries contribute to $\chi(\mathbf{r},\mathbf{r}';\omega)$ for H_2. This is because both the σ_g and σ_u molecular orbitals of H_2 are nonzero along the molecular axis. This is demonstrated by Fig. 5, which shows the charge- density susceptibility of H_2 as a function of y and z with $x = 0$, $\hbar\omega \sim (E_3 - E_0)$, and $\mathbf{r}' = (0,0,0.7)$

. The charge-density susceptibility is singular because Ψ_3 is a ${}^1\Sigma_u$ state, and $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ has the shape of a σ_u orbital because both σ_g and σ_u orbitals contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ when $\mathbf{r}' = (0, 0, 0.7)$. Finally, if $\mathbf{r}$ or $\mathbf{r}'$ is in the xz-plane, only π_x and $\delta_{x^2-y^2}$ orbitals and ${}^1\Pi_x$ and ${}^1\Delta_{x^2-y^2}$ states contribute to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ for H_2.

To test our $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ calculations, we have used $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ to calculate the CISD polarizabilities $\alpha_{xx}(\omega)$, $\alpha_{yy}(\omega)$, and $\alpha_{zz}(\omega)$ for H_2 at $\omega = 0$ and at several other frequencies in the DZ, DZP, and aug-cc-pVDZ basis sets. We compared our static polarizabilities with the corresponding polarizabilities obtained in the finite field approximation using the MOLPRO[17] quantum chemistry software package. The static polarizabilities calculated with the two methods are given in Table 2. There is excellent agreement between the polarizabilities calculated with the two methods. Note that as with the $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ calculations, all polarizability calculations were carried out at the equilibrium bond length of the H_2 molecule.

According to Eq. (30) in Chap. 1, the polarizability $\alpha_{\alpha\beta}(\omega)$ is continuous when $\hbar\omega \neq (E_K - E_0)$. Eq. (30) also indicates that $\alpha_{\alpha\beta}(\omega)$ is singular when $\hbar\omega = (E_K - E_0)$. However, this is not the case for all excited states Ψ_K . Specifically, as with $\chi(\mathbf{r}, \mathbf{r}'; \omega)$, triplet states do not contribute to $\alpha_{\alpha\beta}(\omega)$. This is because Ψ_0 for H_2 is a ${}^1\Sigma_g$ state and μ_α and μ_β are spin-independent operators, so that matrix elements $\langle\Psi_0|\mu_\alpha|\Psi_K\rangle$, $\langle\Psi_K|\mu_\alpha|\Psi_0\rangle$, $\langle\Psi_0|\mu_\beta|\Psi_K\rangle$, and $\langle\Psi_K|\mu_\beta|\Psi_K\rangle$ are nonzero only for singlet states Ψ_K of H_2.

The frequency-dependent polarizability of H_2 is also finite at a number of singlet-state transition energies. We determined which types of singlet states cause $\alpha_{\alpha\beta}(\omega)$ to be singular at $\hbar\omega = (E_K - E_0)$ by determining which symmetries of the components of the matrix elements $\langle\Phi_J|\hat{\mu}_\alpha|\Phi_{J'}\rangle$ (and $\langle\Phi_{J''}|\hat{\mu}_\beta|\Phi_{J'''}\rangle$) in Eq. (37) make the direct product of those symmetries contain the totally symmetric representation of the $D_{\infty h}$ point group. Since $\langle\Phi_J|$ is a determinant in $\langle\Psi_0|$, $\langle\Psi_0|$ must have the same symmetry as $\langle\Phi_J|$. Since $|\Phi_{J'}\rangle$ is in $|\Psi_K\rangle$, $|\Psi_K\rangle$ must have the same symmetry as $|\Phi_{J'}\rangle$. Therefore, we determined the allowable symmetries of $\langle\Psi_0|$ and $|\Psi_K\rangle$ from $\langle\Phi_J|$ and $|\Phi_{J'}\rangle$. Using this analysis, we determined that $\alpha_{zz}(\omega)$ would be singular for singlet Ψ_K states with Σ_u^+ symmetry. Figs. 6 and 7 demonstrate this behavior. In Figs. 6 and 7, $\alpha_{zz}(\omega)$ is singular at two frequencies in the DZ, DZP, and aug-cc-pVDZ basis sets. In each basis set, these two frequencies correspond to the energies of transitions to the $1^1\Sigma_u^+$ and $2^1\Sigma_u^+$ states of H_2. We also determined that $\alpha_{xx}(\omega)$ is singular for singlet Ψ_K states with Π_{u_x} symmetry and that $\alpha_{yy}(\omega)$ is singular for singlet Ψ_K states with Π_{u_y} symmetry. Fig. 8 demonstrates this behavior for $\alpha_{xx}(\omega)$. According to Fig. 8, $\alpha_{xx}(\omega)$ is singular at one frequency in the aug-cc-pVDZ basis set, and this frequency corresponds to the energy of a transition to the $1^1\Pi_{u_x}$ state. Fig. 10 demonstrates this behavior for $\alpha_{yy}(\omega)$. According to Fig. 10, $\alpha_{yy}(\omega)$ is singular at one frequency in the aug-cc-pVDZ basis set, and this frequency corresponds to the energy of a transition to the $1^1\Pi_{u_y}$ state.

The second major topic of this work is intermolecular interactions. We began our study of intermolecular interactions in Chap. 2, where we summarized the main results of several of the major theoretical approaches to intermolecular interactions. In Chap. 3, we reviewed known results for the second-order perturbation correction to the intermolecular interaction energy of two molecules A and B in the polarization approximation. This approximation is valid when the overlap between the electron distributions of the two molecules can be ignored. First, we showed that the second-order intermolecular interaction energy $\Delta E_{0_{AB}}^{(2)}$ is given by Eq. (158), where the first two terms in this equation give the induction energy due to the polarization of each molecule by the field of the permanent dipole of the other. Note that these results are valid within linear response and when we neglect effects caused by the non-uniformity of the field. Second, we used complex contour integration to prove Eq. (159), which is the Casimir-Polder formula with $A = E_{j_A}^{(0)} - E_{0_A}^{(0)}$ and $B = E_{r_B}^{(0)} - E_{0_B}^{(0)}$ from reference 106. Using Eq. (179), we showed that the denominator in the third term of Eq. (158) is given by Eq. (159). At this point, we used the expressions for the frequency-dependent polarizabilities of A and B as given by Eqs. (186) and (187) to show that the third term in Eq. (158) is given by Eq. (188). Eq. (188) is the 2^{nd}-order dispersion energy of interaction of A and B.

In Chap. 4, we derive the third-order perturbation correction to the intermolecular interaction energy $\Delta E_{0_{AB}}^{(3)}$ of two molecules A and B in the polarization approximation. In this derivation, we started with $\Delta E_{0_{AB}}^{(3)}$ as given by Eq. (190), with $\hat{V}^{AB}$ and $\hat{\hat{V}}^{AB}$ given by Eqs. (148) and (196), and with G given by Eqs. (144) - (147), respectively. We show that the third-order intermolecular interaction energy $\Delta E_{0_{AB}}^{(3)}$ is a sum of six terms which are given by Eqs. (214), (222), (230), (253), (271), and (289). Eq. (214), which is first-order in both μ^{A0} and μ^{B0}, describes higher-order induction effects. The permanent dipole on molecule A produces a field, and this field polarizes molecule B. This produces a reaction field at B that acts back on A. Specifically, the reaction field at B polarizes A, which then gives rise to a field acting on B and this alters the energy of the AB pair due to the permanent dipole of B. The energy of the AB pair is also affected by the higher-order induction effect produced by the same mechanism but with the roles of A and B interchanged. Eqs. (230) and (222), which are third-order in μ^{A0} and third-order in μ^{B0}, respectively, describe hyperpolarization effects. The permanent dipole on molecule A produces a field that hyperpolarizes molecule B, and this effect causes an energy change in the AB pair that is given by Eq. (230). Similarly, the permanent dipole on molecule B produces a field that hyperpolarizes molecule A, and this effect causes an energy change in the AB pair that is given by Eq. (222). Eqs. (271) and (253), which are first-order in μ^{A0} and first-order in μ^{B0}, respectively, describe induction-dispersion effects. These effects result from the modification of the AB dispersion energy due to the static fields from the permanent dipoles of A and B. The static field from the permanent dipole of A, together with the field from the fluctuating dipole of A, polarizes B nonlinearly, changing its energy. In addition, the field from the permanent dipole of A

alters the correlations of the spontaneous charge-density fluctuations on B, and this affects the correlation energy (and similarly, with the roles of A and B interchanged).

The induction, hyperpolarization, and induction-dispersion energies given by Eqs. (214), (230), (222), (271), and (253) agree with the results of earlier work. However, Eq. (289), which is zeroth-order in both μ^{A0} and μ^{B0} and corresponds to the dispersion energy of the AB pair, is a new result. This is a pure dispersion effect, associated with correlations in the fluctuating charge densities of A and B *beyond* linear response. Molecule B is hyperpolarized by the fluctuating field from A; also, the fluctuating field from A alters the correlations of the charge-density fluctuations in B. Both mechanisms contribute to the third-order dispersion energy.

In Chap. 5, we use our results for $\Delta E_{0_{AB}}^{(2)}$ and $\Delta E_{0_{AB}}^{(3)}$ obtained in Chaps. 3 and 4, the definitions of $T_{\alpha\beta}$, μ^{A0}, μ^{B0}, $\alpha_{\gamma\epsilon}^{A}(\imath\omega)$ and $\alpha_{\delta\phi}^{B}(\imath\omega)$ as given by Eqs. (149), (297), (186), and (187) to derive approximations to $\Delta E_{0_{AB}}^{(2)}$ and $\Delta E_{0_{AB}}^{(3)}$ for specific geometries of A and B. Eq. (306) gives the second-order correction $\Delta E_{0_{AB}}^{(2)}$ to the energy of the AB complex when A and B are colinear, with each of their molecular axes oriented along the z-axis of the laboratory frame shown in Fig. 12. This equation gives $\Delta E_{0_{AB}}^{(2)}$ in terms of μ_z^{A0}, μ_z^{B0}, α_{zz}^{A}, α_{zz}^{B}, $\alpha_{zz}^{A}(\imath\omega)$, $\alpha_{zz}^{B}(\imath\omega)$, and $\mathbf{R}_{AB}$. Using Eq. (306) and letting A and B be hydrogen fluoride (HF) molecules, we also derived an expression for the second-order correction to the energy of two colinear HF molecules with their molecular axes oriented along the z-axis of the laboratory frame. This expression is given by Eqs. (307), (308), and (309), where the total second-order correction to the energy $\Delta E_{0_{HF-HF}}^{(2)}$ of two HF molecules is the sum of these three equations. These equations are given in terms of $\mu_z^{HF,0}$, α_{zz}^{HF}, $\alpha_{zz}^{FF}(\imath\omega)$, and $\mathbf{R}_{HF-HF}$. We simplified our expression for $\Delta E_{0_{HF-HF}}^{(2)}$ by realizing that for this geometry, we can replace $\mu_z^{HF,0}$ with $\mu^{HF,0}$ in our equations for $\Delta E_{0_{HF-HF}}^{(2)}$. By assuming that the matrix elements in the equation for the static polarizability of HF are real and by using the Unsöld approximation, we have derived an equation which gives $\alpha_{\gamma\epsilon}^{HF}(\imath\omega)$ in terms of the ionization potential E_{IP}^{HF} of HF, the static polarizability $\alpha_{\gamma\epsilon}^{HF}$ of HF, and frequency ω. This expression for $\alpha_{\gamma\epsilon}^{HF}(\imath\omega)$ is given by Eq. (316). We also simplified $\Delta E_{0_{HF-HF}}^{(2)}$ by using Eq. (316) in Eq. (309), giving Eq. (318) for the $\Delta E_{0_{HF-HF}}^{(2)}(0,0)$ component of $\Delta E_{0_{HF-HF}}^{(2)}$. We further simplified $\Delta E_{0_{HF-HF}}^{(2)}(0,0)$ by evaluating the integral over frequencies ω in Eq. (318), giving Eq. (325) for $\Delta E_{0_{HF-HF}}^{(2)}(0,0)$. Finally, using Eqs. (307) and (308) with $\mu_z^{(HF,0)} = \mu^{(HF,0)} = 0.7043$ a. u. and $\alpha_{zz}^{HF} = 6.36$ a. u., we obtained Eq. (310) for both $\Delta E_{0_{HF-HF}}^{(2)}(2,0)$ and $\Delta E_{0_{HF-HF}}^{(2)}(0,2)$. Also, using Eq. (325) with $E_{IP}^{HF} = 0.5896$ a. u., $\alpha_{zz}^{HF} = 6.36$ a. u., and $\alpha_{zz}^{HF} = \alpha_{yy}^{HF} = 5.22$ a. u., we obtained Eq. (326). Multiplying Eq. (310) by two and adding the result to Eq. (326), we obtained Eq. (327) for $\Delta E_{0_{HF-HF}}^{(2)}$. Since Eq. (327) is of the form $C_{6(HF-HF)}/(\mathbf{R}_{HF-HF})^6$. where $C_{6(HF-HF)}$ is a constant, then our results indicate that $C_{6(HF-HF)} = -44.5$ a. u. for two colinear HF molecules.

We have also derived an expression for $\Delta E_{0_{AB}}^{(2)}$ when the internuclear axes of A and B are parallel to each other and to the x-axis of the laboratory frame as shown in Fig. 13. In this geometry, the molecular and laboratory frames are not the same. Therefore, before obtaining a final expression for $\Delta E_{0_{AB}}^{(2)}$ for this geometry, we rotated the nonzero components of the relevant properties of A and B for the parallel geometry shown in Fig. 13 from the molecular frame to the laboratory frame. We obtained the final expression for $\Delta E_{0_{AB}}^{(2)}$ in this geometry by replacing the components in the $\Delta E_{0_{AB}}^{(2)}$ expression for the colinear arrangement of A and B shown in Fig. 12 (Eq. (306)) with the appropriate rotated components. The final expression for $\Delta E_{0_{AB}}^{(2)}$ for parallel A and B as shown in Fig. 13 is given by Eq. (330).

We have used Eq. (330) with $A = B =$HF for $\Delta E_{0_{AB}}^{(2)}$ when A and B are arranged as shown in Fig. 13 to obtain an expression for the second-order correction $\Delta E_{0_{AB}}^{(2)}$ to the energy of interaction between two parallel HF molecules. This expression is given by Eq. (331). We obtain this expression by letting $A = B =$HF in Eq.

(330). We simplified Eq. (331) using essentially the same procedure that we used to simplify Eqs. (307), (308), and (309) for $\Delta E_{0_{AB}}^{(2)}$ of two colinear HF molecules (recall that the sum of Eqs. (307), (308), and (309) gives the total 2^{nd}-order correction to the energy of interaction $\Delta E_{0_{HF-HF}}^{(2)}$ of two colinear HF molecules). After simplifying, we obtained Eq. (337) for $\Delta E_{0_{HF-HF}}^{(2)}$ of two parallel HF molecules. Letting $\mu_x^{HF} = 0.7043$ a. u., $\alpha_{zz}^{HF} = \alpha_{yy}^{HF} = 5.22$ a. u., and $\alpha_{xx}^{HF} = 6.36$ a. u. in Eq. (337), we obtained the final expression for $\Delta E_{0_{AB}}^{(2)}$ of two parallel HF molecules, which is given by Eq. (338). Eq. (338) is of the form $C_{6(HF-HF)}/(\mathbf{R}_{HF-HF})^6$, where $C_{6(HF-HF)}$ is a constant. According to Eq. (338), $C_{6(HF-HF)} = -29.2$ a. u. for two parallel HF molecules.

We have also derived an expression for $\Delta E_{0_{AB}}^{(2)}$ when A and B are perpendicular to each other, as shown in Fig. 14. In this geometry, the laboratory and molecular frames are the same for A, but they are not the same for B. Therefore, before obtaining an expression for $\Delta E_{0_{AB}}^{(2)}$ for this particular geometry, we rotated the nonzero components of the relevant properties of molecule B from its molecular frame to the laboratory frame. After rotating these components, we obtained an expression for $\Delta E_{0_{AB}}^{(2)}$ in this geometry by replacing the components of molecule B in the colinear expression for $\Delta E_{0_{AB}}^{(2)}$ as given by Eqs. (292) - (293) with the appropriate rotated components. The expressions for the $\Delta E_{0_{AB}}^{(2)}(0,2)$, $\Delta E_{0_{AB}}^{(2)}(2,0)$, and $\Delta E_{0_{AB}}^{(2)}(0,0)$ components of $\Delta E_{0_{AB}}^{(2)}$ for this geometry are given by Eqs. (342), (343), and (344).

We have also derived an expression for the second-order correction to the energy of interaction $\Delta E_{0_{ABC}}^{(2)}$ of three molecules A, B, and C. This energy is a sum of the second-order, two-body corrections $\Delta E_{0_{AB}}^{(2)}$, $\Delta E_{0_{AC}}^{(2)}$, and $\Delta E_{0_{BC}}^{(2)}$ due to the interactions between A and B, A and C, and B and C, and an irreducible three-body energy of second-order $\Delta E_{0_{ABC}}^{(2,3)}$. We denote the sum of the second-order two-body corrections $\Delta E_{0_{ABC}}^{(2,2)}$. Each second-order, two-body correction is a sum of three terms, two induction terms and a dispersion term. For example, as shown in Chap.

3, $\Delta E_{0_{AB}}^{(2)}$ is the sum of the induction terms $\Delta E_{0_{AB}}^{(2)}(0,2)$ and $\Delta E_{0_{AB}}^{(2)}(2,0)$, and the dispersion term $\Delta E_{0_{AB}}^{(2)}(0,0)$. Similarly, $\Delta E_{0_{AC}}^{(2)}$ is the sum of $\Delta E_{0_{AC}}^{(2)}(0,2)$, $\Delta E_{0_{AC}}^{(2)}(2,0)$, and $\Delta E_{0_{AC}}^{(2)}(0,0)$, as shown by Eq. (347). Also, as shown by Eq. (348), $\Delta E_{0_{BC}}^{(2)}$ is the sum of $\Delta E_{0_{BC}}^{(2)}(0,2)$, $\Delta E_{0_{BC}}^{(2)}(2,0)$, and $\Delta E_{0_{BC}}^{(2)}(0,0)$. The full nonadditive, 2^{nd}-order correction to the energy $\Delta E_{0_{ABC}}^{(2,3)}$ is given by Eq. (350).

Eq. (351) contains all contributions to the total second-order correction to the energy of the interaction of molecules A, B, and C. Based on this equation, we have obtained an equation for the total second-order correction to the energy of interaction of three colinear hydrogen fluoride molecules. We call the three HF molecules that we use in this derivation HF_1, HF_2, and HF_3, and we call the corresponding 2^{nd}-order correction to the energy of interaction of these three molecules $\Delta E_{0_{HF_1-HF_2-HF_3}}^{(2)}$. The three molecules are arranged so that their internuclear axes lie along the z-axis of the laboratory frame, as shown in Fig. 15. We have denoted the distances between the centers of mass of HF_1 and HF_2, HF_1 and HF_3, and HF_2 and HF_3 by $\mathbf{R}_{HF_1-HF_2}$, $\mathbf{R}_{HF_1-HF_3}$, and $\mathbf{R}_{HF_2-HF_3}$, respectively. We obtain the desired expression for $\Delta E_{0_{HF_1-HF_2-HF_3}}^{(2)}$ by replacing A, B, and C in Eq. (351) with HF_1, HF_2, and HF_3, respectively. This expression for $\Delta E_{0_{HF_1-HF_2-HF_3}}^{(2)}$ is given by Eq. (352). The irreducible three-body energy of interaction $\Delta E_{0_{HF_1-HF_2-HF_3}}^{(2,3)}$ in Eq. (352) is given by Eq. (350) with molecules A, B, and C replaced by HF_1, HF_2, and HF_3. The second-order, two-body terms $\Delta E_{0_{HF_1-HF_2}}^{(2)}$, $\Delta E_{0_{HF_1-HF_3}}^{(2)}$, and $\Delta E_{0_{HF_2-HF_3}}^{(2)}$ in Eq. (352) are given by Eq. (306) with A, B, and C replaced by HF_1, HF_2, and HF_3, respectively. According to Eq. (327), the second-order correction to the energy of interaction of two colinear HF molecules is $\Delta E_{0_{HF-HF}}^{(2)} = -44.5\, a.u./(\mathbf{R}_{HF-HF})^6$. We simplify Eq. (352) for $\Delta E_{0_{HF_1-HF_2-HF_3}}^{(2)}$ by realizing that $\Delta E_{0_{HF_1-HF_2}}^{(2)}$, $\Delta E_{0_{HF_1-HF_3}}^{(2)}$, and $\Delta E_{0_{HF_2-HF_3}}^{(2)}$ are all given by Eq. (327) with the appropriate substitutions of HF_1, HF_2, or HF_3 for HF. We also simplify Eq.

(352) by replacing $\Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}$ in Eq. (352) with a geometry-specific form of $\Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}$, which is given by Eq. (356).

We have also derived an expression for the 2^{nd}-order correction to the energy of interaction $\Delta E^{(2)}_{0_{HF_1-HF_2-HF_3}}$ of HF_1, HF_2, and HF_3 when these three HF molecules ara parallel to each other. The three molecules are arranged so that their internuclear axes are parallel the x-axis of the laboratory frame, as shown in Fig. 16. Although Eq. (352) in our derivation of $\Delta E^{(2)}_{0_{HF_1-HF_2-HF_3}}$ applies to three colinear molecules, it is general enough that we used it as our starting point for deriving $\Delta E^{(2)}_{0_{HF_1-HF_2-HF_3}}$ for three parallel HF molecules. The irreducible three-body energy of interaction $\Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}$ in Eq. (352) for three parallel HF molecules is also given by Eq. (350), with molecules A, B, and C replaced by HF_1, HF_2, and HF_3. According to Eq. (338), the second-order correction to the energy of interaction of two parallel HF molecules is $\Delta E^{(2)}_{0_{HF-HF}} = -29.2\, a.u./(\mathbf{R}_{HF-HF})^6$. We simplify Eq. (352) for this geometry by realizing that $\Delta E^{(2)}_{0_{HF_1-HF_2}}$, $\Delta E^{(2)}_{0_{HF_1-HF_3}}$, and $\Delta E^{(2)}_{0_{HF_2-HF_3}}$ are all given by Eq. (338) with the appropriate substitutions of HF_1, HF_2, and HF_3 for HF. We also simplify Eq. (352) by replacing $\Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}$ in Eq. (352) with a geometry specific form of Eq. $\Delta E^{(2,3)}_{0_{HF_1-HF_2-HF_3}}$, which is given by Eq. (361).

Using the expression for $\Delta E^{(3)}_{0_{AB}}$ derived in Chap. 4, which is correct for any geometry of the AB complex, we have also derived an expression for $\Delta E^{(3)}_{0_{AB}}$ when A and B are colinear. This expression is given by Eq. (290) in Chap. 4, and again by Eq. (362) in Chap. 5. Recall that Eq. (362) consists of six terms, which are $\Delta E^{(3)}_{0_{AB}}(1,1)$, $\Delta E^{(3)}_{0_{AB}}(3,0)$, $\Delta E^{(3)}_{0_{AB}}(0,3)$, $\Delta E^{(3)}_{0_{AB}}(1,0)$, $\Delta E^{(3)}_{0_{AB}}(0,1)$, and $\Delta E^{(3)}_{0_{AB}}(0,0)$. The equations for each of these six terms are listed in Eq. (363). We derive the overall expression for $\Delta E^{(3)}_{0_{AB}}$ when A and B are colinear by deriving the expressions for $\Delta E^{(3)}_{0_{AB}}(1,1)$, $\Delta E^{(3)}_{0_{AB}}(3,0)$, $\Delta E^{(3)}_{0_{AB}}(0,3)$, $\Delta E^{(3)}_{0_{AB}}(1,0)$, $\Delta E^{(3)}_{0_{AB}}(0,1)$, and $\Delta E^{(3)}_{0_{AB}}(0,0)$ separately, and then adding all of the resulting expressions together. Note that in this geometry, the internuclear axes of A and B are oriented along the z-axis of the laboratory frame, as shown in Fig. 12.

First, we show that $\Delta E_{0_{AB}}^{(3)}(1,1)$ in this geometry is given by Eq. (367). In this equation, $\Delta E_{0_{AB}}^{(3)}(1,1)$ is given in terms of μ_z^{A0}, μ_z^{B0}, α_{zz}^{A}, α_{zz}^{B}, and $\mathbf{R}_{AB}$. Next, we show that $\Delta E_{0_{AB}}^{(3)}(0,3)$ and $\Delta E_{0_{AB}}^{(3)}(3,0)$ (in this geometry) are given by Eqs. (370) and (373), respectively. Eq. (370) is given in terms of μ_z^{B0}, β_{zzz}^{A}, and $\mathbf{R}_{AB}$, and Eq. (373) is given in terms of μ_z^{A0}, β_{zzz}^{B} , and $\mathbf{R}_{AB}$. Numerical values of α_{zz} and β_{zzz} are available for many molecules. Also, for this geometry, $\mu_z^{A0} = \mu^{A0}$ and $\mu_z^{B0} = \mu^{B0}$, and numerical values of μ^{A0} and μ^{B0} are also available for many molecules.

We then show that $\Delta E_{0_{AB}}^{(3)}(0,1)$ is given by Eq. (375) which contains T_{xx}, T_{yy}, T_{zz}, μ_z^{B0}, each diagonal component of the frequency-dependent polarizability $\alpha^{A}(\imath\omega)$, and several components of $\beta^{A}(-\imath\omega;\imath\omega,0)$. We simplified Eq. (375) by replacing T_{xx}, T_{yy} , and T_{zz} with the appropriate expressions for these quantities given in terms of $\mathbf{R}_{AB}$, and by replacing μ_z^{B0} with μ^{B0}. We also simplified Eq. (375) by letting HF= A in Eq. (317), and using these expressions for $\alpha_{xx}^{A}(\imath\omega)$, $\alpha_{yy}^{A}(\imath\omega)$, and $\alpha_{zz}^{A}(\imath\omega)$ in Eq. (375). The expressions for the polarizabilities $\alpha_{xx}^{A}(\imath\omega)$, $\alpha_{yy}^{A}(\imath\omega)$, and $\alpha_{zz}^{A}(\imath\omega)$ given by Eq. (317) (with HF= A) are given in terms of the static polarizabilities α_{xx}^{A}, α_{yy}^{A}, α_{zz}^{A}, the ionization potential E_{IP}^{A} of A, and the frequency ω . The static polarizabilities and ionization potential are known for many molecules, so that it is easy to compute $\alpha_{xx}^{A}(\imath\omega)$, $\alpha_{yy}^{A}(\imath\omega)$, and $\alpha_{zz}^{A}(\imath\omega)$ for these molecules.

To complete our simplification of Eq. (375), we needed to replace the various components of $\beta^{A}(-\imath\omega;\imath\omega,0)$ with expressions that contain quantities whose numerical values are known. Using the expression for the frequency-dependent hyperpolarizability $\beta_{\epsilon\alpha\gamma}^{A}(-\imath\omega;\imath\omega,0)$ given by Eq. (394), the Unsöld approximation, and a few manipulations of Eq. (394), we showed that $\beta_{\epsilon\alpha\gamma}^{A}(-\imath\omega;\imath\omega,0)$ is given by Eq. (399). We also used the expression for the static polarizability $\beta_{\epsilon\alpha\gamma}^{A}$ given by Eq. (376), the Unsöld and closure approximations, and other manipulations to show that the matrix elements in Eq. (399) for $\beta^A_{\epsilon\alpha\gamma}(-\imath\omega;\imath\omega,0)$ are given by Eq. (393). We obtained our final expression for $\beta^A_{\epsilon\alpha\gamma}(-\imath\omega;\imath\omega,0)$, given by Eq. (400), by using Eq. (393) in Eq. (399), and by combining the denominators in Eq. (399). Eq. (400) depends on $\beta^A_{\epsilon\alpha\gamma}$, E^A_{IP}, and ω. Since these quantities are known for several molecules, one can easily compute $\beta^A_{\epsilon\alpha\gamma}(-\imath\omega;\imath\omega,0)$ using Eq. (400). Equations for specific components of $\beta^A_{\epsilon\alpha\gamma}(-\imath\omega;\imath\omega,0)$ can be obtained by replacing ϵ, α, and γ in Eq. (400) with the appropriate Cartesian coordinates.

At this point, we obtained a simplified expression for $\Delta E^{(3)}_{0_{AB}}(0,1)$ by replacing $\beta^A_{zxx}(-\imath\omega;\imath\omega,0)$, $\beta^A_{zyy}(-\imath\omega;\imath\omega,0)$, and $\beta^A_{zzz}(-\imath\omega;\imath\omega,0)$ in Eq. (375) with Eq. (400), with the appropriate substitutions for ϵ, α, and γ. This expression for $\Delta E^{(3)}_{0_{AB}}(0,1)$ is given by Eq. (402). We obtained the final expression for $\Delta E^{(3)}_{0_{AB}}(0,1)$, given by Eq. (407), by evaluating the integrals in Eq. (402). We derived the final expression for $\Delta E^{(3)}_{0_{AB}}(1,0)$ by interchanging A and B in Eq. (407). We presented the final expression for $\Delta E^{(3)}_{0_{AB}}(1,0)$ in Eq. (408).

The last step in deriving an expression for $\Delta E^{(3)}_{0_{AB}}$ for the interaction between A and B when they are colinear (with their internuclear axes oriented along the z-axis of the laboratory frame) involved the simplification of the expression for $\Delta E^{(3)}_{0_{AB}}(0,0)$ contained in Eq. (362). The form of $\Delta E^{(3)}_{0_{AB}}(0,0)$ in Eq. (362) for $\Delta E^{(3)}_{0_{AB}}$ is given in Eq. (363). To begin our simplification, we showed that $b^A_{\gamma\alpha\epsilon}(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega')$ is given by Eq. (413). Here, Eq. (413) gives $b^A_{\gamma\alpha\epsilon}(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega')$ in terms of $\beta^A_{\gamma\alpha\epsilon}$, E^A_{IP}, and ω. It is possible to give $b^B_{\delta\beta\phi}(\imath\omega;\imath\omega'-\imath\omega,-\imath\omega')$ and the other frequency-dependent $b^B_{\delta\beta\phi}$ terms contained in $\Delta E^{(3)}_{0_{AB}}(0,0)$ in terms of $\beta^B_{\delta\beta\phi}$, E^B_{IP}, and ω. Since numerical values of static polarizabilities and ionization potentials are available for many molecules, it is possible to use our expression for $\Delta E^{(3)}_{0_{AB}}(0,0)$ to compute $\Delta E^{(3)}_{0_{AB}}(0,0)$ at various $\mathbf{R}_{AB}$ and ω.

There are several possibilities for future work on the charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$. Future applications of the charge-density susceptibility include calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ for several other centrosymmetric diatomic molecules such as N_2,

O_2, Cl_2, and F_2, and also for noncentrosymmetric diatomic molecules such HF, HCl, and CO. We may also calculate $\chi(\mathbf{r},\mathbf{r}';\omega)$ for small polyatomic atomic molecules such as H_2O, and CO_2.

We may also calculate $\chi(\mathbf{r},\mathbf{r}';\omega)$ for H_2 in higher level basis sets and compare $\chi(\mathbf{r},\mathbf{r}';\omega)$ obtained in different basis sets to determine the relative contributions of different orbital types to $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2. We may also calculate $\chi(\mathbf{r},\mathbf{r}';\omega)$ of other molecules mentioned above as a function of basis set. This would allow us to determine the relative contributions of different orbital types to $\chi(\mathbf{r},\mathbf{r}';\omega)$ for these molecules.

We plan to improve our results for $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 by calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 at all of the same conditions as those used in this work, with the exception of the step sizes Δy and Δz between y and z data points (recall that we have $x = 0$). Specifically, we plan on calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2 with step sizes Δy and Δz that are smaller than the current step sizes. This will allow us to determine if $\chi(\mathbf{r},\mathbf{r}';\omega)$ for H_2 calculated with smaller step sizes has features that are unresolved in our results for $\chi(\mathbf{r},\mathbf{r}';\omega)$ of H_2. If we calculate $\chi(\mathbf{r},\mathbf{r}';\omega)$ of other molecules, we can also calculate $\chi(\mathbf{r},\mathbf{r}';\omega)$ of these molecules as a function of step size. From these calculations, we can determine if the shape of $\chi(\mathbf{r},\mathbf{r}';\omega)$ for these molecules is independent of Δy and Δz, or if we resolve more features of $\chi(\mathbf{r},\mathbf{r}';\omega)$ as we decrease Δy and Δz.

Other future work may involve modifying the current program for calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ to improve its efficiency and speed. We could improve the efficiency and speed of our program by explicitly removing triplet states and singlet states with improper symmetries from the sum-over-states calculation of $\chi(\mathbf{r},\mathbf{r}';\omega)$. Depending on the results of $\chi(\mathbf{r},\mathbf{r}';\omega)$ calculations for different molecules, $\mathbf{r}$ values, $\mathbf{r}'$ values, and ω values, it may also be possible to develop programs to approximate $\chi(\mathbf{r},\mathbf{r}';\omega)$.

Another very important future project involves the development of algorithms and would be to develop algorithms and write computer programs that use $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ to calculate other properties, including dipole and higher-order polarizabilities, induction and dispersion energies for interacting molecules, infrared intensities, and nonlocal intramolecular dielectric functions. We have given an extensive list of molecular properties related to $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ in Chap. 1.

Future work on intermolecular interactions will involve comparing the results of the calculations presented here with the corresponding results of similar calculations presented in the literature. For example, we plan to compare the values of C_6 obtained here for $\Delta E^{(2)}_{0_{HF-HF}}$ of two colinear and of two parallel HF molecules with the corresponding values of C_6 obtained by Meath and co-workers,[289] and similarly for two perpendicular HF molecules. We also plan to compare C_9 values for three HF molecules with the corresponding values of Meath *et. al.*.[289]

Appendices

Appendix A. Fortran CISD Code for Calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ and $\alpha_{\alpha\beta}(\omega)$

Appendix A. Fortran CISD Code for Calculating $\chi(\mathbf{r},\mathbf{r}';\omega)$ and $\alpha_{\alpha\beta}(\omega)$

```
      PROGRAM CHICALC
c
c     This program solves the configuration-interaction with singles
c     and doubles (CISD) eigenvalue problem for the specified
c     molecule and computes the charge-density susceptibility of
c     that molecule at coordinates r = x, y, z, and r' = x', y', z'.
c     The program also computes the xx, yy, zz, and xy components
c     of the polarizability of the molecule.
c
c     Declare that all variables with names that begin with letters
c     A-H or O-Z will be double-precision numbers.
c
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
c
c     Description of all variables and/or arrays used in the program:
c
c     NRE = Integer array whose values correspond to the number of
c     irreducible representations in the C1 (1st element) point
c     group; the C2, CS, and CI point groups (2nd element); the C2V,
c     C2H, and D2 (3rd element) point groups; and the D2H point
c     group (4th element).
c
c     MC = Integer array which contains the irreducible represen-
c     tations of the C1, C2, CS, CI, C2V, C2H, D2 and D2H point
c     groups.
c
c     IG = Integer set to the number of irreducible representations
c     in the point group.
c
c     GRP = Point group of molecular system (character variable).
c
c     GRPREP = One-dimensional character array (with at most eight
c     elements) which is set to the list of (symbols for the) ir-
c     reducible representations for the point group of the
c     molecule.
c
c     SYMM1 = One-dimensional array of integers. The value of
c     each element represents the symmetry of a spatial orbital in
c     the molecular system. The symmetries are arranged according
c     to the energies of their corresponding orbitals.
c
c     SYMM2 = One-dimensional array of integers. The value
c     of each element represents the symmetry of a spin orbital in
c     the molecular system. The symmetries are arranged according
c     to the energies of their corresponding orbitals.
c
c     IRREP = Two-dimensional integer array which contains the ir-
c     reducible representations of the symmetries of all spin
c     orbitals in the molecule.
c
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c     NOCC1 = Number of occupied spatial orbitals.
c
c     NUNOCC1 = Number of unoccupied spatial orbitals.
c
c     NTOT1 = Total number of spatial orbitals.
c
c     NTOT2 = Total number of spin orbitals.
c
c     NELEC = Number of electrons in the molecular system.
c
c     SPIN2 = One-dimensional array of integers. The value of an
c     element with an odd index is +1, and the value of an element
c     with an even index is -1. The value of each element corres-
c     ponds to the spin that an electron would have if it were to
c     occupy that spin orbital (and if the value of the element
c     were multiplied by 0.5).
c
c     RSYM2 = Two-dimensional integer array which represents the
c     symmetry of each occupied orbital in the reference deter-
c     minant (each occupied orbital has between one and eight
c     values associated with it, depending on the point group of
c     the molecule. These associated values correspond to the
c     irreducible representation of the orbital's symmetry).
c
c     RTOTSYM2 = One-dimensional integer array which represents
c     the overall symmetry of the reference (the array is the
c     irreducible representation which represents the overall
c     symmetry of the reference determinant).
c
c     C = Two-dimensional array of integers which is used to
c     construct all possible (but not necessarily spin or
c     symmetry allowed) determinants. The first index refers
c     to the determinant number (to count and distinguish
c     between determinants), and the second index refers to
c     a spin orbital. The element corresponding to a par-
c     ticular determinant and orbital will have a value of
c     1 or 0 if the orbital is occupied or unoccupied, res-
c     pectively.
c
c     NC = Integer variable which is used to keep track of the
c     total number of determinants (not necessarily spin or
c     symmetry allowed).
c
c     CSPIN = One-dimensional array whose index corresponds to
c     determinant number, and each of whose elements has a value
c     which (when multiplied by 0.5) corresponds to the total
c     spin of a specific determinant.
c
c     C2 = Two-dimensional array of integers which is used to
c     construct all possible spin-allowed determinants. The
c     first index refers to the determinant number (to count
c     and distinguish between determinants), and the second
c     index refers to a spin orbital. The element corresponding
c     to a particular determinant and orbital will have a value
c     of 1 or 0 if the orbital is occupied or unoccupied,
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c     respectively.
c
c     NC2 = Integer variable which is used to keep track of the
c     total number of spin-allowed determinants.
c
c     CIRREP2 = Two-dimensional integer array which contains the
c     irreducible representations for the overall symmetries of
c     all possible spin-allowed determinants.
c
c     C3 = Two-dimensional array of integers which is used to
c     construct all possible spin- and symmetry-allowed
c     determinants.
c
c     NC3 = Integer variable which is used to keep track of the
c     total number of spin- and symmetry-allowed determinants.
c
c     H = CISD Hamiltonian matrix (consists of all possible mat-
c     rix elements formed from the Hamiltonian operator and two
c     determinants).
c
c     TOTDIFF = Two-dimensional array of integers used to keep
c     track of the total number of occupation differences bet-
c     ween any two spin- and symmetry-allowed determinants. For
c     example, if two electrons are in different orbitals in I
c     and J, then TOTDIFF(I,J) will be set to two.
c
c     E1SPAT = Array of one-electron integrals and indeces.
c     This array is read from the "*.int.out" input file, which
c     is generated by a GAMESS calculation. The integrals and
c     indeces in this array are in terms of spatial orbitals.
c
c     E2SPAT = Array of two-electron integrals and indeces.
c     This array is read from the "*.int.out" input file, which
c     is generated by a GAMESS calculation. The integrals and
c     indeces in this array are in terms of spatial orbitals.
c
c     VNN = Nuclear repulsion energy. Read from "*.int.out"
c     input file.
c
c     INPUT4 = Character variable (length 5) used when
c     reading one- and two-electron integral information
c     from the "*.int.out" input file.
c
c     CJ = Two-dimensional array of coefficients which are
c     produced when the CISD eigenvalue problem is solved.
c     Each CISD wavefunction is a linear combination of deter-
c     minants weighted by these coefficients. The first index
c     in this array corresponds to the determinant number, and
c     the second index corresponds to the state number.
c
c     E = One-dimensional array of energy eigenvalues produced
c     when the CISD eigenvalue problem is solved. The elements
c     of the array are arranged in order of increasing energy.
c
c     FFWORK = One-dimensional array corresponding to the FWORK
```

```
c     array in the rsm subroutine (see rsm subroutine for an
c     explanation of the FWORK array).
c
c     IIWORK = One-dimensional array corresponding to the IWORK
c     array in the rsm subroutine (see rsm subroutine for an
c     explanation of the IWORK array).
c
c     CJSUM = One-dimensional array. Each element contains the
c     sum of the squares of all the CJ coefficients for a par-
c     ticular state.
c
c     NAO = Total number of atomic orbitals.
c
c     NMO = Total number of molecular orbitals.
c
c     OMEGA = Frequency variable, read from input file. This
c     variable indicates what frequency should be used to cal-
c     culate the charge-density susceptibility.
c
c     DOEFF = Two-dimensional array of coefficients for con-
c     verting atomic orbitals into molecular orbitals. Read
c      from the "mod..." input file.
c
c     CHI = Value of the charge-density susceptibility at the
c     r = x, y, z and r' = x', y', z' coordinates (shifted by
c     the nuclear coordintes) of interest.
c
c     AAMU = Three-dimensional array of dipole-moment integ-
c     rals. The first and second indeces in this array corres-
c     pond to atomic orbital number, and the third index, which
c     goes from 1 to 3, corresponds to x (1), y (2) or z (3).
c     This array is read from the "fort.250" input file.
c
c     POLXX = xx-component of the polarizability of the
c     molecule of interest.
c     POLYY = yy-component of the polarizability of the
c     molecule of interest.
c     POLZZ = zz-component of the polarizability of the
c     molecule of interest.
c     POLXY = xy-component of the polarizability of the
c
c     AAO = One-dimensional array of atomic orbitals evaluated
c     at r = x, y, z (shifted by the relevant nuclear coor-
c     dinates). These values are provided by the AOROUT sub
c     routine (the AO array in the AOROUT subroutine is
c     returned to the main program as AAO).
c
c     ARPRIME = One-dimensional array of atomic orbitals
c     evaluated at r' = x', y', z' (shifted by the relevant
c     nuclear coordinates). These values are provided by the
c     AOROUT subroutine (the AO array evaluated at r' = x',
c     y', z' (shifted by nuclear coordinates) in the AOROUT
c     subroutine is returned to the main program as ARPRIME).
c
c     AVEC = One-dimensional array used to facilitate reading
```

```
c     of $VEC group from "mod..." GAMESS input file.
c
c     STUFF, STUFF2 = Character variables 80 characters in
c     length which are used to read lines from the "fort.250"
c     input file.
c
      CHARACTER fileinp*80
      INTEGER MC,NRE
      DIMENSION MC(8,8,4),NRE(4)
c
      CHARACTER GRP*3,GRPREP*3
      DIMENSION GRPREP(8)
      INTEGER SYMM1,SYMM2
      DIMENSION SYMM1(100),SYMM2(200)
      INTEGER IRREP
      DIMENSION IRREP(200,8)
      INTEGER SPIN2
      DIMENSION SPIN2(200)
c
      INTEGER RSYM2,RTOTSYM2
      DIMENSION RSYM2(200,8),RTOTSYM2(8)
c
      INTEGER C,C2,C3
      DIMENSION C(10000,200),C2(10000,200)
      INTEGER CSPIN
      DIMENSION CSPIN(10000)
      INTEGER CIRREP2
      DIMENSION CIRREP2(10000,8)
c
      CHARACTER INPUT4*5,INPUT3*80
      INTEGER TOTDIFF
      DIMENSION TOTDIFF(10000,10000)
c
      COMMON /BLOCK1/ H(10000,10000)
      COMMON /BLOCK2/ E1SPAT(100,100)
      COMMON /BLOCK3/ E2SPAT(100,100,100,100)
      COMMON /BLOCK4/ C3(10000,200)
      COMMON /BLOCK6/ NTOT2
      COMMON /BLOCK12/ NC3
      COMMON /BLOCK15/ NAO
c
      DIMENSION AAO(100),ARPRIME(100)
c
      DIMENSION E(10000)
      DIMENSION CJ(10000,10000)
      DIMENSION FFWORK(80000)
      DIMENSION IIWORK(10000)
      DIMENSION CJSUM(10000)
c
      DIMENSION ABIG1(50,50,50,50)
      DIMENSION ABIG2(50,50,50,50)
c
      DIMENSION AVEC(5)
      DIMENSION DCOEFF(100,100)
c
```

```
      CHARACTER STUFF*80,STUFF2*80
      DIMENSION AAMU(100,100,3)
c
      DIMENSION B(10000,50,50)
      DIMENSION BAO1(10000,50,50)
      DIMENSION BAO(10000,50,50)
      DIMENSION ILEFT(5000,5000)
      DIMENSION IRIGHT(5000,5000)
      DIMENSION ISIGNRHO(5000,5000)
      DIMENSION IOK1(5000)
      DIMENSION IOK2(5000)
c
c     Set all of the elements in each array equal to zero.
c
      DO 472 II=1,100,1
         DO 473 JJ=1,100,1
            DCOEFF(II,JJ)=0.0d0
            DO 2283 KK=1,3,1
               AAMU(II,JJ,KK)=0.0d0
 2283       CONTINUE
  473    CONTINUE
  472 CONTINUE
c
      DO 474 IK=1,5,1
         AVEC(IK)=0.0d0
  474 CONTINUE
c
      DO 6008 I=1,10000,1
         CSPIN(I)=0
         DO 6009 J=1,200,1
            C(I,J)=0
            C2(I,J)=0
 6009    CONTINUE
         DO 6010 J=1,8,1
            CIRREP2(I,J)=0
 6010    CONTINUE
 6008 CONTINUE
c
      DO 6007 I=1,8,1
         RTOTSYM2(I)=0
 6007 CONTINUE
c
      DO 6005 I=1,200,1
         SPIN2(I)=0
         SYMM2(I)=0
         DO 6006 J=1,8,1
            RSYM2(I,J)=0
            IRREP(I,J)=0
 6006    CONTINUE
 6005 CONTINUE
c
      DO 6020 II=1,100,1
         DO 6002 J=1,100,1
            E1SPAT(II,J)=0.0D0
            DO 6003 K=1,100,1
```

```
               DO 6004 L=1,100,1
                  E2SPAT(II,J,K,L)=0.0D0
 6004          CONTINUE
 6003       CONTINUE
 6002    CONTINUE
         SYMM1(II)=0
         AAO(II)=0.0D0
 6020 CONTINUE
c
      DO 6060 IP=1,50,1
         DO 6061 IQ=1,50,1
            DO 6062 IT=1,50,1
               DO 6063 IU=1,50,1
                  ABIG1(IP,IQ,IT,IU)=0.0d0
                  ABIG2(IP,IQ,IT,IU)=0.0d0
 6063          CONTINUE
 6062       CONTINUE
 6061    CONTINUE
 6060 CONTINUE
c
      DO 6130 I=1,10000,1
         DO 6135 M=1,50,1
            DO 6136 N=1,50,1
               B(I,M,N)=0.0d0
 6136       CONTINUE
 6135    CONTINUE
 6130 CONTINUE
c
      DO 222 I=1,10000,1
         E(I)=0.0D0
         CJSUM(I)=0.0D0
         IIWORK(I)=0
         DO 224 J=1,200,1
            C3(I,J)=0
  224    CONTINUE
         DO 223 J=1,10000,1
            H(I,J)=0.0D0
            TOTDIFF(I,J)=0
            CJ(I,J)=0.0D0
  223    CONTINUE
  222 CONTINUE
c
      DO 6000 I=1,80000,1
         FFWORK(I)=0.0D0
 6000 CONTINUE
c
c     Use data groups to set the values in the NRE and MC arrays.
c
      DATA NRE/1,2,4,8/
      DATA MC/
     &1,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,
     &0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,
     &
     & 1,1,0,0,0,0,0,0, 1,-1,0,0,0,0,0,0, 0,0,0,0,0,0,0,0,
     & 0,0,0,0,0,0,0,0, 0,0,0,0,0,0,0,0, 0,0,0,0,0,0,0,0,
```

```
     & 0,0,0,0,0,0,0,0, 0,0,0,0,0,0,0,0,
     &
     & 1,1,1,1,0,0,0,0,      1,1,-1,-1,0,0,0,0, 1,-1,1,-1,0,0,0,0,
     & 1,-1,-1,1,0,0,0,0, 0,0,0,0,0,0,0,0, 0,0,0,0,0,0,0,0,
     & 0,0,0,0,0,0,0,0, 0,0,0,0,0,0,0,0,
     &
     & 1,1,1,1,1,1,1,1,      1,1,1,1,-1,-1,-1,-1,  1,1,-1,-1,1,1,-1,-1,
     & 1,1,-1,-1,-1,-1,1,1,  1,-1,1,-1,1,-1,1,-1,  1,-1,1,-1,-1,1,-1,1,
     & 1,-1,-1,1,1,-1,-1,1,  1,-1,-1,1,-1,1,1,-1/
c
c     Open the input file containing the basic molecular information.
c
      call getenv('INPUT',fileinp)
      open(unit=20,file=fileinp,status='unknown',form='formatted')
c
c     Read the number of occupied orbitals, the number of unoccupied
c     orbitals, and the total number of orbitals from the input file
c     (all spatial orbitals).
c
      READ(20,*)NOCC1,NUNOCC1,NTOT1
c
c     Set the total number of spin orbitals.
c
      NTOT2=NTOT1*2
c
c     Read the point group of the molecular system from the input file.
c
 9998 FORMAT(A3)
      READ(20,9998)GRP
c
c     Read the symmetries of the spatial orbitals into the SYMM1
c     array.
c
      READ(20,*) (SYMM1(I), I=1,NTOT1)
c
c     Compute the number of electrons and set the result to NELEC.
c
      NELEC=NOCC1*2
c
c     Read the frequency to be used for calculating the charge-density
c     susceptibility into OMEGA.
c
      READ(20,*)OMEGA
      WRITE(6,*)'Frequency:',OMEGA
      CALL FLUSH(6)
c
c     Set the symmetries of the spin orbitals (using the symmetries
c     of the spatial orbitals, which are contained in the SYMM1
c     array).
c
      DO 26 I=1,NTOT1,1
         SYMM2((2*I)-1)=SYMM1(I)
         SYMM2(2*I)=SYMM1(I)
   26 CONTINUE
c
```

```
c     Assign spin to each spin orbital in the system.
c
c     (Note: The spins are assigned to orbitals rather than electrons
c     to facilitate computation. Also, the spins are set to integers
c     rather than +1/2 or -1/2 for the same reason).
c
      DO 28 I=1,NTOT1,1
         SPIN2((2*I)-1)=1
         SPIN2(2*I)=-1
   28 CONTINUE
c
c     Set the total number of all possible determinants (not
c     necessarily spin and symmetry-allowed) to 1.
c
      NC=1
c
c     Construct the reference determinant. If a spin orbital is
c     occupied in the reference determinant, the value of the
c     corresponding element will be set to 1. If a spin orbital
c     is not occupied, the value of the corresponding element
c     will be set to zero.
c
      DO 30 I=1,NELEC,1
         C(NC,I)=1
   30 CONTINUE
c
c     Increment the total number of determinants.
c
      NC=NC+1
c
c     Construct all possible (but not necessarily spin or sym-
c     metry allowed) singly-excited determinants. Increment the
c     total number of determinants each time a new determinant
c     is produced.
c
      DO 32 I=1,NELEC,1
         DO 33 J=(NELEC+1),NTOT2,1
            C(NC,J)=1
            DO 34 K=1,NELEC,1
               IF (K.EQ.I) THEN
               ELSE
                  C(NC,K)=1
               ENDIF
   34       CONTINUE
            NC=NC+1
   33    CONTINUE
   32 CONTINUE
c
c     Construct all possible (but not necessarily spin or sym-
c     metry allowed) doubly-excited determinants. Increment the
c     total number of determinants each time a new determinant
c     is produced.
c
      DO 55 I=1,(NELEC-1),1
         DO 56 J=(I+1),NELEC,1
```

```
            DO 57 K=(NELEC+1),NTOT2,1
               DO 58 L=(K+1),NTOT2,1
                  C(NC,K)=1
                  C(NC,L)=1
                  DO 59 M=1,NELEC,1
                     IF (M.EQ.I .OR. M.EQ.J) THEN
                     ELSE
                        C(NC,M)=1
                     ENDIF
   59             CONTINUE
                  NC=NC+1
   58          CONTINUE
   57       CONTINUE
   56    CONTINUE
   55 CONTINUE
c
c     Decrease the total number of determinants by one to
c     prevent improper counting of the total number of
c     singly- and doubly-excited determinants (the previous
c     loop overcounts the total number of determinants).
c
      NC=NC-1
c
c     Determine the total spin of each possible (but not
c     necessarily spin- or symmetry-allowed) determinant.
c
      DO 67 I=1,NC,1
         DO 68 J=1,NTOT2,1
            IF (C(I,J).EQ.1) THEN
               CSPIN(I)=CSPIN(I)+SPIN2(J)
            ELSE
            ENDIF
   68    CONTINUE
   67 CONTINUE
c
c     Set the total number of spin-allowed determinants to
c     one.
c
      NC2=1
c
c     Determine which of the determinants in the C array are
c     spin-allowed. Add the spin-allowed determinants to the
c     C2 array. Increment the total number of spin-allowed
c     determinants each time a determinant in the C array is
c     added to the C2 array.
c
      DO 73 I=1,NC,1
         IF (CSPIN(I).EQ.CSPIN(1)) THEN
            DO 74 J=1,NTOT2,1
               C2(NC2,J)=C(I,J)
   74       CONTINUE
            NC2=NC2+1
         ELSE
         ENDIF
   73 CONTINUE
```

```
c
c     Decrease the total number of spin-allowed determinants
c     by one to prevent improper counting of these deter-
c     minants (the previous loop overcounts the total number
c     of spin-allowed determinants).
c
      NC2=NC2-1
c
c     According to the point group, set the irreducible rep-
c     resentations of the molecule. Point groups that can be
c     handled by this program are: C1, C2, CS, CI, C2V, C2H,
c     D2, and D2H.
c
      IF (GRP.EQ.'C1') THEN
         IG=1
         GRPREP(1)='A'
      ENDIF
      IF (GRP.EQ.'C2') THEN
         IG=2
         GRPREP(1)='A'
         GRPREP(2)='B'
      ENDIF
      IF (GRP.EQ.'CS') THEN
         IG=2
         GRPREP(1)="A'"
         GRPREP(2)="A''"
      ENDIF
      IF (GRP.EQ.'CI') THEN
         IG=2
         GRPREP(1)='Ag'
         GRPREP(2)='Au'
      ENDIF
      IF (GRP.EQ.'C2V') THEN
         IG=3
         GRPREP(1)='A1'
         GRPREP(2)='A2'
         GRPREP(3)='B1'
         GRPREP(4)='B2'
      ENDIF
      IF (GRP.EQ.'D2') THEN
         IG=3
         GRPREP(1)='A'
         GRPREP(2)='B1'
         GRPREP(3)='B2'
         GRPREP(4)='B3'
      ENDIF
      IF (GRP.EQ.'C2H') THEN
         IG=3
         GRPREP(1)='Ag'
         GRPREP(2)='Au'
         GRPREP(3)='Bg'
         GRPREP(4)='Bu'
      ENDIF
      IF (GRP.EQ.'D2H') THEN
         IG=4
```

```
           GRPREP(1)='Ag'
           GRPREP(2)='Au'
           GRPREP(3)='B1g'
           GRPREP(4)='B1u'
           GRPREP(5)='B2g'
           GRPREP(6)='B2u'
           GRPREP(7)='B3g'
           GRPREP(8)='B3u'
        ENDIF
c
c       Set the irreducible representation for the symmetry of each
c       occupied and unoccupied spin orbital in the molecule.
c
        DO 108 I=1,NTOT2,1
           IF (SYMM2(I).EQ.1) THEN
              DO 109 J=1,8,1
                 IRREP(I,J)=MC(1,J,IG)
  109         CONTINUE
           ENDIF
           IF (SYMM2(I).EQ.2) THEN
              DO 110 J=1,8,1
                 IRREP(I,J)=MC(2,J,IG)
  110         CONTINUE
           ENDIF
           IF (SYMM2(I).EQ.3) THEN
              DO 111 J=1,8,1
                 IRREP(I,J)=MC(3,J,IG)
  111         CONTINUE
           ENDIF
           IF (SYMM2(I).EQ.4) THEN
              DO 112 J=1,8,1
                 IRREP(I,J)=MC(4,J,IG)
  112         CONTINUE
           ENDIF
           IF (SYMM2(I).EQ.5) THEN
              DO 113 J=1,8,1
                 IRREP(I,J)=MC(5,J,IG)
  113         CONTINUE
           ENDIF
           IF (SYMM2(I).EQ.6) THEN
              DO 114 J=1,8,1
                 IRREP(I,J)=MC(6,J,IG)
  114         CONTINUE
           ENDIF
           IF (SYMM2(I).EQ.7) THEN
              DO 115 J=1,8,1
                 IRREP(I,J)=MC(7,J,IG)
  115         CONTINUE
           ENDIF
           IF (SYMM2(I).EQ.8) THEN
              DO 116 J=1,8,1
                 IRREP(I,J)=MC(8,J,IG)
  116         CONTINUE
           ENDIF
  108   CONTINUE
```

```
c
c     Set the irreducible representations of each occupied orbital
c     in the reference determinant.
c
      DO 132 I=1,NELEC,1
         DO 133 J=1,8,1
            RSYM2(I,J)=IRREP(I,J)
  133    CONTINUE
  132 CONTINUE
c
c     Set (initialize) each element in the RTOTSYM2 array (the array
c     which will be set to the overall symmetry of the reference
c     determinant) to one.
c
      DO 119 I=1,8,1
         RTOTSYM2(I)=1
  119 CONTINUE
c
c     Determine the overall symmetry of the reference determinant by
c     calculating the product of the irreducible representations (for
c     the symmetries of the orbitals) of all occupied orbitals in the
c     reference determinant.
c
      DO 120 I=1,NELEC,1
         DO 123 J=1,8,1
            RTOTSYM2(J)=RTOTSYM2(J)*RSYM2(I,J)
  123    CONTINUE
  120 CONTINUE
c
c     Set (initialize) the value of each element in the CIRREP2 array
c     to one.
c
      DO 125 I=1,10000,1
         DO 126 J=1,8,1
            CIRREP2(I,J)=1
  126    CONTINUE
  125 CONTINUE
c
c     Determine the overall symmetry of each spin-allowed determinant.
c
      DO 127 I=1,NC2,1
         DO 128 J=1,NTOT2,1
            IF (C2(I,J).EQ.1) THEN
               DO 129 K=1,8,1
                  CIRREP2(I,K)=CIRREP2(I,K)*IRREP(J,K)
  129          CONTINUE
            ELSE
            ENDIF
  128    CONTINUE
  127 CONTINUE
c
c     Set the total number of spin- and symmetry-allowed determinants
c     to one.
c
      NC3=1
```

```
c
c     Determine whether each spin-allowed determinant in the C2 array
c     is also symmetry-allowed. If a determinants in the C2 array is
c     symmetry-allowed, add it to the C3 array.
c
      DO 137 I=1,NC2,1
         DO 138 J=1,8,1
            IF (CIRREP2(I,J).EQ.RTOTSYM2(J)) THEN
               GO TO 139
            ELSE
               GO TO 137
            ENDIF
  139       IF (J.EQ.8) THEN
               DO 140 K=1,NTOT2,1
                  C3(NC3,K)=C2(I,K)
  140          CONTINUE
               NC3=NC3+1
            ELSE
            ENDIF
  138    CONTINUE
  137 CONTINUE
c
c     Decrease the total number of spin- and symmetry-allowed deter-
c     minants by one to prevent improper counting of these deter-
c     minants (the previous loop overcounts the total number of
c     spin- and symmetry-allowed determinants).
c
      NC3=NC3-1
c
c     Write all spin and symmetry allowed determinants.
c
      WRITE(6,*)'Spin- and Symmetry-Allowed Determinants:'
      CALL FLUSH(6)
c
      DO 620 I=1,NC3,1
         WRITE(6,*)'Determinant:    ',I
         CALL FLUSH(6)
         WRITE(6,*)'Occupied Orbitals:'
         CALL FLUSH(6)
         DO 621 J=1,NTOT2,1
            IF (C3(I,J).EQ.1) THEN
               WRITE(6,*)J
               CALL FLUSH(6)
            ENDIF
  621    CONTINUE
  620 CONTINUE
c
c     Close the input file containing the basic molecular
c     information.
c
      CLOSE (20)
c
c     Open the input file containing the one- and two-electron
c     integrals.
c
```

```
      OPEN (UNIT=21,
     &FILE='h2cisd_MBS_C1.int.out',
     &STATUS='OLD')
c
c     Set the number of data-containing lines in the one-
c     and two-electron integral file (represented by the
c     variable NLINE) to zero.
c
      NLINE=0
c
c     Read the first five characters in the input file into INPUT4.
c
  153 FORMAT(A5)
      READ(21,153)INPUT4
c
c     If the first five characters of the input file are not blank
c     spaces (meaning data is present), increment the number of
c     of data-containing lines, and read the first five charac-
c     ters in the next line. Continue to read and count lines
c     until there are no more data-containing lines.
c
 1507 IF (INPUT4.NE.'     ') THEN
         NLINE=NLINE+1
         READ(21,153)INPUT4
         GO TO 1507
      ENDIF
c
c     Return to the beginning of the data-containing lines,
c     backing up one line at a time.
c
      DO 1509 I=1,(NLINE+1),1
         BACKSPACE(21)
 1509 CONTINUE
c
c     Read the first five characters of the current line (this
c     is a check to make sure that we are at the beginning of
c     the data -- if desired, print these characters to find
c     out if we are indeed at the beginning of the data). Then
c     return to the beginning of the current line.
c
      READ(21,153)INPUT4
      BACKSPACE(21)
c
c     Read the two- and one-electron integrals and indeces into
c     the E2SPAT and E1SPAT arrays, respectively. Also, read the
c     nuclear repulsion energy into the variable VNN. Note: The
c     input file's list of integrals does not include all possible
c     one- and two-electron integrals. Therefore, we will complete
c     the list while reading the integrals from the input file.
c     (The variable for the integral values is XXX, and the
c     variable(s) for the integral indeces are IP,IQ,IR, and IS).
c
      DO 1510 I=1,NLINE,1
         READ(21,*) XXX,IP,IQ,IR,IS
         IF (IR.NE.0) THEN
```

```
            E2SPAT(IP,IQ,IR,IS)=XXX
            E2SPAT(IQ,IP,IR,IS)=XXX
            E2SPAT(IP,IQ,IS,IR)=XXX
            E2SPAT(IQ,IP,IS,IR)=XXX
c
            E2SPAT(IR,IS,IP,IQ)=XXX
            E2SPAT(IS,IR,IP,IQ)=XXX
            E2SPAT(IR,IS,IQ,IP)=XXX
            E2SPAT(IS,IR,IQ,IP)=XXX
         ELSE
            IF (IP.NE.0 .AND. IQ.NE.0
     &      .AND. IR.EQ.0 .AND. IS.EQ.0) THEN
               E1SPAT(IP,IQ)=XXX
               E1SPAT(IQ,IP)=XXX
            ELSE
               IF (IP.EQ.0 .AND. IQ.EQ.0 .AND.
     &         IR.EQ.0 .AND. IS.EQ.0) THEN
                  VNN=XXX
               ENDIF
            ENDIF
         ENDIF
 1510 CONTINUE
c
c     Close the input file containing the one- and two-electron
c     integrals.
c
      CLOSE(21)
c
c     For each pair of determinants (I,J) in which J is greater
c     than or equal to I, subtract the occupation number in J
c     from the occupation number in I for each spin orbital in the
c     molecule, sum these differences, and set the result to
c     TOTDIFF(I,J). Then, divide TOTDIFF(I,J) by two to determine
c     the total number of spin-orbital occupation differences
c     between the two determinants. If the two determinants
c     differ by more than two occupancies, set H(I,J) to zero.
c     If I and J differ by two occupancies, call subroutine (SLATER2)
c     for forming two-electron integrals from two determinants that
c     differ by two spin orbital occupancies. If I and J differ by
c     one occupancy, call subroutine (SLATER1) for forming one- and
c     two-electron integrals from two determinants that differ by
c     one spin orbital occupancy.
c
      DO 9100 I=1,NC3,1
         DO 9101 J=1,NC3,1
            IF (J.GE.I) THEN
               DO 149 K=1,NTOT2,1
                  TOTDIFF(I,J)=TOTDIFF(I,J)+
     &            ABS(C3(I,K)-C3(J,K))
  149          CONTINUE
               IF ((TOTDIFF(I,J)/2).GT.2) THEN
                  H(I,J)=0.0D0
               ELSE
               ENDIF
               IF ((TOTDIFF(I,J)/2).EQ.2) THEN
```

```
                  CALL SLATER2(I,J)
               ELSE
               ENDIF
               IF ((TOTDIFF(I,J)/2).EQ.1) THEN
                  CALL SLATER1(I,J)
               ELSE
               ENDIF
c
c     If I and J are the same, determine which spin orbitals are
c     occupied in both I and J. Convert each spin orbital K (if
c     occupied) in I and J to spatial orbital KS. Then, add the
c     one-electron integral in which KS is occupied in both I and
c     and J (E1SPAT(KS,KS)) to the Hamiltonian matrix element
c     H(I,J). Also, for each pair of occupied spin orbitals L and
c     M in I (and in J) in which M is greater than or equal to L,
c     convert L and M to spatial orbitals LS and MS, calculate
c     the spins of LS and MS, and set these spins to LSPIN and
c     MSPIN. Then, if the spins LSPIN and MSPIN are the same, add
c     the antisymmetrized two-electron integral for these orbitals
c     to the Hamiltonian matrix element H(I,J). The antisymmetrized
c     two-electron integral is E2SPAT(LS,LS,MS,MS) -
c     E2SPAT(LS,MS,MS,LS). If spins LSPIN and MSPIN are different,
c     add the two-electron integral E2SPAT(LS,LS,MS,MS) to H(I,J).
c     Note: For an explanation of the calculations of matrix
c     elements H(I,J), review the Slater rules for calculating
c     one- and two-electron matrix elements of the Hamiltonian.
c
               IF ((TOTDIFF(I,J)/2).EQ.0) THEN
                  DO 160 K=1,NTOT2,1
                     IF (C3(I,K).EQ.1) THEN
                        IF (MOD(K,2).EQ.0) THEN
                           KS=(K/2)
                        ELSE
                        ENDIF
                        IF (MOD(K,2).EQ.1) THEN
                           KS=((K+1)/2)
                        ELSE
                        ENDIF
                        H(I,J)=H(I,J)+E1SPAT(KS,KS)
                     ELSE
                     ENDIF
  160             CONTINUE
               ELSE
               ENDIF
               IF ((TOTDIFF(I,J)/2).EQ.0) THEN
                  DO 161 L=1,NTOT2,1
                     DO 162 M=1,NTOT2,1
                        IF (M.GT.L) THEN
                           IF (C3(I,L).EQ.1 .AND.
     &                     C3(I,M).EQ.1) THEN
                              IF (MOD(L,2).EQ.0) THEN
                                 LS=(L/2)
                                 LSPIN=-1
                              ELSE
                              ENDIF
```

```
                              IF (MOD(L,2).EQ.1) THEN
                                 LS=((L+1)/2)
                                 LSPIN=1
                              ELSE
                              ENDIF
                              IF (MOD(M,2).EQ.0) THEN
                                 MS=(M/2)
                                 MSPIN=-1
                              ELSE
                              ENDIF
                              IF (MOD(M,2).EQ.1) THEN
                                 MS=((M+1)/2)
                                 MSPIN=1
                              ELSE
                              ENDIF
                              IF (LSPIN.EQ.MSPIN) THEN
                                 H(I,J)=H(I,J)+
     &                           E2SPAT(LS,LS,MS,MS)-
     &                           E2SPAT(LS,MS,MS,LS)
                              ELSE
                              ENDIF
                              IF (LSPIN.NE.MSPIN) THEN
                                 H(I,J)=H(I,J)+
     &                           E2SPAT(LS,LS,MS,MS)
                              ELSE
                              ENDIF
                           ELSE
                           ENDIF
                        ELSE
                        ENDIF
  162                CONTINUE
  161             CONTINUE
               ELSE
               ENDIF
            ELSE
            ENDIF
 9101    CONTINUE
 9100 CONTINUE
c
c     For each pair of determinants (I,J) with J greater than I, set
c     TOTDIFF(J,I) equal to TOTDIFF(I,J). TOTDIFF(I,J) was calculated
c     in the previous loop. This can be done because the Hamiltonian
c     matrix H(I,J) is Hermetian.
c
      DO 2025 I=1,NC3,1
         DO 2026 J=1,NC3,1
            IF (J.GE.I) THEN
               TOTDIFF(J,I)=TOTDIFF(I,J)
            ENDIF
 2026    CONTINUE
 2025 CONTINUE
c
c     For each pair of determinants (I,J) with J greater than I, set
c     H(J,I) equal to H(I,J). H(I,J) was calculated in the previous
c     loop. This can be done because the Hamiltonian matrix H(I,J)
```

```
c     is Hermetian.
c
      DO 173 IL=1,NC3,1
         DO 174 JL=1,NC3,1
            IF (JL.GE.IL) THEN
               H(JL,IL)=H(IL,JL)
            ENDIF
  174    CONTINUE
  173 CONTINUE
c
c     List the matrix elements of the Hamiltonian.
c
c     WRITE(6,*)'CISD Hamiltonian matrix elements:'
c     CALL FLUSH(6)
c
c     DO 2001 I=1,NC3,1
c        DO 2002 J=1,NC3,1
c           WRITE(6,*)I,J,H(I,J)
c           CALL FLUSH(6)
c2002    CONTINUE
c2001 CONTINUE
c
c     Set each diagonal matrix element within the set H(NC3+1,NC3+1)
c     ...H(10000,10000) to 1000.  This is done to facilitate the
c     operation of the rsm subroutine. This  enables the main program
c     to provide rsm with a fixed-dimension Hamiltonian matrix H
c     without preventing rsm from solving variably-sized CISD eigen-
c     value problems.
c
      DO 2003 NH=NC3+1,10000,1
         H(NH,NH)=1000.0D0
 2003 CONTINUE
c
c     Set the error indicator IIERR (for the rsm subroutine) to 1,000
c     (This will ensure that if the value of IIERR is zero, then it
c     is zero because rsm set it to zero and not by default). Note:
c     IIERR in the main program corresponds to IERR in the rsm sub-
c     routine. Also, if IIERR is zero, the rsm subroutine ran without
c     generating any errors.
c
      IIERR=1000
c
c     Call the subroutine for solving the CISD eigenvalue problem.
c     Note: To determine what each of the arguments in the rsm call
c     statement corresponds to, see the comments for this program
c     and the rsm subroutine.
c
      CALL rsm(10000,10000,H,E,NC3,CJ,FFWORK,IIWORK,IIERR)
c
c     For each eigenvector, calculate the sum of the squares of the
c     coefficients for that eigenvector. Print the sum of the squares
c     of the coefficients, if desired.
c
      DO 2023 LK=1,NC3,1
         DO 2024 LL=1,NC3,1
```

```
            CJSUM(LK)=CJSUM(LK)+(CJ(LL,LK)**2)
 2024    CONTINUE
c        WRITE(6,*)'Eigenvector:',LK,'Sum of squares of coeffs.:',
c    &   CJSUM(LK)
 2023 CONTINUE
c
c     For each state I, calculate and write the difference between
c     the energy of the Ith eigenvector and the 1st eigenvector
c     (i.e., calculate the resonances).
c
      WRITE(6,*)'Resonances:'
      CALL FLUSH(6)
      DO 8821 I=1,NC3,1
         WRITE(6,*)(E(I)-E(1))
         CALL FLUSH(6)
 8821 CONTINUE
c
c     Write the CI coefficients.
c
c     WRITE(6,*)'Determinant      ',
c     'State      ','CJ(Determinant, State)'
c     CALL FLUSH(6)
c     DO 2382 I=1,NC3,1
c        DO 2383 J=1,NC3,1
c           WRITE(6,*)I,J,CJ(I,J)
c           CALL FLUSH(6)
c2383    CONTINUE
c2382 CONTINUE
c
c     Open the "mod..." input file, which is the input file for
c     a GAMESS CISD energy calculation.
c
      OPEN (UNIT=23,
     &FILE='mod_h2cisd_MBS_C1.inp',
     &STATUS='OLD', FORM='FORMATTED')
c
c     Read the first line (actually, the first 80 characters of the
c     line, which is essentially the whole line) of the input file
c     into INPUT3.
c
 6100 FORMAT(A80)
      READ(23,6100)INPUT3
c
c     If the first five characters of the first line in the input
c     file are NOT " $VEC", then read the next line of the input
c     file. Continue reading lines in the input file until the
c     first five characters of the line ARE " $VEC".
c
      DO 6102 WHILE (INPUT3(1:5).NE.' $VEC')
         READ(23,6100)INPUT3
 6102 CONTINUE
c
c     Set ICOUNT (an integer variable which will be used to keep
c     track of the number of lines in the " $VEC" group) to zero.
c
```

```
      ICOUNT=0
c
c     If the first five characters of the current line ARE " $VEC",
c     read the next line in the input file and increment ICOUNT.
c     Continue to read lines and increment ICOUNT until a line
c     whose first five characters are " $END" is read.
c
      IF (INPUT3(1:5).EQ.' $VEC') THEN
         DO 4446 WHILE (INPUT3(1:5).NE.' $END')
            READ(23,6100)INPUT3
            ICOUNT = ICOUNT + 1
 4446    CONTINUE
      ENDIF
c
c     Set a new variable, JCOUNT, equal to ICOUNT plus one.
c
      JCOUNT = ICOUNT + 1
c
c     Return (by rewinding line by line) to the line whose
c     first five characters are " $VEC".
c
      DO 4447 IBACK = 1, JCOUNT
         BACKSPACE (23)
 4447 CONTINUE
c
c     Read the current line. It should be the " $VEC" line (you
c     have to print the contents of the line to make sure).
c     This is the beginning of the GAMESS " $VEC" group.
c     The actual data begins on the next line.
c
      READ(23,6100)INPUT3
c
c     Read the contents of the " $VEC" group into the
c     DCOEFF array. Note: The " $VEC" group always has
c     a very specific format -- the first number in every
c     line is an integer representing the molecular
c     orbital number, the second number is an integer
c     representing the current line number (each molecular
c     orbital has a certain number of lines of coefficients
c     in the " $VEC" group), and the last five numbers are
c     coeffients for converting the atomic orbitals into
c     molecule orbitals. The 4448 statement gives the
c     format for reading these lines.
c
 4448 FORMAT (I2, 1X, I2, 5E15.8)
c
      DO 6103 IVROW=1,ICOUNT-1
        READ (23,4448) IMO,LIN,(AVEC(JVCOL),JVCOL=1,5)
c
        DO 6104 IVCOL=1,5
           IAO=(LIN-1)*5+IVCOL
           DCOEFF(IAO,IMO)=AVEC(IVCOL)
 6104   CONTINUE
 6103 CONTINUE
c
```

```
c     Set the total number of molecular orbitals NMO equal
c     to the number of the molecular orbital IMO whose coefficients
c     were just read into DCOEFF. Set the total number of atomic
c     orbitals IAO equal to the total number of molecular orbitals.
c
      NMO=IMO
      NAO=NMO
c
c     Write (if desired) the coefficients for converting the
c     atomic orbitals to molecular orbitals.
c
c     WRITE(6,*)'Coefficients for converting a.o.s to m.o.s:'
c     CALL FLUSH(6)
c     WRITE(6,*)'ao      mo      coeff'
c     CALL FLUSH(6)
c     DO 8831 I=1,NAO,1
c        DO 8832 J=1,NAO,1
c           WRITE(6,*)I,J,DCOEFF(I,J)
c           CALL FLUSH(6)
c8832    CONTINUE
c8831 CONTINUE
c
c     Close the "mod..." input file.
c
      CLOSE(23)
c
c     Open the file containing the dipole moment integrals.
c
      OPEN (UNIT=25, FILE='fort.250',
     &STATUS='OLD', FORM='FORMATTED')
c
c     Read the first line (actually, the first 80 characters
c     of the first line) into STUFF, and read the second line
c     (again, the first 80 characters of the second line) into
c     STUFF2.
c
 2277 FORMAT(A80)
      READ(25,2277)STUFF
      READ(25,2277)STUFF2
c
c     Calculate the total number of lines of data in the
c     file containing the dipole moment integrals and set
c     this number equal to LIM. This number is obtained
c     by multiplying the square of the number of atomic
c     orbitals (NAO^2) by three.
c
      LIM=(NAO*NAO*3)
c
c     Read the dipole moment integrals into the AAMU array.
c     Also, write these integrals, if desired.
c
c     WRITE(6,*)'IJ   ','KJ   ','LJ   ','AAMU(IJ,KJ,LJ)'
c     CALL FLUSH(6)
      DO 2276 NL=1,LIM,1
         READ(25,*)IJ,KJ,LJ,XXX
```

```
         AAMU(IJ,KJ,LJ)=XXX
c        WRITE(6,*)IJ,KJ,LJ,AAMU(IJ,KJ,LJ)
c        CALL FLUSH(6)
 2276 CONTINUE
c
c     Close the "fort.250" input file.
c
      CLOSE(25)
c
c     Set each matrix element in the ILEFT, IRIGHT, ISIGNRHO,
c     B, BAO1 and BAO arrays equal to zero.
c
      DO 901 IKH=1,NC3,1
         DO 902 JKH=1,NC3,1
            ILEFT(IKH,JKH)=0
            IRIGHT(IKH,JKH)=0
            ISIGNRHO(IKH,JKH)=0
  902    CONTINUE
         DO 903 JKH=1,NTOT1,1
            DO 904 KKH=1,NTOT1,1
               B(IKH,JKH,KKH)=0.0d0
               BAO1(IKH,JKH,KKH)=0.0d0
               BAO(IKH,JKH,KKH)=0.0d0
  904       CONTINUE
  903    CONTINUE
  901 CONTINUE
c
c     ***************************************************
c
c     At this point, we will begin to calculate the
c     matrix elements of the electronic charge-density
c     operator involving determinants that differ by
c     one spin orbital occupancy.
c
c     ***************************************************
c
c     For each pair of configurations (II, JJ), where
c     JJ is less than II and II and JJ differ by
c     only one spin orbital occupancy, determine the
c     spin orbital which is occupied in II and vacant
c     in JJ and set this orbital equal to ILEFTS. Then,
c     convert spin orbital ILEFTS to a spatial orbital
c     and set the result equal to ILEFT(II,JJ). Similarly,
c     determine the spin orbital which is occupied in JJ
c     and vacant in II and set this orbital equal to
c     IRIGHTS. Then, convert spin orbital IRIGHTS to a
c     spatial orbital and set the result equal to
c     IRIGHT(II,JJ).
c
      DO 7001 II=2,NC3,1
         DO 7002 JJ=1,(II-1),1
            IF ((TOTDIFF(II,JJ)/2).EQ.1) THEN
c
               DO 410 KJ=1,NTOT2,1
                  IF ((C3(II,KJ)-C3(JJ,KJ)).EQ.1) THEN
```

```
                  ILEFT(II,JJ)=((KJ+1)/2)
                  ILEFTS=KJ
               ENDIF
               IF ((C3(JJ,KJ)-C3(II,KJ)).EQ.1) THEN
                  IRIGHT(II,JJ)=((KJ+1)/2)
                  IRIGHTS=KJ
               ENDIF
 410        CONTINUE
c
c     Set ISUMLEFT (a variable which will be used to
c     determine the number of occupied spin orbitals
c     in II that are before ILEFTS) and ISUMRIGHT (a
c     variable which will be used to determine the
c     number of occupied spin orbitals in JJ that are
c     before IRIGHTS) equal to zero.
c
            ISUMLEFT=0
            ISUMRIGHT=0
c
c     Count the number of occupied spin orbitals in II
c     that occur before ILEFTS. For each of these
c     occupied orbitals, increment ISUMLEFT. Then,
c     count the number of occupied spin orbitals in JJ
c     that occur before IRIGHTS. For each of these
c     occupied orbitals, increment ISUMRIGHT.
c
            DO 448 ML=1,ILEFTS,1
               IF (C3(II,ML).EQ.1) THEN
                  ISUMLEFT=ISUMLEFT+1
               ENDIF
 448        CONTINUE
            DO 449 MK=1,IRIGHTS,1
               IF (C3(JJ,MK).EQ.1) THEN
                  ISUMRIGHT=ISUMRIGHT+1
               ENDIF
 449        CONTINUE
c
c     Now, we will determine the sign of the matrix element of the
c     electronic charge-density operator involving determinants II
c     and JJ, and set the result equal to ISIGNRHO(II,JJ). The default
c     value of ISIGNRHO is -1. If determinants II and JJ have the
c     same number of occupied spin orbitals before ILEFTS and IRIGHTS
c     (respectively), then set ISIGNRHO equal to 1.
c
            ISIGNRHO(II,JJ)=-1
c
            IF (ISUMLEFT.EQ.ISUMRIGHT) THEN
               ISIGNRHO(II,JJ)=1
            ENDIF
c
         ENDIF
 7002   CONTINUE
 7001 CONTINUE
c
c     *********************************************************
```

```
c
c     At this point, we are almost done calculating the matrix
c     elements of the electronic charge-density operator involving
c     determinants that differ by one spin orbital occupancy.
c     Before finishing this calculation, however, we will begin to
c     calculate the matrix elements of the electronic charge-
c     density operator involving identical determinants.
c
c     ********************************************************
c
c     For each pair of identical determinants (II, II), set the
c     IOK1(II) and IOK2(II) matrix elements equal to zero. Then,
c     find the first occupied spin orbital in determinant II,
c     convert this spin orbital to a spatial orbital, and set
c     the result to IOK1(II). Then, find the second occupied
c     spin orbital in determinant II, convert this spin orbital
c     to a spatial orbital, and set the result to IOK2(II).
c
      DO 7003 II=1,NC3,1
         IOK1(II)=0
         IOK2(II)=0
         DO 415 KJ=1,NTOT2,1
            IF ((C3(II,KJ).EQ.1) .AND. (IOK1(II).NE.0)) THEN
               IOK2(II)=((KJ+1)/2)
            ENDIF
            IF ((C3(II,KJ).EQ.1) .AND. (IOK1(II).EQ.0)) THEN
               IOK1(II)=((KJ+1)/2)
            ENDIF
 415     CONTINUE
7003  CONTINUE
c
c     ********************************************************
c
c     We are almost done calculating the matrix elements of the
c     electronic charge-density operator involving identical
c     determinants. Before finishing this calculation, however,
c     we will finish calculating the matrix elements of the
c     electronic charge-density operator involving determinants
c     that differ by one spin orbital occupancy.
c
c     We now have enough information to begin computing the CI
c     coefficients' contribution to the charge-density
c     susceptibility.
c
c     ********************************************************
c
c     For each determinant II, where II is determinant 2 or
c     larger, set the CI coefficient for the II determinant
c     and state 1 equal (CJ(II,1)) to CJIND. Then, for each
c     pair of determinants (II,JJ), where JJ is less than II
c     and where the two determinants differ by only one spin
c     orbital occupancy, set ILEFT(II,JJ) (determined earlier
c     -- ILEFT(II,JJ) is the spatial orbital corresponding
c     to the spin orbital that is occupied in II but not in
c     JJ) equal to LL1. Also, set IRIGHT(II,JJ) (determined
```

```
c     earlier -- IRIGHT(II,JJ) is the spatial orbital corres-
c     ponding to the spin orbital that is occupied in JJ but
c     not in II) equal to MM1. At this point, we will assign
c     the sign of the matrix element of the electronic charge-
c     density operator involving determinants II and JJ
c     (ISIGHRHO(II,JJ) to the CI coefficients' contribution
c     to the charge-density susceptibility for this matrix
c     element by multiplying ISIGNRHO(II,JJ) by CJIND, setting
c     the result equal to VAL, and multiplying VAL by CJ(JJ,K).
c     Then, we complete the calculation of the CI coefficents'
c     contribution to the charge-density susceptibility for
c     for these matrix elements by determining CJ(JJ,K)*VAL
c     for each excited state K, and setting the result equal
c     to B(K,LL1,MM1).
c
      DO 7004 II=2,NC3,1
         CJIND=CJ(II,1)
         DO 7005 JJ=1,(II-1),1
            IF ((TOTDIFF(II,JJ)/2).EQ.1) THEN
               LL1=ILEFT(II,JJ)
               MM1=IRIGHT(II,JJ)
               VAL=(ISIGNRHO(II,JJ)*CJIND)
               DO 6997 K=2,NC3,1
                  B(K,LL1,MM1)=B(K,LL1,MM1)+(CJ(JJ,K)*VAL)
 6997          CONTINUE
            ENDIF
 7005    CONTINUE
 7004 CONTINUE
c
c     Repeat the process described in the above paragraph for all
c     pairs of determinants (II, JJ), where II and JJ differ by
c     one spin orbital occupancy and where JJ is GREATER than II.
c
      DO 7006 II=1,(NC3-1),1
         CJIND=CJ(II,1)
         DO 7007 JJ=(II+1),NC3,1
            IF ((TOTDIFF(II,JJ)/2).EQ.1) THEN
               LL1=ILEFT(JJ,II)
               MM1=IRIGHT(JJ,II)
               VAL=(ISIGNRHO(JJ,II)*CJIND)
               DO 6998 K=2,NC3,1
                  B(K,LL1,MM1)=B(K,LL1,MM1)+(CJ(JJ,K)*VAL)
 6998          CONTINUE
            ENDIF
 7007    CONTINUE
 7006 CONTINUE
c
c     ********************************************************
c
c     We have finished calculating the CI coefficients'
c     contribution to the charge-density susceptibility
c     for matrix elements of the electronic charge-density
c     operator involving pairs of determinants (II, JJ) that
c     differ by one spin orbital occupancy.
c
```

```
c     Now, we will calculate the CI coefficients' contribution
c     to the charge-density susceptibility for matrix elements
c     of the electronic charge-density operator involving pairs
c     of identical determinants (II, II).
c
c     ******************************************************
c
c     For each determinants II, set the spatial equivalent of
c     the first occupied spin orbital in II (i.e., IOK1(II))
c     equal to LL1, and set the spatial equivalent of the
c     second occupied spin orbital in II (i.e., IOK2(II))
c     equal to MM1. Then, set the CI coefficient for the II
c     determinant and the ground state (i.e., CJ(II,1))
c     equal to CJIND. At this point, we will split the
c     calculation of the CI coefficients' contribution to
c     the charge-density susceptibility for matrix elements
c     of the electronic charge-density operator involving
c     identical determinants (II, II) into two parts: We
c     we calculate the contribution due to spatial orbitals
c     LL1 and MM1 separately. Specifically, for each excited
c     state K, we will calculate the CI coefficients'
c     contribution to the charge-density susceptibility
c     due to orbital LL1 by multiplying the coefficient
c     for determinant II and state K (i.e., CJ(II,K)) by
c     CJIND, and setting this result equal to B(K,LL1,LL1).
c     Similarly, we will calculate the same contribution
c     for each K due to orbital MM1 by multiplying
c     CJ(II,K) by CJIND and setting the result equal to
c     B(K,MM1,MM1).
c
      DO 7008 II=1,NC3,1
         LL1=IOK1(II)
         MM1=IOK2(II)
         CJIND=CJ(II,1)
         DO 6999 K=2,NC3,1
            B(K,LL1,LL1)=B(K,LL1,LL1)+(CJ(II,K)*CJIND)
            B(K,MM1,MM1)=B(K,MM1,MM1)+(CJ(II,K)*CJIND)
 6999    CONTINUE
 7008 CONTINUE
c
c     ******************************************************
c
c     We have finished calculating the CI coefficients'
c     contribution to the charge-density susceptibility.
c
c     Next, calculate the expansion coefficients' (i.e., the
c     coefficients for converting atomic orbitals to molecular
c     orbitals) contribution to the susceptibility, and
c     combine this with the CI coefficients' contribution
c     to the charge-density susceptibility.
c
c     ******************************************************
c
      DO 7014 K=2,NC3,1
         DO 7011 LKH=1,NTOT1,1
```

```
            DO 7012 JKH=1,NTOT1,1
               DO 7013 MKH=1,NTOT1,1
                  BAO1(K,LKH,JKH)=BAO1(K,LKH,JKH)+
     &           (B(K,LKH,MKH)*DCOEFF(JKH,MKH))
 7013          CONTINUE
 7012       CONTINUE
 7011    CONTINUE
         DO 7010 IKH=1,NTOT1,1
            DO 7015 JKH=1,NTOT1,1
               DO 7016 LKH=1,NTOT1,1
                  BAO(K,IKH,JKH)=BAO(K,IKH,JKH)+
     &            (BAO1(K,LKH,JKH)*DCOEFF(IKH,LKH))
 7016          CONTINUE
 7015       CONTINUE
 7010    CONTINUE
 7014 CONTINUE
c
c     Write the contents of the BAO array, if desired.
c
      WRITE(6,*)'K,KK,LL,BAO(K,KK,LL)'
      CALL FLUSH(6)
      DO 6034 K=2,NC3,1
         DO 6035 KK=1,NAO,1
            DO 6036 LL=1,NAO,1
               WRITE(6,*)K,KK,LL,BAO(K,KK,LL)
               CALL FLUSH(6)
 6036       CONTINUE
 6035    CONTINUE
 6034 CONTINUE
c
c     ***************************************************************
c
c     Complete the calculation of the contribution of all coefficients
c     to the charge-density susceptibilty, and add the frequency
c     dependence to the susceptibility.
c
c     ***************************************************************
c
      DO 6040 NP=1,NAO,1
         DO 6041 NQ=1,NAO,1
            DO 6042 NT=1,NAO,1
               DO 6043 NU=1,NAO,1
                  DO 6044 K=2,NC3,1
                     ABIG1(NP,NQ,NT,NU)=ABIG1(NP,NQ,NT,NU)
     &              +((BAO(K,NP,NQ)*BAO(K,NT,NU))/(E(K)-E(1)-OMEGA))
                     ABIG2(NP,NQ,NT,NU)=ABIG2(NP,NQ,NT,NU)
     &              +((BAO(K,NP,NQ)*BAO(K,NT,NU))/(E(K)-E(1)+OMEGA))
 6044             CONTINUE
 6043          CONTINUE
 6042       CONTINUE
 6041    CONTINUE
 6040 CONTINUE
c
c     Write the ABIG arrays, if desired.
c
```

```
c     DO 6045 NP=1,NAO,1
c        DO 6046 NQ=1,NAO,1
c           DO 6047 NT=1,NAO,1
c              DO 6048 NU=1,NAO,1
c                 WRITE(6,*)NP,NQ,NT,NU,
c    &            ABIG1(NP,NQ,NT,NU)
c                 CALL FLUSH(6)
c6048          CONTINUE
c6047       CONTINUE
c6046    CONTINUE
c6045 CONTINUE
c
c     DO 6049 NP=1,NAO,1
c        DO 6050 NQ=1,NAO,1
c           DO 6051 NT=1,NAO,1
c              DO 6052 NU=1,NAO,1
c                 WRITE(6,*)NP,NQ,NT,NU,
c    &            ABIG2(NP,NQ,NT,NU)
c                 CALL FLUSH(6)
c6052          CONTINUE
c6051       CONTINUE
c6050    CONTINUE
c6049 CONTINUE
c
c     *****************************************************
c
c     Calculate the charge-density susceptibility at each
c     specified x, y, z and x', y', z'. For each x, y, z
c     and x', y', z', calculate the contribution of the
c     atomic orbitals evaluated at these points to the
c     susceptibility, and combine this result with the
c     coefficients' contribution to the susceptibility.
c
c     Also, calculate the xx, yy, zz, and xy components
c     of the polarizability. Unlike the susceptibility,
c     however, the polarizability components will only
c     be calculated once, since these quantities are
c     calculated from integrals over all x, y, z.
c
c     *****************************************************
c
c     Set the values of x', y' and z' to XRP, YRP, and ZRP,
c     respectively.
c
      XRP=0.0d0
      YRP=0.0d0
      ZRP=0.0d0
c
c     Call the subroutine (i. e., subroutine AOROUT) for
c     evaluating the atomic orbitals
c     at any x, y, z or x', y', z'. Obtain the values of the
c     atomic orbitals evaluated at x', y', and z' from
c     AOROUT. These values will be returned from AOROUT in
c     the AAO array.
c
```

```
      CALL AOROUT(XRP,YRP,ZRP,AAO)
c
c     Write x', y', and z'.
c
      WRITE(6,*)'r-prime:',XRP,YRP,ZRP
      CALL FLUSH(6)
c
c     Set each AAO(N) equal an ARPRIME(N) (essentially,
c     create an array which is identical to AAO and name
c     it ARPRIME).
c
      DO 6369 N=1,NAO,1
         ARPRIME(N)=AAO(N)
 6369 CONTINUE
c
c     Write the ARPRIME array, if desired.
c
c     DO 6871 J=1,NAO,1
c        WRITE(80,*)ARPRIME(J)
c6871 CONTINUE
c
c     Use the three nested do loops that immediately follow
c     to choose the grid of x, y, z points at which to
c     calculate the spatial dependent part of the
c     susceptibility. Use the I, J, and K loops to set up
c     the x, y, and z coordinates, respectively. Each x
c     coordinate (XX) is selected by taking the value of I
c     (where I essentially corresponds to the number of
c     the x point), multiplying this by DELTAXX (which is
c     the x increment), and adding this to XX0 (the initial
c     x). The y (YY) and z (ZZ) coordinates are set up in
c     the same way.
c
c     When I, J, and K are all equal to one, set the
c     variables used for calculating the xx, yy, zz, and
c     xy components of the polarizability equal to zero.
c     Note: POLXX1, POLXX2, POLYY1, POLYY2, POLZZ1, POLZZ2,
c     POLXY1, and POLXY2 are intermediate variables used
c     in calculating the xx (POLXX), yy (POLYY), zz (POLZZ),
c     and xy (POLXY) components of the polarizability.
c
      DO 6361 I=1,1
         DO 6362 J=1,1
            DO 6363 K=-1,1
c
                  IF (I.EQ.1 .AND. J.EQ.1
     &            .AND. K.EQ.1) THEN
c
                     POLXX1=0.0d0
                     POLXX2=0.0d0
                     POLYY1=0.0d0
                     POLYY2=0.0d0
                     POLZZ1=0.0d0
                     POLZZ2=0.0d0
                     POLXY1=0.0d0
```

```
                     POLXY2=0.0d0
c
                     POLXX=0.0d0
                     POLYY=0.0d0
                     POLZZ=0.0d0
                     POLXY=0.0d0
c
                  ENDIF
c
                  XX0=0.0d0
                  YY0=0.0d0
                  ZZ0=0.0d0
                  DELTAXX=0.0d0
                  DELTAYY=0.0d0
                  DELTAZZ=0.05d0
c
                  XX=(XX0+I*DELTAXX)
                  YY=(YY0+J*DELTAYY)
                  ZZ=(ZZ0+K*DELTAZZ)
c
c     Call the AOROUT subroutine for evaluating the atomic orbitals
c     at x, y, z. The atomic orbitals will be evaluated at XX, YY,
c     ZZ and their values will be returned to the main program in the
c     AAO array.
c
                  CALL AOROUT(XX,YY,ZZ,AAO)
c
c     Write the x (XX), y (yy), and z (ZZ) coordinates, if desired.
c
c                 WRITE(6,*)XX,YY,ZZ
c                 CALL FLUSH(6)
c
                  A1SUM4=0.0d0
                  A2SUM4=0.0d0
                  DO 5365 IM=1,NAO,1
                     A1SUM3=0.0d0
                     A2SUM3=0.0d0
                     DO 5366 JM=1,NAO,1
                        A1SUM2=0.0d0
                        A2SUM2=0.0d0
                        DO 5367 KM=1,NAO,1
                           A1SUM1=0.0d0
                           A2SUM1=0.0d0
                           DO 5368 LM=1,NAO,1
c
                              A1SUM1=A1SUM1+
     &                        (ABIG1(IM,JM,KM,LM)*ARPRIME(LM))
c
                              IF (I.EQ.1 .AND. J.EQ.1 .AND.
     &                        K.EQ.1) THEN
c
                                 POLXX1=POLXX1+
     &                           (ABIG1(IM,JM,KM,LM)*AAMU(IM,JM,1)
     &                           *AAMU(KM,LM,1))
c
```

```
                                 POLXX2=POLXX2+
     &                           (ABIG2(IM,JM,KM,LM)*AAMU(IM,JM,1)
     &                           *AAMU(KM,LM,1))
c
                                 POLYY1=POLYY1+
     &                           (ABIG1(IM,JM,KM,LM)*AAMU(IM,JM,2)
     &                           *AAMU(KM,LM,2))
c
                                 POLYY2=POLYY2+
     &                           (ABIG2(IM,JM,KM,LM)*AAMU(IM,JM,2)
     &                           *AAMU(KM,LM,2))
c
                                 POLZZ1=POLZZ1+
     &                           (ABIG1(IM,JM,KM,LM)*AAMU(IM,JM,3)
     &                           *AAMU(KM,LM,3))
c
                                 POLZZ2=POLZZ2+
     &                           (ABIG2(IM,JM,KM,LM)*AAMU(IM,JM,3)
     &                           *AAMU(KM,LM,3))
c
                                 POLXY1=POLXY1+
     &                           (ABIG1(IM,JM,KM,LM)*AAMU(IM,JM,1)
     &                           *AAMU(KM,LM,2))
c
                                 POLXY2=POLXY2+
     &                           (ABIG2(IM,JM,KM,LM)*AAMU(IM,JM,1)
     &                           *AAMU(KM,LM,2))
c
                              ENDIF
c
                              A2SUM1=A2SUM1+
     &                        (ABIG2(IM,JM,KM,LM)*AAO(LM))

 5368                      CONTINUE
                           A1SUM2=A1SUM2
     &                     +(A1SUM1*ARPRIME(KM))
                           A2SUM2=A2SUM2
     &                     +(A2SUM1*AAO(KM))
 5367                   CONTINUE
                        A1SUM3=A1SUM3+(A1SUM2*AAO(JM))
                        A2SUM3=A2SUM3+(A2SUM2
     &                  *ARPRIME(JM))
 5366                CONTINUE
                     A1SUM4=A1SUM4+(A1SUM3*AAO(IM))
                     A2SUM4=A2SUM4+(A2SUM3*ARPRIME(IM))
 5365             CONTINUE
c
                  CHI=A1SUM4+A2SUM4
c
c     Write the value of the charge-density susceptibility
c     at x (XX), y (YY), z (ZZ).
c
                  WRITE(6,*)CHI
                  CALL FLUSH(6)
c
```

```
c     Write the xx, yy, zz, and xy components of the
c     polarizability. Note: These will only be written once;
c     when I, J, and K equal one.
c
                  IF (I.EQ.1 .AND. J.EQ.1
     &            .AND. K.EQ.1) THEN
c
                     POLXX=POLXX1+POLXX2
                     WRITE(6,*)'POLXX:',POLXX
                     CALL FLUSH(6)
c
                     POLYY=POLYY1+POLYY2
                     WRITE(6,*)'POLYY:',POLYY
                     CALL FLUSH(6)
c
                     POLZZ=POLZZ1+POLZZ2
                     WRITE(6,*)'POLZZ:',POLZZ
                     CALL FLUSH(6)
c
                     POLXY=POLXY1+POLXY2
                     WRITE(6,*)'POLXY:',POLXY
                     CALL FLUSH(6)
c
                  ENDIF
c
 6363       CONTINUE
 6362    CONTINUE
 6361 CONTINUE
c
      END
c
      SUBROUTINE SLATER1(II,JJ)
c
c     This subroutine evaluates the matrix elements of pairs of
c     determinants which differ in the location of one electron.
c
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
c
      INTEGER C3
c
      COMMON /BLOCK1/ H(10000,10000)
      COMMON /BLOCK2/ E1SPAT(100,100)
      COMMON /BLOCK3/ E2SPAT(100,100,100,100)
      COMMON /BLOCK4/ C3(10000,200)
      COMMON /BLOCK6/ NTOT2
      COMMON /BLOCK12/ NC3
      COMMON /BLOCK15/ NAO
c
      I1A=0
      I2A=0
c
c     Determine where (i.e., what spin orbitals) determinants
c     II and JJ differ, and set these orbitals to I1A and I2A.
c
      DO 151 L=1,NTOT2,1
```

```
         IF ((C3(II,L)-C3(JJ,L)).EQ.1
     &   .AND. I1A.EQ.0) THEN
            I1A=L
         ENDIF
         IF (((C3(II,L)-C3(JJ,L)).EQ.(-1))
     &   .AND. I1A.NE.L .AND. I2A.EQ.0) THEN
            I2A=L
         ENDIF
  151 CONTINUE
c
c     Determine the sign of the Hamiltonian matrix element which
c     is being formed from determinants II and JJ, where II and JJ
c     differ in the occupation of one spin orbital.
c
c     First, count the number of occupied orbitals in determinant
c     II that are lower in energy than the first orbital with
c     different occupancies in II and JJ, and set the total to
c
c     (Before beginning, set SUMI1A to zero).
c
      SUMI1A=0.0D0
      DO 448 ML=1,(I1A-1),1
         IF (C3(II,ML).EQ.1) THEN
            SUMI1A=SUMI1A+1.0D0
         ENDIF
  448 CONTINUE
c
c     Multiply SUMI1A by -1 and set the result to SIGNI1A.
c
      SIGNI1A=((-1.0D0)**SUMI1A)
c
c     Count the number of occupied orbitals in determinant
c     JJ that are lower in energy than the second orbital with
c     different occupancies in II and JJ, and set the total to
c     SUMI2A.
c

c     (Before beginning, set SUMI2A to zero).
c
      SUMI2A=0.0D0
      DO 449 MK=1,(I2A-1),1
         IF (C3(JJ,MK).EQ.1) THEN
            SUMI2A=SUMI2A+1.0D0
         ENDIF
  449 CONTINUE
c
c     Multiply SUMI2A by -1 and set the result to SIGNI2A.
c
      SIGNI2A=((-1.0D0)**SUMI2A)
c
c     Determine the overall sign of H(II,JJ)
c     by multiplying SIGNI1A by SIGNI2A and setting the result
c     equal to SIGNIA.
c
      SIGNIA=(SIGNI1A*SIGNI2A)
```

```
c
c     Convert the spin orbitals I1A, I2A to spatial orbitals I1AS and
c     I2AS, respectively. Each unique pair of consecutively-numbered
c     spin orbitals is assigned to the same spatial orbital. Also,
c     set the spins of I1AS and I2AS. If the spin orbital is even,
c     set the spin of I1AS or I2AS to -1, and if the spin
c     orbital is odd, set the spin of I1AS or I2AS to +1.
c     (I1ASPIN=spin of I1AS, I2ASPIN=spin of I2AS)
c
      IF (MOD(I1A,2).EQ.0) THEN
         I1AS=(I1A/2)
         I1ASPIN=-1
      ELSE
         IF (MOD(I1A,2).EQ.1) THEN
            I1AS=((I1A+1)/2)
            I1ASPIN=1
         ENDIF
      ENDIF
c
      IF (MOD(I2A,2).EQ.0) THEN
         I2AS=(I2A/2)
         I2ASPIN=-1
      ELSE
         IF (MOD(I2A,2).EQ.1) THEN
            I2AS=((I2A+1)/2)
            I2ASPIN=1
         ENDIF
      ENDIF
c
c     Determine if the one-electron integral contribution to the
c     Hamiltonian matrix element H(II,JJ) is spin-conserved. If
c     so, add this integral to H(II,JJ).
c
      IF (I1ASPIN.EQ.I2ASPIN) THEN
         H(II,JJ)=H(II,JJ)+E1SPAT(I1AS,I2AS)
      ENDIF
c
c     Convert the two-electron integral contribution(s) to H(II,JJ)
c     to (an) integral(s) over spatial orbitals.
c
      DO 2000 K=1,NTOT2,1
         IF (K.NE.I1A .AND. K.NE.I2A
     &   .AND. C3(II,K).EQ.1) THEN
            IF (MOD(K,2).EQ.0) THEN
               KS=(K/2)
               KSPIN=-1
            ELSE
               IF (MOD(K,2).EQ.1) THEN
                  KS=((K+1)/2)
                  KSPIN=1
               ENDIF
            ENDIF
            IF (I1ASPIN.EQ.I2ASPIN .AND.
     &      I2ASPIN.EQ.KSPIN) THEN
               H(II,JJ)=H(II,JJ)+
```

```
     &         E2SPAT(KS,KS,I1AS,I2AS)-
     &         E2SPAT(KS,I2AS,I1AS,KS)
            ENDIF
            IF (I1ASPIN.EQ.I2ASPIN .AND. I2ASPIN.NE.KSPIN)
     &      THEN
               H(II,JJ)=H(II,JJ)+
     &         E2SPAT(KS,KS,I1AS,I2AS)
            ENDIF
         ENDIF
 2000 CONTINUE
c
      H(II,JJ)=(H(II,JJ)*SIGNIA)
c
      END
c
      SUBROUTINE SLATER2(III,JJJ)
c
c     This subroutine formulates the two-electron integral for a pair
c     of determinants which differ in the locations of two electrons.
c
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
c
      COMMON /BLOCK1/ H(10000,10000)
      COMMON /BLOCK2/ E1SPAT(100,100)
      COMMON /BLOCK3/ E2SPAT(100,100,100,100)
      COMMON /BLOCK4/ C3(10000,200)
      COMMON /BLOCK6/ NTOT2
      COMMON /BLOCK12/ NC3
      COMMON /BLOCK15/ NAO
c
      INTEGER C3
c
c     Set the spin orbitals (in ascending order) which differ in
c     occupation number in determinants I and J to I1,I2,I3 and I4.
c
c     (Before beginning, set I1,I2,I3 and I4 to zero).
c
c     WRITE(6,*) 'slater 2 1st check'
c     CALL FLUSH(6)
c
      I1=0
      I2=0
      I3=0
      I4=0
      DO 150 KK=1,NTOT2,1
         IF ((C3(III,KK)-C3(JJJ,KK)).EQ.1)
     &   THEN
            IF (I1.EQ.0) THEN
               I1=KK
               GO TO 150
            ENDIF
            IF (I1.NE.0 .AND. I2.EQ.0) THEN
               I2=KK
            ENDIF
         ENDIF
```

```
  150 CONTINUE
      DO 170 KK=1,NTOT2,1
         IF ((C3(III,KK)-C3(JJJ,KK)).EQ.(-1))
     &   THEN
            IF (I3.EQ.0) THEN
               I3=KK
               GO TO 170
            ENDIF
            IF (I4.EQ.0) THEN
               I4=KK
            ENDIF
         ENDIF
  170 CONTINUE
c
c     Determine the sign of the matrix element H(III,JJJ).
c
c     First, count the number of occupied orbitals in
c     determinant III that are lower in energy than the 1st
c     orbital in III which has a different occupation number
c     than in JJJ, and set the total to SUMI1.
c
c     (Before beginning, set SUMI1 to zero).
c
      SUMI1=0.0D0
      DO 450 MM=1,(I1-1),1
         IF (C3(III,MM).EQ.1) THEN
            SUMI1=SUMI1+1.0D0
         ENDIF
  450 CONTINUE
c
c     Then, multiply SUMI1 by -1, and set the result to SIGNI1.
c
      SIGNI1=((-1.0D0)**SUMI1)
c
c     Count the number of occupied orbitals in
c     determinant III that are lower in energy than the 2nd
c     orbital in III which has a different occupation number
c     than in JJJ, and set the total to SUMI2.
c
c     (Before beginning, set SUMI2 to zero).
c
      SUMI2=0.0D0
      DO 451 MN=1,(I2-1),1
         IF (C3(III,MN).EQ.1) THEN
            SUMI2=SUMI2+1.0D0
         ENDIF
  451 CONTINUE
c
c     Multiply SUMI2 by -1, and set the result to SIGNI2.
c
      SIGNI2=((-1.0D0)**SUMI2)
c
c     Count the number of occupied orbitals in
c     determinant JJJ that are lower in energy than the 1st
c     orbital in JJJ which has a different occupation number
```

```
c     than in III, and set the total to SUMI3.
c
c     (Before beginning, set SUMI3 to zero).
c
      SUMI3=0.0D0
      DO 452 MO=1,(I3-1),1
         IF (C3(JJJ,MO).EQ.1) THEN
            SUMI3=SUMI3+1.0d0
         ENDIF
  452 CONTINUE
c
c     Multiply SUMI3 by -1, and set the result to SIGNI3.
c
      SIGNI3=((-1.0D0)**SUMI3)
c
c     Count the number of occupied orbitals in
c     determinant JJJ that are lower in energy than the 2nd
c     orbital in JJJ which has a different occupation number
c     than in III, and set the total to SUMI4.
c
c     (Before beginning, set SUMI4 to zero).
c
      SUMI4=0.0D0
      DO 453 MP=1,(I4-1),1
         IF (C3(JJJ,MP).EQ.1) THEN
            SUMI4=SUMI4+1.0d0
         ENDIF
  453 CONTINUE
c
c     Multiply SUMI4 by -1, and set the result to SIGNI4.
c
      SIGNI4=((-1.0D0)**SUMI4)
c
c     Calculate the overall sign of the two-electron integral(s)
c     by multiplying the four signs together and setting the result
c     to SIGNI.
c
      SIGNI=(SIGNI1*SIGNI2*SIGNI3*SIGNI4)
c
c     Convert the spin orbitals I1,I2,I3 and I4 to spatial orbitals
c     IS1,IS2,IS3 and IS4, respectively. Each unique pair of
c     consecutive spin orbitals is assigned to the same spatial
c     orbital. Set the spins of IS1,IS2,IS3 and IS4. If the spin
c     orbital is odd-numbered, set the spin of the spatial orbital
c     to -1, and if the spin orbital is even, set the spin of the
c     spatial orbital to +1. The variables for the spins of IS1,
c     IS2, IS3 and IS4 are I1SPIN, I2SPIN, I3SPIN, and I4SPIN.
c
      IF (MOD(I1,2).EQ.0) THEN
         IS1=(I1/2)
         I1SPIN=-1
      ELSE
         IF (MOD(I1,2).EQ.1) THEN
            IS1=((I1+1)/2)
            I1SPIN=1
```

```
         ELSE
         ENDIF
      ENDIF
c
      IF (MOD(I2,2).EQ.0) THEN
         IS2=(I2/2)
         I2SPIN=-1
      ELSE
         IF (MOD(I2,2).EQ.1) THEN
            IS2=((I2+1)/2)
            I2SPIN=1
         ELSE
         ENDIF
      ENDIF
c
      IF (MOD(I3,2).EQ.0) THEN
         IS3=(I3/2)
         I3SPIN=-1
      ELSE
         IF (MOD(I3,2).EQ.1) THEN
            IS3=((I3+1)/2)
            I3SPIN=1
         ELSE
         ENDIF
      ENDIF
c
      IF (MOD(I4,2).EQ.0) THEN
         IS4=(I4/2)
         I4SPIN=-1
      ELSE
         IF (MOD(I4,2).EQ.1) THEN
            IS4=((I4+1)/2)
            I4SPIN=1
         ELSE
         ENDIF
      ENDIF
c
c     WRITE(6,*) 'slater2, ok here'
c     CALL FLUSH(6)
c
c     Determine the two-electron integral contribution to
c     H(III,JJJ).
c
c     First, determine whether the two-electron integrals
c     formed by applying the Slater rules to determinants
c     III and JJJ are spin-allowed.
c
c     Add each spin-allowed two-electron integral to H(III,JJJ).
c
      IF (I1SPIN.EQ.I3SPIN .AND.
     &I2SPIN.EQ.I4SPIN .AND. I3SPIN.NE.I2SPIN) THEN
         H(III,JJJ)=H(III,JJJ)+E2SPAT(IS1,IS3,IS2,IS4)
      ENDIF
c
      IF (I1SPIN.EQ.I4SPIN .AND.
```

```
     &I2SPIN.EQ.I3SPIN .AND. I1SPIN.NE.I3SPIN) THEN
         H(III,JJJ)=H(III,JJJ)-
     &   E2SPAT(IS1,IS4,IS2,IS3)
      ENDIF
c
      IF (I1SPIN.EQ.I3SPIN .AND.
     &I2SPIN.EQ.I4SPIN .AND. I1SPIN.EQ.I4SPIN) THEN
         H(III,JJJ)=H(III,JJJ)+
     &   E2SPAT(IS1,IS3,IS2,IS4)-
     &   E2SPAT(IS1,IS4,IS2,IS3)
      ENDIF
c
c     Calculate the sign of H(III,JJJ).
c
      H(III,JJJ)=(H(III,JJJ)*SIGNI)
c
      END
c
      subroutine rsm(nm,n,a,w,m,z,fwork,iwork,ierr)
c
      integer n,nm,m,iwork(n),ierr
      integer k1,k2,k3,k4,k5,k6,k7
      double precision a(nm,n),w(n),z(nm,m),fwork(1)
c
c     this subroutine calls the recommended sequence of
c     subroutines from the eigensystem subroutine package (eispack)
c     to find all of the eigenvalues and some of the eigenvectors
c     of a real symmetric matrix.
c
c     on input
c
c        nm  must be set to the row dimension of the two-dimensional
c        array parameters as declared in the calling program
c        dimension statement.
c
c        n  is the order of the matrix  a.
c
c        a  contains the real symmetric matrix.
c
c        m  the eigenvectors corresponding to the first m eigenvalues
c           are to be computed.
c           if m = 0 then no eigenvectors are computed.
c           if m = n then all of the eigenvectors are computed.
c
c     on output
c
c        w  contains all n eigenvalues in ascending order.
c
c        z  contains the orthonormal eigenvectors associated with
c           the first m eigenvalues.
c
c        ierr  is an integer output variable set equal to an error
c           completion code described in the documentation for tqlrat,
c           imtqlv and tinvit.  the normal completion code is zero.
c
```

```
c        fwork  is a temporary storage array of dimension 8*n.
c
c        iwork  is an integer temporary storage array of dimension n.
c
c     questions and comments should be directed to burton s. garbow,
c     mathematics and computer science div, argonne national laboratory
c
c     this version dated august 1983.
c
c     ------------------------------------------------------------------
c
      ierr = 10 * n
      if (n .gt. nm .or. m .gt. nm) go to 50
      k1 = 1
      k2 = k1 + n
      k3 = k2 + n
      k4 = k3 + n
      k5 = k4 + n
      k6 = k5 + n
      k7 = k6 + n
      k8 = k7 + n
      if (m .gt. 0) go to 10
c     .......... find eigenvalues only ..........
      call  tred1(nm,n,a,w,fwork(k1),fwork(k2))
      call  tqlrat(n,w,fwork(k2),ierr)
      go to 50
c     .......... find all eigenvalues and m eigenvectors ..........
   10 call  tred1(nm,n,a,fwork(k1),fwork(k2),fwork(k3))
      call  imtqlv(n,fwork(k1),fwork(k2),fwork(k3),w,iwork,
     x              ierr,fwork(k4))
      call  tinvit(nm,n,fwork(k1),fwork(k2),fwork(k3),m,w,iwork,z,ierr,
     x              fwork(k4),fwork(k5),fwork(k6),fwork(k7),fwork(k8))
      call  trbak1(nm,n,a,fwork(k2),m,z)
   50 return
      end
      double precision function epslon (x)
      double precision x
c
c     estimate unit roundoff in quantities of size x.
c
      double precision a,b,c,eps
c
c     this program should function properly on all systems
c     satisfying the following two assumptions,
c        1.  the base used in representing floating point
c            numbers is not a power of three.
c        2.  the quantity  a  in statement 10 is represented to
c            the accuracy used in floating point variables
c            that are stored in memory.
c     the statement number 10 and the go to 10 are intended to
c     force optimizing compilers to generate code satisfying
c     assumption 2.
c     under these assumptions, it should be true that,
c            a  is not exactly equal to four-thirds,
c            b  has a zero for its last bit or digit,
```

```
c           c  is not exactly equal to one,
c           eps  measures the separation of 1.0 from
c                the next larger floating point number.
c     the developers of eispack would appreciate being informed
c     about any systems where these assumptions do not hold.
c
c     this version dated 4/6/83.
c
      a = 4.0d0/3.0d0
   10 b = a - 1.0d0
      c = b + b + b
      eps = dabs(c-1.0d0)
      if (eps .eq. 0.0d0) go to 10
      epslon = eps*dabs(x)
      return
      end
      subroutine imtqlv(n,d,e,e2,w,ind,ierr,rv1)
c
      integer i,j,k,l,m,n,ii,mml,tag,ierr
      double precision d(n),e(n),e2(n),w(n),rv1(n)
      double precision b,c,f,g,p,r,s,tst1,tst2,pythag
      integer ind(n)
c
c     this subroutine is a variant of  imtql1  which is a translation of
c     algol procedure imtql1, num. math. 12, 377-383(1968) by martin and
c     wilkinson, as modified in num. math. 15, 450(1970) by dubrulle.
c     handbook for auto. comp., vol.ii-linear algebra, 241-248(1971).
c
c     this subroutine finds the eigenvalues of a symmetric tridiagonal
c     matrix by the implicit ql method and associates with them
c     their corresponding submatrix indices.
c
c     on input
c
c        n is the order of the matrix.
c
c        d contains the diagonal elements of the input matrix.
c
c        e contains the subdiagonal elements of the input matrix
c          in its last n-1 positions.  e(1) is arbitrary.
c
c        e2 contains the squares of the corresponding elements of e.
c          e2(1) is arbitrary.
c
c     on output
c
c        d and e are unaltered.
c
c        elements of e2, corresponding to elements of e regarded
c          as negligible, have been replaced by zero causing the
c          matrix to split into a direct sum of submatrices.
c          e2(1) is also set to zero.
c
c        w contains the eigenvalues in ascending order.  if an
c          error exit is made, the eigenvalues are correct and
```

```
c          ordered for indices 1,2,...ierr-1, but may not be
c          the smallest eigenvalues.
c
c        ind contains the submatrix indices associated with the
c          corresponding eigenvalues in w -- 1 for eigenvalues
c          belonging to the first submatrix from the top,
c          2 for those belonging to the second submatrix, etc..
c
c        ierr is set to
c          zero       for normal return,
c          j          if the j-th eigenvalue has not been
c                     determined after 30 iterations.
c
c        rv1 is a temporary storage array.
c
c     calls pythag for  dsqrt(a*a + b*b) .
c
c     questions and comments should be directed to burton s. garbow,
c     mathematics and computer science div, argonne national laboratory
c
c     this version dated august 1983.
c
c     ------------------------------------------------------------------
c
      ierr = 0
      k = 0
      tag = 0
c
      do 100 i = 1, n
         w(i) = d(i)
         if (i .ne. 1) rv1(i-1) = e(i)
  100 continue
c
      e2(1) = 0.0d0
      rv1(n) = 0.0d0
c
      do 290 l = 1, n
         j = 0
c     .......... look for small sub-diagonal element ..........
  105    do 110 m = l, n
            if (m .eq. n) go to 120
            tst1 = dabs(w(m)) + dabs(w(m+1))
            tst2 = tst1 + dabs(rv1(m))
            if (tst2 .eq. tst1) go to 120
c     .......... guard against underflowed element of e2 ..........
            if (e2(m+1) .eq. 0.0d0) go to 125
  110    continue
c
  120    if (m .le. k) go to 130
         if (m .ne. n) e2(m+1) = 0.0d0
  125    k = m
         tag = tag + 1
  130    p = w(l)
         if (m .eq. l) go to 215
         if (j .eq. 30) go to 1000
```

```
         j = j + 1
c     .......... form shift ..........
         g = (w(l+1) - p) / (2.0d0 * rv1(l))
         r = pythag(g,1.0d0)
         g = w(m) - p + rv1(l) / (g + dsign(r,g))
         s = 1.0d0
         c = 1.0d0
         p = 0.0d0
         mml = m - l
c     .......... for i=m-1 step -1 until l do -- ..........
         do 200 ii = 1, mml
            i = m - ii
            f = s * rv1(i)
            b = c * rv1(i)
            r = pythag(f,g)
            rv1(i+1) = r
            if (r .eq. 0.0d0) go to 210
            s = f / r
            c = g / r
            g = w(i+1) - p
            r = (w(i) - g) * s + 2.0d0 * c * b
            p = s * r
            w(i+1) = g + p
            g = c * r - b
  200    continue
c
         w(l) = w(l) - p
         rv1(l) = g
         rv1(m) = 0.0d0
         go to 105
c     .......... recover from underflow ..........
  210    w(i+1) = w(i+1) - p
         rv1(m) = 0.0d0
         go to 105
c     .......... order eigenvalues ..........
  215    if (l .eq. 1) go to 250
c     .......... for i=l step -1 until 2 do -- ..........
         do 230 ii = 2, l
            i = l + 2 - ii
            if (p .ge. w(i-1)) go to 270
            w(i) = w(i-1)
            ind(i) = ind(i-1)
  230    continue
c
  250    i = 1
  270    w(i) = p
         ind(i) = tag
  290 continue
c
      go to 1001
c     .......... set error -- no convergence to an
c                eigenvalue after 30 iterations ..........
 1000 ierr = l
 1001 return
      end
```

```
      subroutine tqlrat(n,d,e2,ierr)
c
      integer i,j,l,m,n,ii,l1,mml,ierr
      double precision d(n),e2(n)
      double precision b,c,f,g,h,p,r,s,t,epslon,pythag
c
c     this subroutine is a translation of the algol procedure tqlrat,
c     algorithm 464, comm. acm 16, 689(1973) by reinsch.
c
c     this subroutine finds the eigenvalues of a symmetric
c     tridiagonal matrix by the rational ql method.
c
c     on input
c
c        n is the order of the matrix.
c
c        d contains the diagonal elements of the input matrix.
c
c        e2 contains the squares of the subdiagonal elements of the
c          input matrix in its last n-1 positions.  e2(1) is arbitrary.
c
c      on output
c
c        d contains the eigenvalues in ascending order.  if an
c          error exit is made, the eigenvalues are correct and
c          ordered for indices 1,2,...ierr-1, but may not be
c          the smallest eigenvalues.
c
c        e2 has been destroyed.
c
c        ierr is set to
c          zero       for normal return,
c          j          if the j-th eigenvalue has not been
c                     determined after 30 iterations.
c
c     calls pythag for  dsqrt(a*a + b*b) .
c
c     questions and comments should be directed to burton s. garbow,
c     mathematics and computer science div, argonne national laboratory
c
c     this version dated august 1983.
c
c     ------------------------------------------------------------------
c
      ierr = 0
      if (n .eq. 1) go to 1001
c
      do 100 i = 2, n
  100 e2(i-1) = e2(i)
c
      f = 0.0d0
      t = 0.0d0
      e2(n) = 0.0d0
c
      do 290 l = 1, n
```

```
         j = 0
         h = dabs(d(l)) + dsqrt(e2(l))
         if (t .gt. h) go to 105
         t = h
         b = epslon(t)
         c = b * b
c     .......... look for small squared sub-diagonal element ..........
  105    do 110 m = l, n
            if (e2(m) .le. c) go to 120
c     .......... e2(n) is always zero, so there is no exit
c                through the bottom of the loop ..........
  110    continue
c
  120    if (m .eq. l) go to 210
  130    if (j .eq. 30) go to 1000
         j = j + 1
c     .......... form shift ..........
         l1 = l + 1
         s = dsqrt(e2(l))
         g = d(l)
         p = (d(l1) - g) / (2.0d0 * s)
         r = pythag(p,1.0d0)
         d(l) = s / (p + dsign(r,p))
         h = g - d(l)
c
         do 140 i = l1, n
  140    d(i) = d(i) - h
c
         f = f + h
c     .......... rational ql transformation ..........
         g = d(m)
         if (g .eq. 0.0d0) g = b
         h = g
         s = 0.0d0
         mml = m - l
c     .......... for i=m-1 step -1 until l do -- ..........
         do 200 ii = 1, mml
            i = m - ii
            p = g * h
            r = p + e2(i)
            e2(i+1) = s * r
            s = e2(i) / r
            d(i+1) = h + s * (h + d(i))
            g = d(i) - e2(i) / g
            if (g .eq. 0.0d0) g = b
            h = g * p / r
  200    continue
c
         e2(l) = s * g
         d(l) = h
c     .......... guard against underflow in convergence test ..........
         if (h .eq. 0.0d0) go to 210
         if (dabs(e2(l)) .le. dabs(c/h)) go to 210
         e2(l) = h * e2(l)
         if (e2(l) .ne. 0.0d0) go to 130
```

```
  210    p = d(1) + f
c     .......... order eigenvalues ..........
         if (l .eq. 1) go to 250
c     .......... for i=l step -1 until 2 do -- ..........
         do 230 ii = 2, l
            i = l + 2 - ii
            if (p .ge. d(i-1)) go to 270
            d(i) = d(i-1)
  230    continue
c
  250    i = 1
  270    d(i) = p
  290 continue
c
      go to 1001
c     .......... set error -- no convergence to an
c                eigenvalue after 30 iterations ..........
 1000 ierr = l
 1001 return
      end
      double precision function pythag(a,b)
      double precision a,b
c
c     finds dsqrt(a**2+b**2) without overflow or destructive underflow
c
      double precision p,r,s,t,u
      p = dmax1(dabs(a),dabs(b))
      if (p .eq. 0.0d0) go to 20
      r = (dmin1(dabs(a),dabs(b))/p)**2
   10 continue
         t = 4.0d0 + r
         if (t .eq. 4.0d0) go to 20
         s = r/t
         u = 1.0d0 + 2.0d0*s
         p = u*p
         r = (s/u)**2 * r
      go to 10
   20 pythag = p
      return
      end
      subroutine tinvit(nm,n,d,e,e2,m,w,ind,z,
     x                  ierr,rv1,rv2,rv3,rv4,rv6)
c
      integer i,j,m,n,p,q,r,s,ii,ip,jj,nm,its,tag,ierr,group
      double precision d(n),e(n),e2(n),w(m),z(nm,m),
     x       rv1(n),rv2(n),rv3(n),rv4(n),rv6(n)
      double precision u,v,uk,xu,x0,x1,eps2,eps3,eps4,norm,order,epslon,
     x       pythag
      integer ind(m)
c
c     this subroutine is a translation of the inverse iteration tech-
c     nique in the algol procedure tristurm by peters and wilkinson.
c     handbook for auto. comp., vol.ii-linear algebra, 418-439(1971).
c
c     this subroutine finds those eigenvectors of a tridiagonal
```

```
c     symmetric matrix corresponding to specified eigenvalues,
c     using inverse iteration.
c
c     on input
c
c        nm must be set to the row dimension of two-dimensional
c          array parameters as declared in the calling program
c          dimension statement.
c
c        n is the order of the matrix.
c
c        d contains the diagonal elements of the input matrix.
c
c        e contains the subdiagonal elements of the input matrix
c          in its last n-1 positions.  e(1) is arbitrary.
c
c        e2 contains the squares of the corresponding elements of e,
c          with zeros corresponding to negligible elements of e.
c          e(i) is considered negligible if it is not larger than
c          the product of the relative machine precision and the sum
c          of the magnitudes of d(i) and d(i-1).  e2(1) must contain
c          0.0d0 if the eigenvalues are in ascending order, or 2.0d0
c          if the eigenvalues are in descending order.  if  bisect,
c          tridib, or  imtqlv  has been used to find the eigenvalues,
c          their output e2 array is exactly what is expected here.
c
c        m is the number of specified eigenvalues.
c
c        w contains the m eigenvalues in ascending or descending order.
c
c        ind contains in its first m positions the submatrix indices
c          associated with the corresponding eigenvalues in w --
c          1 for eigenvalues belonging to the first submatrix from
c          the top, 2 for those belonging to the second submatrix, etc.
c
c     on output
c
c        all input arrays are unaltered.
c
c        z contains the associated set of orthonormal eigenvectors.
c          any vector which fails to converge is set to zero.
c
c        ierr is set to
c          zero       for normal return,
c          -r         if the eigenvector corresponding to the r-th
c                     eigenvalue fails to converge in 5 iterations.
c
c        rv1, rv2, rv3, rv4, and rv6 are temporary storage arrays.
c
c     calls pythag for  dsqrt(a*a + b*b) .
c
c     questions and comments should be directed to burton s. garbow,
c     mathematics and computer science div, argonne national laboratory
c
c     this version dated august 1983.
```

```
c
c     ------------------------------------------------------------------
c
      ierr = 0
      if (m .eq. 0) go to 1001
      tag = 0
      order = 1.0d0 - e2(1)
      q = 0
c     .......... establish and process next submatrix ..........
  100 p = q + 1
c
      do 120 q = p, n
         if (q .eq. n) go to 140
         if (e2(q+1) .eq. 0.0d0) go to 140
  120 continue
c     .......... find vectors by inverse iteration ..........
  140 tag = tag + 1
      s = 0
c
      do 920 r = 1, m
         if (ind(r) .ne. tag) go to 920
         its = 1
         x1 = w(r)
         if (s .ne. 0) go to 510
c     .......... check for isolated root ..........
         xu = 1.0d0
         if (p .ne. q) go to 490
         rv6(p) = 1.0d0
         go to 870
  490    norm = dabs(d(p))
         ip = p + 1
c
         do 500 i = ip, q
  500    norm = dmax1(norm, dabs(d(i))+dabs(e(i)))
c     .......... eps2 is the criterion for grouping,
c                eps3 replaces zero pivots and equal
c                roots are modified by eps3,
c                eps4 is taken very small to avoid overflow ..........
         eps2 = 1.0d-3 * norm
         eps3 = epslon(norm)
         uk = q - p + 1
         eps4 = uk * eps3
         uk = eps4 / dsqrt(uk)
         s = p
  505    group = 0
         go to 520
c     .......... look for close or coincident roots ..........
  510    if (dabs(x1-x0) .ge. eps2) go to 505
         group = group + 1
         if (order * (x1 - x0) .le. 0.0d0) x1 = x0 + order * eps3
c     .......... elimination with interchanges and
c                initialization of vector ..........
  520    v = 0.0d0
c
         do 580 i = p, q
```

```
            rv6(i) = uk
            if (i .eq. p) go to 560
            if (dabs(e(i)) .lt. dabs(u)) go to 540
c     .......... warning -- a divide check may occur here if
c                e2 array has not been specified correctly ..........
            xu = u / e(i)
            rv4(i) = xu
            rv1(i-1) = e(i)
            rv2(i-1) = d(i) - x1
            rv3(i-1) = 0.0d0
            if (i .ne. q) rv3(i-1) = e(i+1)
            u = v - xu * rv2(i-1)
            v = -xu * rv3(i-1)
            go to 580
  540       xu = e(i) / u
            rv4(i) = xu
            rv1(i-1) = u
            rv2(i-1) = v
            rv3(i-1) = 0.0d0
  560       u = d(i) - x1 - xu * v
            if (i .ne. q) v = e(i+1)
  580    continue
c
         if (u .eq. 0.0d0) u = eps3
         rv1(q) = u
         rv2(q) = 0.0d0
         rv3(q) = 0.0d0
c     .......... back substitution
c                for i=q step -1 until p do -- ..........
  600    do 620 ii = p, q
            i = p + q - ii
            rv6(i) = (rv6(i) - u * rv2(i) - v * rv3(i)) / rv1(i)
            v = u
            u = rv6(i)
  620    continue
c     .......... orthogonalize with respect to previous
c                members of group ..........
         if (group .eq. 0) go to 700
         j = r
c
         do 680 jj = 1, group
  630       j = j - 1
            if (ind(j) .ne. tag) go to 630
            xu = 0.0d0
c
            do 640 i = p, q
  640       xu = xu + rv6(i) * z(i,j)
c
            do 660 i = p, q
  660       rv6(i) = rv6(i) - xu * z(i,j)
c
  680    continue
c
  700    norm = 0.0d0
c
```

```
         do 720 i = p, q
  720    norm = norm + dabs(rv6(i))
c
         if (norm .ge. 1.0d0) go to 840
c     .......... forward substitution ..........
         if (its .eq. 5) go to 830
         if (norm .ne. 0.0d0) go to 740
         rv6(s) = eps4
         s = s + 1
         if (s .gt. q) s = p
         go to 780
  740    xu = eps4 / norm
c
         do 760 i = p, q
  760    rv6(i) = rv6(i) * xu
c     .......... elimination operations on next vector
c                iterate ..........
  780    do 820 i = ip, q
            u = rv6(i)
c     .......... if rv1(i-1) .eq. e(i), a row interchange
c                was performed earlier in the
c                triangularization process ..........
            if (rv1(i-1) .ne. e(i)) go to 800
            u = rv6(i-1)
            rv6(i-1) = rv6(i)
  800       rv6(i) = u - rv4(i) * rv6(i-1)
  820    continue
c
         its = its + 1
         go to 600
c     .......... set error -- non-converged eigenvector ..........
  830    ierr = -r
         xu = 0.0d0
         go to 870
c     .......... normalize so that sum of squares is
c                1 and expand to full order ..........
  840    u = 0.0d0
c
         do 860 i = p, q
  860    u = pythag(u,rv6(i))
c
         xu = 1.0d0 / u
c
  870    do 880 i = 1, n
  880    z(i,r) = 0.0d0
c
         do 900 i = p, q
  900    z(i,r) = rv6(i) * xu
c
         x0 = x1
  920 continue
c
      if (q .lt. n) go to 100
 1001 return
      end
```

```
      subroutine trbak1(nm,n,a,e,m,z)
c
      integer i,j,k,l,m,n,nm
      double precision a(nm,n),e(n),z(nm,m)
      double precision s
c
c     this subroutine is a translation of the algol procedure trbak1,
c     num. math. 11, 181-195(1968) by martin, reinsch, and wilkinson.
c     handbook for auto. comp., vol.ii-linear algebra, 212-226(1971).
c
c     this subroutine forms the eigenvectors of a real symmetric
c     matrix by back transforming those of the corresponding
c     symmetric tridiagonal matrix determined by  tred1.
c
c     on input
c
c        nm must be set to the row dimension of two-dimensional
c          array parameters as declared in the calling program
c          dimension statement.
c
c        n is the order of the matrix.
c
c        a contains information about the orthogonal trans-
c          formations used in the reduction by  tred1
c          in its strict lower triangle.
c
c        e contains the subdiagonal elements of the tridiagonal
c          matrix in its last n-1 positions.  e(1) is arbitrary.
c
c        m is the number of eigenvectors to be back transformed.
c
c        z contains the eigenvectors to be back transformed
c          in its first m columns.
c
c     note that trbak1 preserves vector euclidean norms.
c
c     questions and comments should be directed to burton s. garbow,
c     mathematics and computer science div, argonne national laboratory
c
c     this version dated august 1983.
c
c     ------------------------------------------------------------------
c
      if (m .eq. 0) go to 200
      if (n .eq. 1) go to 200
c
      do 140 i = 2, n
         l = i - 1
         if (e(i) .eq. 0.0d0) go to 140
c
         do 130 j = 1, m
            s = 0.0d0
c
            do 110 k = 1, l
  110       s = s + a(i,k) * z(k,j)
```

```
c     .......... divisor below is negative of h formed in tred1.
c                double division avoids possible underflow ..........
               s = (s / a(i,l)) / e(i)
c
               do 120 k = 1, l
  120          z(k,j) = z(k,j) + s * a(i,k)
c
  130    continue
c
  140 continue
c
  200 return
      end
      subroutine tred1(nm,n,a,d,e,e2)
c
      integer i,j,k,l,n,ii,nm,jp1
      double precision a(nm,n),d(n),e(n),e2(n)
      double precision f,g,h,scale
c
c     this subroutine is a translation of the algol procedure tred1,
c     num. math. 11, 181-195(1968) by martin, reinsch, and wilkinson.
c     handbook for auto. comp., vol.ii-linear algebra, 212-226(1971).
c
c     this subroutine reduces a real symmetric matrix
c     to a symmetric tridiagonal matrix using
c     orthogonal similarity transformations.
c
c     on input
c
c        nm must be set to the row dimension of two-dimensional
c          array parameters as declared in the calling program
c          dimension statement.
c
c        n is the order of the matrix.
c
c        a contains the real symmetric input matrix.  only the
c          lower triangle of the matrix need be supplied.
c
c     on output
c
c        a contains information about the orthogonal trans-
c          formations used in the reduction in its strict lower
c          triangle.  the full upper triangle of a is unaltered.
c
c        d contains the diagonal elements of the tridiagonal matrix.
c
c        e contains the subdiagonal elements of the tridiagonal
c          matrix in its last n-1 positions.  e(1) is set to zero.
c
c        e2 contains the squares of the corresponding elements of e.
c          e2 may coincide with e if the squares are not needed.
c
c     questions and comments should be directed to burton s. garbow,
c     mathematics and computer science div, argonne national laboratory
c
```

```
c     this version dated august 1983.
c
c     ------------------------------------------------------------------
c
      do 100 i = 1, n
         d(i) = a(n,i)
         a(n,i) = a(i,i)
  100 continue
c     .......... for i=n step -1 until 1 do -- ..........
      do 300 ii = 1, n
         i = n + 1 - ii
         l = i - 1
         h = 0.0d0
         scale = 0.0d0
         if (l .lt. 1) go to 130
c     .......... scale row (algol tol then not needed) ..........
         do 120 k = 1, l
  120    scale = scale + dabs(d(k))
c
         if (scale .ne. 0.0d0) go to 140
c
         do 125 j = 1, l
            d(j) = a(l,j)
            a(l,j) = a(i,j)
            a(i,j) = 0.0d0
  125    continue
c
  130    e(i) = 0.0d0
         e2(i) = 0.0d0
         go to 300
c
  140    do 150 k = 1, l
            d(k) = d(k) / scale
            h = h + d(k) * d(k)
  150    continue
c
         e2(i) = scale * scale * h
         f = d(l)
         g = -dsign(dsqrt(h),f)
         e(i) = scale * g
         h = h - f * g
         d(l) = f - g
         if (l .eq. 1) go to 285
c     .......... form a*u ..........
         do 170 j = 1, l
  170    e(j) = 0.0d0
c
         do 240 j = 1, l
            f = d(j)
            g = e(j) + a(j,j) * f
            jp1 = j + 1
            if (l .lt. jp1) go to 220
c
            do 200 k = jp1, l
               g = g + a(k,j) * d(k)
```

```
               e(k) = e(k) + a(k,j) * f
  200       continue
c
  220       e(j) = g
  240    continue
c     .......... form p ..........
         f = 0.0d0
c
         do 245 j = 1, l
            e(j) = e(j) / h
            f = f + e(j) * d(j)
  245    continue
c
         h = f / (h + h)
c     .......... form q ..........
         do 250 j = 1, l
  250    e(j) = e(j) - h * d(j)
c     .......... form reduced a ..........
         do 280 j = 1, l
            f = d(j)
            g = e(j)
c
            do 260 k = j, l
  260       a(k,j) = a(k,j) - f * e(k) - g * d(k)
c
  280    continue
c
  285    do 290 j = 1, l
            f = d(j)
            d(j) = a(l,j)
            a(l,j) = a(i,j)
            a(i,j) = f * scale
  290    continue
c
  300 continue
c
      return
c
      end
c
      SUBROUTINE AOROUT(XELEC,YELEC,ZELEC,AO)
c
c     This subroutine uses the input for a GAMESS CISD energy cal-
c     culation to compute the values of all atomic orbitals for a
c     particular atom. Specifically, each atomic orbital is computed
c     at a set of x, y, z electronic coordinates shifted by the X,
c     Y, and Z coordinates of the atomic nucleus on which the atomic
c     orbital is centered. Also, each atomic orbital is constructed
c     from a linear combination of primitive gaussians, as specified
c     by the GAMESS input.
c
c     Declare that all variables with names that begin with letters
c     A-H or O-Z will be double-precision numbers.
c
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
```

```
c
c     Description of all variables and/or arrays used in the sub-
c     routine:
c
c     XATOM = x-coordinate of nucleus of atom
c     YATOM = y-coordinate of nucleus of atom
c     ZATOM = z-coordinate of nucleus of atom
c
c     XELEC = x electronic coordinate
c     YELEC = y electronic coordinate
c     ZELEC = z electronic coordinate
c
c     XDIFF = difference between x electronic coord. and x-coord. of
c     nucleus of atom
c     YDIFF = difference between y electronic coord. and y-coord. of
c     nucleus of atom
c     ZDIFF = difference between z electronic coord. and z-coord. of
c     nucleus of atom.
c
c     XDSQRD = square of difference between x electronic coord. and
c     x-coord. of nucleus of atom
c     YDSQRD = square of difference between y electronic coord. and
c     y-coord. of nucleus of atom
c     ZDSQRD = square of difference between z electronic coord. and
c     z-coord. of nucleus of atom
c
c     R = Sum of XDSQRD,YDSQRD,ZDSQRD.
c
c     SNUMPG, PNUMPG, DNUMPG = Integer variables set to the number
c     of primitive gaussians in an S, P or D atomic orbital
c     (respectively).
c
c     SPGAUSS = 100 x 100 dimension array containing the exponents
c     and coefficients for the primitive gaussians used in a S-type
c     atomic orbital.
c     PPGAUSS = 100 x 100 dimension array containing the exponents
c     and coefficients for the primitive gaussians used in a P-type
c     atomic orbital.
c     DPGAUSS = 100 x 100 dimension array containing the exponents
c     and coefficients for the primitive gaussians used in a D-type
c     atomic orbital.
c
c     SCHIMU = numerical value of a S-type atomic orbital computed
c     at x-Z, y-Y, z-Z
c     PXCHIMU, PYCHIMU, PZCHIMU = numerical values of Px-type,
c     Py-type, and Pz-type atomic orbitals computed the x-Z, y-Y,
c     z-Z
c     DXY, DXZ, DYZ, DXSQRD, DYSQRD, DZSQRD = numerical values of
c     Dxy-type, Dxz-type, Dyz-type, Dxsquared-type, Dysquared-type
c     and Dzsquared-type atomic orbitals computed at the x-X,y-Y,z-Z
c
c     PI = double-precision numerical constant for pi
c
c     INPUT1 = Character variables used to read the lines in the
c     GAMESS input file.
```

```
c
c      SORBTOT, PORBTOT, DORBTOT = Total number of S, P and D basis
c      functions (3 x PORBTOT = total number of P orbitals,
c      6 x DORBTOT = total number of D orbitals).
c
c      PXORBTOT, PYORBTOT, PZORBTOT, DXYTOT, DXZTOT, DYZTOT, DX2TOT,
c      DY2TOT, DZ2TOT = variables representing the total number of Px,
c      Py, Pz, Dxy, Dxz, Dyz, Dxsquared, Dysquared, Dzsquared orbitals,
c      respectively.
c
c      ATOM = character variable used to read the name of the atom on
c      which the molecular orbital is centered.
c
c      NUMELEC = Integer variable used to read the number of electrons
c      in the atom on which the molecular orbital is centered.
c
c      AORBTOT = Integer variable representing the total number of
c      atomic orbitals for an atom.
c
c      AO = One-dimensional array which holds the values of all atomic
c      orbitals at x-X, y-Y, z-Z.
c
c      ATOMTOT = The total number of atoms in the molecule of interest.
c
c      SORB = Two-letter character variable used to read the letter
c      S denoting a S-type basis function from the GAMESS input file.
c      PORB = Two-letter character variable used to read the letter
c      P denoting a P-type basis function from the GAMESS input file.
c      DORB = Two-letter character variable used to read the letter
c      D denoting a D-type basis function from the GAMESS input file.
c
c      NUMATOM = One-dimensional array used to keep track of the
c      number of atomic orbitals for each atom. For example the element
c      corresponding to NUMATOM(1) is the number of atomic orbitals for
c      the first atom (as listed in the GAMESS input file) in the
c      molecule of interest.
c
c      NCOUNT = Integer variable used to keep track of the total number
c      of atomic orbitals for each atom.
c
       DIMENSION SPGAUSS(100, 100), PPGAUSS(100, 100), DPGAUSS(100,100)
       INTEGER SORBTOT, PORBTOT, DORBTOT, PXORBTOT, PYORBTOT, PZORBTOT
       INTEGER DXYTOT, DXZTOT, DYZTOT, DX2TOT, DY2TOT, DZ2TOT, AORBTOT
       CHARACTER INPUT*80, INPUT1*80, ATOM*15
       REAL NUMELEC
       INTEGER SNUMPG, PNUMPG, DNUMPG, ATOMTOT
       CHARACTER SORB*2, PORB*2, DORB*2
       DIMENSION NUMATOM(100)
       DIMENSION AO(100)
c
       COMMON /BLOCK15/ NAO
c
c      Set the value of the constant pi (PI).
c
       PI = DACOS(-1.D0)
```

```
c
c     Set the total number of atoms equal to zero.
c
      ATOMTOT = 0
c
c     Set the total number of atomic orbitals for this atom
c     equal to zero.
c
      AORBTOT = 0
c
c     Open the input file for a GAMESS CISD energy calculation.
c
      OPEN (UNIT=24,
     &FILE='mod_h2cisd_MBS_C1.inp',
     &STATUS='OLD', FORM='FORMATTED')
  100 FORMAT (A80)
c
c     Go back two lines in the input file.
c
 2222 BACKSPACE(24)
      BACKSPACE(24)
c
c     Read the current line in the input file into INPUT
c     (actually, the first 80 characters of this line).
c
      READ(24,100)INPUT
c
c     If the first five characters in the current line
c     are not " $con", then go to line 2222 in the
c     program. Note: " $con" belongs to the " $control"
c     line in the input file. Since " $control" is
c     always the first group in GAMESS input files,
c     reading " $con" indicates that we are at the
c     beginning of the file. Returning to line 2222
c     will allow us to keep reading until we reach
c     the beginning of the input file.
c
      IF (INPUT(1:5).NE.' $con') THEN
         GO TO 2222
      ENDIF
c
c     If we have read " $con", then go back one line
c     in the file (then, once again, we are at the
c     beginning of the file).
c
      BACKSPACE(24)
c
c     Read the next two lines in the input file, one by
c     one, into INPUT.
c
      READ(24,100)INPUT
      READ(24,100)INPUT
c
c     If the first five characters of the current line
c     are not equal to " $dat" or " $DAT" (indicating
```

```
c     that we have reached the " $data"/" $DATA" group
c     in the GAMESS input file), the read the next line
c     in the input file into INPUT. Keep reading until
c     the first five characters ARE " $data" or " $DATA".
c
  101 IF (INPUT(1:5).NE.' $dat' .AND.
     &INPUT(1:5).NE.' $DAT') THEN
        READ(24,100)INPUT
        GO TO 101
      ELSE
      ENDIF
c
c     Once we read the " $data"/" $DATA" group, read the
c     next three lines, one after another, into INPUT.
c
  102 FORMAT (A80)
      IF (INPUT(1:5).EQ.' $dat' .OR. INPUT(1:5).EQ.' $DAT')
     &THEN
        READ(24,102)INPUT
        READ(24,102)INPUT
        READ(24,102)INPUT
      ELSE
      END IF
c
c     Set NCOUNT equal to zero.
c
      NCOUNT=0
c
c     Read the next line in the input file into INPUT.
c
 777  READ(24,102)INPUT
c
c     If the first five characters in the current line are
c     blank spaces, then read the next line into INPUT.
c     Continue reading until a line is read which DOES NOT
c     have blank spaces for its first five characters.
c
      DO 1999 WHILE (INPUT(1:5).EQ.'     ')
         READ(24,102)INPUT
 1999 CONTINUE
c
c     If the current line's first five characters are
c     " $end", indicating that we have reached the end of
c     the data group in the GAMESS input file, then go to
c     line 5000.
c
      IF (INPUT(1:5).EQ.' $end') THEN
         GO TO 5000
      ELSE
      END IF
c
c     Go back to the previous line.
c
      BACKSPACE(24)
c
```

```
c     Read the name of the atom, the number of electrons in the atom,
c     and the x, y, and z coordinates of the atom's nucleus.
c
  103 FORMAT (A15, F2.0, D20.10, D20.10, D20.10)
      READ(24,103)ATOM, NUMELEC, XATOM, YATOM, ZATOM
c
c     Increment the total number of atoms.
c
      ATOMTOT=ATOMTOT+1
c
c     Set the total number of s, p, d, px, py, pz, dxy, dxz, dyz,
c     dx2, dy2 and dz2 atomic orbitals equal to zero.
c
      SORBTOT = 0
      PORBTOT = 0
      DORBTOT = 0
      PXORBTOT = 0
      PYORBTOT = 0
      PZORBTOT = 0
      DXYTOT = 0
      DXZTOT = 0
      DYZTOT = 0
      DX2TOT = 0
      DY2TOT = 0
      DZ2TOT = 0
c
c     Calculate the difference between the x, y, and z electronic
c     coordinates and the x, y, and z coordinates of the atom's
c     nucleus.
c
      XDIFF = XELEC - XATOM
      YDIFF = YELEC - YATOM
      ZDIFF = ZELEC - ZATOM
c
c     Square the differences between the x, y, and z electronic
c     coordinates and the x, y, and z coordinates of the atom's
c     nucleus.
c
      XDSQRD = XDIFF**2
      YDSQRD = YDIFF**2
      ZDSQRD = ZDIFF**2
c
c     Add the squares of the differences between the x, y, and z
c     electronic coordinates and the x, y, and z coordinates of
c     the atom's nucleus.
c
      R = XDSQRD + YDSQRD + ZDSQRD
c
c     Set the INPUT1 character variable equal to the INPUT
c     variable.
c
      INPUT1 = INPUT
c
 9988 FORMAT (A5)
  104 FORMAT (A80)
```

```
c
c     If the first five characters of INPUT1 are NOT all blanks,
c     read the next line in the input file into INPUT1. If the
c     first five characters of INPUT1 are " S   ", then go to
c     line 201. If the first five characters of INPUT1 are
c     " P   ", then go to line 202. If the first five characters
c     of INPUT1 are " D   ", then go to line 203. Note: " S   "
c     indicates that we are about to read data for an
c     s-type orbital, " P   " indicates that we are about to
c     read data for a p-type atomic orbital, and " D   " indicates
c     that we are about to read the data for a d-type atomic
c     orbital.
c
      DO 200 WHILE (INPUT1(1:5).NE.'     ')
         READ(24,104)INPUT1
         IF (INPUT1(1:5).EQ.' S   ') THEN
            GO TO 201
         ELSE IF (INPUT1(1:5).EQ.' P   ') THEN
                 GO TO 202
              ELSE IF (INPUT1(1:5).EQ.' D   ') THEN
                      GO TO 203
                   ELSE
         ENDIF
  200 CONTINUE
c
c     If the first five characters of INPUT1 are blanks, then
c     go to line 4999. Note: If the first five characters of
c     INPUT1 are blanks, this indicates that we have reached
c     the end of the "$data" group in the GAMESS input file.
c
      IF (INPUT1(1:5).EQ.'     ') THEN
         GO TO 4999
      ELSE
      END IF
c
c     This is line 201, which is the line to go to if a
c     " S   " was read into INPUT in the 200 DO loop.
c
c     Go back to the previous line.
c
  201 BACKSPACE(24)
c
c     Read the "S" indicating data for an s-type orbital
c     and the number following the S (which is the number
c     of primitive gaussians in the s-type orbital) into
c     the SORB character variable and the SNUMPG integer
c     variable, respectively.
c
  105 FORMAT (A2, I4)
      READ(24,105)SORB, SNUMPG
c
c     Read the number of the primitive gaussian, the
c     exponent for the gaussian, and the coefficient
c     for the gaussian into the SPGAUSS array. Do this
c     for all primitive gaussians in the s-type atomic
```

```
c     orbital.
c
      READ(24,*) ((SPGAUSS(ISROW,ISCOL), ISCOL=1,3), ISROW=1,SNUMPG)
c
c     Use the primitive gaussians to calculate the value
c     of the s-type atomic orbital at R, and read the value of the
c     atomic orbital into SCHIMU.
c
      DO 106 I = 1, SNUMPG, 1
         SCHIMU = SCHIMU + DEXP(-1.0D0*((SPGAUSS(I,2))*R))*
     &   (((2.0D0*(SPGAUSS(I,2)))/PI)**0.75D0)*(SPGAUSS(I,3))
  106 CONTINUE
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
c
c     Read the value of the s-type atomic orbital into the
c     AO array.
c
      AO(NCOUNT)=SCHIMU
c
c     Increment the total number of s-type orbitals.
c
      SORBTOT = SORBTOT + 1
c
c     Clear the SCHIMU variable.
c
      SCHIMU=0
c
c     Clear the SPGAUSS array.
c
      DO 300 ISROW = 1, SNUMPG, 1
         SPGAUSS(ISROW,1) = 0
         SPGAUSS(ISROW,2) = 0
         SPGAUSS(ISROW,3) = 0
  300 CONTINUE
c
c     Go back to line 200.
c
      GO TO 200
c
c     This is line 202, which is the line to go to if a
c     " P   " was read into INPUT in the 200 DO loop.
c
c     Go back to the previous line.
c
  202 BACKSPACE(24)
c
c     Read the "P" indicating data for an p-type orbital
c     and the number following the P (which is the number
c     of primitive gaussians in the p-type orbital) into
c     the PORB character variable and the PNUMPG integer
c     variable, respectively.
c
```

```
  107 FORMAT (A2, I4)
      READ(24,107)PORB, PNUMPG
c
c     Read the number of the primitive gaussian, the
c     exponent for the gaussian, and the coefficient
c     for the gaussian into the PPGAUSS array. Do this
c     for all primitive gaussians in the p-type atomic
c     orbital.
c
      READ(24,*)
     &((PPGAUSS(IPROW,IPCOL),IPCOL=1,3), IPROW=1,PNUMPG)
c
c     Use the primitive gaussians to calculate the value
c     of the px-type, py-type, and pz-type atomic orbitals
c     at R, and read the values of these atomic orbitals
c     into PXCHIMU, PYCHIMU, and PZCHIMU.
c
      DO 108 J = 1, PNUMPG, 1
         PXCHIMU = PXCHIMU + DEXP(-1.0D0*((PPGAUSS(J,2))*
     &   R))*XDIFF*(PPGAUSS(J,3))*
     &   (((2.0D0**1.75D0)*
     &   ((PPGAUSS(J,2))**1.25D0))/(PI**.75D0))
c
         PYCHIMU = PYCHIMU + DEXP(-1.0D0*((PPGAUSS(J,2))*
     &   R))*YDIFF*(PPGAUSS(J,3))*
     &   (((2.0D0**1.75D0)*
     &   ((PPGAUSS(J,2))**1.25D0))/(PI**.75D0))
c
         PZCHIMU = PZCHIMU + DEXP(-1.0D0*((PPGAUSS(J,2))*
     &   R))*ZDIFF*(PPGAUSS(J,3))*
     &   (((2.0D0**1.75D0)*
     &   ((PPGAUSS(J,2))**1.25D0))/(PI**.75D0))
  108 CONTINUE
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
c
c     Read the value of the px-type atomic orbital into
c     the AO array.
c
      AO(NCOUNT)=PXCHIMU
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
c
c     Read the value of the py-type atomic orbital into
c     the AO array.
c
      AO(NCOUNT)=PYCHIMU
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
```

```
c
c     Read the value of the pz-type atomic orbital into
c     the AO array.
c
      AO(NCOUNT)=PZCHIMU
c
c     Increment the total number of p-type atomic orbitals.
c
      PORBTOT = PORBTOT + 1
c
c     Increment the total number of px-type, py-type, and
c     pz-type atomic orbitals.
c
      PXORBTOT = PXORBTOT + 1
      PYORBTOT = PYORBTOT + 1
      PZORBTOT = PZORBTOT + 1
c
c     Clear the PXCHIMU, PYCHIMU, and PZCHIMU variables.
c
      PXCHIMU = 0
      PYCHIMU = 0
      PZCHIMU = 0
c
c     Clear the PPGAUSS array.
c
      DO 325 IPROW = 1, PNUMPG, 1
         PPGAUSS(IPROW,1) = 0
         PPGAUSS(IPROW,2) = 0
         PPGAUSS(IPROW,3) = 0
  325 CONTINUE
c
c     Return to the 200 DO loop.
c
      GO TO 200
c
c     This is line 203, which is the line to go to if a
c     " D   " was read into INPUT in the 200 DO loop.
c
c     Go back to the previous line.
c
  203 BACKSPACE(24)
c
c     Read the "D" indicating data for an d-type orbital
c     and the number following the D (which is the number
c     of primitive gaussians in the d-type orbital) into
c     the DORB character variable and the DNUMPG integer
c     variable, respectively.
c
  109 FORMAT (A2, I4)
      READ(24,109)DORB, DNUMPG
c
c     Read the number of the primitive gaussian, the
c     exponent for the gaussian, and the coefficient
c     for the gaussian into the DPGAUSS array. Do this
c     for all primitive gaussians in the d-type atomic
```

```
c     orbital.
c
      READ(24,*)((DPGAUSS(IDROW,IDCOL),
     &IDCOL=1,3), IDROW=1,DNUMPG)
c
c     Use the primitive gaussians to calculate the value
c     of the dxy-type, dxz-type, dyz-type, dx2, dy2, and
c     dz2 atomic orbitals
c     at R, and read the values of these atomic orbitals
c     into PXCHIMU, PYCHIMU, and PZCHIMU.
c
      DO 110 K = 1, DNUMPG, 1
         DXY = DXY + DEXP(-1.0D0*((DPGAUSS(K,2))*R))*
     &   XDIFF*YDIFF*(DPGAUSS(K,3))*
     &   (((2.0D0**2.75D0)*
     &   ((DPGAUSS(K,2))**1.75D0))/(PI**.75D0))
c
         DXZ = DXZ + DEXP(-1.0D0*((DPGAUSS(K,2))*R))*
     &   XDIFF*ZDIFF*(DPGAUSS(K,3))*
     &   (((2.0D0**2.75D0)*
     &   ((DPGAUSS(K,2))**1.75D0))/(PI**.75D0))
c
         DYZ = DYZ + DEXP(-1.0D0*((DPGAUSS(K,2))*R))*
     &   YDIFF*ZDIFF*(DPGAUSS(K,3))*
     &   (((2.0D0**2.75D0)*
     &   ((DPGAUSS(K,2))**1.75D0))/(PI**.75D0))
c
         DXSQRD = DXSQRD + DEXP(-1.0D0*((DPGAUSS(K,2))
     &   *R))*XDIFF*XDIFF*(DPGAUSS(K,3))*
     &   (((2.0D0**2.75D0)*
     &   ((DPGAUSS(K,2))**1.75D0))/((3.0D0**0.5D0)*(PI**.75D0)))
c
         DYSQRD = DYSQRD + DEXP(-1.0D0*((DPGAUSS(K,2))
     &   *R))*YDIFF*YDIFF*(DPGAUSS(K,3))*
     &   (((2.0D0**2.75D0)*
     &   ((DPGAUSS(K,2))**1.75D0))/((3.0D0**0.5D0)*(PI**.75D0)))
c
         DZSQRD = DZSQRD + DEXP(-1.0D0*((DPGAUSS(K,2))
     &   *R))*ZDIFF*ZDIFF*(DPGAUSS(K,3))*
     &   (((2.0D0**2.75D0)*
     &   ((DPGAUSS(K,2))**1.75D0))/((3.0D0**0.5D0)*(PI**.75D0)))
  110 CONTINUE
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
c
c     Read the value of the dx2-atomic orbital into the AO array.
c
      AO(NCOUNT)=DXSQRD
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
c
```

```
c     Read the value of the dy2-atomic orbital into the AO array.
c
      AO(NCOUNT)=DYSQRD
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
c
c     Read the value of the dz2-atomic orbital into the AO array.
c
      AO(NCOUNT)=DZSQRD
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
c
c     Read the value of the dxy-atomic orbital into the AO array.
c
      AO(NCOUNT)=DXY
c
c     Increment the total number of atomic orbitals.
c
      NCOUNT=NCOUNT+1
c
c     Read the value of the dxz-atomic orbital into the AO array.
c
      AO(NCOUNT)=DXZ
c
c     Increment the total number of d-type atomic orbitals.
c
      DORBTOT = DORBTOT + 1
c
c     Increment the total number of dxy-type atomic orbitals.
c
      DXYTOT = DXYTOT + 1
c
c     Increment the total number of dxz-type atomic orbitals.
c
      DXZTOT = DXZTOT + 1
c
c     Increment the total number of dyz-type atomic orbitals.
c
      DYZTOT = DYZTOT + 1
c
c     Increment the total number of dx2-type atomic orbitals.
c
      DX2TOT = DX2TOT + 1
c
c     Increment the total number of dy2-type atomic orbitals.
c
      DY2TOT = DY2TOT + 1
c
c     Increment the total number of dz2-type atomic orbitals.
c
      DZ2TOT = DZ2TOT + 1
```

```
c
c     Clear the dxy-type, dxz-type, dyz-type, dx2-type, dy2-type
c     and dz2-type atomic orbitals.
c
      DXY = 0
      DXZ = 0
      DYZ = 0
      DXSQRD = 0
      DYSQRD = 0
      DZSQRD = 0
c
c     Clear the DPGAUSS array.
c
      DO 375 IDROW = 1, DNUMPG, 1
         DPGAUSS(IDROW,1) = 0
         DPGAUSS(IDROW,2) = 0
         DPGAUSS(IDROW,3) = 0
  375 CONTINUE
c
c     At this point, we have finished reading the information for
c     the d-type atomic orbitals and evaluating these orbitals at R.
c     We are ready to read the information for the next atomic
c     orbital, or (if all of the orbital information has already been
c     read) return the evaluated atomic orbitals to the main program.
c     Return to line 200, where we will decide what to do next.
c
      GO TO 200
c
c     We are done reading the information for all atomic orbitals of
c     the atom and evaluating these orbitals at R. Now, we
c     compute the total number of atomic orbitals for the atom.
c
 4999 AORBTOT = SORBTOT + PXORBTOT + PYORBTOT + PZORBTOT + DXYTOT +
     &          DXZTOT + DYZTOT + DX2TOT + DY2TOT + DZ2TOT
c
c     Read the total number of atomic orbitals for the current
c     atom into NUMATOM(ATOMTOT).
c
      NUMATOM(ATOMTOT)=AORBTOT
c
c     Return to line 777.
c
      GO TO 777
c
c     Close the GAMESS CISD input file.
c
 5000 CLOSE(20)
c
c     Return the values of the atomic orbitals (evaluated at R) to
c     the main program, and return to the main program.
c
      RETURN
c
      END
```

Appendix B. Tables

Appendix B. Tables

Table 1. Non-zero terms in the third-order interaction energy of molecules A and B, classified by order in the permanent dipoles of A and B. Note that we have let $\Psi_{0_A}^{(0)} = |0_A\rangle$ and $\Psi_{0_B}^{(0)} = |0_B\rangle$.

Term	μ^{A0} *order*	μ^{B0} *order*	*Name*
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	1	1 – (1, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{A\oplus B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	0	1	2 – (0, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A} \hat{V}^{AB} \vert 0_A 0_B \rangle$	0	3	3 – (0, 3)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A} \mu_\alpha^{A0} T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{A\oplus B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	1	4 – (1, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{B} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{A} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	1	5 – (1, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{B} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{A\oplus B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	0	6 – (1, 0)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{B} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A\oplus B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	1	7 – (1, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{B} \mu_\alpha^{A0} T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	3	0	8 – (3, 0)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A\oplus B} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{A} \hat{V}^{AB} \vert 0_A 0_B \rangle$	0	1	9 – (0, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A\oplus B} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	0	10 – (1, 0)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A\oplus B} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{A\oplus B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	0	0	11 – (0, 0)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A\oplus B} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	1	12 – (1, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A\oplus B} \hat{\overline{\mu}}_\alpha^A T_{\alpha\beta} \mu_\beta^{B0} G^{A\oplus B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	0	1	13 – (0, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A\oplus B} \mu_\alpha^{A0} T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{A} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	1	14 – (1, 1)
$-\langle 0_A 0_B \vert \hat{V}^{AB} G^{A\oplus B} \mu_\alpha^{A0} T_{\alpha\beta} \hat{\overline{\mu}}_\beta^B G^{A\oplus B} \hat{V}^{AB} \vert 0_A 0_B \rangle$	1	0	15 – (1, 0)

Table 2. Comparison of $\alpha_{xx}(\omega)$, $\alpha_{yy}(\omega)$, and $\alpha_{zz}(\omega)$ values calculated by integrating $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ using the algorithm described here and by finite-field calculations performed with the MOLPRO[17] quantum chemistry software package. Polarizabilities were calculated in the DZ, DZP, and aug-cc-pVDZ basis sets, and polarizabilities are given in a.u.

Basis Set	$\alpha_{xx}(\omega)$	$\alpha_{yy}(\omega)$	$\alpha_{zz}(\omega)$
DZ[a]	0.00031451	0.00031451	5.74696714
DZ[b]	0	0	5.74696958
DZP[a]	0.67532473	0.67532473	5.87133714
DZP[b]	0.67532474	0.67532474	5.87133956
aug-cc-pVDZ[a]	4.35229766	4.35229763	6.54719224
aug-cc-pVDZ[b]	4.35229593	4.35229593	6.54717965

[a] MOLPRO[17] results.

[b] These results were obtained by integrating over $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ using the algorithm described in this work.

Appendix C. Figures

Appendix C. Figures

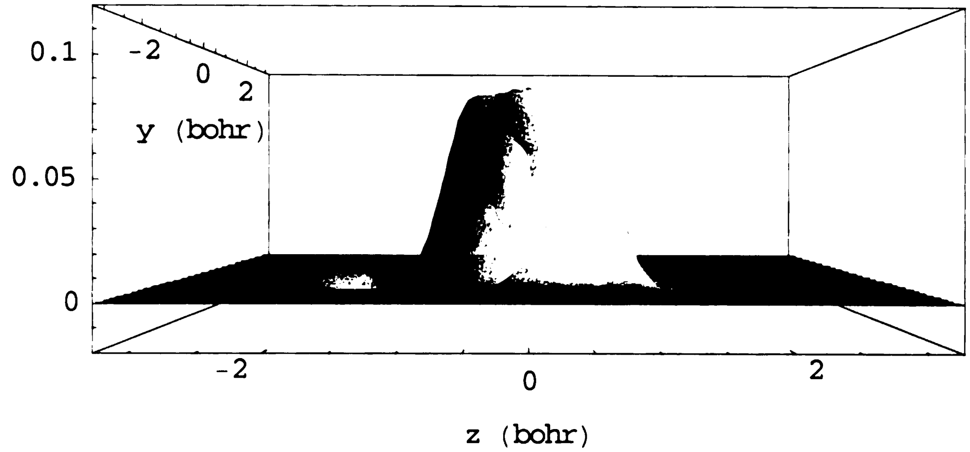

Fig. 1. The charge-density susceptibility of the H_2 molecule at the CISD level with $\omega = 0$ a.u., $\mathbf{r}' = 0,0,0$, $x = 0$, $-3.25 \leq y \leq 3.25$ a.u., $-3.25 \leq z \leq 3.25$ a.u., and $\Delta y = \Delta z = 0.05$ a.u. in the aug-cc-pVDZ basis set. For this calculation, the internuclear axis of H_2 was oriented along the z-axis of the laboratory frame.

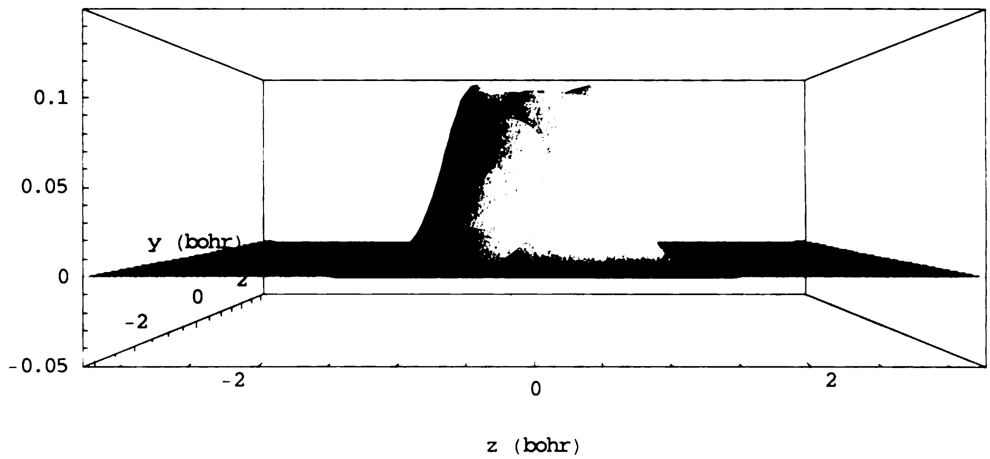

Fig. 2. The charge-density susceptibility of the H_2 molecule at the CISD level with ω = 0.3858668352248763 a.u., $\mathbf{r}'$ = 0,0,0, x = 0, $-3.25 \leq y \leq 3.25$ a.u., $-3.25 \leq z \leq 3.25$ a.u., and $\Delta y = \Delta z = 0.05$ a.u. in the aug-cc-pVDZ basis set. For this calculation, the internuclear axis of H_2 was oriented along the z-axis of the laboratory frame.

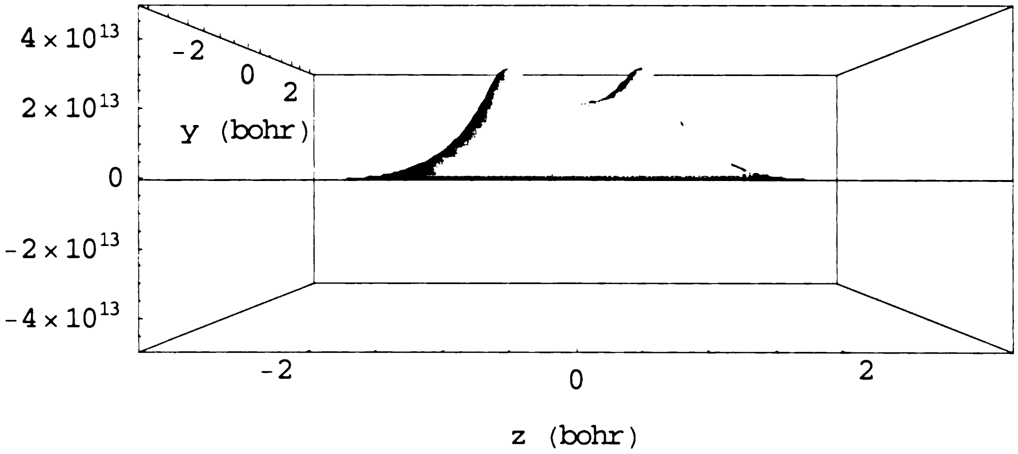

Fig. 3. The charge-density susceptibility of the H_2 molecule at the CISD level with $\omega = 0.4812104263202694$ a.u., $\mathbf{r}' = 0,0,0$, $x = 0$, $-3.25 \le y \le 3.25$ a.u., $-3.25 \le z \le 3.25$ a.u., and $\Delta y = \Delta z = 0.05$ a.u. in the aug-cc-pVDZ basis set. For this calculation, the internuclear axis of H_2 was oriented along the z-axis of the laboratory frame.

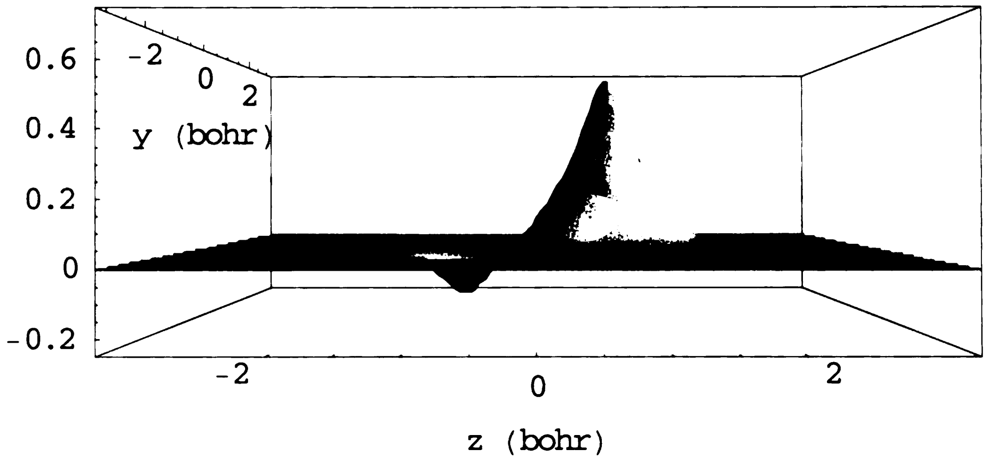

Fig. 4. The charge-density susceptibility of the H_2 molecule at the CISD level with ω = 0.3858668352248763 a.u., $\mathbf{r}' = 0,0,0.7$, $x = 0$, $-3.25 \leq y \leq 3.25$ a.u., $-3.25 \leq z \leq 3.25$ a.u., and $\Delta y = \Delta z = 0.05$ a.u. in the aug-cc-pVDZ basis set. For this calculation, the internuclear axis of H_2 was oriented along the z-axis of the laboratory frame.

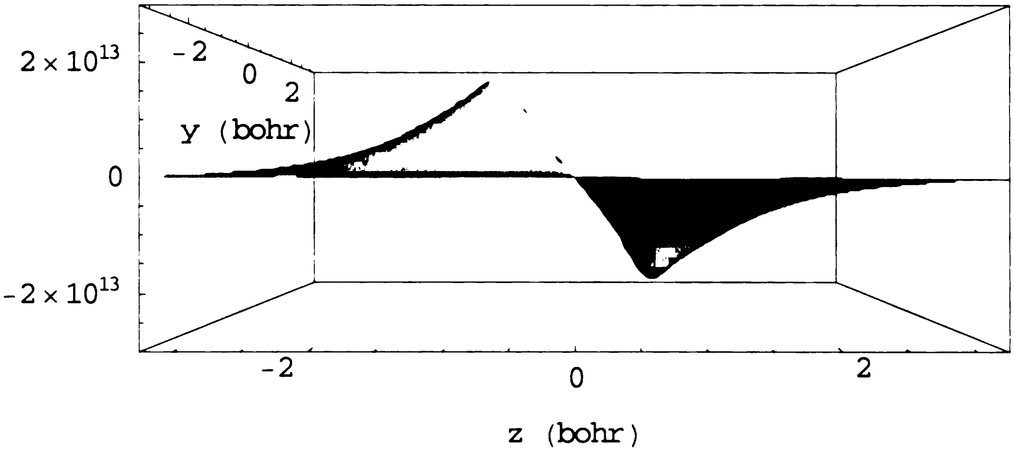

Fig. 5. The charge-density susceptibility of the H_2 molecule at the CISD level with ω = 0.46483806508567789 a.u., **r**′ = 0,0,0.7, $x = 0$, $-3.25 \le y \le 3.25$ a.u., $-3.25 \le z \le 3.25$ a.u., and $\Delta y = \Delta z = 0.05$ a.u. in the aug-cc-pVDZ basis set. For this calculation, the internuclear axis of H_2 was oriented along the z-axis of the laboratory frame.

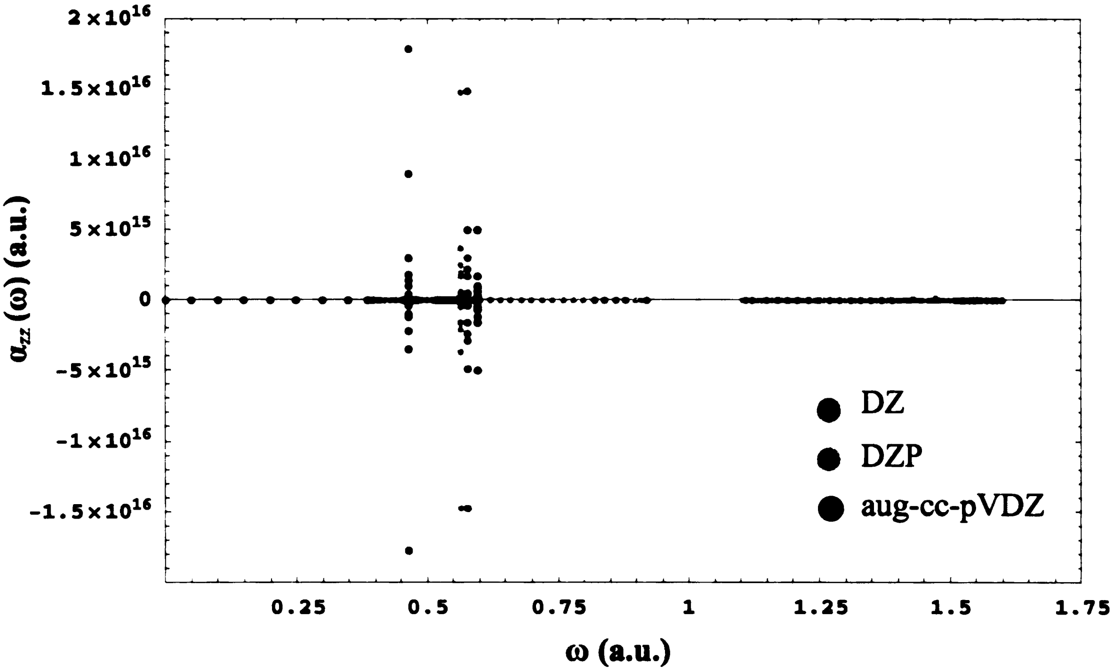

Fig. 6. The *zz* component of the frequency-dependent polarizability $\alpha_{zz}(\omega)$ of H_2 as a function of frequency ω at the CISD level in the DZ, DZP, and aug-cc-pVDZ basis sets.

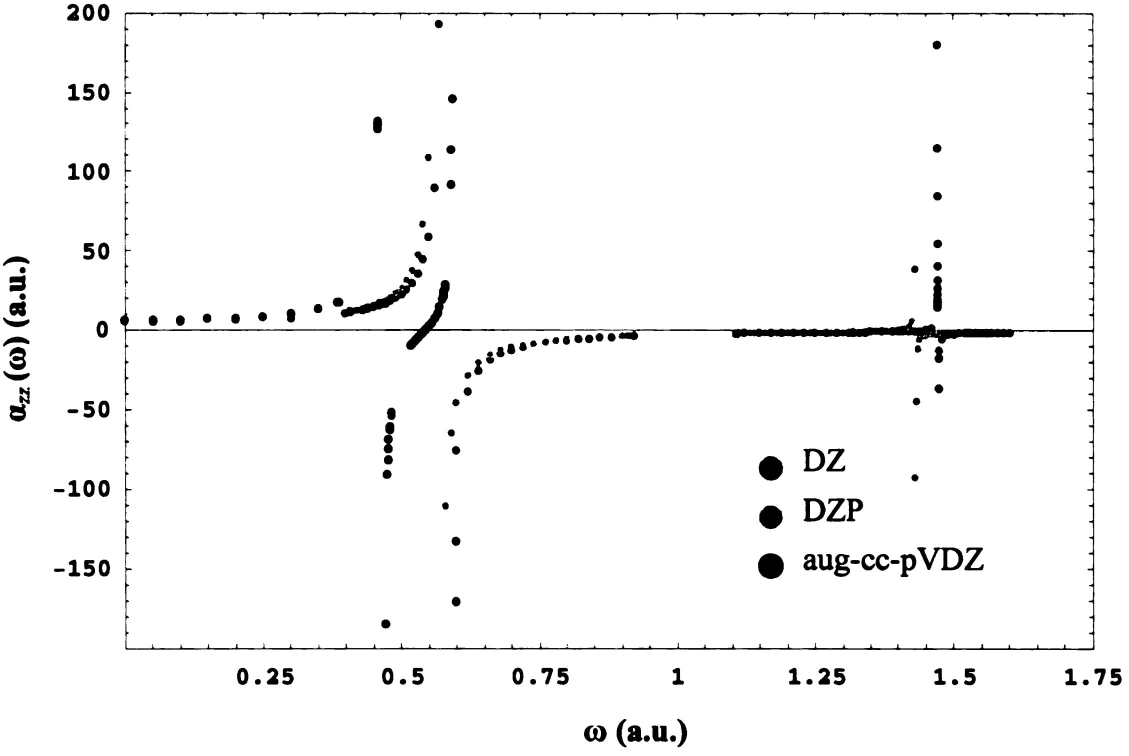

Fig. 7. The *zz* component of the frequency-dependent polarizability $\alpha_{zz}(\omega)$ of H_2 at the CISD level as a function of ω in the DZ, DZP, and aug-cc-pVDZ basis sets. Here, we show the data included in $-200 \leq \alpha_{zz}(\omega) \leq 200$ a.u. in Fig. 6.

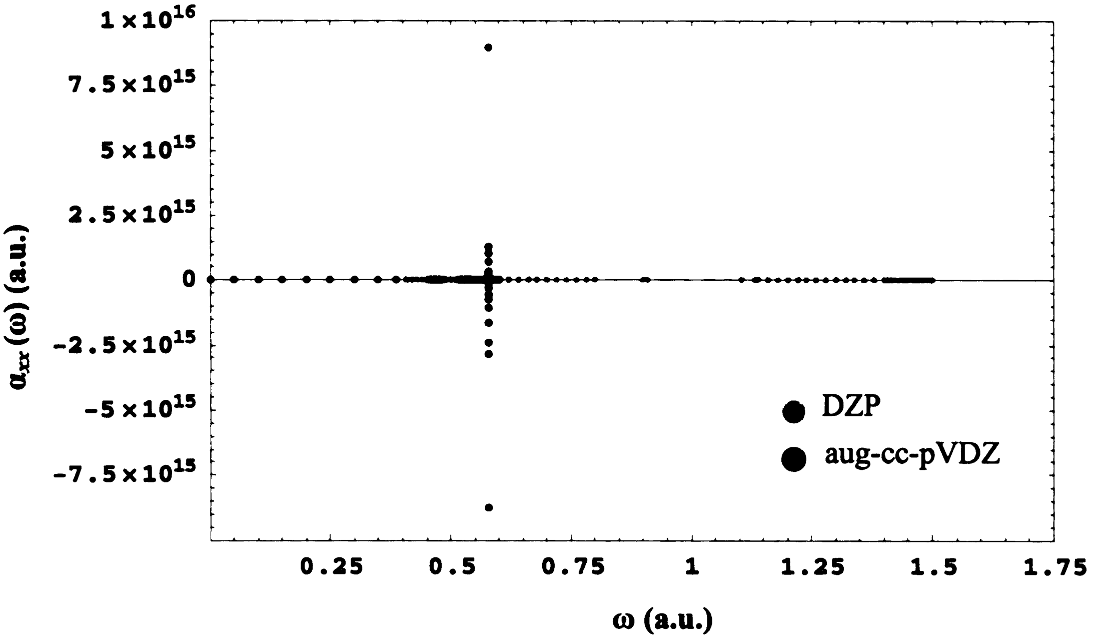

Fig. 8. The *xx* component of the frequency-dependent polarizability $\alpha_{xx}(\omega)$ of H_2 at the CISD level as a function of ω in the DZP and aug-cc-pVDZ basis sets.

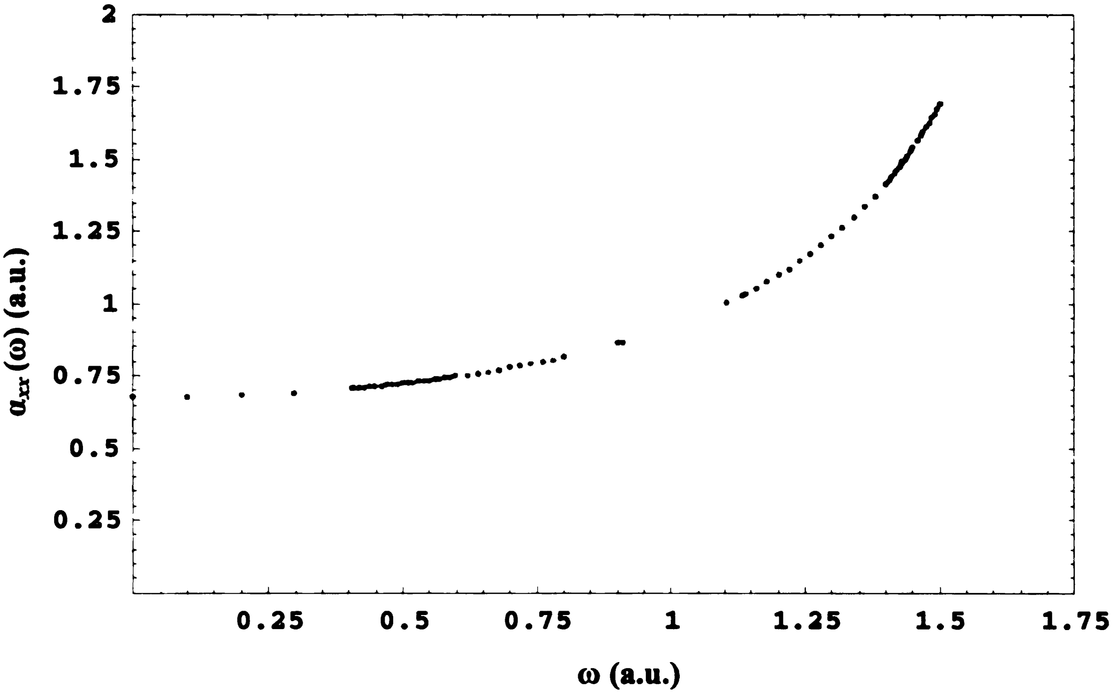

Fig. 9. The *xx* component of the frequency-dependent polarizability α_{xx} (ω) of H_2 at the CISD level as a function of ω in the DZP basis set.

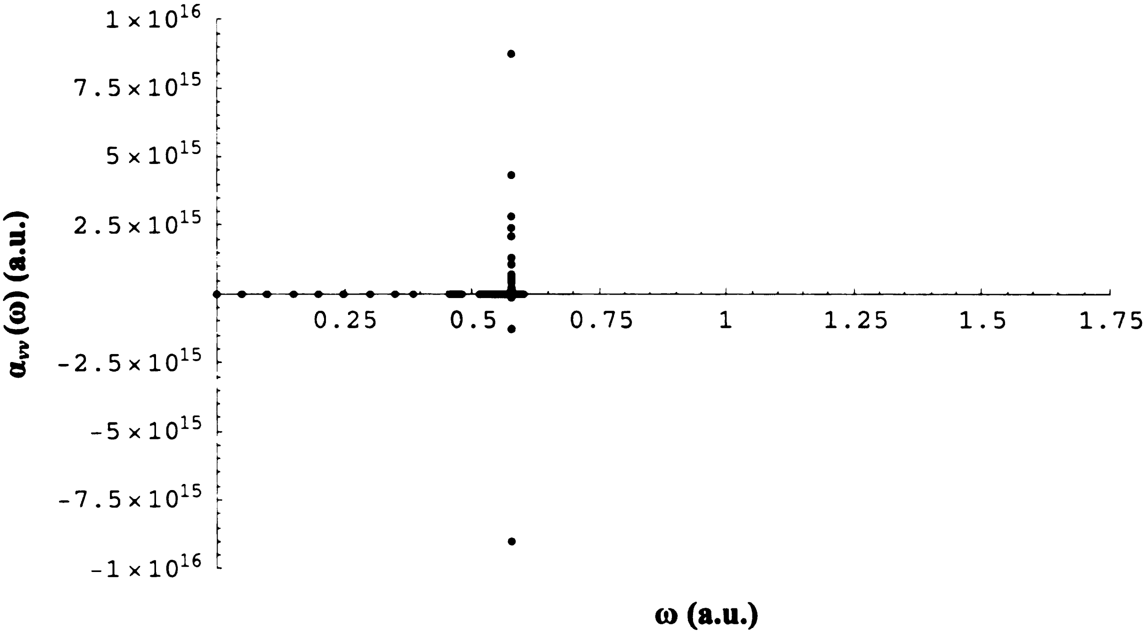

Fig. 10. The *yy* component of the frequency-dependent polarizability $\alpha_{yy}(\omega)$ of H_2 at the CISD level as a function of ω in the aug-cc-pVDZ basis set.

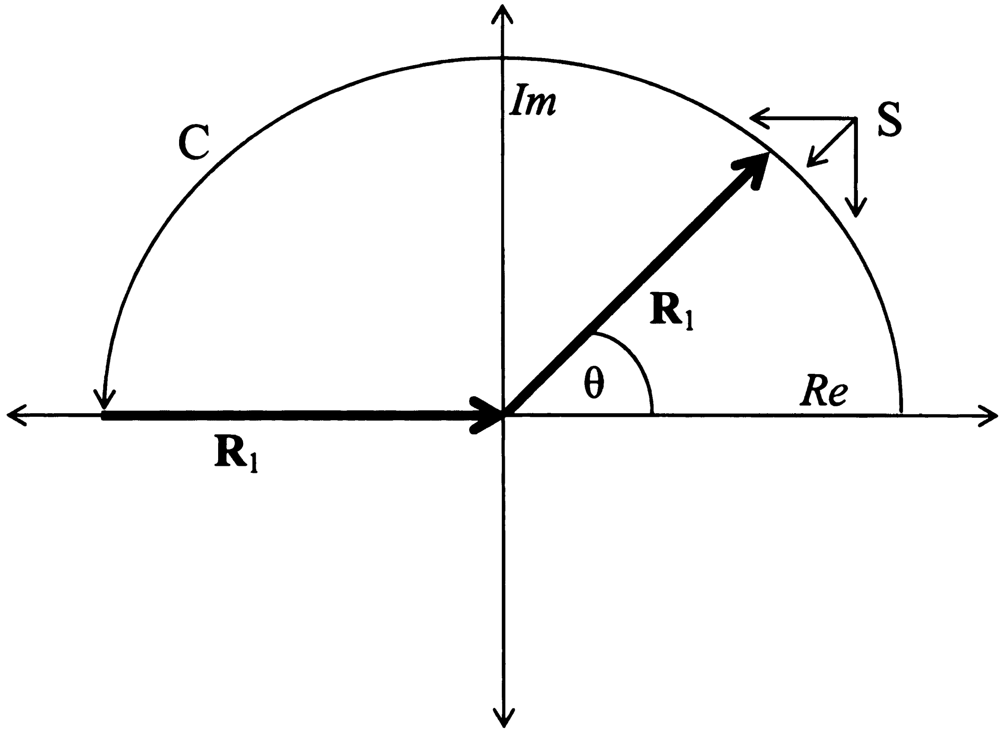

Fig. 11. The semi-circular contour C of radius $\mathbf{R}_l$ in the upper complex half plane. In this figure, *Im* and *Re* denote the imaginary and real axes, respectively. Also, θ is the angle between the real axis and $\mathbf{R}_l$, and S is the portion of C off the real axis.

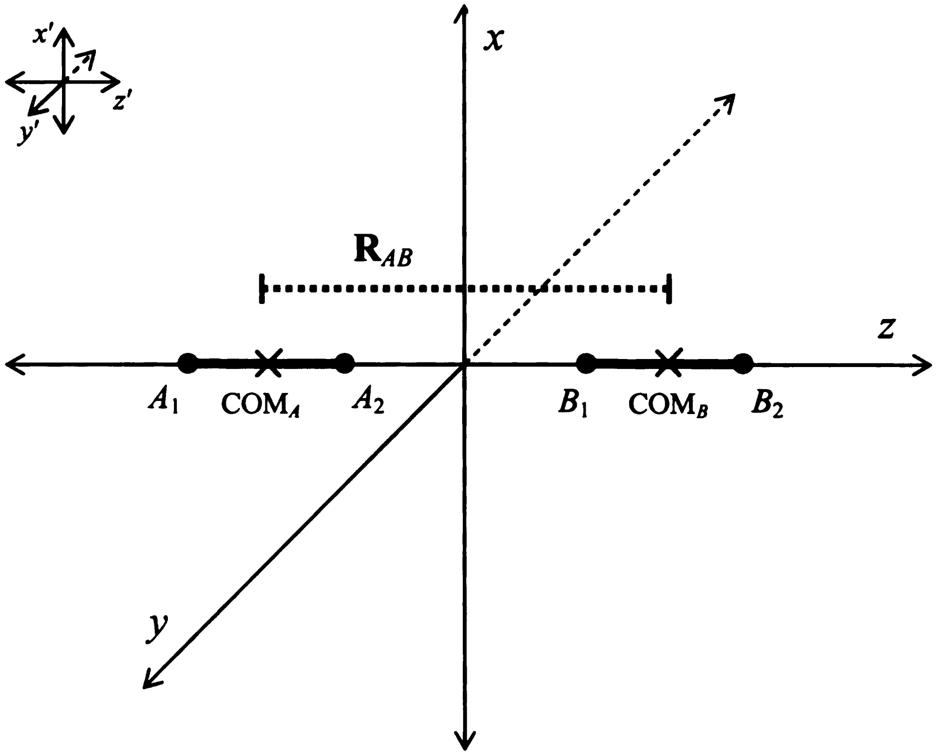

Fig. 12. Colinear arrangement of molecules A and B. In this figure, x, y, and z denote the axes of the laboratory frame, and x', y', and z' denote the axes of the molecular frames of A and B. Also, A_1 and A_2 are the nuclei of molecule A, B_1 and B_2 are the nuclei of molecule B, COM_A and COM_B are the centers of mass of molecules A and B, and $\mathbf{R}_{AB}$ is the distance between the center of mass of A and the center of mass of B.

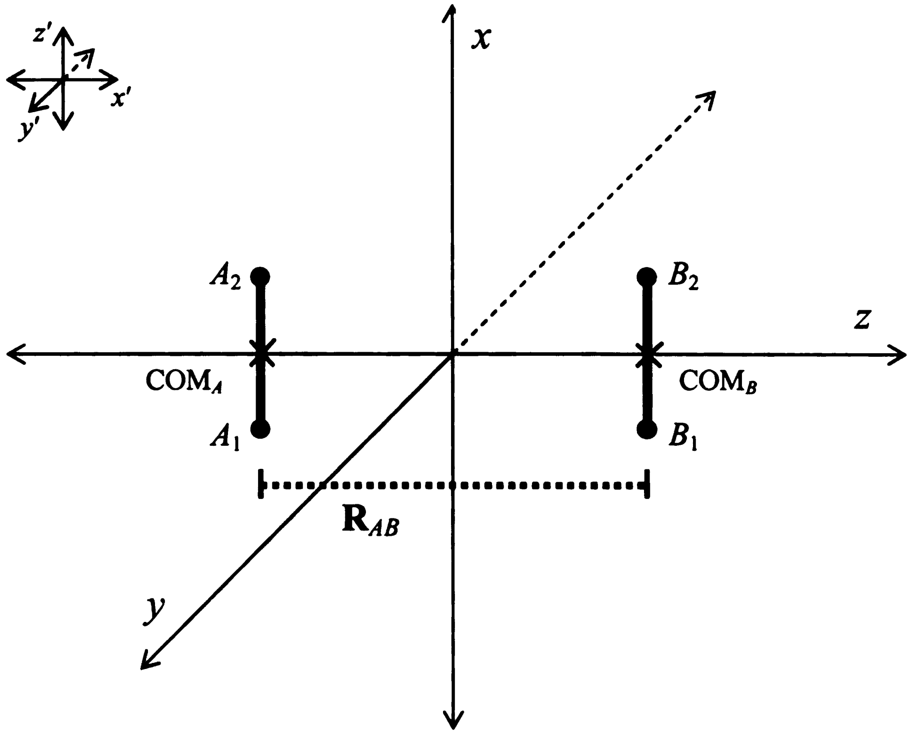

Fig. 13. Parallel arrangement of molecules A and B. In this figure, x, y, and z denote the axes of the laboratory frame, and x', y', and z' denote the axes of the molecular frames of A and B. Also, A_1 and A_2 are the nuclei of molecule A, B_1 and B_2 are the nuclei of molecule B, COM_A and COM_B are the centers of mass of molecules A and B, and $\mathbf{R}_{AB}$ is the distance between the center of mass of A and the center of mass of B.

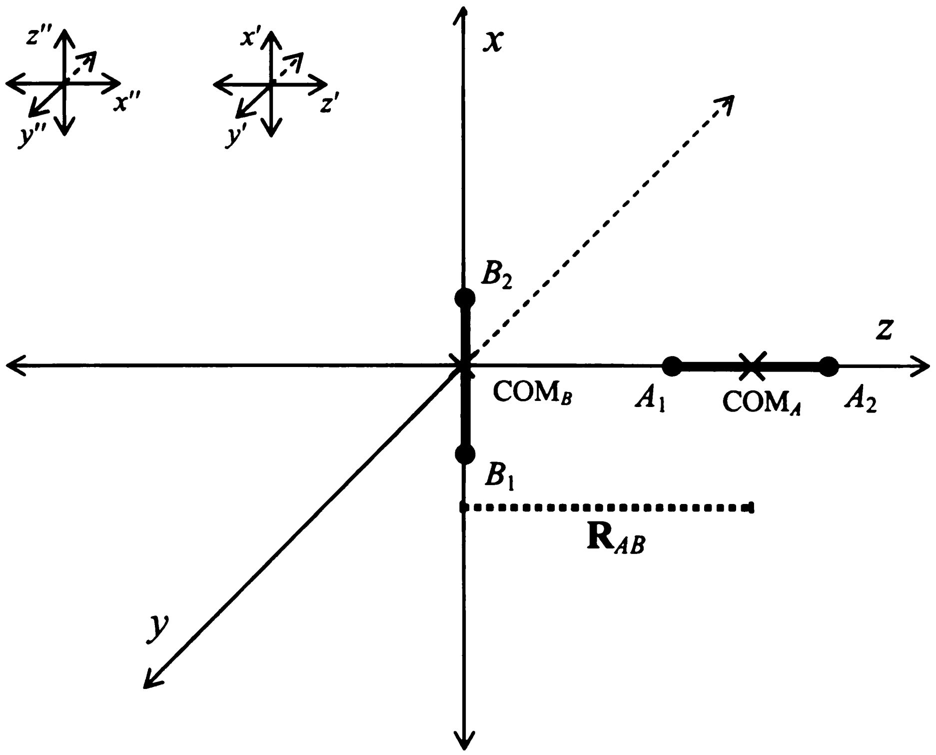

Fig. 14. Perpendicular arrangement of molecules A and B. In this figure, x, y, and z denote the axes of the laboratory frame, x', y', and z' denote the axes of the molecular frame of A, and x'', y'', and z'' denote the axes of the molecular frame of B. Also, A_1 and A_2 are the nuclei of molecule A, B_1 and B_2 are the nuclei of molecule B, COM_A and COM_B are the centers of mass of molecules A and B, and $\mathbf{R}_{AB}$ is the distance between the center of mass of A and the center of mass of B.

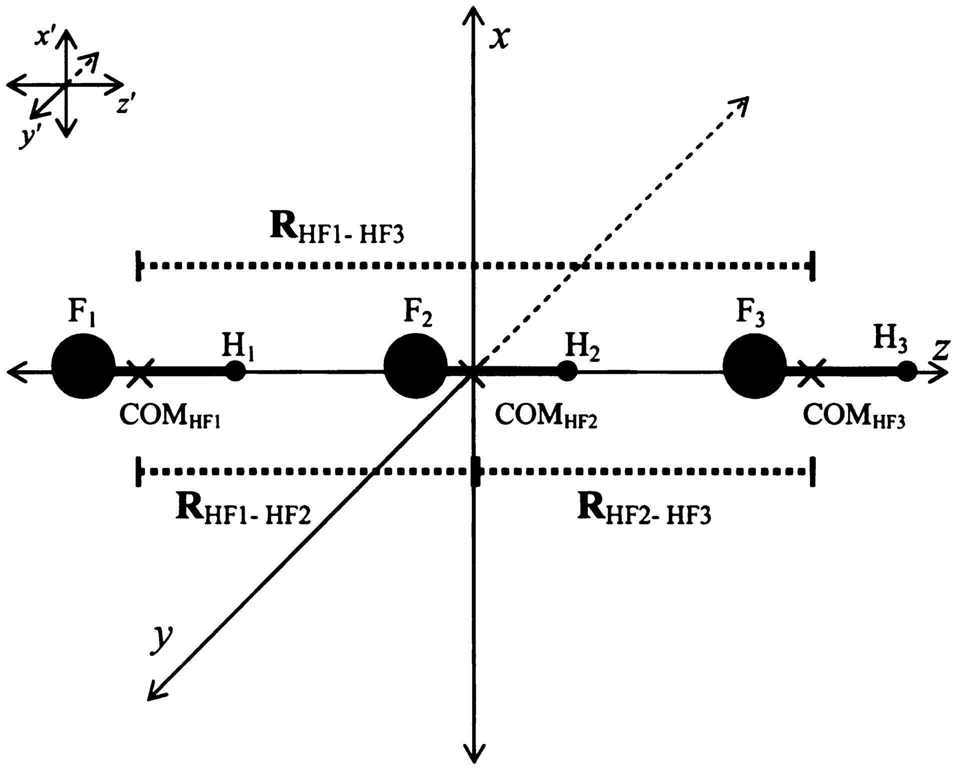

Fig. 15. Colinear arrangement of three HF molecules. In this figure, we have labeled the three HF molecules HF_1, HF_2, and HF_3 in order to distinguish between them. Also, x, y, and z denote the axes of the laboratory frame, x', y', and z' denote the axes of the molecular frames of each HF molecule, H_1, H_2, and H_3 are the hydrogen nuclei in HF_1, HF_2, and HF_3, F_1, F_2 and F_3 are the fluorine nuclei in HF_1, HF_2 and HF_3, and $\mathrm{COM}_{\mathrm{HF1}}$, $\mathrm{COM}_{\mathrm{HF2}}$, and $\mathrm{COM}_{\mathrm{HF3}}$ are the centers of mass of HF_1, HF_2, and HF_3. Finally, $\mathbf{R}_{\mathrm{HF1\text{-}HF2}}$, $\mathbf{R}_{\mathrm{HF1\text{-}HF3}}$, and $\mathbf{R}_{\mathrm{HF2\text{-}HF3}}$ are the distances between the centers of mass of HF_1 and HF_2, HF_1 and HF_3, and HF_2 and HF_3, respectively.

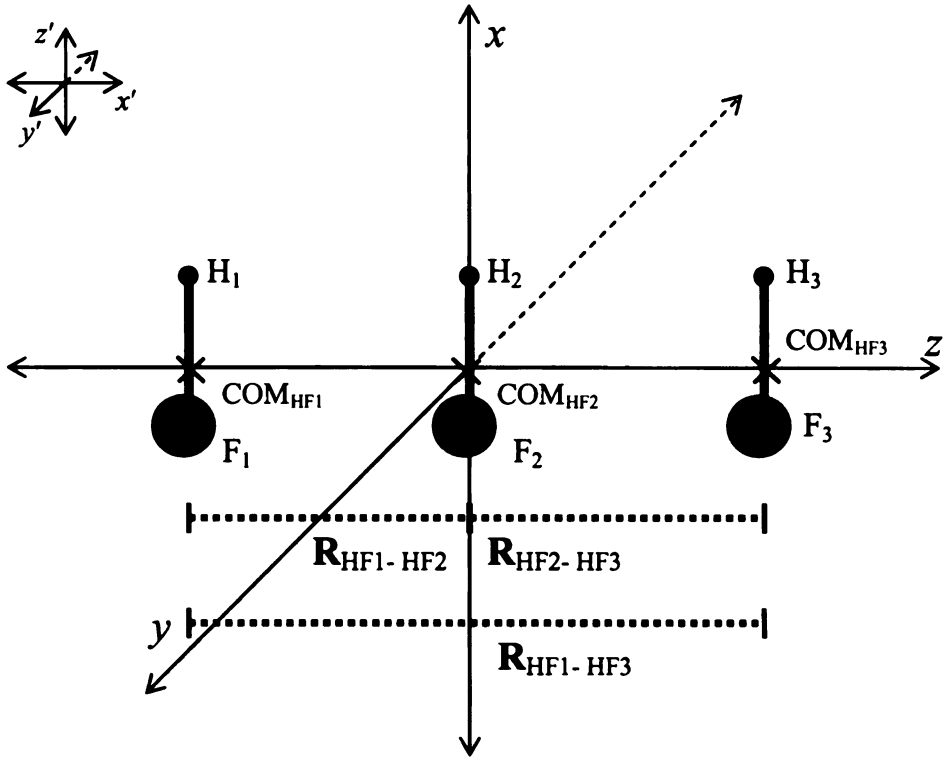

Fig. 16. Parallel arrangement of three HF molecules. In this figure, we have labeled the three HF molecules HF_1, HF_2, and HF_3 in order to distinguish between them. Also, *x*, *y*, and *z* denote the axes of the laboratory frame, *x'*, *y'*, and *z'* denote the axes of the molecular frames of each HF molecule, H_1, H_2, and H_3 are the hydrogen nuclei in HF_1, HF_2, and HF_3, F_1, F_2 and F_3 are the fluorine nuclei in HF_1, HF_2 and HF_3, and COM_{HF1}, COM_{HF2}, and COM_{HF3} are the centers of mass of HF_1, HF_2, and HF_3. Finally, $\mathbf{R}_{HF1\text{-}HF2}$, $\mathbf{R}_{HF1\text{-}HF3}$, and $\mathbf{R}_{HF2\text{-}HF3}$ are the distances between the centers of mass of HF_1 and HF_2, HF_1 and HF_3, and HF_2 and HF_3, respectively.

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