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dissertation entitled

ENERGIES, POLARIZATION, AND POLARIZABILITIES OF MOLECULES INTERACTING AT LONG OR INTERMEDIATE RANGE

presented by

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has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Chemistry

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Date 2/7/95

ENERGIES, POLARIZATION, AND POLARIZABILITIES OF MOLECULES INTERACTING AT LONG OR INTERMEDIATE RANGE

By

Xiaoping Li

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1994

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ABSTRACT

ENERGIES, POLARIZATION, AND POLARIZABILITIES OF MOLECULES INTERACTING AT LONG OR INTERMEDIATE RANGE

by

Xiaoping Li

This thesis presents results for the energies, interaction-induced polarization and polarizabilities of a set of molecules (two or three) interacting at long or intermediate range.

Collision-induced dipoles and polarizabilities have been determined for pairs of centrosymmetric linear molecules interacting at long range. The analysis is complete to order R^{-7} in the intermolecular separation for collision-induced dipoles and to order R^{-6} for collision-induced polarizabilities. For each of the polarization mechanisms, angular momentum algebra has been used to obtain compact results in terms of 6-j and 9-j symbols. Numerical results have been obtained for the polarizabilities of the pairs $H_2 \cdots H_2$, $H_2 \cdots N_2$, and $N_2 \cdots N_2$.

The nonlocal polarizability density $\alpha(\mathbf{r},\mathbf{r}';\omega)$ and hyperpolarizability densities such as $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega_1,\omega_2)$ play an important role in this research. The linear response tensor $\alpha(\mathbf{r},\mathbf{r}';\omega)$ gives the polarization $\mathbf{P}(\mathbf{r},\omega)$ induced at point $\mathbf{r}$ in a molecule by the electric field $\mathbf{F}(\mathbf{r}',\omega)$ acting at another point $\mathbf{r}'$. The hyperpolarizability density $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega_1,\omega_2)$ describes the distribution of the hyperpolarizability in molecules. A method of computing the β hyperpolarizability density has been developed based on its connection to a set of auxiliary functions $\Phi_L^M(k,\omega)$ that determine van der Waals

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interaction energies. For the hydrogen atom in the 1s state, the method yields analytical expressions for the β hyperpolarizability density. The results have been used to compute the damped dispersion-induced dipole in one hydrogen atom, due to its interactions with a second.

Three-body energies and the interaction-induced polarization for molecules interacting at long or intermediate range have been analyzed, assuming that intermolecular exchange effects are negligible. The analysis is complete to third order in the interactions. Distinct polarization mechanisms that contribute to three-body energies and polarization have been identified and clear physical interpretations have been established. These include dispersion, induction, and combined dispersion-induction effects. The induction effect further contains three different polarization mechanisms: the static reaction field, third-body field, and hyperpolarization. Both reaction-field theory and perturbation analysis are used to derive the equations for three-body energies and polarization, giving equivalent results. Polarizability density and hyperpolarizability densities are employed to characterize the nonlocal response of a molecule to the fields from its interacting partners. Thus the results include the direct modifications of the lowest-order electrostatic, induction, and dispersion effects, due to overlap of the molecular charge distributions.

The three-body dispersion energy is calculated for a model system, interacting ground-state hydrogen atoms, to illustrate how overlap modifies three-body interactions. An analytical expression for the damped triple-dipole dispersion energy is obtained and the results are compared to those from the long-range Axilrod-Teller-Muto expression. It is shown that the damped dispersion energy converges as interatomic distances approach zero, while the Axilrod-Teller-Muto equation diverges. The angular dependence of the three-body dispersion energy is also changed appreciably, due to overlap of the charge distributions among interacting hydrogen atoms.

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ACKNOWLEDGMENTS

I would like to thank my research advisor, Dr. Katharine L. C. Hunt, for her direction and encouragement in this research and in the preparation of this thesis.

My thanks are extended to the members of my guidance committee, Dr. James Harrison (who served as second reader), Dr. Richard Schwendeman, Dr. Jeffrey Ledford, and Dr. Milton Smith for their time and kindly help.

My thanks also go to members of Hunt's group for their stimulating discussions and friendship.

Special thanks are given to my wife, Yang Hong, for her constant support during these studies.

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CHAPTER I

INTRODUCTION

This thesis is concerned with the theory of intermolecular forces and the interaction-induced changes in molecular properties such as dipoles and polarizabilities.

The work focuses on two or three molecules interacting at long or intermediate range. The intermolecular separation is assumed to be sufficiently large that overlap between molecular charge distributions is weak and the effects due to exchange of electrons between molecules are negligible. Changes in the energy, polarization, and polarizability of the interacting molecules are analyzed.

In Chapter II, the collision-induced dipoles are determined for pairs of centro-symmetric linear molecules interacting at long range. The analysis is complete to order R^{-7} in the intermolecular separation. Through this order, the collision-induced dipoles are determined by quadrupolar [1] and hexadecapolar induction [2-5] , effects of nonuniformity in the local fields [3-5], back-induction [4], and dispersion [4, 6-8]. For all of these polarization mechanisms, spherical tensor analysis yields the dipole coefficients in terms of 6-j and 9-j symbols. The results are expected to be useful in simplifying collision-induced line shape analyses.

Chapter III gives the long-range contributions to the collision-induced polarizability $\Delta\alpha$ for pairs of centrosymmetric linear molecules through order R^{-6}, including the first- and second-order dipole-induced-dipole (DID) interactions [9], higher-multipole induction, effects of the nonuniformity of the local fields [10, 11], hyperpolarization [12], and dispersion [12-16]. The results have been obtained using spherical tensor analysis and they are given in terms of 6-j and 9-j symbols. The polarization mechanisms included in this work give rise to isotropic rototranslational Raman scattering and to simultaneous rotational transitions on two interacting molecules; both are collision-induced phenomena.

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Transitions with ΔJ up to ± 4 are produced by the R^{-5} and R^{-6} polarization mechanisms treated in this work. For the pairs $H_2 \cdots H_2$, $H_2 \cdots N_2$, and $N_2 \cdots N_2$, *ab initio* results for multipole moments and susceptibilities have been used to evaluate the classical induction contributions to $\Delta\alpha$, and a constant ratio approximation [4, 12, 14] has been used to estimate the dispersion contributions. The relative contributions to $\Delta\alpha$ from different polarization mechanisms are discussed for R values ~0.5 – 1 a.u. outside the isotropic van der Waals minimum of the pair potential.

Chapter IV presents a method of calculating the β hyperpolarizability density and the B hyperpolarizability density, which determine the damped dispersion-induced pair dipole and quadrupole of interacting molecules, respectively [17]. These densities are connected to a set of auxiliary functions denoted by $\Phi_L^M(k,\omega)$ that have been determined via a quantum mechanical variational method [18-21]. For the hydrogen atom in the 1s state, the work yields analytical results for the β and B hyperpolarizability densities.

In Chapter V, the damped dispersion-induced dipoles and quadrupoles are computed for pairs of S-state atoms. It is shown that the equations for damped dispersion dipoles and quadrupoles are convergent as the interatomic separation R goes to zero, while they reduce to the corresponding equations from the multipole expansion at long range. Using the results given in Chapter IV, analytical expressions are obtained for the leading term in the local dispersion dipole $\chi_7 D_7 R^{-7}$ and the leading term in the local dispersion quadrupole $\chi_6 M_6 R^{-6}$ for a pair of ground-state hydrogen atoms; here D_7 and M_6 are the leading long-range dipole and quadrupole coefficients [22-26], respectively, and χ_7 and χ_6 are the damping functions. The functions χ_7 and χ_6 are distinct, but both of them drop to ~0.85 at the van der Waals minimum for H_2 in the triplet state (R = 7.85 a.u.). The leading three dispersion dipole coefficients and the leading three dispersion quadrupole coefficients are also estimated and they compare well with the results from *ab initio* calculations [24-26].

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Chapter VI contains an analysis of nonadditive three-body interaction energies and the interaction-induced polarization. The analysis is complete through third order in the interactions. A reaction-field method is used to identify various polarization mechanisms that contribute to three-body energies and polarization. These include dispersion [27, 28], induction, and combined dispersion-induction effects. The polarizability density and hyperpolarizability densities are used to describe the nonlocal response of a molecule to a nonuniform external field or a local field due to neighboring molecules. Thus this approach accounts for the direct modifications of the lowest-order electrostatic, induction, and dispersion effects due to overlap of the molecular charge distributions. Nonadditive three-body forces are also analyzed in this chapter. An electrostatic interpretation of the three-body forces acting on nuclei is given based on a chain of relations between property derivatives with respect to nuclear coordinates and linear and nonlinear response tensors [29, 30]. For a group of three molecules A, B, and C, it is shown that the three-body dispersion force acting on a nucleus in molecule A results from the electrostatic attraction of that nucleus to the dispersion-induced polarization of the electrons in molecule A *itself*; that is, the three-body dispersion force on a nucleus in A depends only on the perturbed charge distribution of molecule A. This generalizes Hunt's proof [31] of Feynman's conjecture [32] on the origin of two-body dispersion forces to three-body forces. In contrast to the dispersion forces, the three-body induction and induction-dispersion forces on a nucleus in A depend not only on the perturbed charge density of A, but also on that of B and C.

In Chapter VII, the time-independent perturbation theory is used to derive equations for three-body energies and polarization. The results are shown to be equivalent to those obtained in Chapter VI from the reaction-field method.

Finally, in Chapter VIII the three-body dispersion energy [27, 28] is calculated for interacting ground-state hydrogen atoms. The calculation includes the direct effects of

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short-range charge overlap but not exchange. The damped triple-dipole dispersion energy [33] is obtained as an analytical function of the interatomic distances and the geometry of the three atoms. The radial and angular dependence of the dispersion energy is determined.

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CHAPTER II

COLLISION-INDUCED DIPOLES FOR PAIRS OF CENTROSYMMETRIC LINEAR MOLECULES AT LONG RANGE

2.1 Introduction

When two molecules collide, transient dipole moments are induced within each molecule because of the distortion of the charge distributions. These collision-induced dipoles are responsible for infrared [1-3] and far-infrared [4-7] absorption observed in compressed gases and liquids composed of $D_{\infty h}$ molecules, though such absorption is single-molecule forbidden [8]. For quantum mechanical line shape analyses of interaction-induced rototranslational absorption, the net dipole of a pair of molecules A and B is needed in the symmetry adapted form [9, 10]

$$\mu_M(\mathbf{R}) = (4\pi)^{3/2} / \sqrt{3} \sum D_{\lambda_A \lambda_B \lambda L}(R) Y_{\lambda_A}^{m_A}(\Omega^A) Y_{\lambda_B}^{m_B}(\Omega^B) Y_L^{M-m}(\Omega^R)$$

$$\times \langle \lambda_A \, \lambda_B \, m_A \, m_B | \lambda \, m \rangle \langle \lambda \, L \, m \, M-m | 1 \, M \rangle \qquad (1)$$

in terms of the spherical harmonics of the orientation angles Ω^A and Ω^B for the molecular axes $\mathbf{r}^A$ and $\mathbf{r}^B$, and the angles Ω for the vector $\mathbf{R}$ from A to B. In Eq. (1), the summation runs over λ_A, λ_B, λ, L, m_A, m_B, and m; M denotes the spherical tensor component of the dipole moment (M = 1, 0, or -1) and $\langle \lambda_1 \, \lambda_2 \, m_1 \, m_2 | \lambda_3 \, m_3 \rangle$ is a Clebsch-Gordan coefficient. In Eq. (1), the bond lengths in molecules A and B are fixed at the vibrationally averaged values.

Values have been given earlier for the coefficients $D_{\lambda_A \lambda_B \lambda L}$ due to long-range polarization mechanisms through order R^{-7} [9-15]. In this work, angular momentum algebra is u

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algebra is used to obtain the coefficients $D_{\lambda_A\lambda_B\lambda L}$ in terms of 6-j and 9-j symbols. The work explains interrelations among coefficients with different values of λ_A, λ_B, λ and L, for each of the polarization mechanisms, and provides compact new expressions for the coefficients $D_{\lambda_A\lambda_B\lambda L}$, in order to simplify line shape analyses.

2.2 A Spherical Tensor Analysis

For two $D_{\infty h}$ molecules A and B interacting at long range, the net dipole is determined by induction [9-15] and dispersion [14, 16-18, 20]. Through order R^{-7}, the induction term in the dipole of molecule A is

$$\mu_\alpha^{i,A} = 1/3\,\alpha_{\alpha\beta}^A T_{\beta\gamma\delta}(\mathbf{R})\Theta_{\gamma\delta}^B + 1/105\,\alpha_{\alpha\beta}^A T_{\beta\gamma\delta\varepsilon\phi}(\mathbf{R})\Phi_{\gamma\delta\varepsilon\phi}^B$$
$$+1/45\,E_{\alpha,\beta\gamma\delta}^A T_{\beta\gamma\delta\varepsilon\phi}(\mathbf{R})\Theta_{\varepsilon\phi}^B - 1/3\,\alpha_{\alpha\beta}^A T_{\beta\gamma}(\mathbf{R})\alpha_{\gamma\delta}^B T_{\delta\varepsilon\phi}(\mathbf{R})\Theta_{\varepsilon\phi}^A, \qquad (2)$$

where $T_{\alpha\beta\cdots\varepsilon}(\mathbf{R}) = \nabla_\alpha\nabla_\beta\cdots\nabla_\varepsilon(R^{-1})$, with $\mathbf{R}$ the vector from the origin of A to the origin of B. The Einstein convention of summation over repeated Greek subscripts is used in Eq. (2) and below. The induction contribution to the net pair dipole is given by $\mu_\alpha^i = (1-\wp^{AB})\mu_\alpha^{i,A}$, where $\wp^{AB}$ permutes the labels of molecules A and B. The first two terms in Eq. (2) represent quadrupolar [9] and hexadecapolar [12-15] induction, respectively. The third term represents the effects of nonuniformity in the local field acting on molecule A [13-15]: the second gradient of the quadrupolar field due to B induces a dipole in A via the dipole-octopole polarizability E [19]. The final term in Eq. (2) represents back-induction [14]: The field from the quadrupole of A induces a dipole in B; this produces a reaction field at A, thus inducing a dipole at second order in the A-B interaction.

At order R^{-7}, dispersion also contributes to the net pair dipole, for centrosymmetric molecules [14, 16-18, 20]. Both the reaction field method [14, 17] and the third-order, two-center

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two-center perturbation theory [20] show that the dispersion dipole depends upon the polarizability and the dipole-dipole-quadrupole hyperpolarizability B of each molecule, integrated over imaginary frequencies:

$$\mu_\phi^d = \hbar / 3\pi \, (1 - \wp^{AB}) \int_0^\infty d\omega \; T_{\alpha\beta}(\mathbf{R}) \alpha_{\beta\gamma}^A (i\omega) T_{\gamma\delta\varepsilon}(\mathbf{R}) B_{\alpha\phi,\delta\varepsilon}^B (0, i\omega). \tag{3}$$

The leading term in the induced dipole of molecule B, $-1/3\, \alpha_{\alpha\beta}^B T_{\beta\gamma\delta}(\mathbf{R}) \Theta_{\gamma\delta}^A$, stems from the dipole induced in B at first order in the dipole-quadrupole interaction between A and B. This term in the dipole is given by

$$T^{\Theta\alpha} = -1/3\, (1 + C) \langle \Psi_0 | \mu^B G \mu_\alpha^B T_{\alpha\beta\gamma}(\mathbf{R}) \Theta_{\beta\gamma}^A | \Psi_0 \rangle \tag{4}$$

in terms of the wavefunction Ψ_0 for the A-B pair in the absence of interactions, the reduced resolvent $G = (1 - |\Psi_0\rangle\langle\Psi_0|)(H_0 - E_0)^{-1}(1 - |\Psi_0\rangle\langle\Psi_0|)$ for the pair, and the complex conjugation operator C. The quantity $\mu_\alpha^B T_{\alpha\beta\gamma}(\mathbf{R}) \Theta_{\beta\gamma}^A$ in Eq. (4) is related to the direct product $[\mu_B^{(1)} \otimes (T^{(3)} \otimes \Theta_A^{(2)})]^{(0)}$ by

$$\mu_\alpha^B T_{\alpha\beta\gamma}(\mathbf{R}) \Theta_{\beta\gamma}^A = -\sqrt{42}/2\, [\mu_B^{(1)} \otimes (T^{(3)} \otimes \Theta_A^{(2)})]^{(0)}, \tag{5}$$

where the relation between the spherical tensor components $T_p^{(3)}(\mathbf{R})$ ($p = \pm 3, \pm 2, \pm 1$, or 0) and the Cartesian tensor components $T_{\alpha\beta\gamma}(\mathbf{R})$ is assumed to be identical to that of the first-order dipole hyperpolarizability β [21]. Equation (5) has been obtained following the observation that both sides of the above equation are scalar so that they can differ only by a constant. Substitution of Eq. (5) into Eq. (4) gives

$$\begin{aligned} T^{\Theta\alpha} &= \sqrt{42}/6\, (1 + C) \langle \Psi_0 | [\mu_B^{(1)} \otimes G \{\mu_B^{(1)} \otimes [T(\mathbf{R})^{(3)} \otimes \Theta_A^{(2)}]^{(1)}\}^{(0)}]^{(1)} | \Psi_0 \rangle \\ &= \sqrt{42}/6\, (1 + C) \left\langle \Psi_0^B \middle| [\mu_B^{(1)} \otimes G^B \{\mu_B^{(1)} \otimes [T(\mathbf{R})^{(3)} \otimes \Theta_{0A}^{(2)}]^{(1)}\}^{(0)}]^{(1)} \middle| \Psi_0^B \right\rangle. \end{aligned} \tag{6}$$

In Eq. (6), Ψ_0^B and G^B denote the unperturbed wavefunction and reduced resolvent, respectively, for molecule B; $\Theta_{0A}^{(2)}$ is the permanent quadrupole moment of molecule A.

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Use of the tensor-operator methods treated in Refs. 21-23 (and applied to collision-induced polarizabilities in Refs. 24-26) transforms Eq. (6) into

$$T^{\Theta\alpha} = \sqrt{42}/6\sum_{g}\Pi_{g}\begin{Bmatrix}1 & 1 & 0\\ 1 & 1 & g\end{Bmatrix}\{[T(\mathbf{R})^{(3)}\otimes\Theta_{0A}^{(2)}]^{(1)}\otimes(1+C)$$

$$\times\left\langle\Psi_0^B\right|(\mu^B\otimes G^B\mu^B)^{(g)}\left|\Psi_0^B\right\rangle\}^{(1)}$$

$$= \sqrt{42}/6\sum_{g}\Pi_{g}\begin{Bmatrix}1 & 1 & 0\\ 1 & 1 & g\end{Bmatrix}\{[T(\mathbf{R})^{(3)}\otimes\Theta_{0A}^{(2)}]^{(1)}\otimes\alpha_B^{(g)}\}^{(1)}$$

$$= \sqrt{14}/6\sum_{\lambda_B\lambda}\Pi_{\lambda_B\lambda}\begin{Bmatrix}3 & 2 & 1\\ \lambda_B & 1 & \lambda\end{Bmatrix}(-1)^{\lambda}\{[\Theta_{0A}^{(2)}\otimes\alpha_B^{(\lambda_B)}]^{(\lambda)}\otimes T(\mathbf{R})^{(3)}\}^{(1)}, \qquad (7)$$

where $\Pi_{ab\cdots c} = [(2a+1)(2b+1)\cdots(2c+1)]^{1/2}$. For linear molecules, when the only nonvanishing component of the spherical tensor $\gamma^{(p)}$ in the molecule-fixed frame is $\gamma(p,0)$, the tensor components $\gamma(p,q)$ in the space-fixed frame are given by [23]

$$\gamma(p,q) = [4\pi/(2p+1)]^{1/2}\,\gamma(p,0)\,Y_p^q(\Omega). \qquad (8)$$

Equations (7) and (8) imply

$$D^{\Theta\alpha}_{2\lambda_B\lambda 3} = \sqrt{30}/30\,(-1)^{\lambda}\Pi_{\lambda}\begin{Bmatrix}3 & 2 & 1\\ \lambda_B & 1 & \lambda\end{Bmatrix}\Theta^A(2,0)\alpha^B(\lambda_B,0)\,T(3,0)$$

$$= \sqrt{3}(-1)^{\lambda+1}(2\lambda+1)^{1/2}\begin{Bmatrix}3 & 2 & 1\\ \lambda_B & 1 & \lambda\end{Bmatrix}\Theta^A\,\alpha^B(\lambda_B,0)R^{-4}, \qquad (9)$$

where $\alpha(0,0) = -\sqrt{3}\,\bar{\alpha}$, $\alpha(2,0) = 2/\sqrt{6}\ (\alpha_{\Uparrow} - \alpha_{\perp})$, and $T(3,0) = -3\sqrt{10}\,R^{-4}$. This result is consistent with earlier work [9-15]. The corresponding coefficients for the polarization of A by the permanent quadrupole of B are given by

$$D^{\alpha\Theta}_{\lambda_A 2\lambda 3} = (-1)^{\lambda+1}\,\wp^{AB}\,D^{\Theta\alpha}_{2\lambda_B\lambda 3}. \qquad (10)$$

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Similar analysis gives the coefficients for hexadecapolar induction term [12-15] in the form

$$D^{\Phi\alpha}_{4\lambda_B\lambda 5} = \sqrt{5}(-1)^{\lambda+1}(2\lambda+1)^{1/2}\begin{Bmatrix} 5 & 4 & 1 \\ \lambda_B & 1 & \lambda \end{Bmatrix}\Phi^A\alpha^B(\lambda_B,0)R^{-6}, \tag{11}$$

where $\Phi^A = \Phi^A_{zzzz}$, and $D^{\alpha\Phi}_{\lambda_A 4\lambda 5} = (-1)^{\lambda+1}\wp^{AB}D^{\Phi\alpha}_{4\lambda_B\lambda 5}$. The E-tensor term [13-15] satisfies

$$D^{E\Theta}_{\lambda_A 2\lambda 5} = \sqrt{42}(2\lambda+1)^{1/2}\begin{Bmatrix} \lambda_A & 2 & \lambda \\ 5 & 1 & 3 \end{Bmatrix}E^A(\lambda_A,0)\Theta^B R^{-6} \tag{12}$$

with $E(2,0) = -1/\sqrt{21}\ (3E_{z,zzz} - 8E_{x,xxx})$, $E(4,0) = 2/\sqrt{7}\ (E_{z,zzz} + 2E_{x,xxx})$, and $D^{\Theta E}_{2\lambda_B\lambda 5} = (-1)^{\lambda+1}\wp^{AB}D^{E\Theta}_{\lambda_A 2\lambda 5}$. For back-induction [14],

$$D^{b}_{\lambda_A\lambda_B\lambda L} = 15\sqrt{14}\,[1+(-1)^{\lambda+1}\wp^{AB}]\sum_{a,g}(-1)^{\lambda+g+1}(2g+1)\Pi_{a\lambda}\begin{Bmatrix} 1 & 2 & 1 \\ 1 & 3 & 2 \\ \lambda_A & L & g \end{Bmatrix}$$

$$\times\begin{Bmatrix} g & \lambda_B & 1 \\ a & 1 & 2 \end{Bmatrix}\begin{Bmatrix} \lambda_A & \lambda_B & \lambda \\ 1 & L & g \end{Bmatrix}\langle a200|\lambda_B 0\rangle\langle 2300|L0\rangle$$

$$\times\alpha^A(\lambda_A,0)\alpha^B(a,0)\Theta^B R^{-7} \tag{13}$$

with a = 0 or 2. Finally, the coefficients for the dispersion term are given by

$$D^{d}_{\lambda_A\lambda_B\lambda L} = 15\sqrt{14}\,\hbar/\pi\ R^{-7}\langle 2300|L0\rangle\,[1+(-1)^{\lambda+1}\wp^{AB}]\sum_{a,g}(-1)^{\lambda_A+g+a}$$

$$\times(2g+1)\Pi_{a\lambda}\begin{Bmatrix} 1 & 2 & 1 \\ 1 & 3 & 2 \\ \lambda_B & L & g \end{Bmatrix}\begin{Bmatrix} g & \lambda_A & 1 \\ a & 1 & 2 \end{Bmatrix}\begin{Bmatrix} \lambda_B & \lambda_A & \lambda \\ 1 & L & g \end{Bmatrix}$$

$$\times\int_0^\infty d\omega\ B^{(a)}(\lambda_A,0;0,i\omega)\alpha^B(\lambda_B,0;i\omega). \tag{14}$$

In Eq. (14), a = 0, 1, or 2, and

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$$B^{(2)}(0,0;0,i\omega) = 2/\sqrt{30}\,[B_{zz,zz}(0,i\omega) + 2B_{xz,xz}(0,i\omega) + 2B_{zx,xz}(0,i\omega)$$
$$+B_{xx,zz}(0,i\omega) + 4B_{xx,xx}(0,i\omega)], \tag{15a}$$

$$B^{(0)}(2,0;0,i\omega) = -1/\sqrt{3}\,[B_{zz,zz}(0,i\omega) + 2B_{xx,zz}(0,i\omega)], \tag{15b}$$

$$B^{(1)}(2,0;0,i\omega) = 2/\sqrt{3}\,[B_{zx,xz}(0,i\omega) - B_{xz,xz}(0,i\omega)], \tag{15c}$$

$$B^{(2)}(2,0;0,i\omega) = 2/\sqrt{21}\,[-B_{zz,zz}(0,i\omega) - B_{xz,xz}(0,i\omega) - B_{zx,xz}(0,i\omega)$$
$$+3B_{xx,zz}(0,i\omega) + 4B_{xx,xx}(0,i\omega)], \tag{15d}$$

$$B^{(2)}(4,0;0,i\omega) = 2/\sqrt{105}\,[3B_{zz,zz}(0,i\omega) - 4B_{xz,xz}(0,i\omega) - 4B_{zx,xz}(0,i\omega)$$
$$-2B_{xx,zz}(0,i\omega) + 2B_{xx,xx}(0,i\omega)]. \tag{15e}$$

Equations (13) and (14) for the back-induction and dispersion coefficients are structurally similar, because both involve a dipole-dipole interaction between A and B, a dipole-quadrupole interaction, and a dipole expectation value. In Eq. (13), the operators μ^X, μ^X, and Θ^X (X = A or B) are coupled to produce $\alpha^X(a,0)\Theta^X$, while in Eq. (14) the same operators are coupled to yield $B^{(a)}(\lambda_X,0;0,i\omega)$. The results given by Eqs. (9)-(14) also apply to atom-$D_{\infty h}$ molecule interactions, with the index λ_A for the atom always equal to zero [27].

2.3 Summary and Discussion

Angular momentum coupling algebra has been used to derive equations for the dipole coefficients $D_{\lambda_A\lambda_B\lambda L}$ in terms of 6-j and 9-j symbols. The results explain the interrelations among coefficients with different λ_A, λ_B, λ, and L, for each of the polarization mechanisms, and yield compact expressions that simplify line shape analyses.

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Mechanisms giving nonvanishing coefficients $D_{\lambda_A\lambda_B\lambda L}$ can produce rototranslational transitions with ΔJ up to $\pm\lambda_A$ for A and ΔJ up to $\pm\lambda_B$ for B with an isotropic pair potential. The algebraic expressions for the coefficients given by Eqs. (9)-(14) above are consistent with Eqs. (9)-(12), (15)-(19), (24)-(29) and Tables I-IV in Ref. 14, obtained by a direct integration method.

The numerical evaluation of the coefficients due to classical induction effects requires only the multipole moments and static multipole polarizabilities, which are available from *ab initio* calculations for a number of species including H_2 and N_2. In order to determine the dispersion contributions to the coefficients given by Eq. (14), however, it is necessary to obtain the B hyperpolarizability tensor (as well as α tensor) as a function of imaginary frequency. For H_2, values of the imaginary-frequency B tensor components have recently been computed with high accuracy [28], and the dispersion dipole coefficients have been evaluated numerically for pairs containing H_2 [28]. For heavier species such as N_2, where accurate values for $B(0,i\omega)$ are not yet available , Hunt and Bohr [14, 27] have developed a constant ratio approximation that relates the dispersion dipole coefficients to the static multipole polarizability, static hyperpolarizability B, and dispersion energy coefficients (the constant ratio approximation has also been used to estimate dispersion contributions to pair polarizabilities; see Ref. 29 and the next chapter).

Bohr and Hunt have used *ab initio* results for permanent multipole moments and polarizabilities to evaluate the classical induction contribution to $D_{\lambda_A\lambda_B\lambda L}$ for pairs $H_2\cdots H_2$, $H_2\cdots N_2$, and $N_2\cdots N_2$ in Ref. 14. They have estimated the dispersion dipole coefficients based on the constant ratio approximation and discussed the relative contributions of different polarization mechanisms to the collision-induced dipoles of these pairs.

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CHAPTER III

COLLISION-INDUCED POLARIZABILITIES FOR PAIRS OF CENTROSYMMETRIC LINEAR MOLECULES AT LONG RANGE: THEORY AND NUMERICAL RESULTS FOR $H_2 \cdots H_2$, $H_2 \cdots N_2$, AND $N_2 \cdots N_2$

3.1 Introduction

Collision-induced changes $\Delta\alpha$ in polarizabilities occur on the subpicosecond time scale. These changes are detected experimentally in collision-induced Rayleigh and rototranslational Raman scattering [1-4], subpicosecond induced birefringence [5-8], impulsive stimulated scattering [9-12], and measurements of the density dependence of dielectric properties [13, 14] and refractivity [15-17]. The purpose of this work is to provide general, symmetry-adapted equations for the induction and dispersion contributions to $\Delta\alpha$, complete to order R^{-6} in the intermolecular interactions, and to provide numerical results for $H_2 \cdots H_2$, $H_2 \cdots N_2$, and $N_2 \cdots N_2$. These pairs were selected because collision-induced light scattering (CILS) spectra have been obtained in experiments on hydrogen and its isotopic variants [18-28] and nitrogen [29-35] over a wide range of densities and temperatures; and because the multipole moments, susceptibilities, and van der Waals energy coefficients--needed as input parameters for the work--have been evaluated in *ab initio* calculations for these species [36-48].

The calculations are complete to order R^{-6} in the intermolecular separation between a pair of $D_{\infty h}$ molecules. To this order, $\Delta\alpha$ is determined by first- and second-order dipole-induced-dipole (DID) interactions [49], higher-multipole induction by the laser field, dipole induction due to nonuniformities in the local field [35, 50, 51], hyperpolarization [52], and dispersion [52-56]. These polarization mechanisms suffice to predict types of scattering that are single-molecule forbidden, such as isotropic rototranslational

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Raman scattering by centrosymmetric linear molecules during $\Delta J = \pm 2$ and $\Delta J = \pm 4$ transitions, and depolarized rototranslational Raman scattering with $\Delta J = \pm 4$. These mechanisms also yield simultaneous rotational transitions on each of the colliding molecules, with ΔJ up ± 4 for one molecule and ± 2 for its collision partner.

In this work spherical-tensor analysis and angular momentum coupling algebra have been used, as suggested by Samson and Ben-Reuven [57] and by Bancewicz, Glaz, Kazmierczak, and Kielich [58-61; see also 62, 63] to separate the terms in $\Delta\alpha$ according to their transformation properties under rotation of the molecular axes and the intermolecular vector **R**. This casts the results into the symmetry-adapted form needed for line shape analysis [64-67].

This work provides the first full set of results for the dispersion terms $\Delta\alpha^{\mathrm{disp}}$ in the collision-induced polarizability of a pair of linear, centrosymmetric molecules. Here $\Delta\alpha^{\mathrm{disp}}$ has been determined by use of reaction-field theory to find the change in the dispersion energy at second order in an applied field [55], but identical results are obtained from a two-center perturbation treatment taken to fourth-order overall [54]. Two distinct physical effects contribute to $\Delta\alpha^{\mathrm{disp}}$: (1) each molecule is hyperpolarized by the applied field and the fluctuating field of its neighbor [53], and (2) the applied field alters the correlations in the spontaneous quantum mechanical fluctuations of the charge density in each of the molecules, thus affecting the van der Waals interaction energy [55]. Exact analytical results are obtained for the dispersion effects, as integrals over imaginary frequency; terms in the integrands contain the polarizability $\alpha(i\omega)$ of one molecule multiplied by the second hyperpolarizability $\gamma(i\omega, 0, 0)$ of the other. For H_2, both $\alpha(i\omega)$ and $\gamma(i\omega, 0, 0)$ have been determined with high accuracy using explicitly correlated wave functions [39]. For numerical applications to larger molecules, a constant ratio approximation [52, 54, 68, 69] is used to relate $\Delta\alpha^{\mathrm{disp}}$ to the static polarizability, static γ hyperpolarizability, and dispersion energy coefficients, which are more widely available than $\gamma(i\omega, 0, 0)$. Comparisons of the approximation with *ab initio* results for $H \cdots H_2$,

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He$\cdots$$H_2$, and $H_2\cdots H_2$ [39, 70] show that the rms error in the approximation is approximately 20-25%. In the current work on $H_2\cdots H_2$, $H_2\cdots N_2$, and $N_2\cdots N_2$, dispersion is shown to contribute significantly to the collision-induced change in scalar polarizability $\Delta\alpha_0^0$, which determines the spectra for isotropic collision-induced Rayleigh and rototranslational Raman scattering [24]. In fact, if $\Delta\alpha_0^0$ is averaged isotropically over the orientations of each of the interacting molecules and the intermolecular vector, at long range dispersion accounts for ~55% of the total value for $H_2\cdots H_2$, 40% for $H_2\cdots N_2$, and 30% for $N_2\cdots N_2$, based on current estimates. The dispersion terms in the anisotropic polarizability $\Delta\alpha_2^M$ are much smaller for the pairs studied in this work, because the γ hyperpolarizability shows little anisotropy for H_2 and N_2 [39, 41].

In addition to dispersion terms--which are purely quantum mechanical--the calculations include classical induction mechanisms treated in earlier work: First-order DID interactions [49, 71] give the leading R^{-3} terms in $\Delta\alpha$, and hence the dominant contribution to depolarized, collision-induced scattering by pairs of linear molecules [21-35]. Second-order DID terms have been cast in symmetry-adapted form by Bancewicz [58]. Their effects on line shapes and depolarized scattering intensities have been analyzed in molecular dynamics simulations by Ladanyi and Geiger [72, 73].

E-tensor terms vary as R^{-5} [50], and two types contribute to $\Delta\alpha$: The applied field induces a dipole in each molecule; this creates a nonuniform field that induces a dipole in the collision partner, via its dipole-octopole polarizability E [74]. In addition, the applied field induces an octopole in each molecule via E, and the octopolar field polarizes its collision partner. Buckingham and Tabisz [50] have shown that E-tensor induction accounts in part for rotational Raman transitions observed in the far wings of the depolarized scattering spectrum of compressed SF_6 in the gas phase. Bancewicz, Teboul, and Le Duff have analyzed scattering by N_2 [35], with frequency shifts out to 700 cm^{-1}, where the contribution from pressure-broadened allowed transitions is negligible. The region of the spectrum between 300 and 700 cm^{-1} cannot be fit within the DID model for

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$\Delta\alpha$ [35]. Inclusion of the E terms in $\Delta\alpha$ gives the observed line shape, but the fourth-rank component of E determined by fitting the spectra is ~2.5 times the *ab initio* value [75]. The hyperpolarization terms, which depend to leading order on the dipole-dipole-quadrupole hyperpolarizability B [74], tend to be smaller than the E terms (for species studied thus far); but like the E terms, they vary as R^{-5}. The B-tensor terms account for the dipole induced by the external field, acting together with the field gradient of the permanent molecular quadrupole of a neighboring molecule.

The results for $\Delta\alpha$ apply in the outer part of the van der Waals potential well, where overlap between the charge distributions is small. At shorter range, overlap damping, exchange, orbital distortion and charge transfer contribute significantly to $\Delta\alpha$. Short-range effects are not yet well characterized for $H_2\cdots H_2$, $H_2\cdots N_2$, and $N_2\cdots N_2$ since the *ab initio* studies to date [76, 77] have employed basis sets that are small by present standards, and have neglected correlation. Calculations on pairs of inert gas atoms show that the results are very sensitive to the size and quality of the basis [78]. The results given here should be useful in carrying out later *ab initio* work, because they provide the correct limiting form of $\Delta\alpha$ at intermolecular distances where numerical cancellation and Gaussian truncation error make it difficult to obtain accurate results *ab initio* [79]. Additionally, this work identifies single-molecule property tensors (α, Θ, E, B, and γ) that must be reproduced in a basis-set calculation, in order to obtain accurate results for $\Delta\alpha$. Comparison of the observed scattering spectra with the calculated form based on the induction and dispersion terms in $\Delta\alpha$ (given here) should yield predictions about the short-range quantum terms that can be tested in later *ab initio* work. The short-range quantum terms in $\Delta\alpha$ are expected to be important in determining scattering in high-frequency spectral wings [18-35, 78], and in cases where the leading long-range contributions to $\Delta\alpha$ vanish by symmetry [78]. In other cases, the scattered intensity may depend predominantly on $\Delta\alpha$ at intermediate to long range; e.g., this applies to scattering by solid hydrogen and its isotopic variants [80-82], because the separation between H_2 molecules in solid hydrogen i

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hydrogen is slightly larger [80, 83] than R = 6.5 a.u., the isotropic van der Waals minimum of the gas-phase pair potential. Hence long-range models can predict interesting phenomena such as zero-phonon, double transitions in solid HD [27].

This work should be useful in analyzing the experimental light-scattering data that has been obtained for H_2 [18-28], N_2 [29-35], O_2 [84, 85], Cl_2 [86], CO_2 [87-89], and CS_2 [90, 91], in order to obtain information on intermolecular dynamics, as well as short-range polarization effects. In the gas phase, collision-induced scattering contributes to a broad, asymmetric background superimposed on pressure-broadened, allowed lines [92]. In H_2, the first rotational lines are sufficiently well separated in frequency from the origin (the frequency of the incident radiation) that purely translational, collision-induced Rayleigh scattering spectra can be obtained experimentally [18-28]. In this case, potential high-frequency contributions from short-range polarization mechanisms are effectively cut off at ~300 cm^{-1}, because the pressure-broadened wing of the allowed $J = 0 \rightarrow 2$ transitions at $\gamma = 354.4$ cm^{-1} appears in this region [25]. Nearer to the origin, the spectra for ortho-hydrogen show structure that is not found for para-hydrogen at low temperatures [21]: in ortho-hydrogen, the collision-induced scattering is superimposed on the pressure-broadened wing of the allowed $Q_0(1)$ rotational Raman transition [93].

In the liquid phase, the interaction-induced changes in polarizability determine local-field factors for allowed scattering [94], and also generate collision-induced components in the polarizability which transform differently from the single-molecule tensors under rotation of the molecular framework [94-97]. For liquids containing light molecules such as N_2, O_2, Cl_2, and CO_2, molecular dynamics simulations show [71-73, 98-101] that the allowed and collision-induced (CI) components of the polarizability are not well separated in time scale, with the result that significant interference occurs. Collision-induced scattering is predicted to increase the second moment of the depolarized Raman bands for liquid N_2 and O_2 by ~20-30% [71-73], with larger effects expected for Cl_2 and CO_2.

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Experiments using pulsed lasers with 100-femtosecond and shorter time resolution probe $\Delta\alpha$ directly in the time domain [5-12]. In subpicosecond induced birefringence experiments [5-8], a high-intensity laser pulse induces optical anisotropy in the sample, and a weaker, time-delayed pulse probes differences in the refractive index for polarizations parallel or perpendicular to the pump field (the optical Kerr effect, or OKE). In impulsive stimulated scattering (ISS) experiments [9-12], two ultrashort excitation pulses overlap inside a sample, and typically the mean-square scattered probe field is measured. Both OKE and ISS experiments show collision-induced effects on α for liquid CS_2, on the time scale $t < 500$ fs [12, 102]. Finally, collisional effects appear in the second and third refractivity virial coefficients, recently obtained in high-accuracy experiments on H_2 and N_2 [17]: $\Delta\alpha$ determines the second refractivity virial coefficients of compressed gases, and contribute to the second dielectric virial coefficients [103].

Sec. 3.2 of this chapter contains the symmetry analysis for the collision-induced polarizability. Sec. 3.3 gives equations for the coefficients appearing in the scalar component of $\Delta\alpha$, and Sec. 3.4 gives the coefficients for the anisotropic component. Additionally, the implications for rototranslational Raman spectra are discussed in Sec. 3.3 (isotropic scattering) and 3.4 (depolarized scattering). Section 3.5 describes a method of estimating the dispersion contributions to collision-induced polarizabilities in terms of van der Waals energy coefficients, static polarizabilities, and static hyperpolarizabilities. Section 3.6 contains a set of numerical results for $H_2\cdots H_2$, $H_2\cdots N_2$, and $N_2\cdots N_2$ pairs. Sec. 3.7 provides a brief summary and discussion.

3.2 Changes in Polarizability Induced by Long-Range Interactions Between Two Centrosymmetric Linear Molecules

In this section, the collision-induced electronic polarizability $\Delta\alpha$ is determined for a pair of centrosymmetric linear molecules interacting at long range. The results are complete to order R^{-6} in the intermolecular separation R, and to this order $\Delta\alpha$ is a sum of induction and dispersion terms.

To obtain the induction term $\Delta\alpha^{ind}$, the effective multipole moments of two interacting $D_{\infty h}$ molecules A and B in the external field $\mathbf{F}^e$ are determined self-consistently, and then $\Delta\alpha^{ind}$ is derived from the equation

$$lim_{\mathbf{F}^e \to 0} \partial(\mu_\alpha^A + \mu_\alpha^B) / \partial F_\beta^e = \alpha_{\alpha\beta}^A + \alpha_{\alpha\beta}^B + \Delta\alpha_{\alpha\beta}^{ind}. \quad (1)$$

The static local field $\mathbf{F}$ polarizing A is related to $\mathbf{F}^e$,and to the dipole μ^B, quadrupole Θ^B, and octopole Ω^B of molecule B by

$$F_\alpha = F_\alpha^e + T_{\alpha\beta}(\mathbf{R})\mu_\beta^B + 1/3\ T_{\alpha\beta\gamma}(\mathbf{R})\Theta_{\beta\gamma}^B + 1/15\ T_{\alpha\beta\gamma\delta}(\mathbf{R})\Omega_{\beta\gamma\delta}^B + \cdots, \quad (2)$$

where $\mathbf{R}$ is the vector from the origin in molecule A to the origin in molecule B, $T_{\alpha\beta}(\mathbf{R}) = \nabla_\alpha\nabla_\beta(R^{-1})$, $T_{\alpha\beta\gamma}(\mathbf{R}) = \nabla_\alpha\nabla_\beta\nabla_\gamma(R^{-1})$, and $T_{\alpha\beta\gamma\delta}(\mathbf{R}) = \nabla_\alpha\nabla_\beta\nabla_\gamma\nabla_\delta(R^{-1})$. The Einstein convention of summation over repeated Greek suffixes is followed in Eq. (2) and below. For a molecule of $D_{\infty h}$ symmetry in the local field $\mathbf{F}$, the induced dipole moment is related to the field and field gradients at the molecular center of symmetry by

$$\mu_\alpha = \alpha_{\alpha\beta}F_\beta + 1/6\,\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta + 1/15\,E_{\alpha,\beta\gamma\delta}F''_{\beta\gamma\delta} + 1/3\,B_{\alpha,\beta,\gamma\delta}F_\beta F'_{\gamma\delta} + \cdots, \quad (3)$$

where α is the dipole polarizability of the isolated (unperturbed) molecule, γ is the second hyperpolarizability, E is the dipole-octopole polarizability [74], and B is the dipole-dipole-quadrupole hyperpolarizability [74]. The quadrupole and octopole moments of the molecule satisfy

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$$\Theta_{\alpha\beta} = \Theta^{0}_{\alpha\beta} + C_{\alpha\beta,\gamma\delta}F'_{\gamma\delta} + 1/2\ B_{\gamma,\delta,\alpha\beta}F_{\gamma}F_{\delta} + \cdots, \tag{4}$$

$$\Omega_{\alpha\beta\gamma} = E_{\delta,\alpha\beta\gamma}F_{\delta} + \cdots. \tag{5}$$

In Eq. (4), $\Theta^{0}_{\alpha\beta}$ denotes the permanent molecular quadrupole moment, and C is the quadrupole polarizability. The self-consistent solution of Eqs. (1)-(5) yields the induction term [52]

$$\begin{aligned}\Delta\alpha^{ind}_{\alpha\beta} = (1+\wp^{AB})[\alpha^{A}_{\alpha\gamma}\ T_{\gamma\delta}(\mathbf{R})\alpha^{B}_{\delta\beta} + \alpha^{A}_{\alpha\gamma}\ T_{\gamma\delta}(\mathbf{R})\alpha^{B}_{\delta\varepsilon}\ T_{\varepsilon\phi}(\mathbf{R})\alpha^{A}_{\phi\beta} \\ +1/15\,\alpha^{A}_{\alpha\gamma}T_{\gamma\delta\varepsilon\phi}(\mathbf{R})\,E^{B}_{\beta,\delta\varepsilon\phi} + 1/15\,E^{A}_{\alpha,\gamma\delta\varepsilon}T_{\gamma\delta\varepsilon\phi}(\mathbf{R})\alpha^{B}_{\phi\beta} \\ -1/9\,B^{A}_{\alpha,\beta,\gamma\delta}T_{\gamma\delta\varepsilon\phi}(\mathbf{R})\Theta^{0B}_{\varepsilon\phi}].\end{aligned} \tag{6}$$

where $\wp^{AB}$ permutes the labels of molecules A and B in the expression that follows. The first two terms in Eq. (6) give the first- and second-order dipole-induced-dipoles. As noted in Section 3.1, the E-tensor terms in Eq. (6) stem from higher-multipole induction and nonuniformity in the local field, while the B-tensor terms stem from hyperpolarization. The first-order DID terms vary as R^{-3}, E and B terms as R^{-5}, and second-order DID terms as R^{-6}.

At order R^{-6}, dispersion forces also contribute to $\Delta\alpha$, because the dispersion energy of the $A\cdots B$ pair changes in the field $\mathbf{F}^{e}$:

$$\Delta\alpha^{disp}_{\alpha\beta} = -lim_{\mathbf{F}^{e}\to 0}\ \partial^{2}E^{disp}(\mathbf{F}^{e})/\partial F^{e}_{\alpha}\,\partial F^{e}_{\beta}. \tag{7}$$

According to the reaction-field theory for E^{disp} [104-106], spontaneous, quantum mechanical fluctuations in the charge density of molecule A produce a field that polarizes B; the induced polarization of B then creates a reaction field at A. The resulting energy change in A depends upon correlations of the fluctuating polarization within A, which are related to the imaginary part of the polarizability density [104] of A via the fluctuation-dissipation theorem [107]. Similarly, fluctuations in the charge density of B polarize A, leadin

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leading to a reaction field at B, and a second term in the energy change. The external field affects the dispersion energy because $\mathbf{F}^e$ alters the response of each molecule to the fluctuating field of its neighbor, due to hyperpolarization effects [53]; and $\mathbf{F}^e$ also alters the correlations of the spontaneous charge-density fluctuations in each molecule [55]. To leading order, the dispersion term in $\Delta\alpha$ is

$$\Delta\alpha_{\alpha\beta}^{\mathrm{disp}} = \hbar / 2\pi\,(1+\wp^{AB}) \int_0^\infty d\omega\ T_{\gamma\delta}(\mathbf{R})\gamma^B_{\delta\varepsilon\alpha\beta}(i\omega,0,0)T_{\varepsilon\phi}(\mathbf{R})\alpha^A_{\phi\gamma}(i\omega), \tag{8}$$

where $\alpha(i\omega)$ is the polarizability at the imaginary frequency $i\omega$, and $\gamma(i\omega, 0, 0)$ is the imaginary-frequency hyperpolarizability. Through order R^{-6}, the total interaction-induced change in polarizability is the sum of $\Delta\alpha^{\mathrm{ind}}$ from Eq. (6) and $\Delta\alpha^{\mathrm{disp}}$ from Eq. (8).

The polarizability of the interacting molecules A and B is a second-rank Cartesian tensor, with spherical tensor components of ranks 0 and 2. The components are related by [108, 109]:

$$\Delta\alpha_0^0 = 1/\sqrt{3}\,(\Delta\alpha_{XX} + \Delta\alpha_{YY} + \Delta\alpha_{ZZ}), \tag{9}$$

$$\Delta\alpha_2^0 = 1/\sqrt{6}\,(2\Delta\alpha_{ZZ} - \Delta\alpha_{XX} - \Delta\alpha_{YY}), \tag{10}$$

$$\Delta\alpha_2^{\pm1} = \mp 1/2\,[(\Delta\alpha_{XZ} + \Delta\alpha_{ZX}) \pm i(\Delta\alpha_{YZ} + \Delta\alpha_{ZY})], \tag{11}$$

and

$$\Delta\alpha_2^{\pm2} = 1/2\,[(\Delta\alpha_{XX} - \Delta\alpha_{YY}) \pm i(\Delta\alpha_{XY} + \Delta\alpha_{YX})]. \tag{12}$$

In quantum mechanical line shape analyses of collision-induced Rayleigh and rototranslational Raman scattering, the pair polarizability $\Delta\alpha$ is needed in a symmetry-adapted form in terms of the spherical harmonics of the orientation angle Ω^R of the intermolecular vector $\mathbf{R}$ and the orientation angles Ω^A and Ω^B of the axes of molecules A and B. Since $\Delta\alpha_0^0$ is a scalar, it must be obtained by scalar coupling of spherical tensor functions of Ω^A, Ω^B, and Ω^R [71, 93, 110]:

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$$\Delta\alpha_0^0(\mathbf{r}^A,\mathbf{r}^B,\mathbf{R}) = (4\pi)^{3/2}/\sqrt{3}\sum A_{0\lambda_A\lambda_B\lambda L}(r^A,r^B,R)Y_{\lambda_A}^{m_A}(\Omega^A)Y_{\lambda_B}^{m_B}(\Omega^B)$$

$$\times Y_L^{-m}(\Omega^R)\langle\lambda_A\,\lambda_B\,m_A\,m_B|\lambda\,m\rangle\langle\lambda\,L\,m\;-m|0\,0\rangle, \qquad (13)$$

where the summation runs over λ_A, λ_B, λ, L, m_A, m_B, and m. Similarly [71, 93, 110]

$$\Delta\alpha_2^M(\mathbf{r}^A,\mathbf{r}^B,\mathbf{R}) = (4\pi)^{3/2}/\sqrt{3}\sum A_{2\lambda_A\lambda_B\lambda L}(r^A,r^B,R)Y_{\lambda_A}^{m_A}(\Omega^A)Y_{\lambda_B}^{m_B}(\Omega^B)$$

$$\times Y_L^{M-m}(\Omega^R)\langle\lambda_A\,\lambda_B\,m_A\,m_B|\lambda\,m\rangle\langle\lambda\,L\,m\,M-m|2\,M\rangle \qquad (14)$$

with the summation running over the same indices as in Eq. (13). In these equations, the Clebsch-Gordan coefficients are denoted by $\langle\lambda_1\,\lambda_2\,m_1\,m_2|\lambda_3\,m_3\rangle$, and M in Eq. (14) ranges from -2 to 2. This work gives the dependence of $A_{0\lambda_A\lambda_B\lambda L}$ and $A_{2\lambda_A\lambda_B\lambda L}$ on the intermolecular separation R, with the bond lengths held fixed at the vibrationally averaged values [111].

To cast $\Delta\alpha$ from Eqs. (6) and (8) into symmetry-adapted form, it is necessary to separate the multipoles and polarizabilities of A and B into components of different spherical tensor ranks [112, 113]. The polarizability and quadrupole satisfy

$$\alpha_{\alpha\beta} = \bar{\alpha}\,\delta_{\alpha\beta} + 1/3\,(\alpha_{\Uparrow} - \alpha_{\perp})(3\hat{r}_\alpha\hat{r}_\beta - \delta_{\alpha\beta}) \qquad (15)$$

and

$$\Theta_{\alpha\beta} = 1/2\,\Theta(3\hat{r}_\alpha\hat{r}_\beta - \delta_{\alpha\beta}), \qquad (16)$$

in terms of the direction cosine $\hat{r}_\alpha$ between the molecular symmetry axis $\hat{r}$ and the α axis of the space-fixed frame; $\alpha_{\Uparrow}$ is the polarizability for fields along the molecular axis $\hat{r}$, $\alpha_\perp$ for fields perpendicular to the molecular axis, and $\bar{\alpha} = (\alpha_{\Uparrow} + 2\alpha_\perp)/3$. The susceptibilities E, B, and γ are fourth-rank Cartesian tensors, and each has the form [52, 68]

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$$P_{\alpha\beta\gamma\delta} = P_1\,\delta_{\alpha\beta}\,\delta_{\gamma\delta} + P_2\,(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) + P_3\,(3\,\hat{r}_\alpha\,\hat{r}_\beta - \delta_{\alpha\beta})\delta_{\gamma\delta}$$

$$+P_4\,(3\,\hat{r}_\gamma\,\hat{r}_\delta - \delta_{\gamma\delta})\delta_{\alpha\beta} + P_5[(3\,\hat{r}_\alpha\,\hat{r}_\gamma - \delta_{\alpha\gamma})\delta_{\beta\delta} + (3\,\hat{r}_\alpha\,\hat{r}_\delta - \delta_{\alpha\delta})\delta_{\beta\gamma}]$$

$$+P_6[(3\,\hat{r}_\beta\,\hat{r}_\gamma - \delta_{\beta\gamma})\delta_{\alpha\delta} + (3\,\hat{r}_\beta\,\hat{r}_\delta - \delta_{\beta\delta})\delta_{\alpha\gamma}]$$

$$+P_7[35\,\hat{r}_\alpha\,\hat{r}_\beta\,\hat{r}_\gamma\,\hat{r}_\delta - 5(\hat{r}_\alpha\,\hat{r}_\beta\,\delta_{\gamma\delta} + \hat{r}_\alpha\,\hat{r}_\gamma\,\delta_{\beta\delta} + \hat{r}_\alpha\,\hat{r}_\delta\,\delta_{\beta\gamma} + \hat{r}_\beta\,\hat{r}_\gamma\,\delta_{\alpha\delta}$$

$$+\hat{r}_\beta\,\hat{r}_\delta\,\delta_{\alpha\gamma} + \hat{r}_\gamma\,\hat{r}_\delta\,\delta_{\alpha\beta}) + \delta_{\alpha\beta}\,\delta_{\gamma\delta} + \delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}]. \qquad (17)$$

E has spherical tensor components of ranks 2 and 4 only, but B and γ have spherical tensor components of ranks 0, 2, and 4. For $\gamma(i\omega,0,0)$ of a linear molecule, the seven coefficients $P_1 \equiv \gamma_1(i\omega,0,0)$ through $P_7 \equiv \gamma_7(i\omega,0,0)$ are linear combinations of the six independent components of the hyperpolarizability in the molecule-fixed frame:

$$\gamma_j(i\omega,0,0) = a_j\,\gamma_{zzzz}(i\omega,0,0) + b_j\,\gamma_{zzxx}(i\omega,0,0) + c_j\,\gamma_{xxzz}(i\omega,0,0)$$

$$+d_j\,\gamma_{xzxz}(i\omega,0,0) + e_j\,\gamma_{xxyy}(i\omega,0,0) + f_j\,\gamma_{xxxx}(i\omega,0,0) \qquad (18)$$

with expansion coefficients a_j-f_j listed in Table 3.1.

Similarly, the seven coefficients $P_1 \equiv B_1$ through $P_7 \equiv B_7$ are linear combinations of the four independent components of the static B tensor in the molecule-fixed frame for linear molecules:

$$B_j = a_j\,B_{z,z,zz} + b_j\,B_{x,z,xz} + c_j\,B_{x,x,zz} + d_j\,B_{x,x,xx} \qquad (19)$$

with expansion coefficients listed in Table 3.2. For both γ and B, $P_5 \equiv P_6$, but this does not hold for the dipole-octopole polarizability E. For linear molecules, E satisfies Eq. (17) with $E_1 = E_2 = 0$,

$$E_3 = E_5 = 1/63(8\,E_{x,xxx} - 3\,E_{z,zzz}), \qquad (20a)$$

$$E_4 = E_6 = 5/126(3\,E_{z,zzz} - 8\,E_{x,xxx}), \qquad (20b)$$

Table 3.1

γ_j	
γ_1	1
γ_2	1
γ_3	
γ_4	
γ_5	
γ_6	
γ_7	

Table 3

γ_j
B_1
B_2
B_3
B_4
B_5
B_6
B_7

Table 3.1. Expansion coefficients for γ-tensor components, Eq. (18).

γ_j	a_j	b_j	c_j	d_j	e_j	f_j
γ_1	1/15	4/15	4/15	-4/15	1/3	1/15
γ_2	1/15	-1/15	-1/15	2/5	-1/6	7/30
γ_3	1/21	2/7	-1/21	-4/21	-1/3	1/21
γ_4	1/21	-1/21	2/7	-4/21	-1/3	1/21
γ_5	1/21	-1/21	-1/21	1/7	1/6	-5/42
γ_6	1/21	-1/21	-1/21	1/7	1/6	-5/42
γ_7	1/35	-1/35	-1/35	-4/35	0	1/35

Table 3.2. Expansion coefficients for B-tensor components, Eq. (19).

γ_j	a_j	b_j	c_j	d_j
B_1	-1/15	-4/15	-1/15	-4/15
B_2	1/10	2/5	1/10	2/5
B_3	-2/21	-4/21	2/7	8/21
B_4	1/14	-4/21	13/21	8/21
B_5	1/14	1/7	-3/14	-2/7
B_6	1/14	1/7	-3/14	-2/7
B_7	3/70	-4/35	-1/35	1/35

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$$E_7 = 1/14(E_{z,zzz} + 2E_{x,xxx}). \tag{20c}$$

For each of the polarization mechanisms in $\Delta\alpha$, this work has yielded relations among the terms in the coefficients $A_{0\lambda_A\lambda_B\lambda L}$ and $A_{2\lambda_A\lambda_B\lambda L}$ by use of angular momentum algebra, as in the work by Bancewicz [58] on DID interactions. The analysis is illustrated for the E-tensor term $\alpha^A_{\alpha\gamma} T_{\gamma\delta\varepsilon\phi} E^B_{\beta,\delta\varepsilon\phi}$, which stems from the dipole-octopole interaction between molecules A and B, and interactions of both A and B with the external field. For clarity in Eqs. (21)-(23) below, only the spherical-tensor recoupling scheme is shown for the multipole operators of A and B, and the T tensor. The contribution of the α-E term to the Jth rank part of $\Delta\alpha$ transforms as

$$T_{\alpha E} = [\mu^{A(1)} \otimes \{[\mu^{A(1)} \otimes (T^{(4)} \otimes \Omega^{B(3)})^{(1)}]^{(0)} \otimes \mu^{B(1)}\}^{(1)}]^{(J)}, \tag{21}$$

where $\otimes$ denotes the direct product. Then

$$T_{\alpha E} = \sum_h \Pi_h (-1)^h / 3\, [\mu^{A(1)} \otimes \{\mu^{A(1)} \otimes [(T^{(4)} \otimes \Omega^{B(3)})^{(1)} \otimes \mu^{B(1)}]^{(h)}\}^{(1)}]^{(J)} \tag{22}$$

with the notation $\Pi_{ab\cdots z} = [(2a+1)(2b+1)\cdots(2z+1)]^{1/2}$. Further analysis in terms of the 6-j and 9-j symbols gives

$$T_{\alpha E} = \sum_h \sum_k \Pi_{hk} 1/\sqrt{3} \begin{Bmatrix} 4 & 3 & 1 \\ 1 & h & k \end{Bmatrix} [\mu^{A(1)} \otimes \{\mu^{A(1)} \otimes [T^{(4)} \otimes e^{B(k)}]^{(h)}\}^{(1)}]^{(J)}$$

$$= \sum_h \sum_j \sum_k \Pi_{hjk} (-1)^{J+h} \begin{Bmatrix} 4 & 3 & 1 \\ 1 & h & k \end{Bmatrix} \begin{Bmatrix} 1 & 1 & j \\ h & J & 1 \end{Bmatrix} \{a^{A(j)} \otimes [T^{(4)} \otimes e^{B(k)}]^{(h)}\}^{(J)}$$

$$= \sum_h \sum_j \sum_k \sum_\lambda (2h+1) \Pi_{jk\lambda} (-1)^j \begin{Bmatrix} 4 & 3 & 1 \\ 1 & h & k \end{Bmatrix} \begin{Bmatrix} 1 & 1 & j \\ h & J & 1 \end{Bmatrix} \begin{Bmatrix} j & k & \lambda \\ 4 & J & h \end{Bmatrix}$$

$$\times \{[a^{A(j)} \otimes e^{B(k)}]^{(\lambda)} \otimes T^{(4)}\}^{(J)}$$

$$= \sum_j \sum_k \sum_\lambda \Pi_{jk\lambda} (-1)^j \begin{Bmatrix} j & 1 & 1 \\ k & 3 & 1 \\ \lambda & 4 & J \end{Bmatrix} \{[a^{A(j)} \otimes e^{B(k)}]^{(\lambda)} \otimes T^{(4)}\}^{(J)}, \tag{23}$$

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where $a^{A(j)}$ denotes $(\mu^{A(1)} \otimes \mu^{A(1)})^{(j)}$, and $e^{B(k)}$ denotes $(\Omega^{B(3)} \otimes \mu^{B(1)})^{(k)}$. In deriving Eq. (23), Eqs. (4.3), (4.9), (4.19), and (4.24) of Ref. 109 have been used. Equation (23) for the operator structure corresponds to an expression for $\Delta\alpha$ obtained by inserting the reduced resolvent operators, the ground-state bra and ket, and a numerical prefactor, and accounting for different operator-ordering possibilities. In the equation for $\Delta\alpha$, $a^{A(j)}$ and $e^{B(k)}$ become $\alpha^{A(j)}$ and $E^{B(k)}$, respectively.

For species of $D_{\infty h}$ symmetry, when the q = 0 components of the spherical tensors $P(k,q)$ are the only nonzero components in the molecule-fixed frame, the spherical tensor components $P(k,q')$ in the space-fixed frame satisfy [see, e.g., Ref. 109]

$$P(k,q') = D^{k}_{q'0}{}^{*}\, P(k,q=0) = [4\pi/(2k+1)]^{1/2}\, Y_k^{q'}(\theta,\phi) P(k,q=0), \qquad (24)$$

where $D^{k}_{q'0}{}^{*}$ is the conjugate of the Wigner rotation matrix.

From Eqs. (23) and (24), the α-E term in $\Delta\alpha_J^M$ satisfies

$$T(\alpha\text{-}E) = \sum_j \sum_k \sum_\lambda \sum_{p_1} \sum_{p_2} (4\pi)^{3/2} c_J^{\alpha E} \Pi_\lambda (-1)^j / 3 \begin{Bmatrix} j & 1 & 1 \\ k & 3 & 1 \\ \lambda & 4 & J \end{Bmatrix} \alpha^A(j,0) E^B(k,0)$$
$$\times T(4,0) Y_j^{p_1}(\theta^A,\phi^A) Y_k^{p_2}(\theta^B,\phi^B) Y_4^{M-(p_1+p_2)}(\theta^R,\phi^R)$$
$$\times \langle j k p_1 p_2 | \lambda (p_1+p_2) \rangle \langle \lambda 4 (p_1+p_2)[M-(p_1+p_2)] | J M \rangle. \qquad (25)$$

In Eq. (25), $\alpha^A(0,0) = -\sqrt{3}\,\bar{\alpha}^A$ and $\alpha^A(2,0) = 2/\sqrt{6}\,(\alpha^A_{\Uparrow} - \alpha^A_{\perp})$. The relation for $\alpha^A(2,0)$ is consistent with Eq. (10); but $\alpha^A(0,0)$ differs from Eq. (9), where α_0^0 is defined by $1/\sqrt{3}\,\alpha_{\varepsilon\varepsilon}$. This reflects the phase difference between the ordinary scalar product $C^{(k)} \cdot D^{(k)}$ of two tensors C and D of rank k, vs. the rank 0 component of the direct product [109]:

$$[C^{(k)} \otimes D^{(k)}]^{(0)} = (-1)^k (2k+1)^{-1/2}\, C^{(k)} \cdot D^{(k)}. \qquad (26)$$

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The components of the E-tensor in Eq. (25) satisfy $E^B(0,0) = 0$, $E^B(2,0) = 3\sqrt{21}\,E^B_3$, and $E^B(4,0) = 4\sqrt{7}\,E^B_7$. Also $T(4,0) = 6\sqrt{70}\,R^{-5}$, and $c_0^{\alpha E} = -c_2^{\alpha E} = -\sqrt{10}/5$. The ratio of -1 between $c_0^{\alpha E}$ and $c_2^{\alpha E}$ stems from the phase difference noted above. Then from Eq. (25), the $\alpha^A - E^B$ contributions to the polarizability coefficients $A^{\alpha E}_{Jjk\lambda 4}$ are given by

$$A^{\alpha E}_{Jjk\lambda 4} = 4\sqrt{21}\,(2\lambda+1)^{1/2}(-1)^{1+J/2}\begin{Bmatrix} j & 1 & 1 \\ k & 3 & 1 \\ \lambda & 4 & J \end{Bmatrix}\alpha^A(j,0)E^B(k,0)R^{-5}. \tag{27}$$

In deriving Eq. (27), it has been assumed that j is even, for nonzero $\alpha^A(j,0)$; i.e., the antisymmetric part of the polarizability tensor has been neglected. The $E^A - \alpha^B$ contributions are given by

$$A^{E\alpha}_{Jkj\lambda 4} = (-1)^{\lambda}\,\wp^{AB}A^{\alpha E}_{Jjk\lambda 4}. \tag{28}$$

The results for the E-tensor terms are consistent with those of Bancewicz, Glaz, and Kielich [60]; the coefficients depending on the second-rank part of the E-tensor agree with results given by Borysow and Moraldi [51].

A similar analysis for the first-order DID terms gives

$$A^{\alpha\alpha}_{Jjk\lambda 2} = 6\sqrt{2}\,(2\lambda+1)^{1/2}(-1)^{1+J/2}\begin{Bmatrix} j & 1 & 1 \\ k & 1 & 1 \\ \lambda & 2 & J \end{Bmatrix}\alpha^A(j,0)\alpha^B(k,0)R^{-3}. \tag{29}$$

Equation (29) is identical to the result derived by Bancewicz [58].

The $B^A - \Theta^B$ terms satisfy

$$A^{B\Theta}_{Jj2\lambda 4} = -\sqrt{42}\,[(2\lambda+1)/(2J+1)]^{1/2}(-1)^{1+J/2}\begin{Bmatrix} j & 2 & \lambda \\ 4 & J & 2 \end{Bmatrix}B^A(J;j,0)\Theta^B R^{-5}, \tag{30}$$

where the B-tensor components $B^A(J;j,0)$ are given by

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$$B^A(0;2,0) = -2/\sqrt{3}\,(3B_4^A + 4B_5^A), \tag{31a}$$

$$B^A(2;0,0) = 2\sqrt{10/3}\,B_2^A, \tag{31b}$$

$$B^A(2;2,0) = -4/3\sqrt{21}\,B_5^A, \tag{31c}$$

and

$$B^A(2;4,0) = 140/\sqrt{105}\;B_7^A. \tag{31d}$$

Equations (31a)-(31d) follow from the observation that the tensor operators which appear in $B^A(J;j,0)$ have the structure $[(\mu^{A(1)} \otimes \mu^{A(1)})^{(J)} \otimes \Theta^{A(2)}]^{(j)}$. The $\Theta^A - B^B$ coefficients satisfy

$$A_{J2j\lambda 4}^{\Theta B} = (-1)^{\lambda}\,\wp^{AB} A_{Jj2\lambda 4}^{B\Theta}. \tag{32}$$

The second-order DID and dispersion terms are both derived from perturbation expressions with an underlying tensor-operator structure exemplified by

$$T^{AAB} = \{\mu^{A(1)} \otimes [\{[\mu^{A(1)} \otimes (T^{(2)} \otimes \mu^{B(1)})^{(1)}]^{(0)} \otimes [\mu^{A(1)} \otimes (T^{(2)} \otimes \mu^{B(1)})^{(1)}]^{(0)}\}^{(0)} \otimes \mu^{A(1)}]^{(1)}\}^{(J)}. \tag{33}$$

Coupling the four dipole operators for molecule A to produce two factors of polarizability of A gives a second-order DID term, while coupling to produce the hyperpolarizability of A gives a dispersion term.

The coefficients for the second-order DID terms of the type $\alpha^A\alpha^B\alpha^A$ are given by

$$A_{Jjk\lambda L}^{ABA} = (-1)^{1+J/2}\,30\sqrt{3}\sum_a\sum_b\sum_n (2n+1)\Pi_{ab\lambda}\langle a\,b\,0\,0|j\,0\rangle\langle 2\,2\,0\,0|L\,0\rangle \times \begin{Bmatrix} 1 & 1 & 2 \\ 1 & 1 & 2 \\ k & n & L \end{Bmatrix} \begin{Bmatrix} 1 & 1 & a \\ 1 & 1 & b \\ n & J & j \end{Bmatrix} \begin{Bmatrix} j & k & \lambda \\ L & J & n \end{Bmatrix} \alpha^A(a,0)\alpha^A(b,0)\alpha^B(k,0)R^{-6}; \tag{34}$$

correspondingly, the coefficients for the $\alpha^B\alpha^A\alpha^B$ terms satisfy

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$$A^{BAB}_{Jkj\lambda L} = (-1)^{\lambda}\, \wp^{AB} A^{ABA}_{Jjk\lambda L}. \tag{35}$$

The second-order DID coefficients agree with the results of Bancewicz [58].

For the γ^A - α^B dispersion coefficients, the result is

$$A^{\gamma\alpha}_{Jjk\lambda L} = (-1)^{1+J/2}\, 15\sqrt{3} \sum_{a} (\Pi_{\lambda a} / \Pi_J) \begin{Bmatrix} 2 & 1 & 1 \\ 2 & 1 & 1 \\ L & k & a \end{Bmatrix} \begin{Bmatrix} j & k & \lambda \\ L & J & a \end{Bmatrix} \langle 2200 | L\,0 \rangle$$

$$\times \hbar / \pi \int_0^{\infty} \gamma^A(a, J; j, 0 | i\omega, 0, 0)\, \alpha^B(k, 0; i\omega)\, d\omega\, R^{-6}, \tag{36}$$

where

$$\gamma^A(0,0;0,0|i\omega,0,0) = 3\gamma_1^A(i\omega,0,0) + 2\gamma_2^A(i\omega,0,0), \tag{37a}$$

$$\gamma^A(2,2;0,0|i\omega,0,0) = 2\sqrt{5}\,\gamma_2^A(i\omega,0,0), \tag{37b}$$

$$\gamma^A(2,0;2,0|i\omega,0,0) = -\sqrt{2}\,[3\gamma_3^A(i\omega,0,0) + 4\gamma_5^A(i\omega,0,0)], \tag{37c}$$

$$\gamma^A(0,2;2,0|i\omega,0,0) = -\sqrt{2}\,[3\gamma_4^A(i\omega,0,0) + 4\gamma_5^A(i\omega,0,0)], \tag{37d}$$

$$\gamma^A(2,2;2,0|i\omega,0,0) = -2\sqrt{14}\,\gamma_5^A(i\omega,0,0), \tag{37e}$$

and

$$\gamma^A(2,2;4,0|i\omega,0,0) = 2\sqrt{70}\,\gamma_7^A(i\omega,0,0). \tag{37f}$$

In Eq. (36), $\alpha^B(k,0;i\omega)$ is the (k, 0) spherical component of $\alpha^B(i\omega)$. The results in Eqs. (37a)-(37f) for $\gamma^A(a,J;j,0|i\omega,0,0)$ have been obtained from the dipole operator coupling $\{[\mu^{A(1)} \otimes \mu^{A(1)}]^{(a)} \otimes [\mu^{A(1)} \otimes \mu^{A(1)}]^{(J)}\}^{(j)}$. The α^A-γ^B dispersion terms satisfy

$$A^{\alpha\gamma}_{Jkj\lambda L} = (-1)^{\lambda}\, \wp^{AB} A^{\gamma\alpha}_{Jjk\lambda L}. \tag{38}$$

The coefficients in Eqs. (13) and (14) have been evaluated by direct integration using *Mathematica* [114], and by use of Eqs. (27)-(38), with identical results. In Sec. 3.3, explicit expressions for $\Delta\alpha_0^0$ are given and their spectroscopic implications are discussed; results for $\Delta\alpha_2^M$ and their spectroscopic implications are given in Sec. 3.4.

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3.3 Collision-Induced Changes in Scalar Polarizabilities

This section provides results for the coefficients $A_{0\lambda_A\lambda_B\lambda L}$ that determine the induced changes in scalar polarizabilities. Since $\Delta\alpha_0^0$ in Eq. (13) contains terms with nonzero λ_A and/or λ_B, isotropic rototranslational Raman scattering with $\Delta J = \pm 2$ and ± 4 can occur as a purely collision-induced phenomenon.

For a pair at a fixed separation R, the change in effective polarizability averaged over the orientations of $\hat{\mathbf{r}}^A$, $\hat{\mathbf{r}}^B$, and $\mathbf{R}$ is $A_{00000}/3$. Through order R^{-6}, there are two contributions to A_{00000}, one from second-order DID interactions and the other from dispersion

$$A_{00000} = (1+\wp^{AB})\{6\bar{\alpha}^A\bar{\alpha}^B\bar{\alpha}^A + 4/3\,(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)\bar{\alpha}^B(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)$$
$$+3\hbar/\pi\int_0^{\infty} d\omega\,\bar{\alpha}^B(i\omega)[3\gamma_1^A(i\omega,0,0) + 2\gamma_2^A(i\omega,0,0)]\}R^{-6}. \qquad (39)$$

Both DID and dispersion effects increase the effective polarizability of the pair. The coefficient A_{00000} accounts for isotropic, collision-induced Rayleigh scattering [24].

Isotropic scattering with a change in the rotational state of one or both molecules is produced by the polarization effects in nine other coefficients, through order R^{-6}. The coefficient A_{02022} is associated with transitions on molecule A only

$$A_{02022} = 4\sqrt{5}/5\,\bar{\alpha}^B(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)R^{-3} + 2\sqrt{5}/5\,\bar{\alpha}^B(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)(2\bar{\alpha}^A + \bar{\alpha}^B)R^{-6}$$
$$+2\sqrt{5}/15\,(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)[\bar{\alpha}^B(\alpha_{\Uparrow}^A - \alpha_{\perp}^A) + 2/3\,(\alpha_{\Uparrow}^B - \alpha_{\perp}^B)^2]R^{-6}$$
$$+\sqrt{5}\hbar/(5\pi)\,\{\int_0^{\infty} d\omega\,[3\gamma_1^B(i\omega,0,0) + 2\gamma_2^B(i\omega,0,0)][\alpha_{\Uparrow}^A(i\omega) - \alpha_{\perp}^A(i\omega)]$$
$$+3\int_0^{\infty} d\omega\,[3\gamma_3^A(i\omega,0,0) + 4\gamma_5^A(i\omega,0,0)]\bar{\alpha}^B(i\omega)\}R^{-6}. \qquad (40)$$

The set of coefficients A_{022LL} with L=0, 2, or 4 can produce "double transitions", i.e., simultaneous transitions in the rotational Raman spectrum [110]; for these coefficients, the associate

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associated selection rules are $\Delta J = \pm 2$ for each molecule (if the anisotropic terms in the interaction potential are neglected). The coefficients A_{022LL} satisfy

$$A_{022LL} = (1+\wp^{AB})[-\sqrt{14}/15\,\delta_{L2}(\alpha_{\Uparrow}^{A}-\alpha_{\perp}^{A})(\alpha_{\Uparrow}^{B}-\alpha_{\perp}^{B})R^{-3} + 2\sqrt{70}/5\,\delta_{L4}$$

$$[2/21(\alpha_{\Uparrow}^{A}-\alpha_{\perp}^{A})(3E_{z,zzz}^{B}-8E_{x,xxx}^{B}) - \Theta^{A0}(3B_{4}^{B}+4B_{5}^{B})]R^{-5}$$

$$+c_{L}\{2/9(\alpha_{\Uparrow}^{A}-\alpha_{\perp}^{A})(\alpha_{\Uparrow}^{B}-\alpha_{\perp}^{B})[6\,\overline{\alpha}^{A}+(\alpha_{\Uparrow}^{A}-\alpha_{\perp}^{A})]$$

$$+\hbar/\pi\int_{0}^{\infty}d\omega\,[3\gamma_{3}^{A}(i\omega,0,0)+4\gamma_{5}^{A}(i\omega,0,0)][\alpha_{\Uparrow}^{B}(i\omega)-\alpha_{\perp}^{B}(i\omega)]\}R^{-6}]$$

(41)

with $c_0 = \sqrt{5}/25$, $c_2 = \sqrt{14}/35$, and $c_4 = 18\sqrt{70}/175$.

The E-tensor polarization mechanisms give the only nonzero contributions to the coefficients $A_{04\lambda_B\lambda L}$, through order R^{-6}

$$A_{04044} = 8/3\,\overline{\alpha}^{B}(E_{z,zzz}^{A}+2E_{x,xxx}^{A})R^{-5}, \tag{42}$$

$$A_{04244} = -4\sqrt{77}/63\,(\alpha_{\Uparrow}^{B}-\alpha_{\perp}^{B})(E_{z,zzz}^{A}+2E_{x,xxx}^{A})R^{-5}. \tag{43}$$

To order R^{-6} there are three other nonvanishing coefficients in Equation (13) given by $A_{00222} = \wp^{AB}A_{02022}$, $A_{00444} = \wp^{AB}A_{04044}$, and $A_{02444} = \wp^{AB}A_{04244}$.

First-order DID effects generally dominate in collision-induced light scattering spectra, unless the DID coefficients vanish due to symmetry. For changes in the scalar polarizability, first-order DID terms appear in A_{02022}, A_{02222}, and A_{00222} only; A_{02022} and A_{00222} are associated with single transitions with $\Delta J = \pm 2$ for either molecule A or B and A_{02222} with double transitions having $\Delta J = \pm 2$ for both molecules (neglecting the anisotropy of the pair potential). Second-order DID and dispersion effects also appear in A_{02022}, A_{02222}, and A_{00222}. Hence the net contribution of these terms to the scattering intensity is enhanced by the existence of cross-products with the first-order DID effect. E-tensor terms in $\Delta\alpha_0^0$ contribute significantly to scattering in the spectral wings [35], beca

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because they produce transitions with $\Delta J = \pm 4$ for one molecule and ΔJ up to ± 2 for the other. These effects should be easier to distinguish in the isotropic scattering spectra than effects of the other R^{-5} or R^{-6} polarization mechanisms. The leading long-range contributions to isotropic, pure translational (Rayleigh) scattering stem from second-order DID and dispersion terms. Experimental spectra are expected to show substantial short-range overlap contributions to A_{00000}, particularly for lighter, less polarizable species.

3.4 Collision-Induced Changes in Anisotropic Polarizabilities

The collision-induced change in the second-rank tensor component of the polarizability $\Delta\alpha_2^M$ determines the spectra for depolarized rototranslational Raman scattering by $A\cdots B$ pairs. Through order R^{-6}, $\Delta\alpha_2^M$ depends on a total of 38 coefficients $A_{2\lambda_A\lambda_B\lambda L}$.

The collision-induced depolarized Rayleigh spectrum (pure translational light scattering) is determined by the collision-induced anisotropic polarizability $\Delta\alpha_2^M$, averaged isotropically over the orientations of molecules A and B. The averaging gives

$$\Delta\alpha_2^M = (4\pi/3)^{1/2} A_{20002} Y_2^M(\Omega^R) \tag{44}$$

with

$$\begin{aligned} A_{20002} = {} & 6\sqrt{10}/5\,\overline{\alpha}^A\overline{\alpha}^B R^{-3} + (1+\wp^{AB})[3\sqrt{10}/5\,\overline{\alpha}^A\overline{\alpha}^B\overline{\alpha}^A + \sqrt{10}/75 \\ & \times(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)\overline{\alpha}^B(\alpha_{\Uparrow}^A - \alpha_{\perp}^A) + 3\sqrt{10}/5\,\hbar/\pi \\ & \times\int_0^\infty d\omega\, \gamma_2^A(i\omega,0,0)\overline{\alpha}^B(i\omega)]R^{-6}. \end{aligned} \tag{45}$$

From Eq. (45), the first-order DID interactions give the dominant long-range contribution to the polarizability anisotropy of a colliding pair, averaged over the orientations of $\hat{\mathbf{r}}^A$ and $\hat{\mathbf{r}}^B$.

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The remaining coefficients in $\Delta\alpha_2^M$ are categorized below according to the selection rules for rotational transitions they generate, if the anisotropy of the interaction potential is neglected. Three coefficients A_{2202L} generate rotational transitions of molecule A only, with ΔJ limited to ± 2. These are given by:

$$
\begin{aligned}
A_{2202L} = {} & -2\sqrt{7}/5\,\delta_{L2}\,\bar{\alpha}^B(\alpha^A_{\Uparrow} - \alpha^A_{\perp})R^{-3} + 4\sqrt{35}/35\,\delta_{L4}[\bar{\alpha}^B(3E^A_{z,zzz} - 8E^A_{x,xxx}) \\
& - 7B^B_2\,\Theta^{A0}]R^{-5} + \{(\alpha^A_{\Uparrow} - \alpha^A_{\perp})\bar{\alpha}^B[a_L\bar{\alpha}^A + b_L\bar{\alpha}^B + c_L(\alpha^A_{\Uparrow} - \alpha^A_{\perp})] \\
& + d_L(\alpha^B_{\Uparrow} - \alpha^B_{\perp})(\alpha^A_{\Uparrow} - \alpha^A_{\perp})(\alpha^B_{\Uparrow} - \alpha^B_{\perp})\}R^{-6} \\
& + e_L\hbar/\pi\int_0^{\infty} d\omega\,\gamma^B_2(i\omega,0,0)[\alpha^A_{\Uparrow}(i\omega) - \alpha^A_{\perp}(i\omega)]R^{-6} \\
& + \hbar/\pi\int_0^{\infty} d\omega\,[9\sqrt{10}/5\,\delta_{L0}\gamma^A_4(i\omega,0,0) + f_L\,\gamma^A_5(i\omega,0,0)]\bar{\alpha}^B(i\omega)R^{-6},
\end{aligned}
\tag{46}
$$

with the coefficients a_L - f_L listed in Table 3.3.

Two coefficients generate single-molecule transitions of A, with ΔJ up to ± 4

$$
\begin{aligned}
A_{24042} = {} & [12\sqrt{35}/175\,\bar{\alpha}^B(\alpha^A_{\Uparrow} - \alpha^A_{\perp})^2 + 6\sqrt{35}\,\hbar/(5\pi) \\
& \times\int_0^{\infty} d\omega\,\gamma^A_7(i\omega,0,0)\bar{\alpha}^B(i\omega)]R^{-6},
\end{aligned}
\tag{47}
$$

and

$$
A_{24044} = -2\sqrt{154}/21\,\bar{\alpha}^B(E^A_{z,zzz} + 2E^A_{x,xxx})R^{-5}. \tag{48}
$$

The coefficients $A_{222\lambda L}$ are associated double transitions, with selection rules of ΔJ up to ± 2 for molecule A and simultaneously ΔJ up to ± 2 for molecule B

$$
\begin{aligned}
A_{222\lambda L} = {} & a_{\lambda L}(\alpha^A_{\Uparrow} - \alpha^A_{\perp})(\alpha^B_{\Uparrow} - \alpha^B_{\perp})R^{-3} + [(-1)^{\lambda} + \wp^{AB}][b_{\lambda L}B^A_5\Theta^{B0} \\
& - c_{\lambda L}(\alpha^A_{\Uparrow} - \alpha^A_{\perp})(3E^B_{z,zzz} - 8E^B_{x,xxx})]R^{-5} + [(-1)^{\lambda} + \wp^{AB}]
\end{aligned}
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$$\times\{(\alpha_{\Uparrow}^{A}-\alpha_{\perp}^{A})(\alpha_{\Uparrow}^{B}-\alpha_{\perp}^{B})[d_{\lambda L}\,\bar{\alpha}^{A}+e_{\lambda L}(\alpha_{\Uparrow}^{A}-\alpha_{\perp}^{A})]$$

$$+\hbar/\pi\int_{0}^{\infty}d\omega\,[f_{\lambda L}\gamma_{4}^{A}(i\omega,0,0)+g_{\lambda L}\gamma_{5}^{A}(i\omega,0,0)][\alpha_{\Uparrow}^{B}(i\omega)-\alpha_{\perp}^{B}(i\omega)]\}R^{-6}, \tag{49}$$

with coefficients $a_{\lambda L}-g_{\lambda L}$ listed in Table 3.4 (for L=0, 2 or 4). Double transitions are also associated with $A_{242\lambda L}$; in this case, ΔJ up to ±4 for molecule A, and the coefficients satisfy

$$A_{242\lambda L}=[(-1)^{\lambda+1}h_{\lambda L}B_{7}^{A}\Theta^{B0}+(-1)^{\lambda}q_{\lambda L}(\alpha_{\Uparrow}^{B}-\alpha_{\perp}^{B})(E_{z,zzz}^{A}+2E_{x,xxx}^{A})]R^{-5}$$

$$+(-1)^{\lambda}\{s_{\lambda L}(\alpha_{\Uparrow}^{A}-\alpha_{\perp}^{A})^{2}(\alpha_{\Uparrow}^{B}-\alpha_{\perp}^{B})+t_{\lambda L}\hbar/\pi\int_{0}^{\infty}d\omega\,\gamma_{7}^{A}(i\omega,0,0)$$

$$\times[\alpha_{\Uparrow}^{B}(i\omega)-\alpha_{\perp}^{B}(i\omega)]\}R^{-6}, \tag{50}$$

with $h_{\lambda L}$, $q_{\lambda L}$, $s_{\lambda L}$, and $t_{\lambda L}$ given in Table 3.5, for L=0, 2, and 4. The remaining nonzero coefficients are $A_{2022L}=\wp^{AB}A_{2202L}$ (L=0, 2, 4), $A_{2044L}=\wp^{AB}A_{2404L}$ (L=2, 4), and $A_{224\lambda L}=(-1)^{\lambda}\wp^{AB}A_{242\lambda L}$.

First-order DID effects appear in A_{20002}, A_{22022}, A_{20222}, and $A_{222\lambda 2}$, and thus make the leading contributions to collision-induced depolarized Rayleigh scattering (A_{20002}), and to collision-induced depolarized Raman scattering involving either single-molecule rotational transitions with ΔJ of ±2, or double transitions with ΔJ of ±2 for each molecule in a pair. The first-order DID effects generally dominate in each of these terms. In the isotropic induced spectrum, only the E-tensor mechanism gives rise to transitions with ΔJ = ±4 (through order R^{-6}), but in the depolarized scattering spectrum, E-tensor, B-tensor, second-order DID and dispersion terms can all generate ΔJ = ±4: the E-tensor mechanism determines A_{24044} and A_{20444}, and all four effects appear in A_{22024}, A_{20224}, $A_{222\lambda 4}$, $A_{242\lambda 4}$, and $A_{224\lambda 4}$. Second-order DID and dispersion effects determine the remaining nonzero coefficients.

Table

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0
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Table

λ	L
2	0
0	2
1	2
2	2
3	2
4	2
2	4
3	4
4	4

Table 3.3. Coefficients for A_{2202L} in Eq. (46).

L	a_L	b_L	c_L	d_L	e_L	f_L
0	$4\sqrt{10}/5$	$\sqrt{10}/25$	$2\sqrt{10}/15$	$\sqrt{10}/1125$	$\sqrt{10}/25$	$12\sqrt{10}/5$
2	$-2\sqrt{7}/5$	$2\sqrt{7}/35$	$2\sqrt{7}/105$	$2\sqrt{7}/1575$	$2\sqrt{7}/35$	$-6\sqrt{7}/5$
4	0	$36\sqrt{35}/175$	0	$4\sqrt{35}/875$	$36\sqrt{35}/175$	0

Table 3.4. Coefficients for $A_{222\lambda L}$ in Eq. (49).

λ	L	$a_{\lambda L}$	$b_{\lambda L}$	$c_{\lambda L}$	$d_{\lambda L}$	$e_{\lambda L}$	$f_{\lambda L}$	$g_{\lambda L}$
2	0	0	0	0	$-2\sqrt{7}/75$	$2\sqrt{7}/1575$	0	$-2\sqrt{7}/25$
0	2	$2\sqrt{2}/75$	0	0	$2\sqrt{2}/75$	$16\sqrt{2}/1575$	$3\sqrt{2}/25$	$2\sqrt{2}/25$
1	2	0	0	0	$\sqrt{6}/25$	$\sqrt{6}/105$	$3\sqrt{6}/25$	$3\sqrt{6}/25$
2	2	$-2\sqrt{10}/75$	0	0	$31\sqrt{10}/525$	$19\sqrt{10}/2205$	$3\sqrt{10}/25$	$31\sqrt{10}/175$
3	2	0	0	0	$12\sqrt{14}/175$	$2\sqrt{14}/245$	$3\sqrt{14}/25$	$36\sqrt{14}/175$
4	2	$12\sqrt{2}/25$	0	0	$24\sqrt{2}/175$	$34\sqrt{2}/1225$	$9\sqrt{2}/25$	$72\sqrt{2}/175$
2	4	0	$8\sqrt{2}/5$	$4\sqrt{2}/105$	$-24\sqrt{2}/175$	$8\sqrt{2}/1225$	0	$-72\sqrt{2}/175$
3	4	0	$4\sqrt{35}/5$	$2\sqrt{35}/105$	$-12\sqrt{35}/175$	$4\sqrt{35}/1225$	0	$-36\sqrt{35}/175$
4	4	0	$4\sqrt{55}/5$	$2\sqrt{55}/105$	$-12\sqrt{55}/175$	$4\sqrt{55}/1225$	0	$-36\sqrt{55}/175$

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Table 3.5. Coefficients for $A_{242\lambda L}$ in Eq. (50).

λ	L	$h_{\lambda L}$	$q_{\lambda L}$	$s_{\lambda L}$	$t_{\lambda L}$
2	0	0	0	$4\sqrt{35}/875$	$2\sqrt{35}/25$
2	2	0	0	$8\sqrt{2}/1225$	$4\sqrt{2}/35$
3	2	0	0	$4\sqrt{35}/1225$	$2\sqrt{35}/35$
4	2	0	0	$4\sqrt{55}/1225$	$2\sqrt{55}/35$
2	4	$2\sqrt{10}/45$	$2\sqrt{10}/315$	$4\sqrt{10}/6125$	$2\sqrt{10}/175$
3	4	$2\sqrt{14}/9$	$4\sqrt{14}/315$	$4\sqrt{14}/1225$	$2\sqrt{14}/35$
4	4	$2\sqrt{2}$	$-8\sqrt{2}/315$	$36\sqrt{2}/1225$	$18\sqrt{2}/35$
5	4	$14\sqrt{22}/9$	$-2\sqrt{22}/45$	$4\sqrt{22}/175$	$2\sqrt{22}/5$
6	4	$28\sqrt{26}/9$	$8\sqrt{26}/45$	$8\sqrt{26}/175$	$4\sqrt{26}/5$

3.5 Approximations for Dispersion Coefficients

The leading dispersion contributions to $A_{0\lambda_A\lambda_B\lambda L}$ and $A_{2\lambda_A\lambda_B\lambda L}$ can be evaluated either from the values of α and γ as functions of imaginary frequency for each of the interacting molecules, using Eq. (39)-(50), or from sum-over-states calculations of the dispersion-induced changes in polarizability for interacting pairs. At present, accurate quantum mechanical results are available for $H_2\cdots H_2$ for coefficients with λ_A or λ_B equal to zero [39], but not for other cases or other pairs; values for $\gamma(i\omega,0,0)$ are not generally available. Therefore, to estimate the dispersion terms for larger molecules, a "constant ratio" approximation [52, 54, 68, 69] has been developed; it employs the van der Waals energy coefficients $C_n^{L_A L_B M}$, static polarizabilities, and static hyperpolarizabilities.

For example, to find the dispersion term in A_{00000} (represented by A_{00000}^{d}) $\gamma_1^X(i\omega,0,0)/\bar{\alpha}^X(i\omega)$ and $\gamma_2^X(i\omega,0,0)/\bar{\alpha}^X(i\omega)$ for molecule X are approximated by the frequency-independent ratios I_1^X and I_2^X. Then

$$A_{00000}^{d} = -C_6^{000}(1+\wp^{AB})(3I_1^A + 2I_2^A)R^{-6}, \tag{51}$$

where C_6^{000} is the isotropic van der Waals coefficient for the $A\cdots B$ pair, It is f

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$$C_6^{000} = -3\hbar/\pi \int_0^\infty \bar{\alpha}^A(i\omega)\bar{\alpha}^B(i\omega)d\omega . \tag{52}$$

It is further assumed that the relationship between I_j^X and the zero-frequency values of γ_j^X and $\bar{\alpha}^X$ is the same as in the Unsöld approximation, which gives

$$I_j^X = 1/2\, \gamma_j^X(0,0,0)/\bar{\alpha}^X(0). \tag{53}$$

The Unsöld approximation is used only to generate Eq. (53); with Eq. (51) it yields the estimate

$$A_{00000}^d = -1/2\, C_6^{000} R^{-6}(1+\wp^{AB})\{[3\gamma_1^A(0,0,0)+2\gamma_2^A(0,0,0)]/\bar{\alpha}^A\}. \tag{54}$$

The coefficient A_{20002}^d is estimated similarly in terms of C_6^{000}, by

$$A_{20002}^d = -\sqrt{10}/10\, C_6^{000} R^{-6}[\gamma_2^A(0,0,0)/\bar{\alpha}^A + \gamma_2^B(0,0,0)/\bar{\alpha}^B]. \tag{55}$$

To extend the approximation to other coefficients, the anisotropic dispersion energy coefficients $C_n^{L_A L_B M}$ are needed for two centrosymmetric linear molecules. These coefficients fix the long-range dispersion energy ΔE^{disp} [75, 115],

$$\Delta E^{disp}(R,\theta_A,\phi_A,\theta_B,\phi_B) = \sum_{n=6}^{\infty} \sum_{L_A,L_B} \sum_{M=0}^{\min(L_A,L_B)} C_n^{L_A L_B M} R^{-n}$$
$$\times P_{L_A}^M(\cos\theta_A) P_{L_B}^M(\cos\theta_B) \cos M(\phi_A - \phi_B), \tag{56}$$

where $P_L^M(\cos\theta)$ denotes the associated Legendre function, (θ_A,ϕ_A) and (θ_B,ϕ_B) specify the orientations of $\mathbf{r}_A$ and $\mathbf{r}_B$ with respect to a fixed axis system, and $\mathbf{R}$ lies along the z axis of this system. The coefficients $C_n^{L_A L_B M}$ are given by Eq. (52) and

$$C_6^{200} = -\hbar/\pi \int_0^\infty [\alpha_\Uparrow^A(i\omega) - \alpha_\perp^A(i\omega)]\bar{\alpha}^B(i\omega)d\omega , \tag{57}$$

$$C_6^{020} = \wp^{AB} C_6^{200}, \tag{58}$$

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$$C_6^{22M} = a_M \hbar / \pi \int_0^\infty [\alpha_{\Uparrow}^A(i\omega) - \alpha_{\perp}^A(i\omega)][\alpha_{\Uparrow}^B(i\omega) - \alpha_{\perp}^B(i\omega)]\, d\omega \tag{59}$$

with $a_0 = -1$, $a_1 = 2/9$, and $a_2 = -1/36$.

With these relations and the analog of Eq. (53), the dispersion contributions to the remaining isotropic polarizability coefficients are approximated by

$$A_{02022}^{d} = -\sqrt{5}/10\, C_6^{200} R^{-6}[(3\gamma_1^B + 2\gamma_2^B)/\overline{\alpha}^B + 3(3\gamma_3^A + 4\gamma_5^A)/(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)], \tag{60}$$

$$A_{022LL}^{d} = b_L C_6^{220} R^{-6}(1 + \wp^{AB})(3\gamma_3^A + 4\gamma_5^A)/(\alpha_{\Uparrow}^A - \alpha_{\perp}^A), \tag{61}$$

with $b_0 = -\sqrt{5}/50$, $b_2 = -\sqrt{14}/70$, and $b_4 = -9\sqrt{70}/175$.

Similarly, the constant ratio approximation for the dispersion contributions to the remaining anisotropic polarizability coefficients with λ_A and $\lambda_B \leq 2$ yields

$$A_{22020}^{d} = -\sqrt{10}/50\, C_6^{200} R^{-6}[\gamma_2^B/\overline{\alpha}^B + 15(3\gamma_4^A + 4\gamma_5^A)/(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)], \tag{62}$$

$$A_{22022}^{d} = -\sqrt{7}/35\, C_6^{200} R^{-6}[\gamma_2^B/\overline{\alpha}^B - 21\gamma_5^A/(\alpha_{\Uparrow}^A - \alpha_{\perp}^A)], \tag{63}$$

$$A_{22024}^{d} = -18\sqrt{35}/175\, C_6^{200} R^{-6}\gamma_2^B/\overline{\alpha}^B, \tag{64}$$

$$A_{222\lambda L}^{d} = -1/2\, C_6^{220} R^{-6}[(-1)^{\lambda} + \wp^{AB}](f_{\lambda L}\gamma_4^A + g_{\lambda L}\gamma_5^A)/(\alpha_{\Uparrow}^A - \alpha_{\perp}^A), \tag{65}$$

with $f_{\lambda L}$ and $g_{\lambda L}$ given in Table 3.4. To estimate the dispersion terms with λ_A=4 or λ_B =4, the van der Waals coefficients $C_8^{L_A L_B M}$ are required. The coefficients $C_8^{L_A L_B 0}$ with L_A or L_B equal to 4 are related to the fourth-rank tensor invariant of the quadrupole polarizability C,

$$C_4(i\omega) = 1/35\,[2C_{zz,zz}(i\omega) - 4C_{xz,xz}(i\omega) + C_{xx,xx}(i\omega)], \tag{66}$$

and to $E_7(i\omega)$, the fourth-rank part of the dipole-octopole polarizability E, by

$$C_8^{400} = -20\hbar/\pi \int_0^\infty [3C_4^A(i\omega) + 2E_7^A(i\omega)]\overline{\alpha}^B(i\omega)\, d\omega, \tag{67}$$

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$$C_8^{420} = -\hbar/\pi \int_0^\infty [88\,C_4^A(i\omega) + 152/3\,E_7^A(i\omega)][\alpha_{\parallel}^B(i\omega) - \alpha_{\perp}^B(i\omega)]d\omega\,. \qquad (68)$$

Equations for C_8^{42M} with $M \neq 0$ are given in Ref. 68; C_8^{040} and C_8^{240} are obtained by interchanging the molecule labels A and B in Eqs. (67) and (68).

The anisotropic dispersion coefficients with L_A or L_B equal to 4 have been estimated in terms of the anisotropic van der Waals interaction energy coefficients C_8^{400}, C_8^{040}, C_8^{420}, and C_8^{240}, the fourth-rank part of the static γ hyperpolarizability tensor from Table 3.1, and the static values of C_4 and E_7, with the results:

$$A_{24042}^d = -3\sqrt{35}/100\,C_8^{400}R^{-6}\gamma_7^A/(3C_4^A + 2E_7^A), \qquad (69)$$

$$A_{242\lambda L}^d = 3/16\,(-1)^{\lambda+1}C_8^{420}t_{\lambda L}R^{-6}\gamma_7^A/(33C_4^A + 19E_7^A), \qquad (70)$$

in terms of the coefficients $t_{\lambda L}$ given in Table 3.5. The remaining coefficients are given by $A_{20442}^d = \wp^{AB}A_{24042}^d$ and $A_{224\lambda L}^d = (-1)^\lambda \wp^{AB}A_{242\lambda L}^d$.

For small molecules, values of the permanent susceptibilities and dispersion energy coefficients appearing in Eqs. (54), (55), and (60)-(70) are available from *ab initio* calculations [38-48]. Table 3.6 gives the values of α and γ used to estimate the dispersion polarizability coefficients for H_2 and N_2, and Table 3.7 gives the dispersion energy coefficients used. Coefficients not listed and not derivable by symmetry arguments (C_8^{040} and C_8^{240} for $H_2\cdots N_2$, and C_8^{400}, C_8^{040}, C_8^{420}, and C_8^{240} for $N_2\cdots N_2$) have been set to zero in the calculations. This is equivalent to dropping the dispersion contributions associated with the fourth-rank part of the γ hyperpolarizability for N_2; these are expected to be small compared to the contributions from γ components of ranks 0 and 2. Table 3.8 provides a test of the constant ratio approximation, by comparison of the estimates for the dispersion contributions to $A_{J\lambda_A\lambda_B\lambda L}$ for a pair of interacting H_2 molecules with the accurate *ab initio* results recently obtained by Bishop and Pipin [39]. For $H\cdots H_2$, $He\cdots H_2$, and $H_2\cdots H_2$, the rms error in the dispersion polarizability coefficients with $\lambda_A = 0$ or $\lambda_A = 2$ for H_2 is ~20% [39-70]. The rms error for the pair $H_2\cdots H_2$ with λ_A

Table 3
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Table 3.6. Molecular properties (in a.u.) used to calculate collision-induced polarizabilities.

Property	H_2	N_2
Θ^0	0.4828[a]	-1.1131[e]
$\bar{\alpha}$	5.3966[b]	11.675[e]
$\alpha_{\Uparrow} - \alpha_{\perp}$	1.9793[b]	4.648[e]
γ_{zzzz}	743.86[c]	1172[e]
γ_{xxxx}	621.05[c]	639[e]
γ_{xxzz}	229.61[c]	319[e]
$C_{zz,zz}$	6.3926[b]	34.61[e]
$C_{xz,xz}$	4.4441[b]	26.85[e]
$C_{xx,xx}$	5.2032[b]	19.29[e]
$E_{z,zzz}$	4.4424[b]	38.28[e]
$E_{x,xxx}$	-1.7740[b]	-22.00[e]
$B_{z,z,zz}$	-97.671[d]	-174[f]
$B_{x,z,xz}$	-63.417[d]	-102[f]
$B_{x,x,zz}$	36.746[d]	67[f]
$B_{x,x,xx}$	-71.250[d]	-119.5[f]

[a]Ref. 36, value interpolated to $r(H_2) = 1.449$a.u. in Ref. 37.

[b]Ref. 38.

[c]Ref. 39; values of the static γ hyperpolarizability at $r(H_2) = 1.449$a.u. were supplied by D. M. Bishop, personal communication.

[d]Ref. 40; static B values from D. M. Bishop, personal communication.

[e]Ref. 41; Ref. 42 gives $\bar{\alpha} = 11.616$ a.u. and $\alpha_{\Uparrow} - \alpha_{\perp} = 4.654$ a.u.; properties of N_2 at SCF level are given in Refs. 43-45.

[f]Ref. 44; for B values, see also Ref. 45.

Table 3
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C_6^{020}
C_6^{22}
C_8^{400}
C_8^{420}

[a]Re
[b]Re
[c]Re
[d]Re

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Table 3.7. Dispersion energy coefficients (in a.u.) used to calculate collision-induced polarizabilities.

Coefficient	$H_2 \cdots H_2$	$H_2 \cdots N_2$	$N_2 \cdots N_2$
C_6^{000}	-12.058[a]	-29.28[c]	-73.8[d]
C_6^{200}	-1.219[a]	-2.88[c]	-7.82[c]
C_6^{020}	-1.219[a]	-3.59[c]	-7.82[c]
C_6^{220}	-0.390[a]	-1.12[c]	-2.67[c]
C_8^{400}	-1.38[b]	-3.22[c]	—
C_8^{420}	-0.57[b]	-1.62[c]	—

[a]Ref. 38.

[b]Ref. 46 with isotropic C_8 coefficient for H_2 pairs from Ref. 47.

[c]Ref. 46.

[d]Ref. 48.

Table 3.8. Test of the constant ratio approximation for dispersion polarizability coefficients by comparison with accurate *ab initio* results (Ref. 39) for $H_2 \cdots H_2$. Results in a.u. for the coefficients of R^{-6}.

Coefficient	*Ab initio*	Constant ratio approximation
A_{00000}^{d}	2960.8	2471.5
A_{02022}^{d}	90.6	75.9
A_{20002}^{d}	354.8	312.6
A_{22020}^{d}	41.6	31.5
A_{22022}^{d}	-2.34	-2.99
A_{22024}^{d}	38.7	30.4
A_{24042}^{d}	-1.2	-0.6

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or λ_B equal 4 ranges from ~50% - 60%. This may be due to limitations of the approximation. On the other hand, the terms in the fourth-rank component of γ for H_2 nearly cancel, leading to a very small value for γ_7 and high sensitivity to its frequency dependence. In fact, the most recent *ab initio* calculation in Ref. 39 gives a different sign for γ_7 than found in Ref. 116, though both calculations are of high accuracy overall. For more anisotropic molecules, such near-cancellation is not expected.

3.6 Numerical Results for $H_2 \cdots H_2$, $H_2 \cdots N_2$, and $N_2 \cdots N_2$

Table 3.9 lists the contributions to the collision-induced polarizabilities $\Delta\alpha_0^0$, $\Delta\alpha_2^0$, and $\Delta\alpha_2^{\pm 2}$ from first- and second-order DID effects, E-tensor terms, B-tensor terms, and dispersion, for $H_2 \cdots H_2$, $H_2 \cdots N_2$, and $N_2 \cdots N_2$ in collinear and T-shaped configurations. For each of the molecular configurations studied, the intermolecular vector points along the z axis. Molecule pairs are listed as $A \cdots B$. In the T configurations, molecule A points along the x axis and B along z; hence results differ for $H_2 \cdots N_2$ and $N_2 \cdots H_2$ in T shapes. As shown in Table 3.9, first-order DID interactions increase α_0^0 and α_2^0 for these configurations, but decrease $\alpha_2^{\pm 2}$ for T-shaped pairs. Second-order DID and dispersion effects increase α_0^0 and α_2^0, and $\alpha_2^{\pm 2}$ in each case. E terms are positive in α_J^M for collinear pairs, but for T-shaped pairs the E terms are negative in $\Delta\alpha_0^0$ and nonuniform in sign for $\Delta\alpha_2^M$. The signs of the B-tensor terms are nonuniform, because the quadrupoles of H_2 and N_2 are opposite in sign.

The long-range polarization effects have been compared numerically for $H_2 \cdots H_2$ at R=7.5 a.u. (approximately 1 a.u. outside the van der Waals minimum in the isotropic pair potential), for $H_2 \cdots N_2$ at 8.0 a.u., and for $N_2 \cdots N_2$ at 8.5 a.u. (0.5-0.7 a.u. outside the isotropic van der Waals minimum). The results are summarized below, first for the change in scalar polarizability $\Delta\alpha_0^0$ and then for the anisotropic polarizability $\Delta\alpha_2^M$.

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Table 3.9. Long-range contributions to collision-induced polarizabilities $\Delta\alpha_0^0$, $\Delta\alpha_2^0$, and $\Delta\alpha_2^{\pm 2}$ for $H_2 \cdots H_2$, $H_2 \cdots N_2$, and $N_2 \cdots N_2$.[a]

$\Delta\alpha_J^M$	Configuration	A···B	DID-1	DID-2	E tensor	B tensor	Dispersion
$\Delta\alpha_0^0$	Collinear	$H_2 \cdots H_2$	$52.4\ R^{-3}$	$1645\ R^{-6}$	$120\ R^{-5}$	$81\ R^{-5}$	$1640\ R^{-6}$
		$H_2 \cdots N_2$	$118.4\ R^{-3}$	$5747\ R^{-6}$	$362\ R^{-5}$	$-26\ R^{-5}$	$3320\ R^{-6}$
		$N_2 \cdots N_2$	$267.3\ R^{-3}$	$17290\ R^{-6}$	$1110\ R^{-5}$	$-308\ R^{-5}$	$6420\ R^{-6}$
	T, A ⇑ x	$H_2 \cdots H_2$	$10.8\ R^{-3}$	$1175\ R^{-6}$	$-5.5\ R^{-5}$	$-40\ R^{-5}$	$1470\ R^{-6}$
		$H_2 \cdots N_2$	$27.7\ R^{-3}$	$4226\ R^{-6}$	$-349\ R^{-5}$	$13\ R^{-5}$	$2980\ R^{-6}$
		$N_2 \cdots H_2$	$20.9\ R^{-3}$	$3845\ R^{-6}$	$-244\ R^{-5}$	$13\ R^{-5}$	$2680\ R^{-6}$
		$N_2 \cdots N_2$	$54.3\ R^{-3}$	$11950\ R^{-6}$	$-1312\ R^{-5}$	$154\ R^{-5}$	$5230\ R^{-6}$
$\Delta\alpha_2^0$	Collinear	$H_2 \cdots H_2$	$184.0\ R^{-3}$	$1805\ R^{-6}$	$500\ R^{-5}$	$636\ R^{-5}$	$631\ R^{-6}$
		$H_2 \cdots N_2$	$402.4\ R^{-3}$	$6382\ R^{-6}$	$2910\ R^{-5}$	$-163\ R^{-5}$	$1460\ R^{-6}$
		$N_2 \cdots N_2$	$880.3\ R^{-3}$	$19370\ R^{-6}$	$10300\ R^{-5}$	$-2630\ R^{-5}$	$3200\ R^{-6}$
	T, A ⇑ x	$H_2 \cdots H_2$	$148.2\ R^{-3}$	$954\ R^{-6}$	$93\ R^{-5}$	$108\ R^{-5}$	$449\ R^{-6}$
		$H_2 \cdots N_2$	$323.2\ R^{-3}$	$3701\ R^{-6}$	$1770\ R^{-5}$	$-901\ R^{-5}$	$1080\ R^{-6}$
		$N_2 \cdots H_2$	$318.4\ R^{-3}$	$2892\ R^{-6}$	$-834\ R^{-5}$	$814\ R^{-5}$	$716\ R^{-6}$
		$N_2 \cdots N_2$	$694.4\ R^{-3}$	$9797\ R^{-6}$	$1540\ R^{-5}$	$-375\ R^{-5}$	$1730\ R^{-6}$
$\Delta\alpha_2^{\pm 2}$	T, A ⇑ x	$H_2 \cdots H_2$	$-9.4\ R^{-3}$	$76\ R^{-6}$	$9\ R^{-5}$	$5\ R^{-5}$	$29\ R^{-6}$
		$H_2 \cdots N_2$	$-20.0\ R^{-3}$	$216\ R^{-6}$	$-125\ R^{-5}$	$89\ R^{-5}$	$53\ R^{-6}$
		$N_2 \cdots H_2$	$-22.0\ R^{-3}$	$326\ R^{-6}$	$135\ R^{-5}$	$-109\ R^{-5}$	$125\ R^{-6}$
		$N_2 \cdots N_2$	$-47.1\ R^{-3}$	$824\ R^{-6}$	$-50\ R^{-5}$	$19\ R^{-5}$	$234\ R^{-6}$

[a]Results are tabulated in a.u.

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First-order DID interactions (DID-1) make the dominant contribution to $\Delta\alpha_0^0$ for the pairs and distances selected: for collinear pairs, the DID-1 terms give 82%-84% of the total $\Delta\alpha_0^0$, and for T-shaped pairs, 66%-82% of the total. Other polarization mechanisms are significant, however: for the T-shaped pairs, second-order DID interactions (DID-2) amount to 17%-29% of the total, and dispersion terms constitute 13%-21% of the total. E-tensor terms vary substantially in importance: they amount to less than 1% of $\Delta\alpha_0^0$ for T-shaped $H_2 \cdots H_2$, but 27% for T-shaped $N_2 \cdots N_2$. B terms are generally small, not exceeding 3%-4% of $\Delta\alpha_0^0$. The corrections to DID-1 are smaller for collinear pairs, but still significant: DID-2 terms account for 6%-9% of the total, E terms for 3%-5%, B terms for ~1%-2%, and dispersion for 3%-6%. Generally the DID-2 terms are larger for the heavier pairs, in both absolute and relative magnitude, while the dispersion terms are larger in absolute magnitude but smaller in relative magnitude for the heavier pairs.

The first-order DID interactions give better approximation to $\Delta\alpha_2^M$ than to $\Delta\alpha_0^0$. For collinear pairs, the DID-1 terms account for 86%-88% of the total, and for the T-shaped pairs studied, the errors in the first-order DID approximations for $\Delta\alpha_2^M$ do not exceed 6% in any case. DID-2 and dispersion interactions appear to be highly isotropic, with the result that DID-2 terms contribute ~1.5%-3% to $\Delta\alpha_2^M$, and dispersion ~1% or less. The E- and B-tensor contributions to $\Delta\alpha_2^M$ are larger: E terms contribute 4%-14% to $\Delta\alpha_2^0$ of collinear pairs (largest for $N_2 \cdots N_2$), 1%-8% to $\Delta\alpha_2^0$ for T-shaped pairs, and 1.5%-10% to $\Delta\alpha_2^{\pm 2}$ for T-shaped pairs. B terms range from ~1% to 8% of $\Delta\alpha_2^M$. In the T configurations, both E and B terms are more important for the unlike molecule pairs than for the like pairs.

As a general trend, the DID-1, DID-2, E, and dispersion terms increase in absolute value in the order $H_2 \cdots H_2 < N_2 \cdots H_2 <$(or $\cong$) $H_2 \cdots N_2 < N_2 \cdots N_2$. Exceptions are observed for DID-2 and dispersion terms in $\Delta\alpha_2^{\pm 2}$, where the values are appreciably larger for $N_2 \cdots H_2$ than for $H_2 \cdots N_2$. An exception is also found for the E terms in $\Delta\alpha_2^0$ and $\Delta\alpha_2^{\pm 2}$ of the T configurations, where the values for $H_2 \cdots N_2$ are larger than for $N_2 \cdots N_2$.

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The B terms show different trends in absolute value. In $\Delta\alpha_0^0$ for collinear and T configurations, and in $\Delta\alpha_2^0$ for collinear configurations, B terms are larger for the like pairs than for the unlike pairs; in contrast, in $\Delta\alpha_2^M$ for T-shaped pairs, the B terms are larger for the unlike pairs. For the cases studied, the largest relative contribution from DID-2 terms occurs for $\Delta\alpha_0^0$ for the $N_2\cdots N_2$ pair in the T shape, where DID-2 terms are 29% of the total. For E terms, the largest relative contribution is -27%, also for $\Delta\alpha_0^0$ of $N_2\cdots N_2$ in the T shape; the largest relative contribution from dispersion is 21% of $\Delta\alpha_0^0$ for $H_2\cdots H_2$ in the T shape; of the B terms, the largest is 8%, for $\Delta\alpha_2^{\pm 2}$ of $N_2\cdots H_2$ in the T shape.

3.7 Summary and Discussion

Equations (13) and (14) give the general, symmetry-adapted form of the collision-induced changes in polarizabilities $\Delta\alpha_0^0$ and $\Delta\alpha_2^M$ needed to analyze line shapes for Rayleigh and rototranslational Raman scattering, both isotropic and anisotropic [18-35]. Contributions to the polarizability coefficients $A_{0\lambda_A\lambda_B\lambda L}$ and $A_{2\lambda_A\lambda_B\lambda L}$ from first-order dipole-induced-dipole interactions [49, 71] are given in Eq. (29); from octopolar induction and local field nonuniformities [50, 51] in Eqs. (27) and (28); from hyperpolarization [52] in Eqs. (30)-(32); from second-order DID interactions [58] in Eqs. (34) and (35); and from dispersion in Eqs. (36)-(38). These equations have been obtained using spherical tensor analysis, and they are given in terms of 6-j and 9-j symbols. Explicit expressions for the coefficients are analyzed in Sec. 3.3 and 3.4.

Isotropic rototranslational Raman scattering with $\Delta J = \pm 2$ or ± 4 is forbidden for isolated molecules, but it can be produced by the polarization mechanisms treated in this work, because $\Delta\alpha_0^0$ in Eq. (13) contains terms with λ_A or λ_B equal to 2 or 4. Simultaneous rotational transitions [109] on each of the interacting molecules are produced in both the isotropic and depolarized rototranslational Raman spectra. The polarization mechanisms that vary as R^{-5} and R^{-6} contribute to scattering with higher ΔJ and greater shifts from the incident frequencies than the first-order DID terms.

Numerical results are given in Table 3.9 and in Sec. 3.6. For the classical induction mechanisms, the results have been obtained directly with *ab initio* values for the permanent multipole moments and susceptibilities [36-48]. For dispersion effects, a constant ratio approximation [52, 54, 55, 69] has been used to express the results in terms of the static α values, the static γ values, and the van der Waals energy coefficients, since these are available for a broad class of molecules. The γ hyperpolarizabilities at imaginary frequency have been computed in *ab initio* work on H, He, and H_2 [39]. For these pairs, a test of the constant ratio approximation against the accurate *ab initio* results shows the rms errors of ~20% for the coefficients with λ_A and λ_B equal to 0 or 2 [39, 70].

The leading contributions to $\Delta\alpha_0^0$ and $\Delta\alpha_2^M$ for both collinear and T configurations come from the first-order DID interactions, which range from ~66% to ~106% of the long-range total for $H_2\cdots H_2$ at R=7.5 a.u., $H_2\cdots N_2$ at R=8.0 a.u., and $N_2\cdots N_2$ at R=8.5 a.u., outside the van der Waals minima in the isotropic pair potentials by ~0.5-1.0 a.u.. Deviations of the total from the first-order DID results tend to be largest for $\Delta\alpha_0^0$ of the T-shaped pairs. The largest relative contributions from second-order DID terms exceed 20%; this also holds for the E-tensor terms and dispersion. When the change in scalar polarizability $\Delta\alpha_0^0$ is averaged isotropically over the orientations of the interacting molecules and the intermolecular vector **R**, all long-range terms except second-order DID and dispersion drop out. As a consequence, dispersion accounts for an estimated 55% of the total, isotropically averaged for $H_2\cdots H_2$, 40% for $H_2\cdots N_2$, and 30% for $N_2\cdots N_2$ at long range.

The results in this work should prove useful in analyzing the observed two-body Rayleigh and Raman line shapes for H_2 and N_2 [18-35]. The mechanisms in Eqs. (39)-(50) contribute to single-molecule rotational transitions with ΔJ up to ±4, and to double trans

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transitions with $\Delta J = \pm 4$ on one molecule and $\Delta J = \pm 2$ on the other (neglecting the anisotropies in the pair potential [83]). Cross terms with the leading first-order DID effects are possible for both second-order DID and dispersion terms, thus enhancing their net contributions to the collision-induced scattering intensity. Comparison of the experimental spectra with calculated spectra, based on this work and quantum line shape calculations [64-67], should permit an accurate characterization of electronic overlap effects on collision-induced polarizabilities for pairs containing H_2 and N_2.

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CHAPTER IV

CALCULATIONS OF CONTRACTED HYPERPOLARIZABILITY DENSITIES

4.1 Introduction

The nonlocal polarizability density $\alpha(\mathbf{r},\mathbf{r}';\omega)$ is a linear response tensor that gives the polarization $\mathbf{P}(\mathbf{r},\omega)$ induced at point $\mathbf{r}$ by the perturbing field $\mathbf{F}(\mathbf{r}',\omega)$acting at the point $\mathbf{r}'$ [1-6]. It represents the full linear response of a molecule to external fields or local fields due to the neighboring molecules: $\alpha(\mathbf{r},\mathbf{r}';\omega)$ not only determines the induced dipole moment, but also all the induced higher multipole moments in a field, within linear response [5]. Hyperpolarizability densities such as $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega',\omega'')$ describe the effects of nonlinear response: $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega',\omega'')$ is the first-order nonlinear response tensor that determines the polarization $\mathbf{P}(\mathbf{r},\omega'+\omega'')$ induced at point $\mathbf{r}$ by the perturbing fields $\mathbf{F}(\mathbf{r}',\omega')$ and $\mathbf{F}(\mathbf{r}'',\omega'')$ at other two points $\mathbf{r}'$ and $\mathbf{r}''$ [6]. Both $\alpha(\mathbf{r},\mathbf{r}';\omega)$ and $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega',\omega'')$ are fundamental molecular properties. They have applications in theories of local fields and light scattering in condensed media [1-3], and in approximations for dispersion energies [5], collision-induced dipoles, and collision-induced polarizabilities for two weakly overlapped molecules [6-8]. Integration of $\alpha(\mathbf{r},\mathbf{r}';\omega)$ over all space with respect to $\mathbf{r}$ and $\mathbf{r}'$ gives the linear polarizability $\alpha(\omega)$, and integration of $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega',\omega'')$ over all the space with respect to $\mathbf{r}$, $\mathbf{r}'$, and $\mathbf{r}''$ yields the first-order hyperpolarizability $\beta(\omega',\omega'')$ that is responsible for the nonlinear optical effects such as second-order harmonic generation or frequency doubling [9-12].

Recently, Hunt, Liang, Nimalakirthi, and Harris [13] have shown that the hyperpolarizability density $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ also determines the derivatives of polarizability tensor components with respect to nuclear coordinates, and thus the vibrat

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vibrational Raman intensities within the Placzek approximation [14]:

$$\partial\alpha_{\beta\gamma}(\omega)/\partial R^{I}_{\alpha} = Z^{I}\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, T_{\alpha\delta}(\mathbf{R}^{I},\mathbf{r})\,\beta_{\delta\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0), \tag{1}$$

where Z^{I} is the charge on nucleus I, and $T_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ is the dipole propagator:

$$T_{\alpha\beta}(\mathbf{r},\mathbf{r}') = T_{\alpha\beta}(\mathbf{r}-\mathbf{r}') = \nabla_{\alpha}\nabla_{\beta}(|\mathbf{r}-\mathbf{r}'|^{-1}). \tag{2}$$

With information on $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$, Eq. (1) can be used to identify the regions in the electronic charge distribution that make the principal contributions to vibrational Raman intensities for isolated molecules.

A nonlocal polarizability density model based on $\alpha(\mathbf{r},\mathbf{r}';\omega)$, $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega',\omega'')$ and higher-order response tensors can also be used to approximate collision-induced dipoles and polarizabilities for a pair of weakly overlapped molecules [6]. This model allows for the continuous distribution of the polarizability within the interacting molecules. Thus equations for collision-induced dipoles and polarizabilities within the nonlocal polarizability density model include the direct modifications of electrostatic, induction, and dispersion interactions due to overlap of the molecular charge distributions. For example, this approach gives the dispersion-induced dipole for an A···B pair [6, 8]:

$$\Delta\mu^{AB}_{\alpha,\mathrm{disp}} = \hbar/(2\pi)^{7}\int_{0}^{\infty} d\omega \iint d\mathbf{k}\, d\mathbf{k}'\,(1+\wp^{AB})\,\{\alpha^{A}_{\beta\gamma}(\mathbf{k},\mathbf{k}';i\omega)\,\hat{\beta}^{B}_{\delta\varepsilon\alpha}(-\mathbf{k},-\mathbf{k}';i\omega,0)$$

$$\times \exp[i(\mathbf{k}'-\mathbf{k})\mathbf{R}^{B\to A}]\}\, T_{\gamma\varepsilon}(\mathbf{k}')T_{\delta\beta}(\mathbf{k}) \tag{3}$$

In Eq. (3), $\wp^{AB}$ permutes the labels A and B in the expression that follows; $\alpha^{A}(\mathbf{k},\mathbf{k}';i\omega)$ is the spatial Fourier transform of $\alpha^{A}(\mathbf{r},\mathbf{r}';i\omega)$, and $\hat{\beta}^{B}(\mathbf{k},\mathbf{k}';i\omega,0)$ is the contracted hyperpolarizability density, obtained by integrating over all space with respect to the coordinate $\mathbf{r}''$ in $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';i\omega,0)$ and then Fourier transforming; $T_{\alpha\beta}(\mathbf{k}) = -4\pi\, k_{\alpha}k_{\beta}/k^{2}$ is the dipole propagator in **k**-space.

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From the form of Eq. (3), only the longitudinal component of $\alpha(\mathbf{k},\mathbf{k}';\omega)$ and the longitudinal component of $\hat{\beta}(\mathbf{k},\mathbf{k}';\omega,0)$ are required. These longitudinal parts are related to the corresponding susceptibility densities by [5]

$$\alpha^{L}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega) = \hat{k}_{\alpha}\ \hat{k}'_{\beta}\ \chi(\mathbf{k},\mathbf{k}';\omega)/kk', \tag{4}$$

$$\hat{\beta}^{L}_{\alpha\beta\gamma}(\mathbf{k},\mathbf{k}';\omega,0) = \hat{k}_{\alpha}\ \hat{k}'_{\beta}\ \hat{\beta}_{\gamma}(\mathbf{k},\mathbf{k}';\omega,0)/kk'. \tag{5}$$

In these equations, $\chi(\mathbf{k},\mathbf{k}';\omega)$ denotes the linear charge-density susceptibility [5, 15, 22] and $\hat{\beta}_{\gamma}(\mathbf{k},\mathbf{k}';\omega,0)$ represents the γ component of the contracted β susceptibility density defined by Eq.(6) below.

Given an accurate ground-state wavefunction, the charge-density susceptibility $\chi(\mathbf{k},\mathbf{k}';\omega)$ can be obtained by use of pseudo-state techniques [15], a variational principle [16-20], or the Unsöld approximation and molecular structure factors [21, 22]. For example, $\chi(\mathbf{k},\mathbf{k}';\omega)$ has been determined accurately for the hydrogen atom in the 1s state [15] and approximately for helium, argon, and xenon atoms [23-26]. In reference 27, Linder and Kromhout have noted a need for methods of calculating nonlinear charge-density susceptibilities such as $\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0)$. However, no such calculations have been reported so far. In this work, a method has been developed for computing $\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0)$ via its connections to the auxiliary functions denoted by $\Phi^{M}_{L}(\mathbf{k},\mathbf{k}';\omega)$ [16], which can be determined variationally. The same functions $\Phi^{M}_{L}(\mathbf{k},\mathbf{k}';\omega)$ also fix the charge-density susceptibility $\chi(\mathbf{k},\mathbf{k}';\omega)$ [15, 16, 22] and the contracted susceptibility density $\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0)$ that determines the dispersion-induced quadrupole for an $A\cdots B$ pair [see Chapter V].

Section 4.2 of this chapter presents a method of calculating the contracted hyperpolarizability densities $\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0)$ and $\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0)$. In Sec. 4.3, this method is applied to the hydrogen atom in the 1s state to obtain analytical results for these densities. Sec. 4.4 provides a brief summary and discussion.

4.2 A Method of Calculating Contracted Susceptibility Densities

The contracted susceptibility density $\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0)$ is defined by [6]

$$\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0) = [1 + C(\omega \to -\omega)] \times$$

$$[\langle 0|\,\rho(\mathbf{k})\,G(\omega)\,\mu_{\alpha}^{o}\,G(\omega)\,\rho(\mathbf{k}')\,|0\rangle$$
$$+\langle 0|\,\rho(\mathbf{k})\,G(\omega)\,\rho(\mathbf{k}')^{o}\,G(0)\,\mu_{\alpha}\,|0\rangle$$
$$+\langle 0|\,\mu_{\alpha}\,G(0)\,\rho(\mathbf{k})^{o}\,G(\omega)\,\rho(\mathbf{k}')\,|0\rangle] \qquad (6)$$

based on the general form for nonlinear response tensors given by Orr and Ward [28]. Damping has been neglected in Eq. (6); $C(\omega \to -\omega)$ denotes the operator for complex conjugation and replacement of ω by $-\omega$; μ_{α} is the α component of the molecular dipole operator; $\rho(\mathbf{k})$ is the Fourier component of the charge density operator:

$$\rho(\mathbf{k}) = \int d\mathbf{r}\,\exp(i\mathbf{k}\cdot\mathbf{r})\sum_{j} q_j\,\delta(\mathbf{r}-\mathbf{r}_j) = \sum_{j} q_j \exp(i\mathbf{k}\cdot\mathbf{r}_j) \qquad (7)$$

with q_j the charge of particle j, and

$$G(\omega) = (1-\wp_0)(H - E_0 - \hbar\omega)^{-1}(1-\wp_0), \qquad (8)$$

where $\wp_0$ is the ground-state projection operator $|0\rangle\langle 0|$; also, in Eq. (6) $\rho(\mathbf{k})^{o} \equiv \rho(\mathbf{k}) - \langle 0|\,\rho(\mathbf{k})\,|0\rangle$, and similarly for $\rho(\mathbf{k}')^{o}$ and μ_{α}^{o}.

The expression for the contracted susceptibility density $\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0)$ is given by Eq. (6) with the dipole operator μ_{α} replaced by the molecular quadrupole operator $\Theta_{\alpha\beta}$. Thus $\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0)$ and $\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0)$ are two separate contracted susceptibility densities, but they are different contractions of a *single*, underlying hyperpolarizability density $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$. Contraction of $\mathbf{P}(\mathbf{r}'')$ in $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ into the dipole operator μ_{α} and then spatially Fourier transforming gives $\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0)$, while contraction of

$\mathbf{P}(\mathbf{r}'')$ into the quadrupole operator $\Theta_{\alpha\beta}$ and Fourier transforming yields the density $\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0)$.

To simplify Eq. (6), the density $\hat{\beta}_\alpha(\mathbf{k},\mathbf{k}';\omega,0)$ is expanded in terms of the spherical harmonics of the orientation angles of the vectors $\mathbf{k}$ and $\mathbf{k}'$ by substitution of Eq. (7) into Eq. (6) and use of the Rayleigh expansion for $\exp(i\mathbf{k}\cdot\mathbf{r}_j)$:

$$\hat{\beta}_\alpha(\mathbf{k},\mathbf{k}';\omega,0) = \sum_{L=0}^{\infty}\sum_{M=-L}^{L}\sum_{L'=0}^{\infty}\sum_{M'=-L'}^{L'} c_L c_{L'}^{*} Y_L^M(\theta,\phi) Y_{L'}^{M'}(\theta',\phi')^{*} \times \beta_{LL',\alpha}^{MM'}(k,k';\omega,0), \tag{9}$$

where

$$c_L = (-i)^L 2^L L!/(2L)!\,[4\pi/(2L+1)]^{1/2}, \tag{10}$$

and

$$\begin{aligned}\beta_{LL',\alpha}^{MM'}(k,k';\omega,0) = [1+C(\omega\to-\omega)]\times\\ [\langle 0|\,\rho_L^M(\mathbf{k})\,G(\omega)\,\mu_\alpha^o\,G(\omega)\,\rho_{L'}^{M'}(\mathbf{k}')^{*}\,|0\rangle\\ +\langle 0|\,\rho_L^M(\mathbf{k})\,G(\omega)\,\rho_{L'}^{M'}(\mathbf{k}')^{*o}\,G(0)\,\mu_\alpha\,|0\rangle\\ +\langle 0|\,\mu_\alpha\,G(0)\,\rho_L^M(\mathbf{k})^o\,G(\omega)\,\rho_{L'}^{M'}(\mathbf{k}')^{*}\,|0\rangle]\end{aligned} \tag{11}$$

with the generalized multipole moment operator $\rho_l^m(k)$ given by

$$\rho_l^m(k) = \sum_j q_j \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_l^m(\theta_j,\phi_j)\frac{(2l+1)!}{2^l l!} j_l(kr_j), \tag{12}$$

In Eq. (12), $j_l(kr_j)$ denotes the lth spherical Bessel function.

$\beta_{LL',\alpha}^{MM'}(k,k';\omega,0)$ is a first-rank Cartesian tensor, with spherical tensor components of rank 1. The components are related by

$$\beta^{MM'}_{LL',\binom{0}{1}}(k,k';\omega,0) = \beta^{MM'}_{LL',z}(k,k';\omega,0), \tag{13a}$$

$$\beta^{MM'}_{LL',\binom{\pm 1}{1}}(k,k';\omega,0) = \mp 1/\sqrt{2}\,[\beta^{MM'}_{LL',x}(k,k';\omega,0) \pm \beta^{MM'}_{LL',y}(k,k';\omega,0)]. \tag{13b}$$

If the auxiliary functions $\Phi_l^m(k,\omega)$ are defined by [16]

$$\left|\Phi_l^m(k,\omega)\right\rangle = G(-\omega)\,\rho_l^m(k)\left|0\right\rangle, \tag{14}$$

then from Eqs. (11) and (13),

$$\beta^{MM'}_{LL',\binom{q}{1}}(k,k';\omega,0) = [1 + C(\omega \to -\omega)]\Big(\left\langle \Phi_1^q \right| \rho_{L'}^{M'}(k')^{*o} \left| \Phi_L^M(k,\omega) \right\rangle$$

$$+ \left\langle \Phi_{L'}^{M'}(k',\omega) \right| \rho_L^M(k)^o \left| \Phi_1^q \right\rangle + \left\langle \Phi_{L'}^{M'}(k',\omega) \right| \rho_1^{qo} \left| \Phi_L^M(k,\omega) \right\rangle\Big) \tag{15}$$

with q equal to -1, 0, or 1. In Eq. (15), ρ_L^M are the spherical multipole moment operators given by

$$\rho_L^M = \sum_j q_j r_j^L [4\pi/(2L+1)]^{1/2}\, Y_L^M(\theta_j,\phi_j), \tag{16}$$

and the functions Φ_L^M are defined by

$$\left|\Phi_L^M\right\rangle = G(0)\,\rho_L^M\left|0\right\rangle. \tag{17}$$

The susceptibility density $\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0)$ has an expansion similar to Eq. (9),

$$\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0) = \sum_{L=0}^{\infty}\sum_{M=-L}^{L}\sum_{L'=0}^{\infty}\sum_{M'=-L'}^{L'} c_L c_{L'}^* Y_L^M(\theta,\phi) Y_{L'}^{M'}(\theta',\phi')^*$$

$$\times B^{MM'}_{LL',\alpha\beta}(k,k';\omega,0), \tag{18}$$

where $B^{MM'}_{LL',\alpha\beta}(k,k';\omega,0)$ are second-rank Cartesian tensor components, related to the spherical tensor components by

$$B^{MM'}_{LL',\binom{0}{2}}(k,k';\omega,0) = B^{MM'}_{LL',zz}(k,k';\omega,0), \tag{19a}$$

$$B^{MM'}_{LL',\binom{\pm 1}{2}}(k,k';\omega,0) = \mp\sqrt{2/3}\,[B^{MM'}_{LL',xz}(k,k';\omega,0) \pm B^{MM'}_{LL',yz}(k,k';\omega,0)], \tag{19b}$$

and

$$B^{MM'}_{LL',(\substack{\pm 2\\2})}(k,k';\omega,0)=1/\sqrt{6}\,[B^{MM'}_{LL',xx}(k,k';\omega,0)-B^{MM'}_{LL',yy}(k,k';\omega,0)$$

$$\pm 2i\,B^{MM'}_{LL',xy}(k,k';\omega,0)]. \tag{19c}$$

The components $B^{MM'}_{LL',(\substack{q\\2})}(k,k';\omega,0)$ (q = -2, -1, 0, 1, or 2) are given by the right side of Eq. (15) with Φ_1^q replaced by Φ_2^q and ρ_1^q replaced by ρ_2^q.

$\Phi_l^m(k,\omega)$ from Eq. (14) can be approximated by the function Ψ which makes the following functional minimum [16, 17-20],

$$J_l^m(\Psi)=\langle\Psi|H_0-E_0+\hbar\omega\,|\Psi\rangle-\langle 0|\rho_l^m(k)^*\,|\Psi\rangle-\langle\Psi|\rho_l^m(k)|0\rangle \tag{20}$$

subject to the conditions $\langle 0|\Psi\rangle=0$ and $\omega\geq 0$. In Eq. (20), H_0 is the Hamiltonian of the unperturbed molecule, and E_0 is the energy of its ground state.

Eq. (15) and the corresponding expressions for the densities $B^{MM'}_{LL',(\substack{q\\2})}(k,k';\omega,0)$ are the principal results of this section. They express these densities in terms of the variationally determined functions $\Phi_l^m(k,\omega)$ that also fix the linear charge-density susceptibility [15, 16, 22]. In the next section, these results are employed to calculate the contracted β and B susceptibility densities for the hydrogen atom in the 1s state.

4.3 Application to Hydrogen Atoms

To illustrate the method given in Sec. 4.2, the z-component of the contracted β susceptibility density and zz-component of the contracted B susceptibility density are calculated in this section for the ground-state hydrogen atom. The results will be used to evaluate the damped dispersion-induced local dipole μ_z and quadrupole Θ_{zz} for a H···H pair in the next chapter.

Using a trial function of the form

$$|\Psi\rangle = \lambda(k,\omega)\, G(0)\, \rho_L^M |0\rangle \tag{21}$$

and then applying the variational principle (20) to find $\lambda(k,\omega)$, Koide [16] has determined the functions $\Phi_L^M(k,\omega)$ for the hydrogen atom in the 1s state:

$$\Phi_L^M(k,\omega) \cong \left\langle \Phi_L^M \middle| \rho_L^M(k) \middle| 0 \right\rangle \left[\left\langle \Phi_L^M \middle| \rho_L^M \middle| 0 \right\rangle + \omega \left\langle \Phi_L^M \middle| \Phi_L^M \right\rangle \right]^{-1} \Phi_L^M \tag{22}$$

with

$$\Phi_L^M = -\left(\frac{4\pi}{2L+1}\right)^{1/2} Y_L^M(\theta,\phi) \left(\frac{r^{L+1}}{L+1} + \frac{r^L}{L}\right) \frac{e^{-r}}{\sqrt{\pi}}. \tag{23}$$

Atomic units are used in Eqs. (22), (23) and below.

For the z-component of the β density of the hydrogen atom in the 1s state, only the elements $\beta_{L\,L\pm1}^{MM}$ are nonzero [29]. They are given by

$$\beta_{L\,L\pm1}^{MM'}(k,k';\omega,0) = \delta_{MM'} \langle 1\,L\,0\,M | L\pm1\,M \rangle \langle 1\,L\,0\,0 | L\pm1\,0 \rangle \beta_{L\,L\pm1}(k,k';\omega,0), \tag{24}$$

where $\langle L_1\, L_2\, M_1\, M_2 \,|\, L\, M \rangle$ is a Clebsch-Gordan coefficient, and

$$\begin{aligned}\beta_{L\,L\pm1}(k,k';\omega,0) = {} & \frac{2\omega_L a_L}{\omega_L^2 - \omega^2} \left[f_L(k)\, g_{L\pm}(k') - \frac{a_{L\pm1} d_{L\pm}}{\omega_L - \omega_{L\pm1}} f_L(k)\, f_{L\pm1}(k') \right] \\ & + \frac{2\omega_{L\pm1} a_{L\pm1}}{\omega_{L\pm1}^2 - \omega^2} \left[f_{L\pm1}(k')\, h_{L\pm}(k) - \frac{a_L d_{L\pm}}{\omega_L - \omega_{L\pm1}} f_L(k)\, f_{L\pm1}(k') \right]\end{aligned} \tag{25}$$

with $L \geq 1$ for $\beta_{L\,L+1}$ and $L \geq 2$ for $\beta_{L\,L-1}$, and

$$\beta_{01}(k,k';\omega,0) = \frac{2\omega_1 a_1}{\omega_1^2 - \omega^2} f_1(k')\, h_{0+}(k), \tag{26}$$

$$\beta_{10}(k,k';\omega,0) = \frac{2\omega_1 a_1}{\omega_1^2 - \omega^2} f_1(k)\, g_{1-}(k'). \tag{27}$$

In equations (25)-(27), the functions ω_L, a_L and $f_L(k)$ have been given by Koide [16]

$$\omega_L = \frac{\langle \Phi_L^M | \rho_L^M | 0 \rangle}{\langle \Phi_L^M | \Phi_L^M \rangle} = \frac{L(L+1)(L+2)(2L+1)}{L^4 + 11L^3 + 18L^2 + 10L + 2}, \tag{28}$$

$$a_L = \frac{|\langle \Phi_L^M | \rho_L^M | 0 \rangle|^2}{\langle \Phi_L^M | \Phi_L^M \rangle} = \frac{(2L)!(L+1)(L+2)^2(2L+1)^2}{2^{2L+1}(2L^4 + 11L^3 + 18L^2 + 10L + 2)}, \tag{29}$$

and

$$f_L(k) = \frac{\langle \Phi_L^M | \rho_L^M(k) | 0 \rangle}{\langle \Phi_L^M | \rho_L^M | 0 \rangle} = 2L/(2L+1)\ k^L\, x^{L+2}(x + 1/2L), \tag{30}$$

The functions new in this work are $d_{L\pm}$, $g_{L\pm}(k)$, and $h_{L\pm}(k)$; they are given by

$$d_{L+} = \frac{\langle \Phi_{L+1}^M | \rho_1^0 | \Phi_L^M \rangle}{\langle \Phi_{L+1}^M | \rho_{L+1}^M | 0 \rangle \langle \Phi_L^M | \rho_L^M | 0 \rangle} [\langle 1\, L\, 0\, M | L+1\, M \rangle \langle 1\, L\, 0\, 0 | L+1\, 0 \rangle]^{-1}$$

$$= -2^{2L+3}[(L+3)(2L+4)!]^{-1}\,(2L^4 + 17L^3 + 46L^2 + 43L + 9), \tag{31}$$

$$d_{L-} = \frac{\langle \Phi_{L-1}^M | \rho_1^0 | \Phi_L^M \rangle}{\langle \Phi_{L-1}^M | \rho_{L-1}^M | 0 \rangle \langle \Phi_L^M | \rho_L^M | 0 \rangle} [\langle 1\, L\, 0\, M | L-1\, M \rangle \langle 1\, L\, 0\, 0 | L-1\, 0 \rangle]^{-1}$$

$$= -2^{2L}[(2L-1)(L+1)(L+2)(2L)!]^{-1}\,(2L^4 + 9L^3 + 7L^2 - 6L - 3), \tag{32}$$

$$g_{L+}(k) = \frac{\langle \Phi_1^0 | \rho_{L+1}^M(k)^{\bullet\circ} | 0 \rangle}{\langle \Phi_L^M | \rho_L^M | 0 \rangle} [\langle 1\, L\, 0\, M | L+1\, M \rangle \langle 1\, L\, 0\, 0 | L+1\, 0 \rangle]^{-1}$$

$$= -(L+3)/4\ k^{L+1}\, x^{L+3}[2L(L+4)x^2 + (3L+2)x + 1], \tag{33}$$

$$g_{L-}(k) = \frac{\langle \Phi_1^0 | \rho_{L-1}^M(k)^{\bullet\circ} | 0 \rangle}{\langle \Phi_L^M | \rho_L^M | 0 \rangle} [\langle 1\, L\, 0\, M | L-1\, M \rangle \langle 1\, L\, 0\, 0 | L-1\, 0 \rangle]^{-1}$$

$$= -1/2\ k^{L-1}\, x^{L+2}[(L+2)(2L-1)(2L+1)]^{-1}[4L(L+2)(L+3)(L+4)x^3$$

$$-4(L+2)(L+3)(2L-1)x^2 - (L+2)(13L+4)x - 3(L+3)] + 43/6\ \delta_{L1}x^2, \tag{34}$$

$$h_{L+}(k) = \frac{\langle \Phi^M_{L+1} | \rho^M_L(k)^o | \Phi^0_1 \rangle}{\langle \Phi^M_{L+1} | \rho^M_{L+1} | 0 \rangle} [\langle 1\,L\,0\,M | L+1\,M \rangle \langle 1\,L\,0\,0 | L+1\,0 \rangle]^{-1}$$

$$= -1/2\, k^L x^{L+3} [(L+3)(2L+3)^2]^{-1} [4(L+1)(L+3)(L+4)(L+5)x^3$$

$$-4(L+3)(L+4)(2L+1)x^2 - (L+2)(13L+17)x - 3(L+4)] + 43/18\, \delta_{L0} x^2, \tag{35}$$

and

$$h_{L-}(k) = \frac{\langle \Phi^M_{L-1} | \rho^M_L(k)^o | \Phi^0_1 \rangle}{\langle \Phi^M_{L-1} | \rho^M_{L-1} | 0 \rangle} [\langle 1\,L\,0\,M | L-1\,M \rangle \langle 1\,L\,0\,0 | L-1\,0 \rangle]^{-1}$$

$$= -(L+2)(2L+1)/4(2L-1)\, k^L x^{L+2} [2(L-1)(L+3)x^2 + (3L-1)x + 1], \tag{36}$$

where $x \equiv 4/(k^2+4)$.

The zz-component of the B susceptibility density of the ground-state hydrogen atom has nonzero elements $B^{MM}_{L\,L\pm2}$ and B^{MM}_{LL}, which satisfy

$$B^{MM'}_{LL+n}(k,k';\omega,0) = \delta_{MM'} \langle 2\,L\,0\,M | L+n\;M \rangle \langle 2\,L\,0\,0 | L+n\;0 \rangle$$

$$\times B_{L\,L+n}(k,k';\omega,0), \tag{37}$$

where n equals -2, 0 or 2, and

$$B_{L\,L\pm2}(k,k';\omega,0) = \frac{2\omega_L a_L}{\omega_L^2 - \omega^2} [f_L(k)\, A_{LL\pm2}(k') - \frac{a_{L\pm2} D_{LL\pm2}}{\omega_L - \omega_{L\pm2}} f_L(k)\, f_{L\pm2}(k')]$$

$$+ \frac{2\omega_{L\pm2} a_{L\pm2}}{\omega_{L\pm2}^2 - \omega^2} [f_{L\pm2}(k')\, C_{LL\pm2}(k) + \frac{a_L D_{LL\pm2}}{\omega_L - \omega_{L\pm2}} f_L(k)\, f_{L\pm2}(k')] \tag{38}$$

with $L \geq 1$ for B_{LL+2} and $L \geq 3$ for B_{LL-2}, and

$$B_{02}(k,k';\omega,0) = \frac{2\omega_2 a_2}{\omega_2^2 - \omega^2} f_2(k')\, C_{02}(k), \tag{39}$$

$$B_{20}(k,k';\omega,0) = \frac{2\omega_2 a_2}{\omega_2^2 - \omega^2} f_2(k)\, A_{20}(k'), \tag{40}$$

and

$$B_{LL}(k,k';\omega,0)=\frac{2\omega_L a_L}{\omega_L^2-\omega^2}[f_L(k)A_{LL}(k')+f_L(k')C_{LL}(k)]$$

$$+\frac{2a_L^2 D_{LL}(\omega_L^2+\omega^2)}{(\omega_L^2-\omega^2)^2}f_L(k)f_L(k'). \tag{41}$$

In equations (38)-(41), the functions D_{LL+n}, $A_{LL+n}(k)$ and $C_{LL+n}(k)$ (n = -2, 0, or 2) satisfy

$$D_{LL+2}=\frac{\langle\Phi_{L+2}^M|\,\rho_2^0\,|\Phi_L^M\rangle}{\langle\Phi_L^M|\,\rho_L^M\,|0\rangle\langle\Phi_{L+2}^M|\,\rho_{L+2}^M\,|0\rangle}[\langle 2\,L\,0\,M|L+2\;\;M\rangle\langle 2\,L\,0\,0|L+2\;\;0\rangle]^{-1}$$

$$=-2^{2L+3}(2L+3)[(L+4)(2L+5)(2L+4)!]^{-1}$$

$$\times(2L^4+23L^3+86L^2+110L+20), \tag{42}$$

$$D_{LL-2}=\frac{\langle\Phi_{L-2}^M|\,\rho_2^0\,|\Phi_L^M\rangle}{\langle\Phi_L^M|\,\rho_L^M\,|0\rangle\langle\Phi_{L-2}^M|\,\rho_{L-2}^M\,|0\rangle}[\langle 2\,L\,0\,M|L-2\;\;M\rangle\langle 2\,L\,0\,0|L-2\;\;0\rangle]^{-1}$$

$$=(2L+1)/(2L-3)\,D_{L-2L}, \tag{43}$$

$$D_{LL}=\frac{\langle\Phi_L^M|\,\rho_2^0\,|\Phi_L^M\rangle}{\langle\Phi_L^M|\,\rho_L^M\,|0\rangle^2}[\langle 2\,L\,0\,M|L\,M\rangle\langle 2\,L\,0\,0|L\,0\rangle]^{-1}$$

$$=-2^{2L+1}(2L+3)[(L+2)(2L+1)(2L+2)!]^{-1}$$

$$\times(2L^4+15L^3+31L^2+14L+2), \tag{44}$$

$$A_{LL+2}(k)=\frac{\langle\Phi_2^0|\,\rho_{L+2}^M(k)^{*o}\,|\Phi_L^M\rangle}{\langle\Phi_L^M|\,\rho_L^M\,|0\rangle}[\langle 2\,L\,0\,M|L+2\;\;M\rangle\langle 2\,L\,0\,0|L+2\;\;0\rangle]^{-1}$$

$$=-(L+3)(L+4)(2L+3)/24\,k^{L+2}x^{L+4}$$

$$\times[4L(L+5)x^2+4(L+1)x+1], \tag{45}$$

$$A_{LL-2}(k) = \frac{\left\langle \Phi_2^0 \middle| \rho_{L-2}^M(k)^{\bullet o} \middle| \Phi_L^M \right\rangle}{\left\langle \Phi_L^M \middle| \rho_L^M \middle| 0 \right\rangle} [\langle 2\, L\, 0\, M | L-2\;\; M \rangle \langle 2\, L\, 0\, 0 | L-2\;\; 0 \rangle]^{-1}$$

$$= -1/6\,[(2L-1)(2L-3)(L+2)(2L+1)]^{-1}\, k^{L-2} x^{L+2} [16L(L+2)(L+3)$$

$$\times (L+4)(L+5)x^4 + 16(1-8L)(L+2)(L+3)(L+4)x^3 + 48(L+2)(L+3)$$

$$\times (3L-2)x^2 + 60(L+2)(2L+1)x + 15(L+4)] + 107/12\, \delta_{L2} x^2, \qquad (46)$$

$$A_{LL}(k) = \frac{\left\langle \Phi_2^0 \middle| \rho_L^M(k)^{\bullet o} \middle| \Phi_L^M \right\rangle}{\left\langle \Phi_L^M \middle| \rho_L^M \middle| 0 \right\rangle} [\langle 2\, L\, 0\, M | L\, M \rangle \langle 2\, L\, 0\, 0 | L\, 0 \rangle]^{-1}$$

$$= -1/12\,(2L+1)^{-1} k^L x^{L+3} [8L(L+3)(L+4)(L+5)x^3 - 4(L+3)(L+4)$$

$$\times (5L-2)x^2 - 6(L+3)(3L+2)x - 3(L+4)], \qquad (47)$$

$$C_{LL+2}(k) = \frac{\left\langle \Phi_{L+2}^M \middle| \rho_L^M(k)^{\bullet o} \middle| \Phi_2^0 \right\rangle}{\left\langle \Phi_{L+2}^M \middle| \rho_{L+2}^M \middle| 0 \right\rangle} [\langle 2\, L\, 0\, M | L+2\;\; M \rangle \langle 2\, L\, 0\, 0 | L+2\;\; 0 \rangle]^{-1}$$

$$= (2L+1)/(2L+5)\, A_{L+2L}, \qquad (48)$$

$$C_{LL}(k) = A_{LL}(k), \qquad (49)$$

and

$$C_{LL-2}(k) = \frac{\left\langle \Phi_{L-2}^M \middle| \rho_L^M(k)^{\bullet o} \middle| \Phi_2^0 \right\rangle}{\left\langle \Phi_{L-2}^M \middle| \rho_{L-2}^M \middle| 0 \right\rangle} [\langle 2\, L\, 0\, M | L-2\;\; M \rangle \langle 2\, L\, 0\, 0 | L-2\;\; 0 \rangle]^{-1}$$

$$= (2L+1)/(2L-3)\, A_{L-2L}. \qquad (50)$$

4.4 Summary and Discussion

This work has shown that the contracted susceptibility densities $\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0)$ and $\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0)$ are related to the variationally determined functions $\Phi_L^M(k,\omega)$ that have been used to evaluate the linear charge-density susceptibility $\chi(\mathbf{k},\mathbf{k}';\omega)$ [14, 15, 22]. For the hydrogen atom in the 1s state, the work yields analytical expressions for these susceptibility densities. The results will be used in later computational work on the damped local dispersion dipole and quadrupole of a $H\cdots H$ pair (see Chapter V).

The method developed in this work can be extended to the S-state atoms with multiple electrons. In the extension $\hat{\beta}_{\alpha}(\mathbf{k},\mathbf{k}';\omega,0)$ is still given by equations (9), (24)-(27); but the functions ω_L, a_L, $d_{L\pm}$, $f_L(k)$, $g_{L\pm}(k)$, and $h_{L\pm}(k)$ appearing in Eqs. (24)-(27) cannot be evaluated analytically as in the case of the hydrogen atoms. Instead these functions are obtained from the one-electron transition density matrices DA and DB analogous to the matrices DA^{01} and DB^{01} introduced by Krauss and Neumann in the calculations of the charge-density susceptibilities $\chi(\mathbf{k},\mathbf{k}';\omega)$ for inert gas atoms [23]:

$$\omega_L = \alpha_L / \{2\,\mathrm{Tr}[DA(L,L)S]\}, \tag{51}$$

$$a_L = \alpha_L^2 / \{4\,\mathrm{Tr}[DA(L,L)S]\}, \tag{52}$$

$$f_L(k) = 2/\alpha_L \sum_i \sum_j DB_{ji}(L) \left\langle \Phi_i^1 \middle| \rho_L^M(k) \middle| \Phi_j^0 \right\rangle, \tag{53}$$

$$g_{L\pm}(k) = 2/\alpha_L \sum_i \sum_j DA_{ji}(L,1) \left\langle \Phi_i^1 \middle| \rho_{L\pm 1}^M(k)^{*o} \middle| \Phi_j^1 \right\rangle c^{-1}, \tag{54}$$

$$h_{L\pm}(k) = 2/\alpha_{L\pm 1} \sum_i \sum_j DA_{ji}(1,L\pm 1) \left\langle \Phi_i^1 \middle| \rho_L^M(k)^{o} \middle| \Phi_j^1 \right\rangle c^{-1}, \tag{55}$$

$$d_{L\pm} = 4/(\alpha_L \alpha_{L\pm 1}) \sum_i \sum_j DA_{ji}(L,L\pm 1) \left\langle \Phi_i^1 \middle| \rho_1^0 \middle| \Phi_j^1 \right\rangle c^{-1}. \tag{56}$$

In equations (51)-(56), α_L is the static polarizability of order L; $\{\Phi_i^0\}$ and $\{\Phi_j^1\}$ are the zeroth- and first-order basis sets [23], respectively, and the matrices S, DA and DB are given by

$$S_{ij} = \left\langle \Phi_i^1 \middle| \Phi_j^1 \right\rangle, \tag{57}$$

$$DA(L_1, L_2) = M^{-1}\rho(L_1) A \rho(L_2)^+ (M^{-1})^+, \tag{58}$$

$$DB(L) = A \rho(L)^+ (M^{-1})^+, \tag{59}$$

where A is the density matrix for the ground state, and $\rho(L)$ and M are defined by

$$\rho_{ij}(L) = \left\langle \Phi_i^0 \middle| \rho_L^M \middle| \Phi_j^0 \right\rangle, \tag{60}$$

and

$$M_{ij} = \left\langle \Phi_i^0 \middle| H_0 - E_0 \middle| \Phi_j^1 \right\rangle. \tag{61}$$

In Eqs. (54)-(56), the coefficient c satisfies

$$c = \langle 1 L 0 M | L \pm 1 M \rangle \langle 1 L 0 0 | L \pm 1 0 \rangle. \tag{62}$$

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CHAPTER V

DISPERSION DIPOLES AND QUADRUPOLES FOR PAIRS OF ATOMS: EFFECTS OF OVERLAP DAMPING

5.1 Introduction

Interactions between colliding molecules in gases and liquids distort the charge distributions of the collision partners, producing transient dipole moments in the molecular pair. Collision-induced changes in dipole moments give rise to the single-molecule forbidden infrared and far-infrared absorption by nondipolar species such as H_2 [1-2], N_2 [3-5], and inert-gas mixtures [2, 6], and contribute to allowed absorption. In line shape analyses of light absorption spectra, the collision-induced dipoles are needed as functions of intermolecular separation and relative orientation.

For molecules interacting at long range, only classical induction and dispersion effects contribute to collision-induced dipoles; they are given in terms of permanent multipole moments, multipole polarizabilities, and hyperpolarizabilities of isolated molecules [7-12]. Long range dipoles of inert-gas heterodiatoms have been determined accurately in quantum perturbation calculations [9]. The net dipoles for pairs involving H, He, H_2, and N_2 are known to a good approximation at long range [11, 12].

At shorter range, when overlap and exchange effects are significant, *ab initio* methods can be used to compute pair dipoles. Because large basis sets are often required in pair property calculations, accurate *ab initio* calculations (including correlation effects) for pair dipoles have been limited to small systems such as He$\cdots$H [13, 14], He$\cdots$Ar [15], He$\cdots H_2$ [16, 17], and $H_2 \cdots H_2$ [18, 19]. This prompts interest in developing long-range models that include overlap effects and yield good results in the regions near to the van der Waals minima. In these regions it is often difficult to obtain accurate results *ab initio* due to numerical cancellation and basis limitations. Therefore, long-range models, corrected for overlap damping, complement *ab initio* calculations at short range. Additionally, these models can be compared with experimental results or *ab initio* calculations to extract useful information on the short-range exchange effects on pair properties.

A nonlocal polarizability density model developed by Hunt [20] serves this purpose. In the model the distribution of polarizable matter in the interacting molecules is represented by means of the linear response tensor $\alpha(\mathbf{r},\mathbf{r}';\omega)$, the nonlinear response tensor $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega',\omega-\omega')$, and higher-order tensors. These tensors give the ω-frequency component of the polarization induced at point $\mathbf{r}$ in a molecule by a perturbing field acting at other points. Earlier, Hunt [20] has used this model to derive equations for induction and dispersion contributions to collision-induced dipoles and polarizabilities, with overlap effects included. The equations have been applied to a $\mathrm{H}\cdots\mathrm{H}$ pair to evaluate analytically the lowest-order damped induction contributions to local dipoles, quadrupoles, and pair polarizabilities [20]. However, no calculations of damped dispersion dipoles have been reported so far because a method of obtaining the required β susceptibility density has not been available until recently. In Chapter IV, the β susceptibility density has been shown to be related to a set of variationally determined auxiliary functions $\Phi_L^M(k,\omega)$. For a ground-state hydrogen atom, analytical results have been obtained for the β susceptibility density. The purpose of this chapter is to derive equations for the damped dispersion dipoles for atomic pairs, and to provide numerical values for the atomic dipole and pair quadrupole of a $\mathrm{H}\cdots\mathrm{H}$ pair, based on the results given in the last chapter.

The dispersion contribution to the dipole for an $\mathrm{A}\cdots\mathrm{B}$ pair is related to the dispersion energy between A and B in the presence of a static, uniform applied field $\mathbf{F}$ by [21]

$$\Delta\mu_\alpha^{\mathrm{disp}} = -\partial\,\Delta E^{\mathrm{disp}} / \partial F_\alpha|_{\mathbf{F}=0}. \tag{1}$$

The dispersion interaction results from the correlations in the fluctuating charge distributions of molecules A and B: The spontaneous, fluctuating charge density of molecule A polarizes B; the induced polarization in B gives rise to a reaction field at A, causing an energy change in A. The reaction field at B associated with the fluctuating charge distribution of B determines the energy change in B, the second term in the total energy change in the pair. Two distinct physical effects contribute to $\Delta\mu^{\mathrm{disp}}$: (1) Each molecule is hyperpolarized by the simultaneous action of the applied field and the fluctuating field due to its neighbor, and (2) the applied field changes the correlations in the fluctuating charge distribution of each of the molecules, thus affecting the van der Waals interaction energy. The dispersion contribution to the pair dipole depends on the polarizability density of one molecule and the contracted β susceptibility density of the other, both taken at imaginary frequencies [22]:

$$\Delta\mu^{AB}_{\alpha,\mathrm{disp}} = \hbar/(2\pi)^7 \int_0^\infty d\omega \iint d\mathbf{k}\, d\mathbf{k}'\, (1+\wp^{AB})\, \{\alpha^{A}_{\beta\gamma}(\mathbf{k},\mathbf{k}';i\omega)\hat{\beta}^{B}_{\delta\varepsilon\alpha}(-\mathbf{k},-\mathbf{k}';i\omega,0)$$
$$\times \exp[i(\mathbf{k}'-\mathbf{k})\mathbf{R}^{B\to A}]\}\, T_{\gamma\varepsilon}(\mathbf{k}')T_{\delta\beta}(\mathbf{k}) \qquad (2)$$

The above equation is equivalent to the expression for the dispersion dipole obtained by Linder and Kromhout [23], using second-order perturbation theory.

Equation (2) is valid for any interacting molecules with arbitrary symmetry, but the work in this chapter is restricted to interacting S-state atoms. In Sec. 5.2, partial wave analysis is used to analyze dispersion dipoles and quadrupoles. It is shown that the equations for damped dispersion dipoles and quadrupoles are convergent at short range, while they approach the inverse power series of the multipole expansion at long range. Sec. 5.3 contains a numerical application to a pair of ground-state hydrogen atoms. The leading term in the local dispersion dipole (i.e., the dispersion dipole of one H atom in the pair) and the leading term in the local dispersion quadrupole for the pair $H\cdots H$ are obtained as analytical functions of the interatomic distance R.

5.2 Damped Dispersion Dipoles and Quadrupoles

The dipole induced in A by dispersion interactions with B is given by the term generated by $\wp^{AB}$ in Eq. (2). It can be recast into a computationally useful form

$$\Delta\mu^{A}_{\alpha,\mathrm{disp}} = \hbar/(8\pi)^5 \int d\mathbf{k}\, \exp(-i\mathbf{k}\cdot\mathbf{R}^{AB})k^{-2} \int d\mathbf{k}'\, \exp(i\mathbf{k}'\cdot\mathbf{R}^{AB})k'^{-2}$$

$$\times \int_0^\infty d\omega\, \chi^{B}(\mathbf{k},\mathbf{k}';i\omega)\, \hat{\beta}^{A}_{\alpha}(-\mathbf{k},-\mathbf{k}';i\omega,0), \tag{3}$$

where $\chi(\mathbf{k},\mathbf{k}';i\omega)$ is the imaginary-frequency charge-density susceptibility, $\hat{\beta}_\alpha(-\mathbf{k},-\mathbf{k}';i\omega,0)$ is the contracted susceptibility density defined by equation (6) in Chapter IV, and $\mathbf{R}^{AB}$ is the vector from the center of symmetry of molecule A to the center of symmetry of molecule B.

In order to simplify Eq. (3), $\chi(\mathbf{k},\mathbf{k}';\omega)$ and $\hat{\beta}_\alpha(-\mathbf{k},-\mathbf{k}';\omega,0)$ are first resolved into partial waves [24, 25]:

$$\chi(\mathbf{k},\mathbf{k}';\omega) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'} c_l c^*_{l'} Y^m_l(\theta,\phi) Y^{m'}_{l'}(\theta',\phi')^* \alpha^{mm'}_{ll'}(k,k';\omega), \tag{4}$$

and

$$\hat{\beta}_\alpha(-\mathbf{k},-\mathbf{k}';\omega,0) = \sum_{L=0}^{\infty}\sum_{M=-L}^{L}\sum_{L'=0}^{\infty}\sum_{M'=-L'}^{L'} c^*_L c_{L'} Y^M_L(\theta,\phi)^* Y^{M'}_{L'}(\theta',\phi')$$

$$\times \beta^{MM'}_{LL',\alpha}(k,k';\omega,0)^*. \tag{5}$$

In Eqs. (4) and (5), $Y^m_l(\theta,\phi)$ denotes the spherical harmonic function, c_L and $\beta^{MM'}_{LL',\alpha}(k,k';\omega,0)$ are given by Eqs. (4.10) and (4.11) (in Chapter IV), respectively, and

$$\alpha^{mm'}_{ll'}(k,k';\omega) = 2/\hbar \sum_{n\neq 0} \omega_{n0}(\omega^2_{n0}-\omega^2)^{-1}\langle 0|\rho^m_l(k)^*|n\rangle\langle n|\rho^{m'}_{l'}(k')|0\rangle \tag{6}$$

with the generalized multipole moment operator $\rho^m_l(k)$ given by Eq. (4.12).

Specialized to a pair of S-state atoms, equations (4) and (5) simplify because

$$\beta^{MM'}_{LL',\alpha}(k,k';\omega,0)=\delta_{MM'}[\delta_{L\,L'+1}\,\beta^{MM}_{LL-1,\alpha}(k,k';\omega,0)+\delta_{L\,L'-1}\,\beta^{MM}_{LL+1,\alpha}(k,k';\omega,0)],$$

(7)

and

$$\alpha^{mm'}_{ll'}(k,k';\omega)=\delta_{ll'}\,\delta_{mm'}\,\alpha_l(k,k';\omega). \tag{8}$$

Substitution of Eqs. (4) and (5) into (3) and use of Eqs. (7) and (8) gives

$$\Delta\mu^{A}_{z,disp}=\sum_{l}^{\infty}\sum_{L}^{\infty}\left[\Delta\mu^{+}(l,L)+\Delta\mu^{-}(l,L)\right] \tag{9}$$

with

$$\begin{aligned}\Delta\mu^{\pm}(l,L)=\hbar/8\pi^5\left|c_l c_L\right|^2\int d\mathbf{k}\exp(-i\mathbf{k}\cdot\mathbf{R})\,k^{-2}\int d\mathbf{k}'\exp(i\mathbf{k}'\cdot\mathbf{R})\,k'^{-2}\\ \times Y^m_l(\theta,\phi)\,Y^m_l(\theta',\phi')^*\,Y^M_L(\theta,\phi)^*\,Y^M_{L\pm1}(\theta',\phi')\\ \times\int_0^\infty d\omega\,\alpha^B_l(k,k';i\omega)\,\beta^{MM(A)}_{LL\pm1,z}(k,k';i\omega,0),\end{aligned} \tag{10}$$

where $\mathbf{R}\equiv\mathbf{R}^{AB}$, and the z axis is chosen to be along the interatomic vector $\mathbf{R}$. It should be noted that the x and y components of the dispersion dipole vanish for a pair of spherically symmetric atoms.

Equation (10) can further be simplified by substitution of the Rayleigh expansions for $\exp(-i\mathbf{k}\cdot\mathbf{R})$ and $\exp(i\mathbf{k}'\cdot\mathbf{R})$

$$\exp(i\mathbf{k}\cdot\mathbf{R})=\sum_J[4\pi(2L+1)]^{1/2}\,i^J\,Y^0_J(\theta,\phi)\,j_J(kR), \tag{11}$$

and integration with respect to the polar angles (θ,ϕ) and (θ',ϕ'). This gives

$$\begin{aligned}\Delta\mu^{\pm}(l,L)=p_{lL\pm}\sum_{J=|L-l|}^{L+l}\;\sum_{J'=|L\pm1-l|}^{L\pm1+l}q^{JJ'}_{lL\pm}\,(2/\pi)^2\int_0^\infty dk\,j_J(kR)\int_0^\infty dk'\,j_{J'}(k'R)\\ \times\hbar/2\pi\int_0^\infty d\omega\,\alpha^B_l(k,k';i\omega)\,\beta^A_{LL\pm1}(k,k';i\omega,0),\end{aligned} \tag{12}$$

where

$$p_{lL\pm} = \frac{2^{2L\pm1}}{(2l+1)(2L+1)}\left[\frac{2^l l!}{(2l)!}\right]^2 \frac{L!(L\pm1)!}{(2L)!(2L\pm2)!}, \tag{13}$$

$$q_{lL\pm}^{JJ'} = (-i)^{J\pm1} i^{J'}(2J+1)(2J'+1)\langle 1\,L\,0\,0|L\pm1\;0\rangle\langle J\,l\,0\,0|L\,0\rangle\langle J'\,L\pm1\,0\,0|l\,0\rangle$$
$$\times\sum_M \langle 1\,L\,0\,M|L\pm1\,M\rangle\langle J\,l\,0\,M|L\,M\rangle\langle J'\,L\pm1\,0\,M|l\,M\rangle, \tag{14}$$

and

$$\beta_{LL\pm1}(k,k';i\omega,0) = \beta_{LL\pm1}^{MM}(k,k';i\omega,0)[\langle 1\,L\,0\,M|L\pm1\,M\rangle\langle 1\,L\,0\,0|L\pm1\,0\rangle]^{-1}. \tag{15}$$

In Eqs. (14) and (15), $\langle L_1\;L_2\;M_1\;M_2|L_3\;M_3\rangle$ denotes a Clebsch-Gordan coefficient.

Next the limiting expressions for $\Delta\mu^{\pm}(l,L)$ are derived as the interatomic separation R approaches zero and infinity: Use of the expansion

$$j_J(kR) = 2^J J!/(2J+1)!\,(kR)^J + O(R^{J+2}), \tag{16}$$

gives

$$\Delta\mu^{\pm}(l,L) \sim R^{J+J'} \text{ as } R \to 0 \tag{17}$$

with the consequence that the dispersion dipole vanishes at zero separation R. In the limit as $R \to \infty$, Eq. (12) reduces to

$$\Delta\mu^{\pm}(l,L) = D^{\pm}(l,L)R^{-(2l+2L+2\pm1)}, \tag{18}$$

after use of the relation

$$4/\pi^2 \int_0^\infty dk\, j_J(kR)\int_0^\infty dk'\, j_J(k'R)\alpha_l(k,k';i\omega)\beta_{LL\pm1}(k,k';i\omega,0)$$
$$= \delta_{Jl+L}\delta_{J'l+L\pm1}(2l+2L)!(2l+2L\pm2)![2^{2l+2L\pm1}(l+L)!(l+L\pm1)!]^{-1}$$
$$\times\alpha_l(i\omega)\beta_{LL\pm1}(i\omega,0)R^{-(2l+2L+2\pm1)} \text{ as } R \to \infty, \tag{19}$$

where

$$D^{\pm}(l,L) = p_{lL\pm}\, q_{lL\pm}^{(l+L)\,(l+L\pm1)}(2l+2L)!(2l+2L\pm2)![2^{2l+2L\pm1}(l+L)!(l+L\pm1)!]^{-1}$$

$$\times\hbar/2\pi\int_0^{\infty} d\omega\, \alpha_l(i\omega)\beta_{L\,L\pm1}(i\omega,0), \tag{20}$$

$$\alpha_l(i\omega) = lim_{k\to0}\, lim_{k'\to0}\, \alpha_l(k,k';i\omega)k^{-l}k'^{-l}, \tag{21}$$

and

$$\beta_{L\,L\pm1}(i\omega,0) = lim_{k\to0}\, lim_{k'\to0}\, \beta_{L\,L\pm1}(k,k';i\omega,0)k^{-L}k'^{-(L\pm1)}. \tag{22}$$

Equation (19) has been derived by an analysis similar to that given in Appendix 1 of reference 24.

Eq. (18) gives the long-range form of the dispersion-induced dipole for a pair of distinct, spherically symmetric atoms,

$$\Delta\mu = D_7\,R^{-7} + D_9\,R^{-9} + D_{11}\,R^{-11} + \cdots. \tag{23}$$

The coefficients D_7, D_9, D_{11}, and higher-order coefficients can be computed from Eq. (20) for $D^{\pm}(l,L)$. For example, the leading dispersion dipole coefficient D_7 is given by

$$D_7 = D^{+}(1,1) + D^{+}(2,0) + D^{-}(1,2) + D^{-}(2,1). \tag{24}$$

The quadrupole moment induced in A by dispersion interactions with B satisfies

$$\Delta\Theta^{A}_{\alpha\beta,disp} = \hbar/(8\pi)^5 \int d\mathbf{k}\, \exp(-i\mathbf{k}\cdot\mathbf{R})k^{-2}\int d\mathbf{k}'\, \exp(i\mathbf{k}'\cdot\mathbf{R})k'^{-2}$$

$$\times\int_0^{\infty} d\omega\, \chi^{B}(\mathbf{k},\mathbf{k}';i\omega)\,\hat{B}^{A}_{\alpha\beta}(-\mathbf{k},-\mathbf{k}';i\omega,0), \tag{25}$$

where

$$\hat{B}_{\alpha\beta}(\mathbf{k},\mathbf{k}';\omega,0) = \sum_{L=0}^{\infty}\sum_{M=-L}^{L}\sum_{L'=0}^{\infty}\sum_{M'=-L'}^{L'} c_L c^{*}_{L'}\, Y^{M}_{L}(\theta,\phi)Y^{M'}_{L'}(\theta',\phi')^{*}$$

$$\times\, B^{MM'}_{LL',\alpha\beta}(k,k';\omega,0) \qquad (26))$$

with $B^{MM'}_{LL',\alpha\beta}(k,k';\omega,0)$ given by Eqs. (4.19a)-(4.19c) and an equation analogous to

Eq. (4.15).

For simplicity, only the zz-component of the dispersion-induced quadrupole for a pair of S-state atoms is considered here. Then only the components $B^{MM}_{LL,zz}$ and $B^{MM}_{LL\pm2,zz}$ in Eq. (26) are nonzero. By an analysis similar to the derivation that led to equations (9) and (10), the following results are obtained:

$$\Delta\Theta^{A}_{zz,disp} = \sum_{l}\sum_{L}[\Delta\Theta_{-2}(l,L) + \Delta\Theta_{0}(l,L) + \Delta\Theta_{-2}(l,L)], \tag{27}$$

where

$$\Delta\Theta_{\alpha}(l,L) = s^{\alpha}_{lL}\sum_{J=|L-l|}^{L+l}\sum_{J'=|L+\alpha-l|}^{L+\alpha-l} t^{JJ'\alpha}_{lL}\,(2/\pi)^2\int_0^\infty dk\, j_J(kR)\int_0^\infty dk'\, j_{J'}(k'R)$$
$$\times\hbar/2\pi\int_0^\infty d\omega\,\alpha^{B}_{l}(k,k';i\omega)\,B^{A}_{LL+\alpha}(k,k';i\omega,0) \tag{28}$$

with $\alpha = 0, \pm 2$. The coefficients s^{α}_{lL} and $t^{JJ'\alpha}_{lL}$ satisfy

$$s^{\alpha}_{lL} = \frac{2^{2L+\alpha}}{(2l+1)(2L+1)}\left[\frac{2^{l}l!}{(2l)!}\right]^2\frac{L!(L+\alpha)!}{(2L)!(2L+2\alpha)!}, \tag{29}$$

$$t^{JJ'\alpha}_{lL} = (-i)^{J+\alpha}i^{J'}(2J+1)(2J'+1)\langle 2\,L\,0\,0|L+\alpha\;0\rangle\langle J\,l\,0\,0|L\,0\rangle\langle J'\,L+\alpha\;0\,0|l\,0\rangle$$
$$\times\sum_{M}\langle 2\,L\,0\,M|L+\alpha\;M\rangle\langle J\,l\,0\,M|L\,M\rangle\langle J'\,L+\alpha\;0\,M|l\,M\rangle, \tag{30}$$

and

$$B_{LL+\alpha}(k,k';i\omega,0) = B^{MM}_{LL+\alpha}(k,k';i\omega,0)[\langle 1\,L\,0\,M|L+\alpha\;M\rangle\langle 1\,L\,0\,0|L+\alpha\;0\rangle]^{-1}. \tag{31}$$

It can be shown that $\Delta\Theta_{\alpha}(l,L)$ vanishes as $R\to 0$. As $R\to\infty$, an analysis similar to that leading to Eqs. (18) and (20) gives:

$$\Delta\Theta_{\alpha}(l,L) = M_{\alpha}(l,L)R^{-(2l+2L+2+\alpha)} \tag{32}$$

with

$$M_\alpha(l,L) = s^\alpha_{lL}\, t_{lL}^{(l+L)(l+L+\alpha)\alpha} (2l+2L)!\,(2l+2L+2\alpha)!\,[2^{2l+2L+\alpha}(l+L)!(l+L+\alpha)!]^{-1}$$

$$\times \hbar/2\pi \int_0^\infty d\omega\, \alpha_l(i\omega) B_{L\,L+\alpha}(i\omega,0), \tag{33}$$

where $\alpha = 0, \pm 2$, and

$$B_{L\,L+\alpha}(i\omega,0) = lim_{k\to 0}\, lim_{k'\to 0}\, B_{L\,L+\alpha}(k,k';i\omega,0)\, k^{-L} k'^{-(L+\alpha)}. \tag{34}$$

Equation (32) gives the long-range form of the local dispersion quadrupole in an atomic pair:

$$\Theta_{zz} = M_6 R^{-6} + M_8 R^{-8} + M_{10} R^{-10} + \cdots, \tag{35}$$

where the coefficients M_6, M_8, $\cdots$ can be obtained from $M_\alpha(l,L)$ given by Eq. (33). For example, the leading local dispersion quadrupole coefficient M_6 satisfies

$$M_6 = M_{-2}(1,2) + M_{-2}(2,1) + M_0(1,1) + M_0(1,0). \tag{36}$$

5.3 Application to Hydrogen Atoms

For the hydrogen atom in the 1s state, the z-component of the β susceptibility density and the zz-component of the B susceptibility density have been determined in Chapter IV. They satisfy

$$\beta_{L\,L\pm1}(k,k';\omega,0) = \frac{2\omega_L a_L}{\omega_L^2 - \omega^2}\left[f_L(k)\, g_{L\pm}(k') - \frac{a_{L\pm1} d_{L\pm}}{\omega_L - \omega_{L\pm1}} f_L(k)\, f_{L\pm1}(k')\right]$$

$$+ \frac{2\omega_{L\pm1} a_{L\pm1}}{\omega_{L\pm1}^2 - \omega^2}\left[f_{L\pm1}(k')\, h_{L\pm}(k) - \frac{a_L d_{L\pm}}{\omega_L - \omega_{L\pm1}} f_L(k)\, f_{L\pm1}(k')\right] \tag{37}$$

with $L \geq 1$ for $\beta_{L\,L+1}$ and $L \geq 2$ for $\beta_{L\,L-1}$, and

$$\beta_{01}(k,k';\omega,0) = \frac{2\omega_1 a_1}{\omega_1^2 - \omega^2} f_1(k')\, h_{0+}(k), \tag{38}$$

$$\beta_{10}(k,k';\omega,0) = \frac{2\omega_1 a_1}{\omega_1^2 - \omega^2} f_1(k)\, g_{1-}(k'), \tag{39}$$

and

$$B_{L\,L\pm2}(k,k';\omega,0)=\frac{2\omega_L a_L}{\omega_L^2-\omega^2}[f_L(k)\,A_{L\,L\pm2}(k')-\frac{a_{L\pm2}D_{L\,L\pm2}}{\omega_L-\omega_{L\pm2}}f_L(k)\,f_{L\pm2}(k')]$$

$$+\frac{2\omega_{L\pm2}\,a_{L\pm2}}{\omega_{L\pm2}^2-\omega^2}[f_{L\pm2}(k')\,C_{L\,L\pm2}(k)+\frac{a_L D_{L\,L\pm2}}{\omega_L-\omega_{L\pm2}}f_L(k)\,f_{L\pm2}(k')] \tag{40}$$

with $L \geq 1$ for B_{LL+2} and $L \geq 3$ for B_{LL-2}, and

$$B_{02}(k,k';\omega,0)=\frac{2\omega_2\,a_2}{\omega_2^2-\omega^2}f_2(k')\,C_{02}(k), \tag{41}$$

$$B_{20}(k,k';\omega,0)=\frac{2\omega_2\,a_2}{\omega_2^2-\omega^2}f_2(k)\,A_{20}(k'), \tag{42}$$

and

$$B_{LL}(k,k';\omega,0)=\frac{2\omega_L\,a_L}{\omega_L^2-\omega^2}[f_L(k)\,A_{LL}(k')+f_L(k')C_{LL}(k)]$$

$$+\frac{2a_L^2\,D_{LL}\,(\omega_L^2+\omega^2)}{(\omega_L^2-\omega^2)^2}f_L(k)f_L(k'). \tag{43}$$

The linear charge-density susceptibility in Eqs. (12) and (28) has been obtained by Koide [24]:

$$\alpha_l(k,k';\omega)=\frac{2\omega_l\,a_l}{\omega_l^2-\omega^2}f_l(k)\,f_l(k'). \tag{44}$$

The functions ω_L, a_L, $f_L(k)$, $d_{L\pm}$, $g_{L\pm}(k)$, $h_{L\pm}(k)$, D_{LL+n}, $A_{LL+n}(k)$, and $C_{LL+n}(k)$ ($n=-2$, 0, or 2) appearing in Eqs. (37)-(44) have been evaluated analytically and they are given by Eqs. (4.28)-(4.36) and (4.42)-(4.50).

From Eqs. (20) and (33), the leading three local dipole coefficients (D_7, D_9, and D_{11}) and the leading three local quadrupole coefficients (M_6, M_8, and M_{10}) have been obtained for a pair of ground-state hydrogen atoms. The results are listed in Table 5.1.

The *ab initio* values for D_7, D_9, and M_6 [26-29] are also given in Table 5.1 for comparison. Table 5.1 shows that the relative error is 6% for D_7, 5% for D_9, and 12% for M_6. These errors stem from the approximations introduced in obtaining the function $\Phi_L^M(k,\omega)$ from Eq. (4.22).

Table 5.1. Local dispersion dipole coefficients and quadrupole coefficients (in a.u.) for H(1s)···H(1s).

Coefficients	This work	*Ab initio* calculations
D_7	-416.4	-394.51[a] -394.5106[b] -393.5[c]
D_9	-13420	-12800[d]
D_{11}	-544000	
M_6	-58.3	-52.2[b]
M_8	-5873	
M_{10}	-257000	

[a]Ref. [26].
[b]Ref. [27].
[c]Ref. [28].
[d]Ref. [29].

Substitution of Eq. (37) for $\beta_{L\,L\pm 1}(k,k';\omega,0)$ and Eq. (44) for $\alpha_l(k,k';\omega)$ into Eq. (12) gives the dipole induced in one hydrogen atom by dispersion interactions with the second, with direct charge-overlap effects included:

$$\Delta\mu^{\pm}(l,L) = 4/\pi^2\; p_{l\,L\pm} \sum_{J=|L-l|}^{L+l} \sum_{J'=|L\pm 1-l|}^{L\pm 1+l} q_{l\,L\pm}^{J\,J'} \{a_l\, a_L (\omega_l+\omega_L)^{-1} \int_0^\infty dk\, j_J(kR)\, f_l(k)\, f_L(k)$$

$$\times [\int_0^\infty dk'\, j_{J'}(k'R)\, f_l(k')\, g_{L\pm}(k') - a_{L\pm 1}\, d_{L\pm}(\omega_L - \omega_{L\pm 1})^{-1}$$

$$\times \int_0^\infty dk'\, j_{J'}(k'R) f_l(k') f_{L\pm 1}(k')]$$

$$+ a_l\, a_{L\pm 1} (\omega_l + \omega_{L\pm 1})^{-1} \int_0^\infty dk'\, j_{J'}(k'R) f_l(k') f_{L\pm 1}(k')$$

$$\times [\int_0^\infty dk\, j_J(kR) f_l(k) h_{L\pm}(k) + a_L d_{L\pm}(\omega_L - \omega_{L\pm 1})^{-1}$$

$$\times \int_0^\infty dk\, j_J(kR) f_l(k) f_L(k)]\} \qquad (45)$$

with $l \ge 1$, $L \ge 1$ for $\mu^+(l,L)$, and $l \ge 1$, $L \ge 2$ for $\mu^-(l,L)$, and

$$\Delta\mu^+(l,0) = 4/\pi^2\; p_{l0} \sum_{J'=|l-1|}^{l+1} q_{l0}^{l\,J'}\, a_1\, a_l (\omega_1 + \omega_l)^{-1} \int_0^\infty dk\, j_l(kR) f_l(k) h_{0+}(k)$$

$$\times \int_0^\infty dk'\, j_{J'}(k'R) f_1(k') f_l(k'), \qquad (46)$$

$$\Delta\mu^-(l,1) = 4/\pi^2\; p_{l1-} \sum_{J=|l-1|}^{l+1} q_{l1-}^{J\,l}\, a_1\, a_l (\omega_1 + \omega_l)^{-1} \int_0^\infty dk\, j_J(kR) f_1(k) f_l(k)$$

$$\times \int_0^\infty dk'\, j_l(k'R) f_l(k') g_{1-}(k'). \qquad (47)$$

In deriving Eqs. (45)-(47), the intergral identity

$$\int_0^\infty d\omega\, a\, b (a^2+\omega^2)^{-1} (b^2+\omega^2)^{-1} = \pi/2\,(a+b)^{-1} \qquad (48)$$

has been used for a, b > 0.

The lowest-order contribution to the local dispersion dipole in the pair H$\cdots$H is the sum of two terms, $\Delta\mu^+(1,0)$ and $\Delta\mu^-(1,1)$. From Eq. (18), both of these terms might be expected to lead an R^{-5} behavior as $R \to \infty$. Thus this contribution is denoted by $\mu_5(R)$:

$$\mu_5(R) = \Delta\mu^+(1,0) + \Delta\mu^-(1,1). \tag{49}$$

The long-range coefficient D_5 vanishes, so $\mu_5(R)$ is purely an overlap effect. This is consistent with the fact that the leading term of the long-range dispersion dipole for an atomic pair varies as R^{-7}. $\mu_5(R)$ can be evaluated analytically as a function of the interatomic separation R, as shown in Appendix A. It is plotted against R in Figure 5.1.

Similarly, the function $\mu_7(R)$ that reduces to the leading R^{-7} term as $R \to \infty$ is the sum of four terms:

$$\mu_7(R) = \Delta\mu^+(1,1) + \Delta\mu^+(2,0) + \Delta\mu^-(1,2) + \Delta\mu^-(2,1) = \chi_7(R) D_7 R^{-7} \tag{50}$$

with D_7 listed in Table 5.1. $\mu_7(R)$ is also given analytically in Appendix A, and it is plotted in Figure 5.1. The damping function $\chi_7(R)$ is shown in Figure 5.2.

The local dispersion quadrupole of $H \cdots H$ pair, which approaches the leading R^{-6} term at long range, includes three terms:

$$\Theta_6(R) = \Delta\Theta_0(1,1) + \Delta\Theta_2(1,0) + \Delta\Theta_{-2}(1,2) = \chi_6(R) M_6 R^{-6}, \tag{51}$$

where M_6 is listed in Table 5.1, and $\Delta\Theta_0(1,1)$, $\Delta\Theta_2(1,0)$, and $\Delta\Theta_{-2}(1,2)$ are obtained by substitution of Eqs. (40)-(44) into Eq. (28) and use of the identity (48), as well as the identity

$$\int_0^\infty d\omega\, \omega^2 (a^2 + \omega^2)^{-1} (b^2 + \omega^2)^{-2} = \pi/4\; b^{-1} (a+b)^{-2} \tag{52}$$

for a, b> 0. This yields

$$\begin{aligned}\Delta\Theta_0(1,1) = 4/\pi^2 s_{11}^0 \sum_{J=0,2} \sum_{J'=0,2} t_{11}^{JJ'0} \{ & a_1^2/(2\omega_1) [\int_0^\infty dk\, j_J(kR) f_1^2(k) \\ & \times \int_0^\infty dk'\, j_{J'}(k'R) f_1(k') A_{11}(k') \\ & + \int_0^\infty dk'\, j_{J'}(k'R) f_1^2(k') \int_0^\infty dk\, j_J(kR) f_1(k) C_{11}(k)] \\ & + a_1^3 D_{11}/(4\omega_1^2) \int_0^\infty dk\, j_J(kR) f_1^2(k) \int_0^\infty dk'\, j_{J'}(k'R) f_1^2(k') \},\end{aligned} \tag{53}$$

$$\Delta\Theta_2(1,0) = 4/\pi^2 s_{10}^2 \sum_{J'=1,3} t_{10}^{1J'2} a_1 a_2/(\omega_1+\omega_2)\int_0^\infty dk\, j_1(kR) f_1(k) C_{02}(k)$$

$$\times\int_0^\infty dk' j_{J'}(k'R) f_1(k') f_2(k'), \tag{54}$$

and

$$\Delta\Theta_{-2}(1,2) = \Delta\Theta_2(1,0). \tag{55}$$

The function $\Theta_6(R)$ is evaluated analytically in Appendix A. It is plotted in Figure 5.3. The corresponding damping function $\chi_6(R)$ is plotted in Figure 5.2.

The net quadrupole of the $H\cdots H$ pair with respect to the center of mass satisfies

$$\Theta_6^{HH}(R) = 2\Theta_6(R) - 2R\mu_7(R). \tag{56}$$

The dependence of $\Theta_6^{HH}(R)$ on R is illustrated in Figure 5.4.

Figure 5.2 shows that the dispersion dipole and quadrupole are damped differently, but both χ_6 and χ_7 drop to ~0.85 at van der Waals minimum (R = 7.85 a.u.) for H_2 in the triplet state.

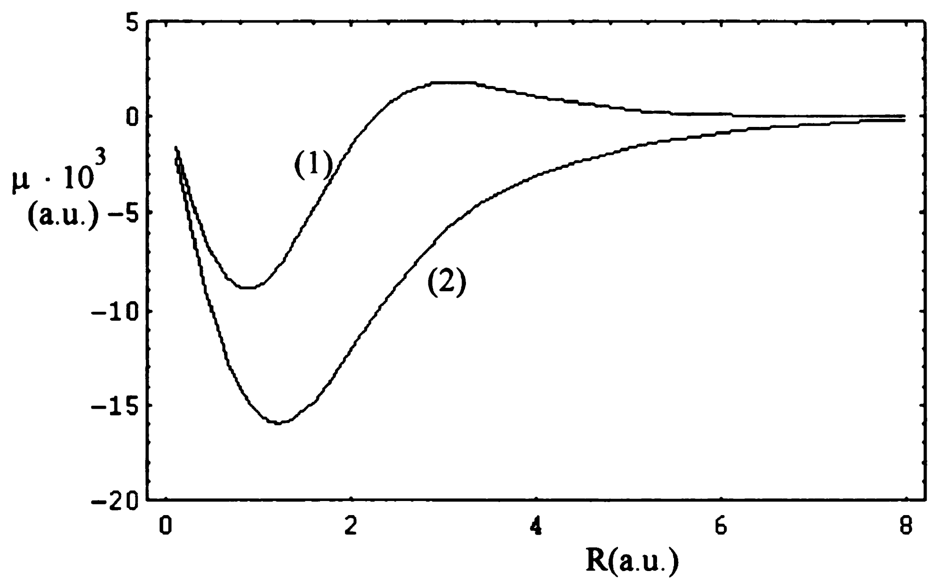

Figure 5.1. The dipole moment induced in one hydrogen atom by dispersion interactions with a second, displaced by a distance R along the z axis. (1) $\mu_5(R)$ defined by Eq. (49), and (2) $\mu_7(R)$ defined by Eq. (50).

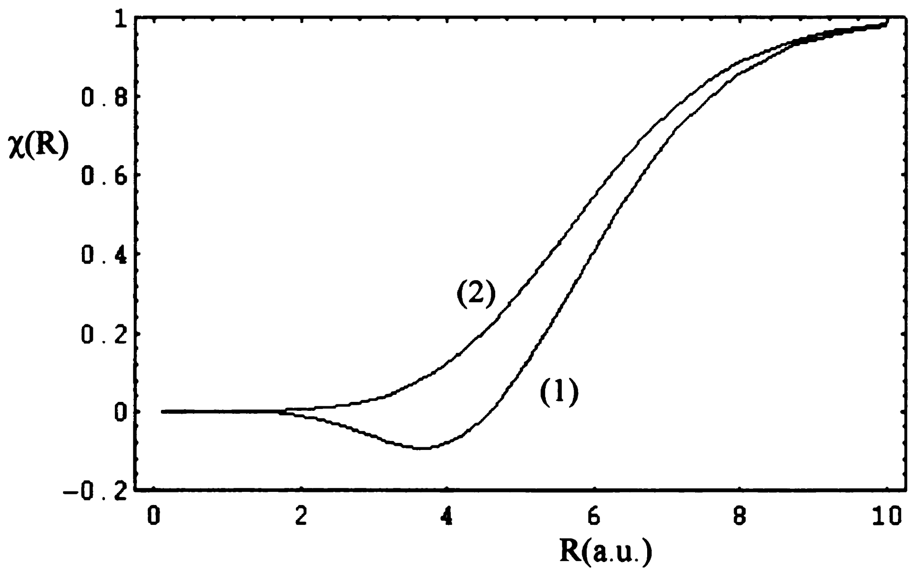

Figure 5.2. The damping functions $\chi_6(R)$ and $\chi_7(R)$ defined by Eq. (51) and Eq. (50), respectively. (1) $\chi_6(R)$, and (2) $\chi_7(R)$.

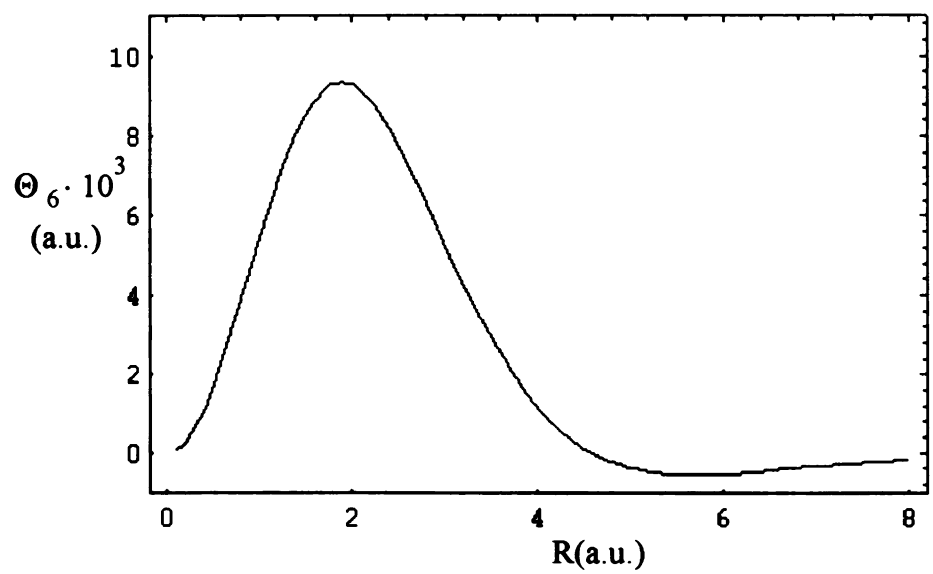

Figure 5.3. The leading term in the local quadrupole moment Θ_6 induced in one hydrogen atom by dispersion interactions with a second, displaced by a distance R along the z axis.

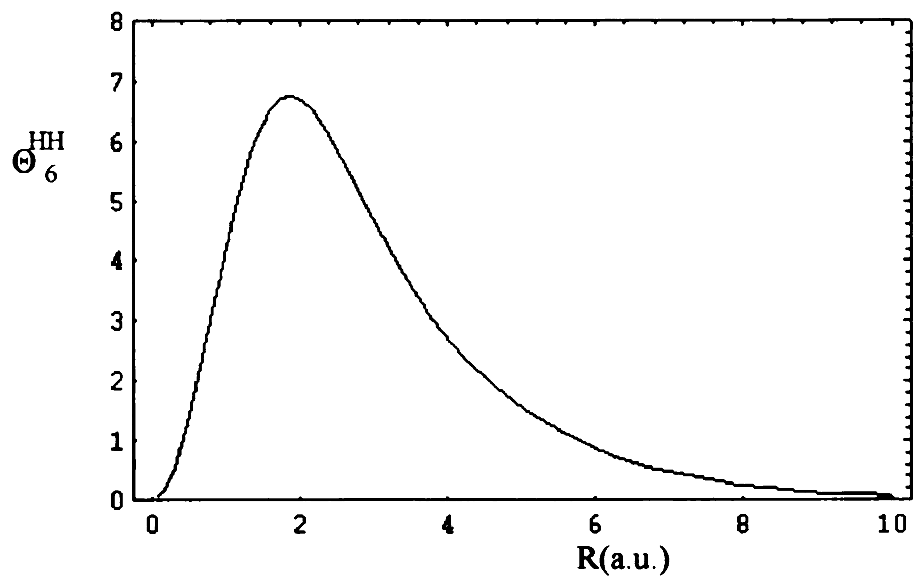

Figure. 5.4 The leading term in the pair quadrupole moment of a H$\cdots$H pair given by Eq. (56).

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CHAPTER VI

NONADDITIVE THREE-BODY ENERGIES, DIPOLES, AND FORCES: AN APPROACH BASED ON NONLOCAL RESPONSE THEORY

6.1 Introduction

Effects of nonadditive three-body forces [1, 2] can be detected experimentally in measurements of third virial coefficients [3-8], binding energies of rare-gas crystals at lower temperatures [8-11], collision-induced far-infrared absorption by compressed gases [12-15], and rotational and vibrational spectra of van der Waals trimers [16-27]. The purpose of this work is to analyze the nonadditive three-body energies and polarization for molecules interacting at intermediate or long range where intermolecular exchange effects are negligible.

The analysis is based on a nonlocal response theory. In the theory, the polarizability density $\alpha(\mathbf{r},\mathbf{r}')$ and hyperpolarizability densities such as $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ and $\gamma(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''')$ [28-31] are used to describe the nonlocal response of a molecule to external fields or local fields due to its interacting partners. Thus equations for three-body energies and polarization within the nonlocal response theory include the direct modifications of the lowest-order induction and dispersion effects due to overlap of the electronic charge distributions of the interacting molecules. These equations reduce to those from the multipole expansion at long range, while at short range they are substantially damped.

The analysis is complete to third order in the intermolecular interactions. To this order, dispersion [1, 2, see also 32-39], classical induction, and combined induction-dispersion effects all contribute to the total interaction energies.

In Sec. 6.2, polarizability densities are used to analyze three-body dispersion energies. The analysis establishes a simple physical picture of three-body dispersion interactions. In this picture, the spontaneously fluctuating polarization of one molecule polarizes a second, polarizing a third, and producing a reaction field at the first molecule. The resulting energy change of the first molecule depends on the correlation of the fluctuating polarization. There are similar energy changes associated with their polarization fluctuations in the second and third molecules. The sum of the energy changes in all three molecules gives the three-body dispersion energy.

In addition to dispersion interactions, the work also identifies other polarization mechanisms that contribute to nonadditive three-body energies. Induction energies, arising from polarization of molecules due to the fields from permanent molecular charge distributions, appear at second order as well as at third order. Combined induction-dispersion effects occur at third order. They reflect the perturbation of two-body dispersion interactions by the static field due to the permanent charge distribution of the third body. These are treated in Sec. 6.3.

Sec. 6.4 contains an analysis of the three-body interaction-induced polarization. The three-body polarization $\mathbf{P}^{(3)}(\mathbf{r})$ is obtained by first finding the change in the three-body energy $\Delta E^{(3)}$ due to the application of a static, spatially nonuniform external electric field $\mathbf{F}^{e}(\mathbf{r})$, and then calculating the functional derivative $-\delta\Delta E^{(3)}/\delta\mathbf{F}^{e}(\mathbf{r})$. The results are expressed in terms of fundamental molecular properties such as the permanent polarization, polarizability density, and hyperpolarizability densities. Spatial integration of $\mathbf{P}^{(3)}(\mathbf{r})$ over all space gives the three-body interaction-induced dipoles [13-15, 40-44]. Three-body dipoles (as well as three-body potentials) are responsible for the component in collision-induced far-infrared spectra of compressed gases that is proportional to the third power of the density of the gas [13].

In Sec. 6.5, the forces acting on the nuclei in molecule A due to its interactions with B and C are calculated. An electrostatic interpretation of nonadditive three-body forces on nuclei is given based on a chain of relations that connect property derivatives with respect to nuclear coordinates, linear response tensors, and nonlinear response tensors [45-47]. It is proven explicitly that the three-body dispersion force on a nucleus in molecule A results from the classical electrostatic attraction of the nucleus to the three-body dispersion-induced polarization of the electrons on molecule A *itself*. This generalizes Hunt's proof [48] of Feynman's conjecture [49] about the origin of two-body dispersion forces to three-body dispersion forces. In contrast to the dispersion forces, the classical induction and induction-dispersion forces on a nucleus in A depend not only on the interaction-induced polarization of electrons on A, but also on B and C.

6.2 Nonadditive Three-body Dispersion Energy

In this section, the three-body dispersion energy is analyzed using nonlocal polarizability densities to account for the distribution of polarizable matter in a set of interacting molecules A, B, and C. The analysis includes the effects of direct charge overlap on the dispersion energy, but not the effects due to exchange or charge transfer.

The nonadditive three-body dispersion energy $\Delta E^{(3)}_{\text{disp}}$ results from correlations in the fluctuating polarization of molecules A, B, and C. The instantaneous polarization $\mathbf{P}_{\text{fl}}(\mathbf{r},\omega)$ of molecule 1 polarizes molecule 2, which in turn polarizes molecule 3; the reaction field from molecule 3 acts on molecule 1, to produce an energy shift. $\Delta E^{(3)}_{\text{disp}}$ is the sum of six energy-shift terms, generated by all permutations of A, B, and C among the molecule labels 1, 2, and 3. The three-body component of the reaction field $\mathbf{F}^{\text{A}}_{\text{fl}}(\mathbf{r}^{\text{v}},\omega)$ at molecule A, due to fluctuations $\mathbf{P}_{\text{fl}}(\mathbf{r},\omega)$ originating in A, is given by

$$\mathbf{F}^{\text{A}}_{\text{fl}}(\mathbf{r}^{\text{v}},\omega) = (1+\wp^{\text{BC}})\int d\mathbf{r}\cdots d\mathbf{r}^{\text{iv}}\, \mathbf{T}(\mathbf{r}^{\text{v}},\mathbf{r}^{\text{iv}})\cdot\alpha^{\text{C}}(\mathbf{r}^{\text{iv}},\mathbf{r}''';\omega)$$
$$\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')\cdot\alpha^{\text{B}}(\mathbf{r}'',\mathbf{r}';\omega)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\mathbf{P}^{\text{A}}_{\text{fl}}(\mathbf{r},\omega), \qquad (1)$$

where $\wp^{BC}$ permutes the labels B and C in the expression that follows, and $T(\mathbf{r},\mathbf{r}')$ is the dipole propagator,

$$T_{\alpha\beta}(\mathbf{r},\mathbf{r}') = T_{\alpha\beta}(\mathbf{r}-\mathbf{r}') = \nabla_\alpha \nabla_\beta (|\mathbf{r}-\mathbf{r}'|^{-1})$$
$$= [3(r_\alpha - r'_\alpha)(r_\beta - r'_\beta) - \delta_{\alpha\beta}|\mathbf{r}-\mathbf{r}'|^2]/(|\mathbf{r}-\mathbf{r}'|^5) - 4\pi/3\,\delta_{\alpha\beta}\,\delta(\mathbf{r}-\mathbf{r}') \quad (2)$$

with retardation effects neglected. The energy shift of molecule A in the field $\mathbf{F}_{fl}^{A}(\mathbf{r}^{v},\omega)$ is

$$\Delta E_A^{(3)} = -1/2 \int d\mathbf{r}^{v} \langle \mathbf{P}_{fl}^{A}(\mathbf{r}^{v},t)\cdot \mathbf{F}_{fl}^{A}(\mathbf{r}^{v},t)\rangle. \quad (3)$$

Substitution of the frequency Fourier representations for $\mathbf{P}_{fl}^{A}(r^{v},t)$ and $\mathbf{F}_{fl}^{A}(r^{v},t)$ gives

$$\Delta E_A^{(3)} = -1/2\,(1+\wp^{BC})\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \int d\mathbf{r}\cdots d\mathbf{r}^{v} \langle \mathbf{P}_{fl}^{A}(\mathbf{r}^{v},\omega')$$
$$\cdot \mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot \alpha^{C}(\mathbf{r}^{iv},\mathbf{r}''';\omega)\cdot \mathbf{T}(\mathbf{r}''',\mathbf{r}'')\cdot \alpha^{B}(\mathbf{r}'',\mathbf{r}';\omega)$$
$$\cdot \mathbf{T}(\mathbf{r}',\mathbf{r})\cdot \mathbf{P}_{fl}^{A}(\mathbf{r},\omega)\rangle \exp[-i(\omega+\omega')t]. \quad (4)$$

The term given explicitly in Eq. (4) represents the polarization route $A \to B \to C \to A$, and the term generated by $\wp^{BC}$ represents the route $A \to C \to B \to A$. Similar expressions for $\Delta E_B^{(3)}$ and $\Delta E_C^{(3)}$ are obtained by finding the reaction fields acting on B and C.

The average energy change $\Delta E_A^{(3)}$ depends on the correlation in the fluctuating polarization of molecule A at points $\mathbf{r}$ and $\mathbf{r}^{v}$. According to the fluctuation-dissipation theorem [50, 51], the correlation is related to the imaginary part of the nonlocal polarizability density $\alpha^{A''}(\mathbf{r},\mathbf{r}^{v};\omega)$ by

$$1/2\langle P_{fl,\phi}^{A}(\mathbf{r},\omega)P_{fl,\alpha}^{A}(\mathbf{r}^{v},\omega') + P_{fl,\alpha}^{A}(\mathbf{r}^{v},\omega')P_{fl,\phi}^{A}(\mathbf{r},\omega)\rangle$$
$$= \hbar/2\pi\,\alpha_{\phi\alpha}^{A''}(\mathbf{r},\mathbf{r}^{v};\omega)\delta(\omega+\omega')\coth(\hbar\omega/2kT). \quad (5)$$

To illustrate the quantum mechanical nature of the fluctuations given by Eq. (5), the limit as $T \to 0$ is considered, with infinitesimal damping; then $\alpha''_{\phi\alpha}(\mathbf{r},\mathbf{r}^{v};\omega)$ for the molecular ground state $|0\rangle$ is given by [52]

$$\alpha''_{\phi\alpha}(\mathbf{r},\mathbf{r}^{\mathrm{v}};\omega) = \pi/\hbar \sum_{m\neq 0} [\langle 0|P_\phi(\mathbf{r})|m\rangle\langle m|P_\alpha(\mathbf{r}^{\mathrm{v}})|0\rangle\delta(\omega-\omega_{m0})$$

$$-\langle 0|P_\phi(\mathbf{r})|m\rangle\langle m|P_\alpha(\mathbf{r}^{\mathrm{v}})|0\rangle\delta(\omega+\omega_{m0})], \qquad (6)$$

assuming for simplicity that the states $|m\rangle$ are real. As $T \to 0$, $\coth(\hbar\omega/2kT) \to [\theta(\omega) - \theta(-\omega)]$, where $\theta(\omega)$ is the Heaviside step function. Thus Eq. (5) gives

$$1/2\left\langle P_{fl,\phi}(\mathbf{r},\omega)P_{fl,\alpha}(\mathbf{r}^{\mathrm{v}},\omega') + P_{fl,\alpha}(\mathbf{r}^{\mathrm{v}},\omega')P_{fl,\phi}(\mathbf{r},\omega)\right\rangle$$

$$= 1/2 \sum_{m\neq 0} \langle 0|P_\phi(\mathbf{r})|m\rangle\langle m|P_\alpha(\mathbf{r}^{\mathrm{v}})|0\rangle[\delta(\omega-\omega_{m0})+\delta(\omega+\omega_{m0})]\delta(\omega+\omega') \qquad (7)$$

or equivalently

$$1/2\left\langle P_{fl,\phi}(\mathbf{r},t)P_{fl,\alpha}(\mathbf{r}^{\mathrm{v}},t') + P_{fl,\alpha}(\mathbf{r}^{\mathrm{v}},t')P_{fl,\phi}(\mathbf{r},t)\right\rangle$$

$$= 1/2 \sum_{m\neq 0} \langle 0|P_\phi(\mathbf{r})|m\rangle\langle m|P_\alpha(\mathbf{r}^{\mathrm{v}})|0\rangle\{\exp[-i\omega_{m0}(t-t')] + \exp[i\omega_{m0}(t-t')]\}. \qquad (8)$$

A direct computation of the dynamical correlations of the fluctuating polarization in the ground state yields

$$1/2\left\langle P_{fl,\phi}(\mathbf{r},t)P_{fl,\alpha}(\mathbf{r}^{\mathrm{v}},t') + P_{fl,\alpha}(\mathbf{r}^{\mathrm{v}},t')P_{fl,\phi}(\mathbf{r},t)\right\rangle$$

$$= 1/2\langle 0|\{\exp(iHt/\hbar)P_\phi(r)\exp[-iH(t-t')/\hbar]P_\alpha(\mathbf{r}^{\mathrm{v}})\exp(-iHt')$$

$$+\exp(iHt'/\hbar)P_\alpha(\mathbf{r}^{\mathrm{v}})\exp[-iH(t'-t)/\hbar]P_\phi(\mathbf{r})\exp(-iHt)\}|0\rangle$$

$$-\langle 0|P_\phi(\mathbf{r})|0\rangle\langle 0|P_\alpha(\mathbf{r}^{\mathrm{v}})|0\rangle. \qquad (9)$$

In equation (9), the static polarization product has been subtracted from the expression; static reaction field effects are treated separately in Sec. 6.3. Eqs. (8) and (9) are equivalent. The fluctuation correlations persist in the limit as $T \to 0$, where they are determined by the intrinsic, quantum mechanical fluctuations of the polarization in the molecular ground state.

Substitution of Eq. (5) into Eq. (4) gives

$$\Delta E_A^{(3)} = -\hbar/4\pi\,(1+\wp^{BC})\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\cdots d\mathbf{r}^{v}\, \mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C}(\mathbf{r}^{iv},\mathbf{r}''';\omega)$$

$$\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')\cdot\alpha^{B}(\mathbf{r}'',\mathbf{r}';\omega)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A_{*}}(\mathbf{r},\mathbf{r}^{v};\omega)]\coth(\hbar\omega/2kT), \quad (10)$$

where

$$\mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C}(\mathbf{r}^{iv},\mathbf{r}''';\omega)\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')\cdot\alpha^{B}(\mathbf{r}'',\mathbf{r}';\omega)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A_{*}}(\mathbf{r},\mathbf{r}^{v};\omega)]$$

$$\equiv T_{\alpha\beta}(\mathbf{r}^{v},\mathbf{r}^{iv})\alpha^{C}_{\beta\gamma}(\mathbf{r}^{iv},\mathbf{r}''';\omega)T_{\gamma\delta}(\mathbf{r}''',\mathbf{r}'')\alpha^{B}_{\delta\varepsilon}(\mathbf{r}'',\mathbf{r}';\omega)$$

$$\times T_{\varepsilon\phi}(\mathbf{r}',\mathbf{r})\alpha^{A_{*}}_{\phi\alpha}(\mathbf{r},\mathbf{r}^{v};\omega), \quad (11)$$

and the Einstein convention of summation over repeated Greek subscripts is followed in Eq. (11) and below. Then in the limit $T \to 0$,

$$\Delta E_A^{(3)} = -\hbar/2\pi\,(1+\wp^{BC})\mathit{Re}\int_{0}^{\infty} d\omega \int d\mathbf{r}\cdots d\mathbf{r}^{v}\, \mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C}(\mathbf{r}^{iv},\mathbf{r}''';\omega)$$

$$\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')\cdot\alpha^{B}(\mathbf{r}'',\mathbf{r}';\omega)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A_{*}}(\mathbf{r},\mathbf{r}^{v};\omega)], \quad (12)$$

where *Re* denotes the real part of the expression that follows. Use of

$$\mathit{lim}_{\varepsilon\to 0}[(x-\omega)-i\varepsilon]^{-1} = P(x-\omega)^{-1} + i\pi\delta(x-\omega) \quad (13)$$

and the Kramers-Kronig relation [53] between the real and imaginary parts of the polarizability density

$$\alpha'(\mathbf{r},\mathbf{r}';\omega) = 1/\pi\; P\int_{-\infty}^{\infty} dx\,\alpha''(\mathbf{r},\mathbf{r}';x)(x-\omega)^{-1} \quad (14)$$

(where P denotes the Cauchy principal value of the integral) gives

$$\alpha(\mathbf{r},\mathbf{r}';\omega) = \alpha'(\mathbf{r},\mathbf{r}';\omega) + i\,\alpha''(\mathbf{r},\mathbf{r}';\omega)$$

$$= \mathit{lim}_{\varepsilon\to 0}\, 1/\pi \int_{-\infty}^{\infty} dx\,\alpha''(\mathbf{r},\mathbf{r}';x)(x-\omega-i\varepsilon)^{-1}$$

$$= \mathit{lim}_{\varepsilon\to 0}\, 2/\pi \int_{0}^{\infty} dx\, x\,\alpha''(\mathbf{r},\mathbf{r}';x)[x^2-(\omega+i\varepsilon)^2]^{-1}. \quad (15)$$

In the transformation between the second and third lines of Eq. (15), use has been made of the fact that $\alpha''(\mathbf{r},\mathbf{r}';x)$ is an odd function of the frequency x. From Eqs. (12) and (15),

$$\Delta E_A^{(3)} = -2\hbar/\pi^3 (1+\wp^{BC})\, lim_{\varepsilon\to 0} \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz\, Re\{x[x^2-(z+i\varepsilon)^2]^{-1}$$

$$\times y[y^2-(z+i\varepsilon)^2]^{-1}\} \int d\mathbf{r}\cdots d\mathbf{r}^{v}\, \mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C_n}(\mathbf{r}^{iv},\mathbf{r}''';x)$$

$$\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')\cdot\alpha^{B_m}(\mathbf{r}'',\mathbf{r}';y)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A_n}(\mathbf{r},\mathbf{r}^{v};z)]\,. \qquad (16)$$

Adding the corresponding expressions for $\Delta E_B^{(3)}$ and $\Delta E_C^{(3)}$ to Eq. (16) and taking the limit as $\varepsilon \to 0$ yields

$$\Delta E_{disp}^{(3)} = -2\hbar/\pi^3 \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz\,(x+y+z)(x+y)^{-1}(y+z)^{-1}(z+x)^{-1}$$

$$\times \int d\mathbf{r}\cdots d\mathbf{r}^{v}\, \{\mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C_n}(\mathbf{r}^{iv},\mathbf{r}''';x)\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')$$

$$\cdot\alpha^{B_m}(\mathbf{r}'',\mathbf{r}';y)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A_n}(\mathbf{r},\mathbf{r}^{v};z)]$$

$$+\mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{B_m}(\mathbf{r}^{iv},\mathbf{r}''';y)\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')$$

$$\cdot\alpha^{C_n}(\mathbf{r}'',\mathbf{r}';x)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A_n}(\mathbf{r},\mathbf{r}^{v};z)]\}. \qquad (17)$$

Use of the Born symmetry of the nonlocal polarizability density [28, 30],

$$\alpha_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega) = \alpha_{\beta\alpha}(\mathbf{r}',\mathbf{r};\omega), \qquad (18)$$

and the symmetry of the **T** tensor, $\mathbf{T}(\mathbf{r},\mathbf{r}') = \mathbf{T}(\mathbf{r}',\mathbf{r})$, transforms Eq. (17) into

$$\Delta E_{disp}^{(3)} = -4\hbar/\pi^3 \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz\,(x+y+z)(x+y)^{-1}(y+z)^{-1}(z+x)^{-1}$$

$$\times \int d\mathbf{r}\cdots d\mathbf{r}^{v}\, \mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C_n}(\mathbf{r}^{iv},\mathbf{r}''';x)\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')$$

$$\cdot\alpha^{B_m}(\mathbf{r}'',\mathbf{r}';y)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A_n}(\mathbf{r},\mathbf{r}^{v};z)]\,. \qquad (19)$$

The frequency integrals over x, y, and z can be converted into independent quadratures using the identity

$$(x+y+z)(x+y)^{-1}(y+z)^{-1}(z+x)^{-1}$$

$$= 2/\pi \int_0^\infty d\omega\, x\,y\,z\,(x^2+\omega^2)^{-1}(y^2+\omega^2)^{-1}(z^2+\omega^2)^{-1}\,. \qquad (20)$$

From Eq. (6), which holds in the limit of infinitesimal damping,

$$\int_0^\infty dz\, z(z^2+\omega^2)^{-1}\alpha_{\alpha\beta}^{A''}(\mathbf{r},\mathbf{r}^{v};z)$$

$$= \pi/\hbar \sum_{m\neq 0}\omega_{m0}(\omega_{m0}^2+\omega^2)^{-1}\langle 0|P_\alpha(\mathbf{r})|m\rangle\langle m|P_\beta(\mathbf{r}^{v})|0\rangle$$

$$= \pi/2\,\alpha_{\alpha\beta}^{A}(\mathbf{r},\mathbf{r}^{v};i\omega). \tag{21}$$

Equations (19)-(21) imply

$$\Delta E_{disp}^{(3)} = -\hbar/\pi \int_0^\infty d\omega \int d\mathbf{r}\cdots d\mathbf{r}^{v}\, \mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C}(\mathbf{r}^{iv},\mathbf{r}''';i\omega)\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')$$
$$\cdot\alpha^{B}(\mathbf{r}'',\mathbf{r}';i\omega)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A}(\mathbf{r},\mathbf{r}^{v};i\omega)]\,. \tag{22}$$

Equation (22) gives the principal result of this section; it expresses the nonadditive, three-body dispersion energy as a tensor product of the dipole propagators and the imaginary-frequency nonlocal polarizability densities of the three interacting molecules A, B, and C. Within the nonlocal response model, $\Delta E_{disp}^{(3)}$ has a simple physical interpretation in terms of polarization fluctuations and the energy of polarization in the reaction field: A spontaneous fluctuation in the polarization on molecule A polarizes B, which in turn polarizes C; the induced polarization in C produces a reaction field acting at A. This polarization route e.g. $A \to B \to C \to A$ gives one term in the energy shift of A, with the second term generated by the route $A \to C \to B \to A$. Similarly, there are energy shifts of B and C associated with the polarization fluctuations in these molecules. The net three-body dispersion energy is the sum of the energy shift of A, the energy shift of B, and the energy shift of C.

6.3 Nonadditive Induction and Induction-Dispersion Energies

Three-body nonadditivity appears at second order in the intermolecular interactions. At this order, the three-body energy is the sum of three induction terms,

$$\Delta E^{(2)} = \Delta E^{(2)}_{CAB} + \Delta E^{(2)}_{ABC} + \Delta E^{(2)}_{BCA}, \tag{23}$$

where $\Delta E^{(2)}_{CAB}$ represents the energy change in molecule A due to the static fields from the permanent polarization of B and C,

$$\Delta E^{(2)}_{CAB} = -\int d\mathbf{r} \cdots d\mathbf{r}''' \, \mathbf{P}_0^C(\mathbf{r}''') \cdot \mathbf{T}(\mathbf{r}''', \mathbf{r}') \cdot \alpha^A(\mathbf{r}', \mathbf{r}) \cdot \mathbf{T}(\mathbf{r}, \mathbf{r}'') \cdot \mathbf{P}_0^B(\mathbf{r}''), \tag{24a}$$

$$\Delta E^{(2)}_{ABC} = \wp^{AB} \Delta E^{(2)}_{CAB}, \tag{24b}$$

and

$$\Delta E^{(2)}_{BCA} = \wp^{AC} \Delta E^{(2)}_{CAB}. \tag{24c}$$

Equivalently, $\Delta E^{(2)}_{CAB}$ can be viewed as the interaction energy between $\mathbf{P}_0^C(\mathbf{r}''')$ and the polarization induced in A by $\mathbf{P}_0^B(\mathbf{r}'')$ (or similarly, with the roles of B and C interchanged). $\Delta E^{(2)}_{ABC}$ and $\Delta E^{(2)}_{BCA}$ represent the energy changes in B and C, respectively, in the fields due to the permanent polarization of their interaction partners.

At third order, the total nonadditive three-body energy is the sum of the dispersion energy from Eq. (22), the classical induction energy, and a combined induction-dispersion term:

$$\Delta E^{(3)} = \Delta E^{(3)}_{disp} + \Delta E^{(3)}_{ind} + \Delta E^{(3)}_{i+d}. \tag{25}$$

The classical three-body induction terms can be further categorized into three groups, according to their physical origins. These terms stem from (1) static reaction fields, (2) third-body fields, and (3) hyperpolarization:

$$\Delta E^{(3)}_{ind} = \Delta E^{(3)}_{srf} + \Delta E^{(3)}_{tbf} + \Delta E^{(3)}_{hyp}. \tag{26}$$

The static reaction-field effects correspond to the dynamic reaction field effects considered in Sec. 6.2, but they originate in the permanent molecular polarization, rather than the fluctuating polarization treated in Sec. 6.2. The static field due to the permanent polarization of molecule A polarizes B; the induced polarization of B sets up a field that polarizes C, and C in turn produces a reaction field at A, causing an energy shift that depends on the scalar product of the reaction field with the permanent polarization of A (and similarly, with the roles of A, B, and C interchanged). The static reaction field term associated with the permanent polarization of molecule A is

$$\Delta E^{(3)}_{\mathrm{srf},A} = -\int d\mathbf{r}\cdots d\mathbf{r}^{\mathrm{v}}\, \mathbf{P}_0^A(\mathbf{r})\cdot\mathbf{T}(\mathbf{r},\mathbf{r}')\cdot\alpha^B(\mathbf{r}',\mathbf{r}'')\cdot\mathbf{T}(\mathbf{r}'',\mathbf{r}''')$$
$$\cdot\alpha^C(\mathbf{r}''',\mathbf{r}^{\mathrm{iv}})\cdot\mathbf{T}(\mathbf{r}^{\mathrm{iv}},\mathbf{r}^{\mathrm{v}})\cdot\mathbf{P}_0^A(\mathbf{r}^{\mathrm{v}}). \qquad (27)$$

The net contribution to $\Delta E^{(3)}$ from static reaction-field effects is obtained by adding $\Delta E^{(3)}_{\mathrm{srf},A}$ from Eq. (27) and the terms associated with the permanent polarization of B and C:

$$\Delta E^{(3)}_{\mathrm{srf}} = \Delta E^{(3)}_{\mathrm{srf},A} + \Delta E^{(3)}_{\mathrm{srf},B} + \Delta E^{(3)}_{\mathrm{srf},C}. \qquad (28)$$

The quantity $\Delta E^{(3)}_{\mathrm{srf}}$ can be viewed as lowest-order screening term. From Eq. (27), this interpretation for $\Delta E^{(3)}_{\mathrm{srf},A}$ holds as follows: the induction energy of molecule B, due to its polarization in the field from $\mathbf{P}_0^A(\mathbf{r})$, is altered by the presence of C, since C is also polarized by $\mathbf{P}_0^A(\mathbf{r})$. The simultaneous action of the direct field from $\mathbf{P}_0^A(\mathbf{r})$ and the screened field from the polarization induced in C by A causes an energy change in B. The same interpretation holds with the roles of B and C interchanged, due to the symmetry of the **T** tensor. Equivalently, $\Delta E^{(3)}_{\mathrm{srf},A}$ can be viewed as the interaction energy of the dipoles induced in B and C at first order, by $\mathbf{P}_0^A(\mathbf{r})$.

Third-body field and reaction field effects are related, but the polarization routes that contribute to the third-body field terms begin and end at different molecules: as an example, the route $C \to A \to B \to A$ is considered; that is, C polarizes A, which polarizes

B, producing a field at A and changing the energy. The term in $\Delta E^{(3)}$ associated with this route is

$$\Delta E^{(3)}_{\mathrm{tbf,CAB}} = -\int d\mathbf{r}\cdots d\mathbf{r}^{\mathrm{v}}\, \mathbf{P}_0^{C}(\mathbf{r})\cdot \mathbf{T}(\mathbf{r},\mathbf{r}')\cdot \alpha^{A}(\mathbf{r}',\mathbf{r}'')\cdot \mathbf{T}(\mathbf{r}'',\mathbf{r}''')$$

$$\cdot\, \alpha^{B}(\mathbf{r}''',\mathbf{r}^{\mathrm{iv}})\cdot \mathbf{T}(\mathbf{r}^{\mathrm{iv}},\mathbf{r}^{\mathrm{v}})\cdot \mathbf{P}_0^{A}(\mathbf{r}^{\mathrm{v}}). \tag{29}$$

The net contribution to $\Delta E^{(3)}$ from third-body field effects is the sum of $\Delta E^{(3)}_{\mathrm{tbf,CAB}}$ from Eq. (29) and five additional terms from the remaining permutations of A, B, and C in the polarization route:

$$\Delta E^{(3)}_{\mathrm{tbf}} = \Delta E^{(3)}_{\mathrm{tbf,CAB}} + \Delta E^{(3)}_{\mathrm{tbf,ABC}} + \Delta E^{(3)}_{\mathrm{tbf,BCA}} + \Delta E^{(3)}_{\mathrm{tbf,ACB}}$$

$$+\Delta E^{(3)}_{\mathrm{tbf,CBA}} + \Delta E^{(3)}_{\mathrm{tbf,BAC}}. \tag{30}$$

In this equation, $\Delta E^{(3)}_{\mathrm{tbf,XYZ}}$ denotes the right hand side of Eq. (29), after the label changes $C \to X$, $A \to Y$, and $B \to Z$.

The third group of induction terms stem from static hyperpolarization. For example, the hyperpolarization energy of A due to the concerted action of the fields from the permanent polarization of B and C is

$$\Delta E^{(3)}_{\mathrm{hyp,A}} = -(1+\wp^{BC})1/2\int d\mathbf{r}\cdots d\mathbf{r}^{\mathrm{v}}\, \beta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}''):[\mathbf{T}(\mathbf{r},\mathbf{r}''')\cdot \mathbf{P}_0^{B}(\mathbf{r}''')]$$

$$\times [\mathbf{T}(\mathbf{r}',\mathbf{r}^{\mathrm{iv}})\cdot \mathbf{P}_0^{B}(\mathbf{r}^{\mathrm{iv}})]\,[\mathbf{T}(\mathbf{r}'',\mathbf{r}^{\mathrm{v}})\cdot \mathbf{P}_0^{C}(\mathbf{r}^{\mathrm{v}})]. \tag{31}$$

The net hyperpolarization contribution is

$$\Delta E^{(3)}_{\mathrm{hyp}} = \Delta E^{(3)}_{\mathrm{hyp,A}} + \Delta E^{(3)}_{\mathrm{hyp,B}} + \Delta E^{(3)}_{\mathrm{hyp,C}}, \tag{32}$$

and the full three-body, third-order classical induction energy is the sum of $\Delta E^{(3)}_{\mathrm{srf}}$ from Eq. (28), $\Delta E^{(3)}_{\mathrm{tbf}}$ from Eq. (30), and $\Delta E^{(3)}_{\mathrm{hyp}}$ from Eq. (32).

Nonadditive combined induction and dispersion effects also appear at third order. The dispersion energy between molecules A and B is altered by the presence of a third molecule C, because the permanent polarization of C acts as the source of a static field that perturbs the A-B interaction. An applied static field $\mathbf{F}^e$ affects the A-B dispersion interaction in two ways [31, 54]: First, each of the molecules A and B is hyperpolarized by the simultaneous action of $\mathbf{F}^e$ and the fluctuating field from its partner (A or B). This effect is represented by use of an external-field dependent polarizability density $\alpha(\mathbf{r},\mathbf{r}';\omega,\mathbf{F}^e)$ to describe the response of each molecule to the field from its neighbor. Second, the correlations of the spontaneous, quantum mechanical fluctuations in the polarization of A and B are changed by $\mathbf{F}^e$. For example, the application of an external field to a centrosymmetric molecule introduces correlations between dipolar and quadrupolar charge density fluctuations; these correlations vanish in the absence of the applied field. The applied field also alters the correlations of the fluctuating dipoles, at first order for non-centrosymmetric molecules and at second order for centrosymmetric molecules. To account for this effect, the field-dependence of the imaginary part of the polarizability density is included in the fluctuation-dissipation relation:

$$1/2\left\langle P^A_{fl,\phi}(\mathbf{r},\omega)P^A_{fl,\alpha}(\mathbf{r}^v,\omega')+P^A_{fl,\alpha}(\mathbf{r}^v,\omega')P^A_{fl,\phi}(\mathbf{r},\omega)\right\rangle_{\mathbf{F}^e}$$
$$=\hbar/2\pi\,\alpha^{A''}_{\phi\alpha}(\mathbf{r},\mathbf{r}^v;\omega,\mathbf{F}^e)\delta(\omega+\omega')\coth(\hbar\omega/2kT). \qquad (33)$$

Previously, Hunt and Bohr [54] have developed a theory for the dispersion dipole of an A-B pair, based on the change in the dispersion energy due to a uniform, static external field. After modification to allow for the nonuniformity of the field $\mathbf{F}^C_0$ due to the permanent charge distribution of C, the same analysis applies here, with the external field replaced by $\mathbf{F}^C_0$. Then the nonadditive induction-dispersion energy associated with polarization fluctuations in A and B is

$$\Delta E^{(3)}_{(A\cdots B)\leftarrow C}=-(1+\wp^{AB})\hbar/2\pi\int_0^\infty d\omega\int d\mathbf{r}\cdots d\mathbf{r}^v\,\beta^A_{\beta\gamma\alpha}(\mathbf{r}',\mathbf{r}'',\mathbf{r};i\omega,0)T_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''')$$
$$\times\alpha^B_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv};i\omega)T_{\varepsilon\beta}(\mathbf{r}^{iv},\mathbf{r}')T_{\alpha\phi}(\mathbf{r},\mathbf{r}^v)P^C_{0\phi}(\mathbf{r}^v), \quad (34)$$

and the nonadditive, three-body induction-dispersion energy at third order is

$$\Delta E^{(3)}_{i+d} = \Delta E^{(3)}_{(A\cdots B)\leftarrow C} + \Delta E^{(3)}_{(B\cdots C)\leftarrow A} + \Delta E^{(3)}_{(C\cdots A)\leftarrow B}; \tag{35}$$

that is, $\Delta E^{(3)}_{i+d}$ is the sum of the change in the $A\cdots B$ dispersion energy due to the permanent polarization of C, the change in $B\cdots C$ dispersion energy due to the permanent polarization of A, and the change in $C\cdots A$ dispersion energy due to the permanent polarization of B.

6.4 Nonadditive Dispersion Dipoles, Classical Induction, and Induction-Dispersion Dipoles

In this section, nonlocal response tensors and reaction field theory are used to derive the nonadditive three-body polarization induced in molecules A, B, and C. The method is illustrated with the calculation of the dispersion polarization; then the results for the classical induction and induction-dispersion polarization are summarized.

The three-body dispersion polarization $\mathbf{P}^{(3)}_{disp}(\mathbf{r})$ is determined by the functional derivative of $\Delta E^{(3)}_{disp}$ with respect to a static external electric field $\mathbf{F}^e$, which may be spatially nonuniform:

$$\mathbf{P}^{(3)}_{disp}(\mathbf{r}) = -\delta\, \Delta E^{(3)}_{disp} / \delta \mathbf{F}^e(\mathbf{r})|_{\mathbf{F}^e=0}. \tag{36}$$

As noted in the previous section, application of an external field alters the dispersion energy via hyperpolarization and via field-induced fluctuation correlations. These effects are treated by allowing for the $\mathbf{F}^e$-dependence of both the real and the imaginary parts of the nonlocal polarizability densities. Then the same analysis that led to Eq. (22) gives

$$\Delta E^{(3)}_{disp} = -\hbar/\pi \int_0^\infty d\omega \int d\mathbf{r}\cdots d\mathbf{r}^{v}\, \mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C}(\mathbf{r}^{iv},\mathbf{r}''';i\omega,\mathbf{F}^e)\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')$$
$$\cdot\alpha^{B}(\mathbf{r}'',\mathbf{r}';i\omega,\mathbf{F}^e)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A}(\mathbf{r},\mathbf{r}^{v};i\omega,\mathbf{F}^e)]. \tag{37}$$

The polarization $\mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r})$ is the sum of three terms, the polarization $\mathbf{P}_{\text{disp}}(\mathbf{r})^{A\leftarrow B,C}$ induced in A by the dispersion interactions with B and C, and the polarization induced in B and C by dispersion:

$$\mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r}) = \mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r})^{A\leftarrow B,C} + \mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r})^{B\leftarrow A,C} + \mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r})^{C\leftarrow A,B}. \tag{38}$$

The polarization $\mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r})^{A\leftarrow B,C}$ specific to molecule A is obtained by allowing for the external-field dependence of the properties of A alone. Thus, $\mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r})^{A\leftarrow B,C}$ satisfies

$$\mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r})^{A\leftarrow B,C} = \hbar/\pi \int_0^\infty d\omega \int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, \mathrm{Tr}[\mathbf{T}(\mathbf{r}^{vi},\mathbf{r}^{v})\cdot\alpha^{C}(\mathbf{r}^{v},\mathbf{r}^{iv};i\omega)\cdot\mathbf{T}(\mathbf{r}^{iv},\mathbf{r}''')$$
$$\cdot\alpha^{B}(\mathbf{r}''',\mathbf{r}'';i\omega)\cdot\mathbf{T}(\mathbf{r}'',\mathbf{r}')\cdot\delta\alpha^{A}(\mathbf{r}',\mathbf{r}^{vi};i\omega,\mathbf{F}^{e})/\delta\mathbf{F}^{e}(\mathbf{r})|_{\mathbf{F}^{e}=0}]. \tag{39}$$

Expanding $\alpha^{A}(\mathbf{r}',\mathbf{r}^{vi};i\omega,\mathbf{F}^{e})$ as a series in powers of $\mathbf{F}^{e}(\mathbf{r})$ gives [31]

$$\alpha^{A}(\mathbf{r}',\mathbf{r}^{vi};i\omega,\mathbf{F}^{e}) = \alpha^{A}(\mathbf{r}',\mathbf{r}^{vi};i\omega) + \int d\mathbf{r}\,\beta^{A}(\mathbf{r}',\mathbf{r}^{vi},\mathbf{r};i\omega,0)\cdot\mathbf{F}^{e}(\mathbf{r}) + \cdots. \tag{40}$$

Therefore

$$\delta\alpha_{\lambda\beta}^{A}(\mathbf{r}',\mathbf{r}^{vi};i\omega,\mathbf{F}^{e})/\delta F_{\alpha}^{e}(\mathbf{r})|_{\mathbf{F}^{e}=0} = \beta_{\lambda\beta\alpha}^{A}(\mathbf{r}',\mathbf{r}^{vi},\mathbf{r};i\omega,0), \tag{41}$$

and

$$P_{\alpha,\text{disp}}^{(3)}(\mathbf{r})^{A\leftarrow B,C} = \hbar/\pi \int_0^\infty d\omega \int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, T_{\beta\gamma}(\mathbf{r}^{vi},\mathbf{r}^{v})\alpha_{\gamma\delta}^{C}(\mathbf{r}^{v},\mathbf{r}^{iv};i\omega)T_{\delta\varepsilon}(\mathbf{r}^{iv},\mathbf{r}''')$$
$$\times\alpha_{\varepsilon\phi}^{B}(\mathbf{r}''',\mathbf{r}'';i\omega)T_{\phi\lambda}(\mathbf{r}'',\mathbf{r}')\beta_{\lambda\beta\alpha}^{A}(\mathbf{r}',\mathbf{r}^{vi},\mathbf{r};i\omega,0). \tag{42}$$

Equation (42) gives a key result: the polarization induced in molecule A by its dispersion interactions with B and C depends on the imaginary-frequency hyperpolarizability density $\beta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';i\omega,0)$ of A and the polarizability densities $\alpha^{B}(\mathbf{r},\mathbf{r}';i\omega)$ and $\alpha^{C}(\mathbf{r},\mathbf{r}';i\omega)$ of B and C, integrated over frequency.

The nonadditive three-body dispersion dipole is obtained from Eqs. (38), (42), and the corresponding equations for the dispersion-induced polarization of B and C, by integrating $\mathbf{P}_{\text{disp}}^{(3)}(\mathbf{r})$ over all space with respect to $\mathbf{r}$.

The three-body, classical induction contribution to the polarization of A is obtained from Eqs. (23)-(32) and the analog of Eq. (36), by allowing for the $\mathbf{F}^{\mathrm{e}}$-dependence of the polarization $\mathbf{P}_0^{\mathrm{A}}(\mathbf{r})$ and susceptibility densities $\alpha^{\mathrm{A}}(\mathbf{r},\mathbf{r}')$ and $\beta^{\mathrm{A}}(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ of molecule A alone. At second order, the induction contribution is

$$\begin{aligned}\mathbf{P}_{\mathrm{ind}}^{(2)}(\mathbf{r})^{\mathrm{A}\leftarrow\mathrm{B,C}} &= \int d\mathbf{r}'\cdots d\mathbf{r}^{\mathrm{iv}}\,\beta^{\mathrm{A}}(\mathbf{r},\mathbf{r}',\mathbf{r}''):[\mathbf{T}(\mathbf{r}',\mathbf{r}''')\cdot\mathbf{P}_0^{\mathrm{B}}(\mathbf{r}''')][\mathbf{T}(\mathbf{r}'',\mathbf{r}^{\mathrm{iv}})\cdot\mathbf{P}_0^{\mathrm{C}}(\mathbf{r}^{\mathrm{iv}})] \\ &\quad+(1+\wp^{\mathrm{BC}})\int d\mathbf{r}'\cdots d\mathbf{r}^{\mathrm{iv}}\,\alpha^{\mathrm{A}}(\mathbf{r},\mathbf{r}')\cdot\mathbf{T}(\mathbf{r}',\mathbf{r}'')\cdot\alpha^{\mathrm{B}}(\mathbf{r}'',\mathbf{r}''') \\ &\qquad\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}^{\mathrm{iv}})\cdot\mathbf{P}_0^{\mathrm{C}}(\mathbf{r}^{\mathrm{iv}}). \end{aligned} \tag{43}$$

The first term in Eq. (43) gives the lowest order of the polarization induced in A due to the simultaneous action of the fields from the permanent polarization of B and C. The term given explicitly in the second line of Eq. (43) represents the polarization induced in A due to the field from B, which is polarized by the permanent charge density of C.

The induction contribution from third-order effects is the sum of three terms:

$$\mathbf{P}_{\mathrm{ind}}^{\mathrm{A}(3)}(\mathbf{r}) = \mathrm{T}_1 + \mathrm{T}_2 + \mathrm{T}_3, \tag{44}$$

separated according to the highest order of the susceptibility of molecule A contained in the term. The T_1 term depends on the linear response tensor of molecule A; it is given by

$$\begin{aligned}\mathrm{T}_1 &= (1+\wp^{\mathrm{BC}})\int d\mathbf{r}'\cdots d\mathbf{r}^{\mathrm{vi}}\,\{\alpha^{\mathrm{A}}(\mathbf{r},\mathbf{r}')\cdot\mathbf{T}(\mathbf{r}',\mathbf{r}'')\cdot\alpha^{\mathrm{B}}(\mathbf{r}'',\mathbf{r}''')\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}^{\mathrm{iv}}) \\ &\qquad\cdot\alpha^{\mathrm{C}}(\mathbf{r}^{\mathrm{iv}},\mathbf{r}^{\mathrm{v}})\cdot\mathbf{T}(\mathbf{r}^{\mathrm{v}},\mathbf{r}^{\mathrm{vi}})\cdot\mathbf{P}_0^{\mathrm{A}}(\mathbf{r}^{\mathrm{vi}}) \\ &\quad+\alpha^{\mathrm{A}}(\mathbf{r},\mathbf{r}')\cdot\mathbf{T}(\mathbf{r}',\mathbf{r}'')\cdot\alpha^{\mathrm{B}}(\mathbf{r}'',\mathbf{r}''')\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}^{\mathrm{iv}})\cdot\alpha^{\mathrm{C}}(\mathbf{r}^{\mathrm{iv}},\mathbf{r}^{\mathrm{v}})\cdot\mathbf{T}(\mathbf{r}^{\mathrm{v}},\mathbf{r}^{\mathrm{vi}})\cdot\mathbf{P}_0^{\mathrm{B}}(\mathbf{r}^{\mathrm{vi}}) \\ &\quad+\alpha^{\mathrm{A}}(\mathbf{r},\mathbf{r}')\cdot\mathbf{T}(\mathbf{r}',\mathbf{r}'')\cdot\alpha^{\mathrm{B}}(\mathbf{r}'',\mathbf{r}''')\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}^{\mathrm{iv}})\cdot\alpha^{\mathrm{A}}(\mathbf{r}^{\mathrm{iv}},\mathbf{r}^{\mathrm{v}})\cdot\mathbf{T}(\mathbf{r}^{\mathrm{v}},\mathbf{r}^{\mathrm{vi}})\cdot\mathbf{P}_0^{\mathrm{C}}(\mathbf{r}^{\mathrm{vi}}) \\ &\quad+\alpha^{\mathrm{A}}(\mathbf{r},\mathbf{r}')\cdot\mathbf{T}(\mathbf{r}',\mathbf{r}'')\cdot\beta^{\mathrm{B}}(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{\mathrm{iv}}):[\mathbf{T}(\mathbf{r}''',\mathbf{r}^{\mathrm{v}})\cdot\mathbf{P}_0^{\mathrm{A}}(\mathbf{r}^{\mathrm{v}})][\mathbf{T}(\mathbf{r}^{\mathrm{iv}},\mathbf{r}^{\mathrm{vi}})\cdot\mathbf{P}_0^{\mathrm{C}}(\mathbf{r}^{\mathrm{vi}})] \\ &\quad+1/2\,\alpha^{\mathrm{A}}(\mathbf{r},\mathbf{r}')\cdot\mathbf{T}(\mathbf{r}',\mathbf{r}'')\cdot\beta^{\mathrm{B}}(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{\mathrm{iv}}):[\mathbf{T}(\mathbf{r}''',\mathbf{r}^{\mathrm{v}})\cdot\mathbf{P}_0^{\mathrm{C}}(\mathbf{r}^{\mathrm{v}})] \\ &\qquad\times[\mathbf{T}(\mathbf{r}^{\mathrm{iv}},\mathbf{r}^{\mathrm{vi}})\cdot\mathbf{P}_0^{\mathrm{C}}(\mathbf{r}^{\mathrm{vi}})]\}. \end{aligned} \tag{45}$$

The first three terms in Eq. (45) give the polarization induced in A due to sequential linear response to the permanent polarization of A, B or C. The polarization routes represented by the first three terms given explicitly in Eq. (45) are $A \rightarrow C \rightarrow B \rightarrow A$, $B \rightarrow C \rightarrow B \rightarrow A$, and $C \rightarrow A \rightarrow B \rightarrow A$, respectively. The final two terms listed in Eq. (45) give the polarization induced in A by linear response to the hyperpolarization of B, either bilinear in $\mathbf{P}_0^A$ and $\mathbf{P}_0^C$ (fourth term) or quadratic in $\mathbf{P}_0^C$ (fifth term). The operator $\wp^{BC}$ permutes B and C in the five terms given explicitly, completing the set of induction mechanisms that involve linear response by molecule A.

The field at A due to the permanent polarization of B (or C) and the field at A due to the induced polarization in B (or C) act together, to polarize A via its static β hyperpolarizability density, $\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'')$. The T_2 term represents this effect:

$$\begin{aligned}
T_2 = (1+\wp^{BC})\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\,\{&\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}''):[\mathbf{T}(\mathbf{r}',\mathbf{r}''')\cdot\mathbf{P}_0^B(\mathbf{r}''')] \\
&\times[\mathbf{T}(\mathbf{r}'',\mathbf{r}^{iv})\cdot\alpha^C(\mathbf{r}^{iv},\mathbf{r}^{v})\cdot\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{vi})\cdot\mathbf{P}_0^B(\mathbf{r}^{vi})] \\
&+\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}''):[\mathbf{T}(\mathbf{r}',\mathbf{r}''')\cdot\mathbf{P}_0^B(\mathbf{r}''')][\mathbf{T}(\mathbf{r}'',\mathbf{r}^{iv})\cdot\alpha^C(\mathbf{r}^{iv},\mathbf{r}^{v}) \\
&\cdot\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{vi})\cdot\mathbf{P}_0^A(\mathbf{r}^{vi})] \\
&+\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}''):[\mathbf{T}(\mathbf{r}',\mathbf{r}''')\cdot\mathbf{P}_0^B(\mathbf{r}''')][\mathbf{T}(\mathbf{r}'',\mathbf{r}^{iv})\cdot\alpha^B(\mathbf{r}^{iv},\mathbf{r}^{v}) \\
&\cdot\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{vi})\cdot\mathbf{P}_0^C(\mathbf{r}^{vi})]\}. \qquad (46)
\end{aligned}$$

The terms given explicitly in Eq. (46) account for the effects due to $\mathbf{P}_0^B(\mathbf{r}''')$ and an induced polarization. In these terms, the induced polarization in C stems either from the field of $\mathbf{P}_0^B$ or from the field of $\mathbf{P}_0^A$; the induced polarization in B stems from $\mathbf{P}_0^C$. A corresponding term with the integrand $\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}''):[\mathbf{T}(\mathbf{r}',\mathbf{r}''')\cdot\mathbf{P}_0^B(\mathbf{r}''')][\mathbf{T}(\mathbf{r}'',\mathbf{r}^{iv})$ $\cdot\alpha^B(\mathbf{r}^{iv},\mathbf{r}^{v})\cdot\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{vi})\cdot\mathbf{P}_0^A(\mathbf{r}^{vi})]$ is not included here, because it represents a third-order, *two-body* effect.

The third classical induction term T_3 in the polarization of A reflects the γ hyper-polarization of A by the simultaneous action of the fields due to $\mathbf{P}_0^B$ and $\mathbf{P}_0^C$:

$$T_3 = (1+\wp^{BC})1/2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\ \gamma^A(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}'''):[\mathbf{T}(\mathbf{r}',\mathbf{r}^{iv})\cdot\mathbf{P}_0^B(\mathbf{r}^{iv})]$$
$$\times[\mathbf{T}(\mathbf{r}'',\mathbf{r}^{v})\cdot\mathbf{P}_0^B(\mathbf{r}^{v})][\mathbf{T}(\mathbf{r}''',\mathbf{r}^{vi})\cdot\mathbf{P}_0^C(\mathbf{r}^{vi})]. \tag{47}$$

In deriving Eq. (47), the following relation has been used [47]:

$$\delta\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega_1,\omega_2,\mathbf{F}^e)/\delta\mathbf{F}^e(\mathbf{r}''')|_{\mathbf{F}^e=0} = \gamma^A(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega_1,\omega_2,0). \tag{48}$$

The final component of the polarization of A is the induction-dispersion term, obtained from Eqs. (34), (35), and the analog of Eq. (36):

$$P^A_{\alpha,i+d}(\mathbf{r}) = (1+\wp^{BC})\hbar/2\pi\int_0^\infty d\omega\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}$$
$$\times[\gamma^A_{\beta\gamma\delta\alpha}(\mathbf{r}',\mathbf{r}'',\mathbf{r}''',\mathbf{r};i\omega,0,0)\,T_{\gamma\varepsilon}(\mathbf{r}'',\mathbf{r}^{iv})\,\alpha^B_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v};i\omega)\,T_{\phi\beta}(\mathbf{r}^{v},\mathbf{r}')$$
$$\times T_{\delta\eta}(\mathbf{r}''',\mathbf{r}^{vi})\,P^C_{0\eta}(\mathbf{r}^{vi})$$
$$+\beta^B_{\beta\gamma\delta}(\mathbf{r}',\mathbf{r}'',\mathbf{r}''';i\omega,0)\,T_{\gamma\varepsilon}(\mathbf{r}'',\mathbf{r}^{iv})\,\beta^A_{\varepsilon\phi\alpha}(\mathbf{r}^{iv},\mathbf{r}^{v},\mathbf{r};i\omega,0)\,T_{\phi\beta}(\mathbf{r}^{v},\mathbf{r}')$$
$$\times T_{\delta\eta}(\mathbf{r}''',\mathbf{r}^{vi})\,P^C_{0\eta}(\mathbf{r}^{vi})$$
$$+\beta^B_{\beta\gamma\delta}(\mathbf{r}',\mathbf{r}'',\mathbf{r}''';i\omega,0)\,T_{\gamma\varepsilon}(\mathbf{r}'',\mathbf{r}^{iv})\,\alpha^C_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v};i\omega)\,T_{\phi\beta}(\mathbf{r}^{v},\mathbf{r}')$$
$$\times T_{\delta\eta}(\mathbf{r}''',\mathbf{r}^{vi})\alpha^A_{\eta\alpha}(\mathbf{r}^{vi},\mathbf{r};0)]. \tag{49}$$

The terms in Eq. (49) are interpreted by comparison with the result for the polarization of A due to dispersion interactions with B in the absence of C [48]:

$$P^{A\leftarrow B}_{\alpha,disp}(\mathbf{r}) = \hbar/2\pi\int_0^\infty d\omega\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\ \beta^A_{\beta\gamma\alpha}(\mathbf{r}',\mathbf{r}'',\mathbf{r};i\omega,0)\,T_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''')$$
$$\times\alpha^B_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv};i\omega)\,T_{\varepsilon\beta}(\mathbf{r}^{iv},\mathbf{r}'). \tag{50}$$

Thus, the first term gives the change in the dispersion polarization of A due to the lowest-order static field from C acting on A. The second term gives the change in $P^{A\leftarrow B}_{\alpha,\mathrm{disp}}(\mathbf{r})$ due to the same field acting on B. The third term gives the polarization induced in A by the field from $P^{B\leftarrow C}_{\alpha,\mathrm{disp}}(\mathbf{r})$, that is, the polarization induced in B by two-body dispersion interactions between B and C.

6.5 The Electrostatic Interpretation of Nonadditive Three-body Forces on Nuclei

The nonadditive three-body force on nucleus K in molecule A is obtained by differentiating $\Delta E^{(2)}$ and $\Delta E^{(3)}$ with respect to the coordinate $\mathbf{R}^K$ of K:

$$\Delta F_\alpha^{K(2)} = -\partial \Delta E^{(2)} / \partial R_\alpha^K, \tag{51}$$

$$\Delta F_\alpha^{K(3)} = -\partial \Delta E^{(3)} / \partial R_\alpha^K, \tag{52}$$

where $\Delta E^{(2)}$ is given by Eq. (23), and $\Delta E^{(3)}$ is given by Eq. (25). To find the derivatives with respect to $\mathbf{R}^K$, use is also made of a chain of relations that link the permanent polarization, linear response tensors, and nonlinear response tensors [45-47]:

$$\partial P_{0\alpha}^{el}(\mathbf{r}) / \partial R_\beta^K = Z^K \int d\mathbf{r}'\, \alpha_{\alpha\gamma}(\mathbf{r},\mathbf{r}';0)\, T_{\gamma\beta}(\mathbf{r}',\mathbf{R}^K), \tag{53}$$

$$\partial \alpha_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega) / \partial R_\gamma^K = Z^K \int d\mathbf{r}''\, \beta_{\alpha\beta\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)\, T_{\delta\gamma}(\mathbf{r}'',\mathbf{R}^K), \tag{54}$$

and

$$\partial \beta_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega_1,\omega_2) / \partial R_\delta^K = Z^K \int d\mathbf{r}'''\, \gamma_{\alpha\beta\gamma\varepsilon}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega_1,\omega_2,0)\, T_{\varepsilon\delta}(\mathbf{r}''',\mathbf{R}^K). \tag{55}$$

In these equations, Z^K represents the charge on nucleus K, and $\mathbf{P}_0^{el}(\mathbf{r})$ denotes the electronic component of the permanent polarization. A common explanation holds for Eqs. (53)-(55): When a nucleus shifts within a molecule, the electrons respond to the resulting change in the nuclear Coulomb field via the *same* polarizability densities that characterize the response to external fields.

First the third-order forces $\Delta\mathbf{F}^{K(3)}$ are evaluated. $\Delta\mathbf{F}^{K(3)}$ can be categorized into dispersion, induction, and induction-dispersion forces according to the terms in $\Delta E^{(3)}$ with which the forces are associated. The three-body dispersion force on nucleus K in molecule A is obtained from Eqs. (52) and (54):

$$\Delta F^{K(3)}_{\alpha,\mathrm{disp}} = \hbar/\pi\, Z^K \int_0^\infty d\omega \int d\mathbf{r}\cdots d\mathbf{r}^{vi}\, T_{\beta\gamma}(\mathbf{r}^{vi},\mathbf{r}^{v})\alpha^{C}_{\gamma\delta}(\mathbf{r}^{v},\mathbf{r}^{iv};i\omega)T_{\delta\varepsilon}(\mathbf{r}^{iv},\mathbf{r}''')$$

$$\times\alpha^{B}_{\varepsilon\phi}(\mathbf{r}''',\mathbf{r}'';i\omega)T_{\phi\eta}(\mathbf{r}'',\mathbf{r}')\beta^{A}_{\eta\beta\lambda}(\mathbf{r}',\mathbf{r}^{vi},\mathbf{r};i\omega,0)T_{\lambda\alpha}(\mathbf{r},\mathbf{R}^K). \quad (56)$$

A comparison of Eq. (56) and Eq. (42) for $P^{A\leftarrow B,C}_{\alpha,\mathrm{disp}}(\mathbf{r})$ shows that the three-body dispersion force on nucleus K in molecule A is the classical Coulomb force of attraction of nucleus K to the three-body, dispersion polarization of the electrons on the *same* molecule:

$$\Delta\mathbf{F}^{K(3)}_{\mathrm{disp}} = Z^K \int d\mathbf{r}\, \mathbf{T}(\mathbf{R}^K,\mathbf{r})\cdot\mathbf{P}^{A\leftarrow B,C}_{\mathrm{disp}}(\mathbf{r}). \quad (57)$$

To leading order, the dispersion force on a nucleus in A depends on the perturbed electronic charge density of A alone, not on the charge densities of B or C. This proves that Feynman's statement about the origin of two-body dispersion forces between atoms in S states generalizes to three-body dispersion forces among molecules, without restrictions on symmetry [48, 49].

The nonadditive induction-dispersion force on nucleus K in molecule A is

$$\Delta\mathbf{F}^{K(3)}_{i+d} = Z^K \int d\mathbf{r}\, \mathbf{T}(\mathbf{R}^K,\mathbf{r})\cdot[\mathbf{P}^{A}_{i+d}(\mathbf{r}) + \mathbf{P}^{B\leftarrow C}_{\mathrm{disp}}(\mathbf{r}) + \mathbf{P}^{C\leftarrow B}_{\mathrm{disp}}(\mathbf{r})], \quad (58)$$

where $\mathbf{P}^{B\leftarrow C}_{\mathrm{disp}}(\mathbf{r})$ denotes the polarization induced in B by its *two-body* dispersion interactions with C. In deriving Eq. (58), the transformation

$$\int d\mathbf{r}^{v}\, \partial\mathbf{P}^{\mathrm{nuc}(A)}_0(\mathbf{r}^{v})/\partial\mathbf{R}^K\, \mathbf{T}(\mathbf{r},\mathbf{r}^{v}) = Z^K\mathbf{T}(\mathbf{r},\mathbf{R}^K), \quad (59)$$

has been used. In Eq. (59), $\mathbf{P}^{\mathrm{nuc}(A)}_0(\mathbf{r}^{v})$ represents the nuclear contribution to the permanent polarization of A. Equation (58) contrasts with Eq. (57): the induction-dispersion force involves not only the attraction of nucleus K to the electrons of A, but also to those of B and C.

Similarly, the third-order induction force on nucleus K in molecule A is

$$\Delta\mathbf{F}_{\text{ind}}^{K(3)} = Z^K \int d\mathbf{r}\, \mathbf{T}(\mathbf{R}^K, \mathbf{r}) \cdot [\mathbf{P}_{\text{ind}}^{A(3)}(\mathbf{r}) + \mathbf{P}_{\text{ind}}^{B(2)}(\mathbf{r}) + \mathbf{P}_{\text{ind}}^{C(2)}(\mathbf{r})], \tag{60}$$

where $\mathbf{P}_{\text{ind}}^{B(2)}(\mathbf{r})$ denotes the classical polarization induced in B by interactions with A and C at second order. $\mathbf{P}_{\text{ind}}^{B(2)}(\mathbf{r})$ satisfies

$$\begin{aligned}
\mathbf{P}_{\text{ind}}^{B(2)}(\mathbf{r}) = \int d\mathbf{r}' \cdots d\mathbf{r}^{iv} [&\alpha^B(\mathbf{r}, \mathbf{r}') \cdot \mathbf{T}(\mathbf{r}', \mathbf{r}'') \cdot \alpha^C(\mathbf{r}'', \mathbf{r}''') \cdot \mathbf{T}(\mathbf{r}''', \mathbf{r}^{iv}) \cdot \mathbf{P}_0^A(\mathbf{r}^{iv}) \\
&+ \alpha^B(\mathbf{r}, \mathbf{r}') \cdot \mathbf{T}(\mathbf{r}', \mathbf{r}'') \cdot \alpha^A(\mathbf{r}'', \mathbf{r}''') \cdot \mathbf{T}(\mathbf{r}''', \mathbf{r}^{iv}) \cdot \mathbf{P}_0^C(\mathbf{r}^{iv}) \\
&+ \alpha^B(\mathbf{r}, \mathbf{r}') \cdot \mathbf{T}(\mathbf{r}', \mathbf{r}'') \cdot \alpha^C(\mathbf{r}'', \mathbf{r}''') \cdot \mathbf{T}(\mathbf{r}''', \mathbf{r}^{iv}) \cdot \mathbf{P}_0^B(\mathbf{r}^{iv})] \\
+ \int d\mathbf{r}' \cdots d\mathbf{r}^{iv}\, &\beta^B(\mathbf{r}, \mathbf{r}', \mathbf{r}'') : [\mathbf{T}(\mathbf{r}'', \mathbf{r}^{iv}) \cdot \mathbf{P}_0^C(\mathbf{r}^{iv})] \\
&\times [\mathbf{T}(\mathbf{r}', \mathbf{r}''') \cdot \mathbf{P}_0^A(\mathbf{r}''') + 1/2\, \mathbf{T}(\mathbf{r}', \mathbf{r}''') \cdot \mathbf{P}_0^C(\mathbf{r}''')].
\end{aligned} \tag{61}$$

The nonadditive three-body force on nucleus K in A at second order is obtained from equations (23) and (51):

$$\Delta\mathbf{F}_{\text{ind}}^{K(2)} = Z^K \int d\mathbf{r}\, \mathbf{T}(\mathbf{R}^K, \mathbf{r}) \cdot [\mathbf{P}_{\text{ind}}^{(2)}(\mathbf{r})^{A \leftarrow B,C} + \mathbf{P}_{\text{ind}}^{(1)}(\mathbf{r})^{B \leftarrow C} + \mathbf{P}_{\text{ind}}^{(1)}(\mathbf{r})^{C \leftarrow B}], \tag{62}$$

where $\mathbf{P}_{\text{ind}}^{(1)}(\mathbf{r})^{B \leftarrow C}$ is the polarization induced in B by the permanent polarization of C, at first order:

$$\mathbf{P}_{\text{ind}}^{(1)}(\mathbf{r})^{B \leftarrow C} = \int d\mathbf{r}'\, d\mathbf{r}''\, \alpha^B(\mathbf{r}, \mathbf{r}') \cdot \mathbf{T}(\mathbf{r}', \mathbf{r}'') \cdot \mathbf{P}_0^C(\mathbf{r}''). \tag{63}$$

Eqs. (57), (58), (60), and (62) provide an electrostatic interpretation of all of the nonadditive three-body forces on nuclei in interacting molecules A, B, and C.

6.6 Summary and Discussion

Nonadditive three-body dispersion interactions appear at third order; they result from the correlations of the spontaneous, quantum mechanical fluctuations in the polarization of the three interacting molecules A, B and C. The three-body dispersion energy is given by Eq. (22) as a tensor product of the dipole propagators and imaginary-frequency polarizability densities of molecules A, B, and C, integrated over frequency. Unlike the three-body dispersion energy, which is a third-order effect, the classical nonadditive three-body induction energy includes a contribution from second order. The second-order induction energy is the sum of $\Delta E^{(2)}_{CAB}$, $\Delta E^{(2)}_{ABC}$, and $\Delta E^{(2)}_{BCA}$, where $\Delta E^{(2)}_{XYZ}$ represents the lowest-order energy change in Y due to the static fields from the permanent polarization of X and Z. $\Delta E^{(2)}_{CAB}$ is given by Eq. (24a). At third order, the classical induction energy contains three types of terms: (1) a static reaction field term $\Delta E^{(3)}_{srf}$, (2) a third-body field term $\Delta E^{(3)}_{tbf}$, and (3) a hyperpolarization term $\Delta E^{(3)}_{hyp}$. The mechanism that gives rise to $\Delta E^{(3)}_{srf}$ is related to the dynamic reaction field effects in the dispersion interaction, but it originates in the permanent polarization, rather than the fluctuating polarization. The static field due to the permanent charge density of molecule A polarizes B, which then polarizes C, and the polarization induced in C produces a reaction field at A. The resulting energy change in A depends upon the permanent polarization of A and the polarizability densities of B and C. This term $\Delta E^{(3)}_{srf,A}$ is given by Eq. (27), and the total energy $\Delta E^{(3)}_{srf}$ from this mechanism is obtained by adding $\Delta E^{(3)}_{srf,A}$ to additional two terms $\Delta E^{(3)}_{srf,B}$ and $\Delta E^{(3)}_{srf,C}$, the energy changes in B and C originating in the permanent charge distributions of B and C, respectively. The third-body field terms depend on the permanent polarization of two molecules, rather than one molecule as in the static reaction field terms, because the polarization routes that contribute to $\Delta E^{(3)}_{tbf}$ begin and end at different molecules. One representative term is $\Delta E^{(3)}_{tbf,CAB}$ given by Eq. (29). The polarization route associated with this term is $C \rightarrow A \rightarrow B \rightarrow A$; that is, C polarizes A, polarizing B, producing a field at A and changing the energy. $\Delta E^{(3)}_{tbf}$ includes five additional terms obtained from the remaining permutations of A, B, and C. In addition to the static reaction-field and third-body field effects, hyperpolarization also contributes to the pure induction energy at third order. In this mechanism, the concerted action of the fields due to the permanent polarization of molecules B and C produces an energy change in A via the β hyperpolarizability density of A. The hyperpolarization energy of A $\Delta E^{(3)}_{hyp,A}$ satisfies Eq. (31), and the total hyperpolarization energy is the sum of $\Delta E^{(3)}_{hyp,A}$, $\Delta E^{(3)}_{hyp,B}$, and $\Delta E^{(3)}_{hyp,C}$. Nonadditive effects of induction and dispersion also occur at third order. For example, the dispersion energy between molecules A and B is changed by the static field from the permanent polarization of C. The induction-dispersion energy $\Delta E^{(3)}_{(A\cdots B)\leftarrow C}$ depends on the scalar product of the static field from $\mathbf{P}^{C}_{0}(\mathbf{r})$ and the dispersion-induced polarization in each of the molecules A and B. The expression for $\Delta E^{(3)}_{(A\cdots B)\leftarrow C}$ is given by equation (34), and the net contribution from the induction-dispersion effects is obtained by adding $\Delta E^{(3)}_{(A\cdots B)\leftarrow C}$ to additional two terms $\Delta E^{(3)}_{(B\cdots C)\leftarrow A}$ and $\Delta E^{(3)}_{(C\cdots A)\leftarrow B}$.

The three-body polarization $\mathbf{P}^{(3)}(\mathbf{r})$ is derived based on the change in the three-body energy due to a static external electric field $\mathbf{F}^{e}$, which may be spatially nonuniform: $\mathbf{P}^{(3)}(\mathbf{r})$ is obtained from the functional derivative of $\Delta E^{(3)}$ with respect to $\mathbf{F}^{e}$. The three-body polarization $\mathbf{P}^{(3)}(\mathbf{r})$ can also be categorized into dispersion, classical induction, and induction-dispersion terms, depending on the term in the interaction energy with which $\mathbf{P}^{(3)}(\mathbf{r})$ is associated. The dispersion polarization $\mathbf{P}^{A(3)}_{disp}(\mathbf{r})$ induced in molecule A by its interaction with B and C is given by Eq. (42), which depends on the imaginary-frequency β hyperpolarizability density of A and the imaginary-frequency polarizability densities of B and C. Two distinct physical effects contribute to $\mathbf{P}_{\text{disp}}^{A(3)}(\mathbf{r})$: (1) the applied field changes the response of a molecule to the local fields from the neighboring molecules, due to hyperpolarization effects, and (2) the external field also alters the correlations of the spontaneous polarization fluctuations in the molecules because the imaginary part of the polarizability density depends on the applied field.

The three-body, classical induction contribution to the polarization of A is obtained by allowing for the $\mathbf{F}^e$-dependence of the permanent polarization $\mathbf{P}_0^A(\mathbf{r})$, the polarizability density $\alpha^A(\mathbf{r},\mathbf{r}')$, and the hyperpolarizability density $\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'')$. This yields a total of 9 terms, given by Eqs. (45)-(47). Finally, the induction-dispersion contribution to the polarization of A satisfies Eq. (49).

The three-body dispersion force acting on nucleus K in molecule A is given by Eq. (56) or equivalently by Eq. (57). Eq. (57) shows that this force can be understood as the electrostatic attraction of the nucleus K to the three-body dispersion-induced polarization of the electrons in molecule A *itself*. This provides the generalization of Hunt's proof [48] of Feynman's conjecture [49] about the origin of two-body dispersion forces to three-body dispersion forces.

In the next chapter, time-independent perturbation theory is used to analyze nonadditive three-body energies and polarization through third order in the intermolecular interactions. By proving the equivalence with the results given in this chapter, the reaction-field method and the perturbation analysis are unified.

This work should prove useful in later computational work on the long-range contributions to nonadditive three-body potentials. From equations (22)-(35) and (42)-(49), it is easy to derive the corresponding long-range expressions for three-body interaction energies and dipoles. The results are obtained in terms of single-molecule properties such as permanent multipole moments, polarizabilities, and hyperpolarizabilities. Given *ab initio* values for these properties, the long-range model should yield accurate three-body potentials and dipoles at large intermolecular distances where numerical cancellation and basis limitations make it difficult to obtain accurate results from an *ab initio* approach. Additionally, useful information on short-range exchange effects [55-60] may be obtained by comparison of long-range models and *ab initio* calculations [61-66] or experimental data. Experiments that are relevant to three-body interactions include measurements of third virial coefficients of compressed gases [3-8], binding energies of rare-gas crystals at low temperature [8-11], collision-induced far-infrared absorption by dense gases [12-15], and rotational and vibrational spectra of van der Waals trimers [16-27].

Referen

[1] B. M

[2] Y. M

[3] T. K

[4] S. K

[5] H. V

[6] H. V

[7] A. E

[8] J. A

[9] B. N

[10] R.
J.

[11] W

[12] G.

[13] B

[14] B

[15] B

[16] H
C

[17] T
P

[18] T
P

[19] T

[20] M

[21] M

[22] M

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CHAPTER VII

NONADDITIVE THREE-BODY INTERACTION ENERGIES AND DIPOLES: PERTURBATION ANALYSIS

7.1 Nonadditive Three-body Interaction Energy at Second Order

For three interacting molecules A, B, and C, the Hamiltonian is

$$H = H_A + H_B + H_C + V_{AB} + V_{BC} + V_{CA} = H_0 + V, \tag{1}$$

where H_X is the Hamiltonian for molecule X when isolated, the unperturbed Hamiltonian H_0 is the sum $H_A + H_B + H_C$, V_{AB} is the perturbation due to interaction between A and B, (similarly for V_{BC} and V_{CA}), and $V = V_{AB} + V_{BC} + V_{CA}$. Here the intermolecular exchange effects are neglected, and thus the eigenstates of H_0 can be written as direct products $|k\,l\,m\rangle$ of eigenstates $|k\rangle$ of H_A, $|l\rangle$ of H_B, and $|m\rangle$ of H_C.

At second order, the change in the ground state energy of the interacting molecules A, B, and C is [1]

$$\Delta E^{(2)} = -\langle \Psi_0 | V\,G\,V | \Psi_0 \rangle. \tag{2}$$

In Eq. (2) $|\Psi_0\rangle$ denotes the three-body ground state $|000\rangle$, and G is the reduced resolvent operator, given by

$$G = (1 - \wp_{000})(H_0 - E_0)^{-1}(1 - \wp_{000}), \tag{3}$$

where $\wp_{000}$ is the ground-state projection operator, $\wp_{000} = |000\rangle\langle 000|$, and E_0 is the unperturbed ground state energy. For a set of interacting molecules A, B, and C, G can be split into 7 terms, to reflect different possible molecular excitation patterns:

$$G = G^A \wp_0^B \wp_0^C + G^B \wp_0^A \wp_0^C + G^C \wp_0^A \wp_0^B$$

$$+G^{A\oplus B} \wp_0^C + G^{A\oplus C} \wp_0^B + G^{B\oplus C} \wp_0^A + G^{A\oplus B\oplus C}. \tag{4}$$

In Eq. (4), G^A is the reduced resolvent for an isolated molecule A, and $\wp_0^A$ is its ground-state projection operator. $G^{A\oplus B} \wp_0^C$ contains the terms in the sum-over-states expression of Eq. (3) with both molecules A and B in excited states, but C in the ground state, while $G^{A\oplus B\oplus C}$ contains the terms with all three molecules excited.

Substituting $V = V_{AB} + V_{BC} + V_{CA}$ and then expanding the sum in Eq. (2) gives 9 terms. Of these, there are three additive two-body terms, $-\langle \Psi_0 | V_{AB}\, G\, V_{AB} | \Psi_0 \rangle$, $-\langle \Psi_0 | V_{BC}\, G\, V_{BC} | \Psi_0 \rangle$, and $-\langle \Psi_0 | V_{CA}\, G\, V_{CA} | \Psi_0 \rangle$. The remaining 6 terms give the nonadditive three-body energy. All of the nonadditive terms are treated here. First the two terms involving the perturbation operators V_{AB} and V_{CA} are analyzed:

$$-\langle \Psi_0 | V_{AB}\, G\, V_{CA} | \Psi_0 \rangle - \langle \Psi_0 | V_{CA}\, G\, V_{AB} | \Psi_0 \rangle$$

$$= -\langle \Psi_0 | V_{AB}\, G^A \wp_0^B \wp_0^C\, V_{CA} | \Psi_0 \rangle - \langle \Psi_0 | V_{CA}\, G^A \wp_0^B \wp_0^C\, V_{AB} | \Psi_0 \rangle$$

$$= -\int d\mathbf{r}' \cdots d\mathbf{r}'''\, T_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') P_{0\gamma}^B(\mathbf{r}'') T_{\beta\delta}(\mathbf{r}', \mathbf{r}''') P_{0\delta}^C(\mathbf{r}''')$$

$$\times [\langle 0 | P_\alpha^A(\mathbf{r}) G^A P_\beta^A(\mathbf{r}') | 0 \rangle + \langle 0 | P_\beta^A(\mathbf{r}') G^A P_\alpha^A(\mathbf{r}) | 0 \rangle]$$

$$= -\int d\mathbf{r}' \cdots d\mathbf{r}'''\, \alpha_{\alpha\beta}^A(\mathbf{r}, \mathbf{r}') T_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') P_{0\gamma}^B(\mathbf{r}'') T_{\beta\delta}(\mathbf{r}', \mathbf{r}''') P_{0\delta}^C(\mathbf{r}'''), \tag{5}$$

where the Einstein convention of summation over repeated Greek subscripts has been used in Eq. (5) and below, and the perturbation V_{AB} has been written in the form

$$V_{AB} = -\int d\mathbf{r}\, d\mathbf{r}'\, P_\alpha^A(\mathbf{r}) T_{\alpha\beta}(\mathbf{r}, \mathbf{r}') P_\beta^B(\mathbf{r}') \tag{6}$$

with $P_\alpha(\mathbf{r})$ denoting the α-component of the polarization operator and $T_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \nabla_\alpha \nabla_\beta (|\mathbf{r} - \mathbf{r}'|^{-1})$, the dipole propagator. In Eq. (5), $P_{0\alpha}(\mathbf{r}) \equiv \langle 0 | P_\alpha(\mathbf{r}) | 0 \rangle$, and the nonlocal polarizability density $\alpha_{\alpha\beta}^A(\mathbf{r}, \mathbf{r}')$ is defined by

$$\alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \langle 0|P^{A}_{\alpha}(\mathbf{r})G^{A}\,P^{A}_{\beta}(\mathbf{r}')|0\rangle + \langle 0|P^{A}_{\beta}(\mathbf{r}')\,G^{A}\,P^{A}_{\alpha}(\mathbf{r})|0\rangle. \tag{7}$$

Eq. (5) is equivalent to Eq. (6.24a) for $\Delta E^{(2)}_{CAB}$ because of the symmetry of the T-tensor $T_{\alpha\beta}(\mathbf{r},\mathbf{r}') = T_{\beta\alpha}(\mathbf{r}',\mathbf{r})$ and the Born symmetry [2, 4] of the polarizability density $\alpha_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \alpha_{\beta\alpha}(\mathbf{r}',\mathbf{r})$. It gives the lowest-order energy change in molecule A due to the fields from the permanent polarization of B and C. Equivalently, equation (5) can be viewed as the interaction energy between $\mathbf{P}^{C}_{0}(\mathbf{r}''')$ and the polarization induced in A by $\mathbf{P}^{B}_{0}(\mathbf{r}'')$ (or similarly, with the roles of B and C interchanged). The sum of the two terms containing operators V_{AB} and V_{BC} is identical to Eq. (6.24b) for $\Delta E^{(2)}_{ABC}$, and the sum of the two terms containing operators V_{BC} and V_{CA} is equivalent to Eq.(6.24c) for $\Delta E^{(2)}_{BCA}$.

7.2 Nonadditive Three-body Energy at Third order: "Circuit" Terms

At third order, the change in the ground state energy of the interacting molecules A, B, and C is given by [1]

$$\Delta E^{(3)} = \langle \Psi_0 | V\,G\,V^{o}\,G\,V | \Psi_0 \rangle, \tag{8}$$

where $V^{o} = V - \langle 000|V|000\rangle$.

Substituting $V = V_{AB} + V_{BC} + V_{CA}$ and then expanding Eq. (8) gives 27 terms. Of these, there are three additive two-body terms, in which a single perturbation operator such as V_{AB} appears three times; the remaining 24 represent the nonadditive three-body terms. All of these three-body terms are considered here; but in this section, attention is focused on the six terms with interactions of "circuit" type. These terms contain the operators V_{AB}, V_{BC}, and V_{CA}, each appearing once. A representative term of this set is $\langle \Psi_0 | V_{AB}\,G\,V^{o}_{BC}\,G\,V_{CA} | \Psi_0 \rangle$. From Eq. (4) for G, retaining only the nonzero terms yields

$$\langle\Psi_0|V_{AB}\,G\,V^{o}_{BC}\,G\,V_{CA}|\Psi_0\rangle$$
$$=\langle\Psi_0|V_{AB}\,G^{A}\wp_0^{B}\,\wp_0^{C}\,V^{o}_{BC}\,G^{A\oplus C}\,\wp_0^{B}\,V_{CA}|\Psi_0\rangle$$
$$+\langle\Psi_0|V_{AB}\,G^{B}\wp_0^{A}\,\wp_0^{C}\,V^{o}_{BC}\,G^{C}\,\wp_0^{A}\,\wp_0^{B}\,V_{CA}|\Psi_0\rangle$$
$$+\langle\Psi_0|V_{AB}\,G^{A\oplus B}\,\wp_0^{C}\,V^{o}_{BC}\,G^{A}\,\wp_0^{B}\,\wp_0^{C}\,V_{CA}|\Psi_0\rangle$$
$$+\langle\Psi_0|V_{AB}\,G^{A\oplus B}\,\wp_0^{C}\,V^{o}_{BC}\,G^{A\oplus C}\,\wp_0^{B}\,V_{CA}|\Psi_0\rangle. \tag{9}$$

The sum of the "circuit" terms in $\Delta E^{(3)}$ is

$$\Delta E^{(3)}_{cir}=(1+\wp^{AB}+\wp^{BC}+\wp^{AC}+\wp^{ABC}+\wp^{ACB})\langle\Psi_0|V_{AB}\,G\,V^{o}_{BC}\,G\,V_{CA}|\Psi_0\rangle, \tag{10}$$

where $\wp^{AB}$ interchanges the molecule labels A and B, $\wp^{ABC}$ permutes the labels $A\rightarrow B\rightarrow C\rightarrow A$, and similarly for the remaining permutation operators. In $\Delta E^{(3)}_{cir}$, induction and dispersion effects are separate and additive. The first three terms in Eq. (9) and the terms into which they transform under the permutations in Eq. (10) represent induction, while the fourth term and its transforms represent dispersion. This follows from an expansion of Eq. (10) into its component matrix elements, using Eq. (6) for V_{AB}, its analogs for V_{BC} and V_{CA}, and a sum-over-states representation of G from Eq. (4).

From Eq. (10), the terms that contain ground-state matrix elements of the polarization operator for molecule A, and transition matrix elements for molecules B and C are selected, and they are denoted by $\Delta E^{(3)}_{cir,A}$. For simplicity, it is assumed that the molecular eigenstates may be taken as real. Then

$$\begin{aligned}\Delta E^{(3)}_{cir,A}=&-\int d\mathbf{r}\cdots d\mathbf{r}^{v}\langle 0|P^{A}_{\alpha}(\mathbf{r})|0\rangle\langle 0|P^{A}_{\phi}(\mathbf{r}^{v})|0\rangle\\&\times{\sum_{k,m}}'\langle 0|P^{B}_{\beta}(\mathbf{r}')|k\rangle\langle k|P^{B}_{\gamma}(\mathbf{r}'')|0\rangle\langle 0|P^{C}_{\delta}(\mathbf{r}''')|m\rangle\\&\times\langle m|P^{C}_{\varepsilon}(\mathbf{r}^{iv})|0\rangle[2\,\Delta_k^{-1}\Delta_m^{-1}+2\,\Delta_k^{-1}(\Delta_k+\Delta_m)^{-1}\\&\quad+2\,\Delta_m^{-1}(\Delta_k+\Delta_m)^{-1}]\,T_{\alpha\beta}(\mathbf{r},\mathbf{r}')\,T_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''')\,T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v}).\end{aligned} \tag{11}$$

The prime on the summation in Eq. (11) implies that k = 0 and m = 0 are excluded from the sum; Δ_k denotes $E_k - E_0$, the difference in the energies of the unperturbed states k and 0 for molecule B (and similarly for Δ_m). Following algebraic simplification and using Eq. (7) for the definition of the nonlocal polarizability density, Eq. (11) transforms to

$$\Delta E^{(3)}_{cir,A} = -\int d\mathbf{r}\cdots d\mathbf{r}^{v}\, P^{A}_{0\alpha}(\mathbf{r})\, T_{\alpha\beta}(\mathbf{r},\mathbf{r}')\alpha^{B}_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''')$$

$$\times\, \alpha^{C}_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v})\, P^{A}_{0\phi}(\mathbf{r}^{v}). \qquad (12)$$

Equation (12) shows that the three-body "circuit" induction can be understood as a static reaction-field effect, where the permanent polarization of A polarizes B, polarizing C, giving a reaction field back at A, with an energy shift that depends on the permanent polarization of A. Eq. (12) is identical to Eq. (6.27) from the reaction-field method. The net contribution to the induction energy from the "circuit" terms is given by $\Delta E^{(3)}_{cir,A} + \Delta E^{(3)}_{cir,B} + \Delta E^{(3)}_{cir,C}$, which is equivalent to Eq. (6.28).

The final component of $\Delta E^{(3)}_{cir}$ comes from the fourth term in Eq. (9) and the corresponding terms generated by the permutations in Eq. (10). It represents the nonadditive three-body dispersion effects. This component is denoted by $\Delta E^{(3)}_{disp}$; in matrix element form

$$\Delta E^{(3)}_{disp} = -\int d\mathbf{r}\cdots d\mathbf{r}^{v} \times \sum_{j,k,m}{}' \langle 0|P^{A}_{\alpha}(\mathbf{r})|j\rangle\langle j|P^{A}_{\phi}(\mathbf{r}^{v})|0\rangle$$

$$\times \langle 0|P^{B}_{\beta}(\mathbf{r}')|k\rangle\langle k|P^{B}_{\gamma}(\mathbf{r}'')|0\rangle\langle 0|P^{C}_{\delta}(\mathbf{r}''')|m\rangle\langle m|P^{C}_{\varepsilon}(\mathbf{r}^{iv})|0\rangle$$

$$\times [2(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1} + 2(\Delta_j+\Delta_k)^{-1}(\Delta_k+\Delta_m)^{-1}$$

$$+ 2(\Delta_j+\Delta_m)^{-1}(\Delta_k+\Delta_m)^{-1}]T_{\alpha\beta}(\mathbf{r},\mathbf{r}')T_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''')T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v}). \qquad (13)$$

The quantity in brackets in Eq. (13) simplifies to $4(\Delta_j+\Delta_k+\Delta_m)(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_k+\Delta_m)^{-1}$. Then with Eq. (6.20), Eq. (13) transforms to

$$\Delta E^{(3)}_{disp} = -\hbar/\pi \int_0^\infty d\omega \int d\mathbf{r}\cdots d\mathbf{r}^{v}\, \mathrm{Tr}[\mathbf{T}(\mathbf{r}^{v},\mathbf{r}^{iv})\cdot\alpha^{C}(\mathbf{r}^{iv},\mathbf{r}''';i\omega)\cdot\mathbf{T}(\mathbf{r}''',\mathbf{r}'')$$

$$\cdot\alpha^{B}(\mathbf{r}'',\mathbf{r}';i\omega)\cdot\mathbf{T}(\mathbf{r}',\mathbf{r})\cdot\alpha^{A}(\mathbf{r},\mathbf{r}^{v};i\omega)]\,. \qquad (14)$$

This is identical to the dynamical reaction-field result for the dispersion energy given by Eq. (6.22); in this case, the fluctuating polarization of A acts as the source of the field polarizing B, which polarizes C, giving *a dynamic* reaction field at A, and an energy shift depending on the correlations in the fluctuating polarization of A. The results from Eqs. (12) and (14) thus give a unified physical picture of the "circuit" terms in $\Delta E^{(3)}$, as a combination of static and dynamic reaction-field effects.

7.3 Third-body Perturbation of Two-body Interactions

Next, the remaining three-body contributions to the interaction energy $\Delta E^{(3)}$ are analyzed from Eq. (8). In Sec. 7.2, the 6 terms in which V_{AB}, V_{BC}, and V_{CA} each appear once have been calculated; here 18 terms are evaluated in which one of the perturbations appears twice, one appears once, and the third perturbation does not appear. The sum of terms given by

$$\Delta E^{(3)}(AB,AB,AC) = \langle\Psi_0|V_{AB}\,G\,V^{o}_{AB}\,G\,V_{AC}|\Psi_0\rangle + \langle\Psi_0|V_{AB}\,G\,V^{o}_{AC}\,G\,V_{AB}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AC}\,G\,V^{o}_{AB}\,G\,V_{AB}|\Psi_0\rangle \qquad (15)$$

is representative of this set. By permuting the molecule labels in Eq. (15), 15 other distinct terms, in 5 sets of 3, are generated. The set $\Delta E^{(3)}(AB,AB,AC)$ can be categorized as the perturbation of the two-body A-B interactions, due to C acting on A.

From Eq. (4) for the reduced resolvent operator,

$$\langle\Psi_0|V_{AB}\,G\,V^{o}_{AB}\,G\,V_{AC}|\Psi_0\rangle$$

$$= \langle\Psi_0|V_{AB}\,G^{A}\wp^{B}_{0}\,\wp^{C}_{0}\,V^{o}_{AB}\,G^{A}\wp^{B}_{0}\,\wp^{C}_{0}\,V_{AC}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AB}\,G^B\wp_0^A\,\wp_0^C\,V_{AB}^o\,G^A\wp_0^B\,\wp_0^C\,V_{AC}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AB}\,G^{A\oplus B}\,\wp_0^C\,V_{AB}^o\,G^A\wp_0^B\,\wp_0^C\,V_{AC}|\Psi_0\rangle, \tag{16}$$

and

$$\langle\Psi_0|V_{AB}\,G\,V_{AC}^o\,G\,V_{AB}|\Psi_0\rangle$$

$$=\langle\Psi_0|V_{AB}\,G^A\wp_0^B\,\wp_0^C\,V_{AC}^o\,G^A\wp_0^B\,\wp_0^C\,V_{AB}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AB}\,G^B\,\wp_0^A\wp_0^C\,V_{AC}^o\,G^{A\oplus B}\,\wp_0^C\,V_{AB}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AB}\,G^{A\oplus B}\,\wp_0^C\,V_{AC}^o\,G^B\,\wp_0^A\wp_0^C\,V_{AB}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AB}\,G^{A\oplus B}\,\wp_0^C\,V_{AC}^o\,G^{A\oplus B}\,\wp_0^C\,V_{AB}|\Psi_0\rangle. \tag{17}$$

$\langle\Psi_0|V_{AC}\,G\,V_{AB}^o\,G\,V_{AB}|\Psi_0\rangle$ is the complex conjugate of $\langle\Psi_0|V_{AB}\,G\,V_{AB}^o\,G\,V_{AC}|\Psi_0\rangle$ from Eq. (16).

$\Delta E^{(3)}(AB, AB, AC)$ can be separated into 3 sets $S_1 - S_3$:

$$\Delta E^{(3)}(AB, AB, AC) = S_1 + S_2 + S_3, \tag{18}$$

according to the types of matrix elements appearing in each. S_1 terms are given by

$$S_1 = \langle\Psi_0|V_{AB}\,G^A\wp_0^B\,\wp_0^C\,V_{AB}^o\,G^A\wp_0^B\,\wp_0^C\,V_{AC}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AC}\,G^A\wp_0^B\,\wp_0^C\,V_{AB}^o\,G^A\wp_0^B\,\wp_0^C\,V_{AB}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AB}\,G^A\wp_0^B\,\wp_0^C\,V_{AC}^o\,G^A\wp_0^B\,\wp_0^C\,V_{AB}|\Psi_0\rangle, \tag{19}$$

In matrix element form,

$$S_1 = -\int d\mathbf{r}\cdots d\mathbf{r}^{v}\sum_{j,l}{}' [\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^{oA}(\mathbf{r}')|l\rangle\langle l|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$+\langle 0|P_\gamma^A(\mathbf{r}'')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\beta^A(\mathbf{r}')|0\rangle$$

$$+\langle 0|P_{\alpha}^{A}(\mathbf{r})|j\rangle\langle j|P_{\gamma}^{oA}(\mathbf{r}'')|l\rangle\langle l|P_{\beta}^{A}(\mathbf{r}')|0\rangle]\Delta_j^{-1}\Delta_l^{-1}$$

$$\times P_{0\delta}^{B}(\mathbf{r}''')P_{0\varepsilon}^{B}(\mathbf{r}^{iv})P_{0\phi}^{C}(\mathbf{r}^{v})T_{\alpha\delta}(\mathbf{r},\mathbf{r}''')T_{\beta\varepsilon}(\mathbf{r}',\mathbf{r}^{iv})T_{\gamma\phi}(\mathbf{r}'',\mathbf{r}^{v}). \quad (20)$$

From the definition of the β hyperpolarizability density [3],

$$\beta_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';-\omega_\sigma;\omega_1,\omega_2)$$

$$=[1+C(\omega_1\to-\omega_1,\omega_2\to-\omega_2,\omega_\sigma\to-\omega_\sigma)]$$

$$\times[\langle 0|P_\alpha(\mathbf{r})G(\omega_\sigma)P_\beta^{o}(\mathbf{r}')G(\omega_2)P_\gamma(\mathbf{r}'')|0\rangle$$

$$+\langle 0|P_\alpha(\mathbf{r})G(\omega_\sigma)P_\gamma^{o}(\mathbf{r}'')G(\omega_1)P_\beta(\mathbf{r}')|0\rangle$$

$$+\langle 0|P_\gamma(\mathbf{r}'')G^{*}(-\omega_2)P_\alpha^{o}(\mathbf{r})G(\omega_1)P_\beta(\mathbf{r}')|0\rangle], \quad (21)$$

Eq. (20) transforms to

$$S_1=-1/2\int d\mathbf{r}\cdots d\mathbf{r}^{v}\,\beta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0;0,0)\vdots[\mathbf{T}(\mathbf{r},\mathbf{r}''')\cdot\mathbf{P}_0^{B}(\mathbf{r}''')]$$

$$\times[\mathbf{T}(\mathbf{r}',\mathbf{r}^{iv})\cdot\mathbf{P}_0^{B}(\mathbf{r}^{iv})]\,[\mathbf{T}(\mathbf{r}'',\mathbf{r}^{v})\cdot\mathbf{P}_0^{C}(\mathbf{r}^{v})]. \quad (22)$$

In equation (21), $\omega_\sigma\equiv\omega_1+\omega_2$; $C(\omega_1\to-\omega_1,\omega_2\to-\omega_2,\omega_\sigma\to-\omega_\sigma)$ denotes the operator for complex conjugation and replacement of ω_1 by $-\omega_1$, ω_2 by $-\omega_2$, and ω_σ by $-\omega_\sigma$; the frequency-dependent reduced resolvent operator $G(\omega)$ is given by

$$G(\omega)=(1-|0\rangle\langle 0|)(H_0-E_0-\hbar\omega)^{-1}(1-|0\rangle\langle 0|). \quad (23)$$

The S_1 term from Eq. (22) reflects the hyperpolarization of A by the fields from the permanent polarization of B (taken twice) and the permanent polarization of C.

S_2 terms satisfy

$$S_2=(1+C)[\langle\Psi_0|V_{AB}\,G^{B}\wp_0^{A}\,\wp_0^{C}\,V_{AB}^{o}\,G^{A}\wp_0^{B}\,\wp_0^{C}\,V_{AC}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AB}\,G^{B}\,\wp_0^{A}\wp_0^{C}\,V_{AC}^{o}\,G^{A\oplus B}\,\wp_0^{C}\,V_{AB}|\Psi_0\rangle]$$

$$=-\int d\mathbf{r}\cdots d\mathbf{r}^{v}\,P_{0\alpha}^{A}(\mathbf{r})\sum_{j,k}{}'[\langle 0|P_\beta^{A}(\mathbf{r}')|j\rangle\langle j|P_\gamma^{A}(\mathbf{r}'')|0\rangle\langle 0|P_\delta^{B}(\mathbf{r}''')|k\rangle$$

$$\times\langle k|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle][2\Delta_j^{-1}\Delta_k^{-1}+2(\Delta_j+\Delta_k)^{-1}\Delta_k^{-1}]P_{0\phi}^C(\mathbf{r}^v)$$

$$\times T_{\alpha\delta}(\mathbf{r},\mathbf{r}''')T_{\beta\varepsilon}(\mathbf{r}',\mathbf{r}^{iv})T_{\gamma\phi}(\mathbf{r}'',\mathbf{r}^v). \tag{24}$$

The S_2 terms further separate into two sets. In the first, designated $S_{2,ind}$, the field from the unperturbed charge density of C polarizes A, which in turn polarizes B; the induced polarization in B produces a field at A, giving rise to an energy shift that depends on the scalar product of this field and the permanent polarization of A. $S_{2,ind}$ satisfies

$$S_{2,ind}=-\int d\mathbf{r}\cdots d\mathbf{r}^v\,\mathbf{P}_0^C(\mathbf{r})\cdot\mathbf{T}(\mathbf{r},\mathbf{r}')\cdot\alpha^A(\mathbf{r}',\mathbf{r}'')\cdot\mathbf{T}(\mathbf{r}'',\mathbf{r}''')$$

$$\cdot\alpha^B(\mathbf{r}''',\mathbf{r}^{iv})\cdot\mathbf{T}(\mathbf{r}^{iv},\mathbf{r}^v)\cdot\mathbf{P}_0^A(\mathbf{r}^v). \tag{25}$$

The second set of S_2 terms gives one part of the contribution to the induction-dispersion energy, as discussed below. This part is $S_2-S_{2,ind}$; in matrix element form

$$S_2-S_{2,ind}=\int d\mathbf{r}\cdots d\mathbf{r}^v\,P_{0\alpha}^A(\mathbf{r})\sum_{j,k}{}'\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\gamma^A(\mathbf{r}'')|0\rangle\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle$$

$$\times\langle k|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle\,[2\Delta_j^{-1}(\Delta_j+\Delta_k)^{-1}]P_{0\phi}^C(\mathbf{r}^v)$$

$$\times T_{\alpha\delta}(\mathbf{r},\mathbf{r}''')T_{\beta\varepsilon}(\mathbf{r}',\mathbf{r}^{iv})T_{\gamma\phi}(\mathbf{r}'',\mathbf{r}^v). \tag{26}$$

S_3 contains the remaining terms,

$$S_3=\langle\Psi_0|V_{AB}\,G^{A\oplus B}\,\wp_0^C\,V_{AB}^o\,G^A\wp_0^B\,\wp_0^C\,V_{AC}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AC}\,G^A\wp_0^B\,\wp_0^C\,V_{AB}^o\,G^{A\oplus B}\,\wp_0^C\,V_{AB}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{AB}\,G^{A\oplus B}\,\wp_0^C\,V_{AC}^o\,G^{A\oplus B}\,\wp_0^C\,V_{AB}|\Psi_0\rangle. \tag{27}$$

The matrix element form of S_3 is given by

$$S_3=-\int d\mathbf{r}\cdots d\mathbf{r}^v\sum_{j,l,k}{}'[2\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|l\rangle\langle l|P_\gamma^A(\mathbf{r}'')|0\rangle(\Delta_j+\Delta_k)^{-1}\Delta_l^{-1}$$

$$+\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\gamma^{oA}(\mathbf{r}'')|l\rangle\langle l|P_\beta^A(\mathbf{r}')|0\rangle(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}]$$

$$\times \langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle P_{0\phi}^C(\mathbf{r}^v)T_{\alpha\delta}(\mathbf{r},\mathbf{r}''')$$

$$\times T_{\beta\varepsilon}(\mathbf{r}',\mathbf{r}^{iv})T_{\gamma\phi}(\mathbf{r}'',\mathbf{r}^v). \tag{28}$$

Adding $S_2 - S_{2,\text{ind}}$ from Eq. (26) to S_3 converts the element $\langle j|P_\beta^A(\mathbf{r}')|l\rangle$ in the first line of Eq. (28) into $\langle j|P_\beta^{oA}(\mathbf{r}')|l\rangle$. This gives

$$S_2 - S_{2,\text{ind}} + S_3 = -\hbar/2\pi\int_0^\infty d\omega \int d\mathbf{r}\cdots d\mathbf{r}^v\, \beta_{\beta\gamma\alpha}^A(\mathbf{r}',\mathbf{r}'',\mathbf{r};-i\omega;i\omega,0)\,T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')$$

$$\times \alpha_{\delta\varepsilon}^B(\mathbf{r}''',\mathbf{r}^{iv};i\omega)\,T_{\gamma\varepsilon}(\mathbf{r}'',\mathbf{r}^{iv})\,T_{\alpha\phi}(\mathbf{r},\mathbf{r}^v)\,P_{0\phi}^C(\mathbf{r}^v), \tag{29}$$

after use of the integral identities

$$\int_0^\infty dx\,[2a(a^2+x^2)^{-1}][2b(b^2+x^2)^{-1}] = 2\pi\,(a+b)^{-1}, \tag{30}$$

and

$$\int_0^\infty dx\,2a(a^2+x^2)^{-1}[(b+ix)^{-1}(c+ix)^{-1}+(b-ix)^{-1}(c-ix)^{-1}]$$

$$= 2\pi(a+b)^{-1}(a+c)^{-1} \tag{31}$$

for a, b, c > 0.

Earlier, Hunt [4, 5] has shown that the two-body dispersion interactions between A and B produce a change in the polarization of A given by

$$P_{\alpha,\text{disp}}^{A\leftarrow B}(\mathbf{r}) = \hbar/2\pi\int_0^\infty d\omega \int d\mathbf{r}\cdots d\mathbf{r}^v\, \beta_{\beta\gamma\alpha}^A(\mathbf{r}',\mathbf{r}'',\mathbf{r};-i\omega;i\omega,0)\,T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')$$

$$\times \alpha_{\delta\varepsilon}^B(\mathbf{r}''',\mathbf{r}^{iv};i\omega)\,T_{\gamma\varepsilon}(\mathbf{r}'',\mathbf{r}^{iv}); \tag{32}$$

that is, $P_{\alpha,\text{disp}}^{A\leftarrow B}(\mathbf{r})$ depends on the imaginary-frequency hyperpolarizability density of A and the imaginary-frequency polarizability density of B. A comparison of Eq. (32) and (29) gives

$$S_2 - S_{2,\text{ind}} + S_3 = -\int d\mathbf{r}\,d\mathbf{r}'\, P_{\alpha,\text{disp}}^{A\leftarrow B}(\mathbf{r})\,T_{\alpha\beta}(\mathbf{r},\mathbf{r}')\,P_{0\beta}^C(\mathbf{r}'). \tag{33}$$

The right side of Eq. (33) represents the electrostatic interaction between the unperturbed polarization of C and the dispersion-induced change in polarization of A, which is due to the two-body interactions between A and B. This energy term is denoted by S_{i+d}. Then from Eq. (33),

$$S_2 + S_3 = S_{2,\mathrm{ind}} + S_{i+d}. \tag{34}$$

The quantity $\Delta E^{(3)}(AB, AB, AC)$ is the sum of S_1 from Eq. (22), $S_{2,\mathrm{ind}}$ from Eq. (25), and S_{i+d} from Eq. (29). The 18 third-body perturbation terms covered in this section sum to give

$$\begin{aligned}\Delta E^{(3)}_{\mathrm{tbp}} &= \Delta E^{(3)}(AB, AB, AC) + \Delta E^{(3)}(AB, AB, BC) + \Delta E^{(3)}(AC, AC, AB) \\ &\quad + \Delta E^{(3)}(AC, AC, BC) + \Delta E^{(3)}(BC, BC, AB) + \Delta E^{(3)}(BC, BC, AC),\end{aligned} \tag{35}$$

which is identical to the results for $\Delta E^{(3)}_{\mathrm{tbf}} + \Delta E^{(3)}_{\mathrm{hyp}} + \Delta E^{(3)}_{i+d}$ from the reaction-field analysis in Sec. 6.3 of Chapter VI. The full third-order interaction energy is

$$\Delta E^{(3)} = \Delta E^{(3)}_{\mathrm{cir}} + \Delta E^{(3)}_{\mathrm{tbp}} \tag{36}$$

with $\Delta E^{(3)}_{\mathrm{cir}}$ given in Sec. 7.2.

7.4. Three-body Polarization at Second Order

In this section, the nonadditive components of the three-body polarization at second order are evaluated. The second-order term in an arbitrary property ϑ is obtained from

$$\begin{aligned}\vartheta &= \langle \Psi_0 + \Psi_1 + \Psi_2 + \cdots | \vartheta | \Psi_0 + \Psi_1 + \Psi_2 + \cdots \rangle / \\ &\quad \langle \Psi_0 + \Psi_1 + \Psi_2 + \cdots | \Psi_0 + \Psi_1 + \Psi_2 + \cdots \rangle\end{aligned} \tag{37}$$

as

$$\vartheta^{(2)} = \langle \Psi_0 | \vartheta | \Psi_2 \rangle + \langle \Psi_2 | \vartheta | \Psi_0 \rangle + \langle \Psi_1 | \vartheta | \Psi_1 \rangle - \langle \Psi_0 | \vartheta | \Psi_0 \rangle \langle \Psi_1 | \Psi_1 \rangle, \tag{38}$$

where Ψ_1 and Ψ_2 are first- and second-order corrections to Ψ_0 due to the perturbation V,

$$\Psi_1 = -G\,V\,\Psi_0, \tag{39}$$

and

$$\Psi_2 = G\,V^o\,G\,V\Psi_0. \tag{40}$$

In equation (40) $V^o \equiv V - \langle\Psi_0|V|\Psi_0\rangle$. From Eqs. (38)-(40),

$$\begin{aligned}\vartheta^{(2)} &= \langle\Psi_0|\vartheta\,G\,V^o\,G\,V|\Psi_0\rangle + \langle\Psi_0|V\,G\,V^o\,G\,\vartheta|\Psi_0\rangle \\ &\quad + \langle\Psi_0|V\,G\,\vartheta\,G\,V|\Psi_0\rangle - \langle\Psi_0|\vartheta|\Psi_0\rangle\langle\Psi_0|V\,G\;G\,V|\Psi_0\rangle \\ &= \langle\Psi_0|\vartheta\,G\,V^o\,G\,V|\Psi_0\rangle + \langle\Psi_0|V\,G\,V^o\,G\,\vartheta|\Psi_0\rangle + \langle\Psi_0|V\,G\,\vartheta^o\,G\,V|\Psi_0\rangle.\end{aligned} \tag{41}$$

With substitution $V = V_{AB} + V_{BC} + V_{CA}$, equation (41) expands to yield 27 terms. Of these, there are 9 additive two-body terms, in which the same perturbation operators such as V_{AB} appears twice. The remaining 18 terms represent the nonadditive three-body interactions. All these 18 terms are considered here. The operator ϑ is taken as $P_\alpha^A(\mathbf{r})$ and $P_\alpha^A(\mathbf{r})$ is abbreviated by P^A in the following equations. First the sum of the six terms containing operators V_{AB} and V_{CA} is calculated,

$$\begin{aligned}Q_1 &= \langle\Psi_0|P^A\,G\,V_{AB}^o\,G\,V_{CA}|\Psi_0\rangle + \langle\Psi_0|P^A\,G\,V_{CA}^o\,G\,V_{AB}|\Psi_0\rangle \\ &\quad + \langle\Psi_0|V_{AB}G\,V_{CA}^o\,G\,P^A|\Psi_0\rangle + \langle\Psi_0|V_{CA}\,G\,V_{AB}^o\,G\,P^A|\Psi_0\rangle \\ &\quad + \langle\Psi_0|V_{AB}G\,P^{oA}\,G\,V_{CA}|\Psi_0\rangle + \langle\Psi_0|V_{CA}\,G\,P^{oA}\,G\,V_{AB}|\Psi_0\rangle \\ &= \langle\Psi_0|P^A\,G^A\wp_0^B\wp_0^C\,V_{AB}^o\,G^A\wp_0^B\wp_0^C\,V_{CA}|\Psi_0\rangle \\ &\quad + \langle\Psi_0|P^A\,G^A\wp_0^B\,\wp_0^C\,V_{CA}^o\,G^A\wp_0^B\,\wp_0^C\,V_{AB}|\Psi_0\rangle \\ &\quad + \langle\Psi_0|V_{AB}G^A\wp_0^B\,\wp_0^C\,V_{CA}^o\,G^A\wp_0^B\,\wp_0^C\,P^A|\Psi_0\rangle \\ &\quad + \langle\Psi_0|V_{CA}\,G^A\wp_0^B\,\wp_0^C\,V_{AB}^o\,G^A\wp_0^B\,\wp_0^C\,P^A|\Psi_0\rangle\end{aligned}$$

$$+\langle\Psi_0|V_{AB}G^A\wp_0^B\wp_0^C P^{oA}\, G^A\wp_0^B\wp_0^C V_{CA}|\Psi_0\rangle$$

$$+\langle\Psi_0|V_{CA}\, G^A\wp_0^B\wp_0^C P^{oA}\, G^A\wp_0^B\wp_0^C V_{AB}|\Psi_0\rangle. \tag{42}$$

The matrix element form of Eq. (42) is

$$Q_1 = \int d\mathbf{r}'\cdots d\mathbf{r}^{iv}\, T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')T_{\gamma\varepsilon}(\mathbf{r}'',\mathbf{r}^{iv})\, P_{0\delta}^B(\mathbf{r}''')P_{0\varepsilon}^C(\mathbf{r}^{iv})$$
$$\times\sum_{j,n}{}'[\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^{oA}(\mathbf{r}')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$
$$+\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\gamma^{oA}(\mathbf{r}'')|n\rangle\langle n|P_\beta^A(\mathbf{r}')|0\rangle$$
$$+\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\gamma^{oA}(\mathbf{r}'')|n\rangle\langle n|P_\alpha^A(\mathbf{r})|0\rangle$$
$$+\langle 0|P_\gamma^A(\mathbf{r}'')|j\rangle\langle j|P_\beta^{oA}(\mathbf{r}')|n\rangle\langle n|P_\alpha^A(\mathbf{r})|0\rangle$$
$$+\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$
$$+\langle 0|P_\gamma^A(\mathbf{r}'')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|n\rangle\langle n|P_\beta^A(\mathbf{r}')|0\rangle]\Delta_j^{-1}\Delta_n^{-1}. \tag{43}$$

Equation (43) is equivalent to

$$Q_1 = \int d\mathbf{r}'\cdots d\mathbf{r}^{iv}\, \beta_{\alpha\beta\gamma}^A(\mathbf{r},\mathbf{r}',\mathbf{r}'')T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')P_{0\delta}^B(\mathbf{r}''')T_{\gamma\varepsilon}(\mathbf{r}'',\mathbf{r}^{iv})P_{0\varepsilon}^C(\mathbf{r}^{iv}), \tag{44}$$

where $\beta_{\alpha\beta\gamma}^A(\mathbf{r},\mathbf{r}',\mathbf{r}'') \equiv \beta_{\alpha\beta\gamma}^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';0;0,0)$. The Q_1 term represents the lowest-order hyperpolarization of molecule A due to the simultaneous action of the static fields from the permanent charge densities of molecules B and C.

The sum of the six terms containing operators V_{AB} and V_{BC} is given by

$$Q_2 = \langle\Psi_0|P^A\, G\, V_{AB}^o\, G\, V_{BC}|\Psi_0\rangle + \langle\Psi_0|P^A\, G\, V_{BC}^o\, G\, V_{AB}|\Psi_0\rangle$$
$$+\langle\Psi_0|V_{AB}G\, V_{BC}^o\, G\, P^A|\Psi_0\rangle + \langle\Psi_0|V_{BC}\, G\, V_{AB}^o\, G\, P^A|\Psi_0\rangle$$
$$+\langle\Psi_0|V_{AB}\, G\, P^{oA}\, G\, V_{BC}|\Psi_0\rangle + \langle\Psi_0|V_{BC}\, G\, P^{oA}\, G\, V_{AB}|\Psi_0\rangle$$

$$= \langle \Psi_0 | P^A G^A \wp_0^B \wp_0^C V_{AB}^o G^A \wp_0^B \wp_0^C V_{BC} | \Psi_0 \rangle$$

$$+ \langle \Psi_0 | P^A G^A \wp_0^B \wp_0^C V_{BC}^o G^{A\oplus B} \wp_0^C V_{AB} | \Psi_0 \rangle$$

$$+ \langle \Psi_0 | V_{AB} G^{A\oplus B} \wp_0^C V_{BC}^o G^A \wp_0^B \wp_0^C P^A | \Psi_0 \rangle$$

$$+ \langle \Psi_0 | V_{BC} G^B \wp_0^A \wp_0^C V_{AB}^o G^A \wp_0^B \wp_0^C P^A | \Psi_0 \rangle$$

$$+ \langle \Psi_0 | V_{AB} G^{A\oplus B} \wp_0^C P^{oA} G^B \wp_0^A \wp_0^C V_{BC} | \Psi_0 \rangle$$

$$+ \langle \Psi_0 | V_{BC} G^B \wp_0^A \wp_0^C P^{oA} G^{A\oplus B} \wp_0^C V_{AB} | \Psi_0 \rangle, \qquad (45)$$

or in a matrix element form,

$$Q_2 = \int d\mathbf{r}' \cdots d\mathbf{r}^{iv}\, T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'') T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv}) P_{0\varepsilon}^C(\mathbf{r}^{iv})$$
$$\times \sum_j{}' \langle 0 | P_\alpha^A(\mathbf{r}) | j \rangle \langle j | P_\beta^A(\mathbf{r}') | 0 \rangle \sum_k{}' \langle 0 | P_\gamma^B(\mathbf{r}'') | k \rangle \langle k | P_\delta^B(\mathbf{r}''') | 0 \rangle$$
$$\times [\Delta_j^{-1}\Delta_k^{-1} + \Delta_j^{-1}(\Delta_j+\Delta_k)^{-1} + \Delta_j^{-1}(\Delta_j+\Delta_k)^{-1} + \Delta_j^{-1}\Delta_k^{-1}$$
$$+ \Delta_k^{-1}(\Delta_j+\Delta_k)^{-1} + \Delta_k^{-1}(\Delta_j+\Delta_k)^{-1}]$$
$$= 4\int d\mathbf{r}' \cdots d\mathbf{r}^{iv}\, T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'') T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv}) P_{0\varepsilon}^C(\mathbf{r}^{iv})$$
$$\times \sum_j{}' \langle 0 | P_\alpha^A(\mathbf{r}) | j \rangle \langle j | P_\beta^A(\mathbf{r}') | 0 \rangle \sum_k{}' \langle 0 | P_\gamma^B(\mathbf{r}'') | k \rangle \langle k | P_\delta^B(\mathbf{r}''') | 0 \rangle\, \Delta_j^{-1}\Delta_k^{-1}. \qquad (46)$$

Equation (46) can be recast into the form

$$Q_2 = \int d\mathbf{r}' \cdots d\mathbf{r}^{iv}\, \alpha_{\alpha\beta}^A(\mathbf{r},\mathbf{r}') T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'') \alpha_{\gamma\delta}^B(\mathbf{r}'',\mathbf{r}''') T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv}) P_{0\varepsilon}^C(\mathbf{r}^{iv}) \qquad (47)$$

in terms of the polarizability densities of molecules A and B.

The Q_2 term gives the lowest-order three-body component of the polarization induced in A due to the field from the permanent charge distribution of C. The full second-order, three-body polarization of A is given by $< P_\alpha^A(\mathbf{r}) >^{(2)} = Q_1 + (1+\wp^{BC})Q_2$.

7.5 Three-body Polarization: "Circuit" Terms

In this section, the "circuit" contributions (third-order effects) to the three-body polarization are calculated; they are analogous to the "circuit" terms in the energy analyzed in Sec. 7.2. The third-order term in an arbitrary property ϑ is obtained from

$$\vartheta = \langle \Psi_0 + \Psi_1 + \Psi_2 + \Psi_3 + \cdots | \vartheta | \Psi_0 + \Psi_1 + \Psi_2 + \Psi_3 + \cdots \rangle / \\ \langle \Psi_0 + \Psi_1 + \Psi_2 + \Psi_3 + \cdots | \Psi_0 + \Psi_1 + \Psi_2 + \Psi_3 + \cdots \rangle \tag{48}$$

as

$$\vartheta^{(3)} = (1+C)[\langle \Psi_0 | \vartheta | \Psi_3 \rangle + \langle \Psi_1 | \vartheta | \Psi_2 \rangle - \langle \Psi_1 | \Psi_1 \rangle \langle \Psi_0 | \vartheta | \Psi_1 \rangle \\ - \langle \Psi_1 | \Psi_2 \rangle \langle \Psi_0 | \vartheta | \Psi_0 \rangle] \tag{49}$$

assuming that all of the corrections Ψ_j to the wavefunction are orthogonal to Ψ_0. The corrections Ψ_1 and Ψ_2 are given by Eqs. (39) and (40), respectively, and Ψ_3 is given by

$$\Psi_3 = -G\,V^o\,G\,V^o\,G\,V\,\Psi_0 + \langle \Psi_0 | V\,G\,V | \Psi_0 \rangle G\,G\,V\,\Psi_0. \tag{50}$$

Then

$$\vartheta^{(3)} = (1+C)[-\langle \Psi_0 | \vartheta\,G\,V^o\,G\,V^o\,G\,V\,| \Psi_0 \rangle - \langle \Psi_0 | V\,G\,\vartheta^o G\,V^o\,G\,V\,| \Psi_0 \rangle \\ + \langle \Psi_0 | V\,G\,V\,| \Psi_0 \rangle \langle \Psi_0 | \vartheta\,G\,G\,V\,| \Psi_0 \rangle + \langle \Psi_0 | V\,G\,G\,V\,| \Psi_0 \rangle \langle \Psi_0 | \vartheta\,G\,V\,| \Psi_0 \rangle]. \tag{51}$$

With the substitution $V = V_{AB} + V_{BC} + V_{CA}$, each of the terms in Eq. (51) expands to give 27 terms. In this section, the sets of 6 of "circuit" type, which contain V_{AB}, V_{BC}, and V_{CA}, each appearing once, are analyzed. As used in the last section, the α-component of the polarization operator for molecule A, $P_\alpha^A(\mathbf{r})$, is taken as ϑ, and $P_\alpha^A(\mathbf{r})$ is abbreviated as P^A in the following equations.

A representative circuit term from Eq. (51) is $\langle\Psi_0|\mathrm{P^A\,G\,V^o_{AB}\,G\,V^o_{BC}\,G\,V_{CA}}\,|\Psi_0\rangle$. With Eq. (4) for G, a direct expansion of $\langle\Psi_0|\mathrm{P^A\,G\,V^o_{AB}\,G\,V^o_{BC}\,G\,V_{CA}}\,|\Psi_0\rangle$ generates 7^3 terms; but of these, only 4 are nonzero and

$$\begin{aligned}
&\langle\Psi_0|\mathrm{P^A\,G\,V^o_{AB}\,G\,V^o_{BC}\,G\,V_{CA}}|\Psi_0\rangle\\
&\qquad=\langle\Psi_0|\mathrm{P^A\,G^A}\,\wp_0^{\mathrm{B}}\wp_0^{\mathrm{C}}\,\mathrm{V^o_{AB}\,G^A}\,\wp_0^{\mathrm{B}}\wp_0^{\mathrm{C}}\,\mathrm{V^o_{BC}\,G^{A\oplus C}}\,\wp_0^{\mathrm{B}}\mathrm{V_{CA}}\,|\Psi_0\rangle\\
&\qquad\quad+\langle\Psi_0|\,\mathrm{P^A\,G^A}\,\wp_0^{\mathrm{B}}\wp_0^{\mathrm{C}}\,\mathrm{V^o_{AB}\,G^B}\,\wp_0^{\mathrm{A}}\,\wp_0^{\mathrm{C}}\,\mathrm{V^o_{BC}\,G^C}\,\wp_0^{\mathrm{A}}\,\wp_0^{\mathrm{B}}\mathrm{V_{CA}}\,|\Psi_0\rangle\\
&\qquad\quad+\langle\Psi_0|\,\mathrm{P^A\,G^A}\,\wp_0^{\mathrm{B}}\wp_0^{\mathrm{C}}\,\mathrm{V^o_{AB}\,G^{A\oplus B}}\,\wp_0^{\mathrm{C}}\,\mathrm{V^o_{BC}\,G^A}\,\wp_0^{\mathrm{B}}\wp_0^{\mathrm{C}}\,\mathrm{V_{CA}}\,|\Psi_0\rangle\\
&\qquad\quad+\langle\Psi_0|\,\mathrm{P^A\,G^A}\,\wp_0^{\mathrm{B}}\wp_0^{\mathrm{C}}\,\mathrm{V^o_{AB}\,G^{A\oplus B}}\,\wp_0^{\mathrm{C}}\,\mathrm{V^o_{BC}\,G^{A\oplus C}}\,\wp_0^{\mathrm{B}}\,\mathrm{V_{CA}}\,|\Psi_0\rangle. \qquad (52)
\end{aligned}$$

The full expansion of the terms within square brackets in Eq. (51) yields 68 nonzero "circuit" terms. These can be grouped into four sets $\mathrm{T_1 - T_4}$, which are given explicitly in Appendix B, so that

$$\left\langle \mathrm{P^A_\alpha}(\mathbf{r})\right\rangle^{(3)}_{\mathrm{cir}} = \mathrm{T_1 + T_2 + T_3 + T_4}. \qquad (53)$$

From Eqs. (B1) and (B5)-(B10) for the $\mathrm{T_1}$ term,

$$\begin{aligned}
\mathrm{T_1} = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,l,m}{}' &[\langle 0|\,\mathrm{P^A_\alpha}(\mathbf{r})\,|j\rangle\langle j|\,\mathrm{P^{oA}_\beta}(\mathbf{r}')\,|l\rangle\langle l|\,\mathrm{P^A_\gamma}(\mathbf{r}'')|0\rangle\\
&+\langle 0|\,\mathrm{P^A_\beta}(\mathbf{r}')\,|j\rangle\langle j|\mathrm{P^{oA}_\alpha}(\mathbf{r})\,|l\rangle\langle l|\,\mathrm{P^A_\gamma}(\mathbf{r}'')|0\rangle\\
&+\langle 0|\,\mathrm{P^A_\alpha}(\mathbf{r})|\,j\rangle\langle j|\mathrm{P^{oA}_\gamma}(\mathbf{r}'')|l\rangle\langle l|\mathrm{P^A_\beta}(\mathbf{r}')|0\rangle]\\
&\times \mathrm{P^B_{0\delta}}(\mathbf{r}''')\,\mathrm{P^B_{0\varepsilon}}(\mathbf{r}^{iv})\,\langle 0|\,\mathrm{P^C_\lambda}(\mathbf{r}^{v})\,|m\rangle\langle m|\,\mathrm{P^C_\phi}(\mathbf{r}^{vi})\,|0\rangle\\
&\times 2\,\Delta_j^{-1}\Delta_l^{-1}\Delta_m^{-1}]\,\mathrm{T}_{\beta\delta}(\mathbf{r}',\mathbf{r}''')\,\mathrm{T}_{\varepsilon\lambda}(\mathbf{r}^{iv},\mathbf{r}^{v})\,\mathrm{T}_{\phi\gamma}(\mathbf{r}^{vi},\mathbf{r}'')\\
= \int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, &\beta^{\mathrm{A}}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0;0,0)\,\mathrm{T}_{\beta\delta}(\mathbf{r}',\mathbf{r}''')\,\mathrm{P^B_{0\delta}}(\mathbf{r}''')\\
&\times \mathrm{T}_{\gamma\phi}(\mathbf{r}'',\mathbf{r}^{vi})\,\alpha^{\mathrm{C}}_{\phi\lambda}(\mathbf{r}^{vi},\mathbf{r}^{v})\,\mathrm{T}_{\lambda\varepsilon}(\mathbf{r}^{v},\mathbf{r}^{iv})\,\mathrm{P^B_{0\varepsilon}}(\mathbf{r}^{iv}). \qquad (54)
\end{aligned}$$

These terms represent the hyperpolarization of A by the direct field from the unperturbed charge density of B, acting together with the field from the polarization induced in C by $\mathbf{P}_0^B(\mathbf{r}^{iv})$. The analogous hyperpolarization contribution associated with the unperturbed charge density of C is given by $\wp^{BC}\, T_1$, where $\wp^{BC}$ permutes the molecule labels B and C.

In Appendix B, the linear induction contribution $T_{3,ind}$ is separated out from T_3; here $T_{3,ind}$ satisfies

$$T_{3,ind} = (1+\wp^{BC})\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, \alpha^A_{\alpha\beta}(\mathbf{r},\mathbf{r}')\,T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')\,\alpha^B_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv}) \times T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v})\,\alpha^C_{\phi\lambda}(\mathbf{r}^{v},\mathbf{r}^{vi})\,T_{\lambda\gamma}(\mathbf{r}^{vi},\mathbf{r}'')\,P^A_{0\gamma}(\mathbf{r}''), \tag{55}$$

or in matrix element form

$$T_{3,ind} = 2(1+\wp^{BC})\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,k,m}{}' \langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\beta(\mathbf{r}')|0\rangle P^A_{0\gamma}(\mathbf{r}'') \times\langle 0|P^B_\delta(\mathbf{r}''')|k\rangle\langle k|P^B_\varepsilon(\mathbf{r}^{iv})|0\rangle\langle 0|P^C_\phi(\mathbf{r}^{v})|m\rangle\langle m|P^C_\lambda(\mathbf{r}^{vi})|0\rangle \times 4\,\Delta_j^{-1}\Delta_k^{-1}\,\Delta_m^{-1}\,T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v})T_{\gamma\lambda}(\mathbf{r}'',\mathbf{r}^{vi}). \tag{56}$$

The dispersion contribution to $P^A_\alpha(\mathbf{r})$ is given by $T_{disp} = T_4 + (T_3 - T_{3,ind})$. It satisfies

$$\begin{aligned} T_{disp} = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,l,k,m}{}' \{&[\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\gamma(\mathbf{r}'')|l\rangle\langle l|P^A_\beta(\mathbf{r}')|0\rangle \\ &+\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\beta(\mathbf{r}')|l\rangle\langle l|P^A_\gamma(\mathbf{r}'')|0\rangle] f_{4a}(\Delta_j,\Delta_l,\Delta_k,\Delta_m) \\ &+\langle 0|P^A_\beta(\mathbf{r}')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|l\rangle\langle l|P^A_\gamma(\mathbf{r}'')|0\rangle f_{4c}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)\} \\ &\times\langle 0|P^B_\delta(\mathbf{r}''')|k\rangle\langle k|P^B_\varepsilon(\mathbf{r}^{iv})|0\rangle\langle 0|P^C_\phi(\mathbf{r}^{v})|m\rangle\langle m|P^C_\lambda(\mathbf{r}^{vi})|0\rangle \\ &\times T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')\,T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v})\,T_{\gamma\lambda}(\mathbf{r}'',\mathbf{r}^{vi}), \end{aligned} \tag{57}$$

where $f_{4a}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)$ is given by Eq. (B14), and

$$f_{4c}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)=(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_l+\Delta_m)^{-1}$$
$$+(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_k+\Delta_m)^{-1}$$
$$+(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_l+\Delta_m)^{-1}$$
$$+(\Delta_j+\Delta_m)^{-1}(\Delta_k+\Delta_m)^{-1}(\Delta_l+\Delta_m)^{-1}. \qquad (58)$$

Eq. (57) can be recast in terms of the β hyperpolarizability density of A and the polarizability densities of B and C, taken at imaginary frequencies. To prove this, complex contour integration methods are used to write

$$f_{4a}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)=4/\pi\int_0^{\infty}dx\,\Delta_j^{-1}\Delta_l(\Delta_l^2+x^2)^{-1}\Delta_k(\Delta_k^2+x^2)^{-1}\Delta_m(\Delta_m^2+x^2)^{-1}, \qquad (59)$$

and

$$f_{4c}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)=4/\pi\int_0^{\infty}dx[(\Delta_j+ix)(\Delta_l+ix)+(\Delta_j-ix)(\Delta_l-ix)]$$
$$\times\Delta_k(\Delta_k^2+x^2)^{-1}\Delta_m(\Delta_m^2+x^2)^{-1}. \qquad (60)$$

Then Eq. (57) transforms to

$$T_{disp}=\hbar/\pi\int_0^{\infty}d\omega\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\,T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')\alpha^{B}_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv};i\omega)\,T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v})$$
$$\times\alpha^{C}_{\phi\lambda}(\mathbf{r}^{v},\mathbf{r}^{vi};i\omega)\,T_{\lambda\gamma}(\mathbf{r}^{vi},\mathbf{r}'')\,\beta^{A}_{\gamma\beta\alpha}(\mathbf{r}'',\mathbf{r}',\mathbf{r};i\omega,0), \qquad (61)$$

which is equivalent to Eq. (6.42) for $P^{(3)}_{\alpha,disp}(\mathbf{r})^{A\leftarrow B,C}$ obtained by the reaction-field method in Sec. 6.4 of Chapter VI.

7.6 Three-body Polarization: "Noncircuit" Terms

This section presents the analysis of the remaining 18 nonadditive terms in the polarization induced in A by its interactions with B and C. In these terms, one of the three perturbations V_{AB}, V_{BC}, and V_{CA} appears twice, the second appears once, and the third does not appear. These can further be categorized into three distinct sets, according to the perturbation operators involved. The first set contains operators V_{AB}, V_{AB}, and V_{BC}, the second contains V_{BC}, V_{BC}, and V_{AB}, and the third contains V_{AB}, V_{AB}, and V_{AC}. The first set of terms are first analyzed. A representative term in this set is $-\langle\Psi_0|P^A\, G\, V_{AB}^o\, G\, V_{AB}^o\, G\, V_{BC}|\Psi_0\rangle$. Substitution of Eq. (4) for G into this yields three nonzero terms

$$
\begin{aligned}
&-\langle\Psi_0|P^A\, G\, V_{AB}^o\, G\, V_{AB}^o\, G\, V_{BC}|\Psi_0\rangle \\
&\quad= -\langle\Psi_0|P^A\, G^A\, \wp_0^B\, \wp_0^C\, V_{AB}^o\, G^A\, \wp_0^B\, \wp_0^C\, V_{AB}^o\, G^B\, \wp_0^A\, \wp_0^C\, V_{BC}|\Psi_0\rangle \\
&\quad\quad -\langle\Psi_0|P^A\, G^A\, \wp_0^B\, \wp_0^C\, V_{AB}^o\, G^B\, \wp_0^A\, \wp_0^C\, V_{AB}^o\, G^B\, \wp_0^A\, \wp_0^C\, V_{BC}|\Psi_0\rangle \\
&\quad\quad -\langle\Psi_0|P^A\, G^A\, \wp_0^B\, \wp_0^C\, V_{AB}^o\, G^{A\oplus B}\, \wp_0^C\, V_{AB}^o\, G^B\, \wp_0^A\, \wp_0^C\, V_{BC}|\Psi_0\rangle. \qquad (62)
\end{aligned}
$$

The full expansion in Eq. (51) gives 27 terms of this type. These can be grouped into three sets $U_1 - U_3$ so that

$$
\left\langle P_\alpha^A(\mathbf{r})\right\rangle^{(3)} = U_1 + U_2 + U_3, \qquad (63)
$$

where the terms U_1, U_2, and U_3 are analyzed in Appendix C. The matrix element form of U_1 is given by Eq. (C2). The U_1 term contains an induction term $U_{1,\mathrm{ind}}$, which satisfies

$$
\begin{aligned}
U_{1,\mathrm{ind}} = \int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, &\alpha_{\alpha\beta}^A(\mathbf{r},\mathbf{r}')\, T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')\, \beta_{\gamma\delta\varepsilon}^B(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{iv}) \\
&\times T_{\delta\lambda}(\mathbf{r}''',\mathbf{r}^{v})\, P_{0\lambda}^A(\mathbf{r}^{v})\, T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi})\, P_{0\eta}^C(\mathbf{r}^{vi}). \qquad (64)
\end{aligned}
$$

In matrix element form,

$$U_{1,\mathrm{ind}} = 4\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, P^{A}_{0\lambda}(\mathbf{r}^{v})\langle 0|P^{A}_{\alpha}(\mathbf{r})|j\rangle\langle j|P^{A}_{\beta}(\mathbf{r}')|0\rangle$$

$$\times[\langle 0|P^{B}_{\gamma}(\mathbf{r}'')|k\rangle\langle k|P^{oB}_{\delta}(\mathbf{r}''')|m\rangle\langle m|P^{B}_{\varepsilon}(\mathbf{r}^{iv})|0\rangle$$

$$+\langle 0|P^{B}_{\gamma}(\mathbf{r}'')|k\rangle\langle k|P^{oB}_{\varepsilon}(\mathbf{r}^{iv})|m\rangle\langle m|P^{B}_{\delta}(\mathbf{r}''')|0\rangle$$

$$+\langle 0|P^{B}_{\varepsilon}(\mathbf{r}^{iv})|k\rangle\langle k|P^{oB}_{\gamma}(\mathbf{r}'')|m\rangle\langle m|P^{B}_{\delta}(\mathbf{r}''')|0\rangle]$$

$$\times P^{C}_{0\eta}(\mathbf{r}^{vi})\,\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}\,T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')\,T_{\delta\lambda}(\mathbf{r}''',\mathbf{r}^{v})\,T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi}). \tag{65}$$

In $U_{1,\mathrm{ind}}$, the fields from the permanent polarization of A and C hyperpolarize B; the induced polarization in B gives rise to a field that polarizes A. The dispersion contribution to the polarization from the U_1 term is $U_1 - U_{1,\mathrm{ind}}$.

The U_2 term given by Eq. (C6) contains the permanent polarization of B and C. It reflects the hyperpolarization of A by the simultaneous action of the direct field from $\mathbf{P}_0^B(\mathbf{r})$ and the field from the polarization induced in B by $\mathbf{P}_0^C(\mathbf{r})$. This effect is designated by $U_{2,\mathrm{ind}}$, which is given by

$$U_{2,\mathrm{ind}} = \int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, \beta^{A}_{\alpha\beta\lambda}(\mathbf{r},\mathbf{r}',\mathbf{r}^{v})\,T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')\,P^{B}_{0\gamma}(\mathbf{r}'')$$

$$\times\, T_{\lambda\delta}(\mathbf{r}^{v},\mathbf{r}''')\,\alpha^{B}_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})\,T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi})\,P^{C}_{0\eta}(\mathbf{r}^{vi})$$

$$= 4\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\sum_{j,l,k}{}'\,[\langle 0|P^{A}_{\alpha}(\mathbf{r})|j\rangle\langle j|P^{oA}_{\beta}(\mathbf{r}')|l\rangle\langle l|P^{A}_{\lambda}(\mathbf{r}^{v})|0\rangle$$

$$+\langle 0|P^{A}_{\alpha}(\mathbf{r})|j\rangle\langle j|P^{oA}_{\lambda}(\mathbf{r}^{v})|l\rangle\langle l|P^{A}_{\beta}(\mathbf{r}')|0\rangle$$

$$+\langle 0|P^{A}_{\beta}(\mathbf{r}')|j\rangle\langle j|P^{oA}_{\alpha}(\mathbf{r})|l\rangle\langle l|P^{A}_{\lambda}(\mathbf{r}^{v})|0\rangle]$$

$$\times\langle 0|P^{B}_{\delta}(\mathbf{r}''')|k\rangle\langle k|P^{B}_{\varepsilon}(\mathbf{r}^{iv})|0\rangle\,P^{B}_{0\gamma}(\mathbf{r}'')\,P^{C}_{0\eta}(\mathbf{r}^{vi})$$

$$\times\,\Delta_j^{-1}\Delta_l^{-1}\Delta_k^{-1}\,T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')\,T_{\delta\lambda}(\mathbf{r}''',\mathbf{r}^{v})\,T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi}). \tag{66}$$

The dispersion contribution to the polarization from the U_2 term is $U_2 - U_{2,\mathrm{ind}}$.

The dispersion component in the polarization U_{disp} is $U_1 - U_{1,ind} + U_2 - U_{2,ind} + U_3$, and U_{disp} satisfies

$$
\begin{aligned}
U_{disp} = \int d\mathbf{r}' \cdots d\mathbf{r}^{vi} \sum_{j,l,k,m}{}' \{ & [\langle 0|P_\lambda^A(\mathbf{r}^v)|j\rangle\langle j|P_\beta^{oA}(\mathbf{r}')|l\rangle\langle l|P_\alpha^A(\mathbf{r})|0\rangle \\
& + \langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\lambda^{oA}(\mathbf{r}^v)|l\rangle\langle l|P_\alpha^A(\mathbf{r})|0\rangle] \\
& \times[\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\gamma^{oB}(\mathbf{r}'')|m\rangle\langle m|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle \Delta_l^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1} \\
& + \langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\varepsilon^{oB}(\mathbf{r}^{iv})|m\rangle\langle m|P_\gamma^B(\mathbf{r}'')|0\rangle \Delta_l^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1} \\
& + \langle 0|P_\gamma^B(\mathbf{r}'')|k\rangle\langle k|P_\delta^{oB}(\mathbf{r}''')|m\rangle\langle m|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle \Delta_l^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}] \\
& + \langle 0|P_\lambda^A(\mathbf{r}^v)|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\beta^A(\mathbf{r}')|0\rangle \\
& \times[\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\gamma^{oB}(\mathbf{r}'')|m\rangle\langle m|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle (\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}\Delta_m^{-1} \\
& + \langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\varepsilon^{oB}(\mathbf{r}^{iv})|m\rangle\langle m|P_\gamma^B(\mathbf{r}'')|0\rangle \\
& \times((\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_l+\Delta_m)^{-1} + (\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1} \\
& \times(\Delta_l+\Delta_m)^{-1}) \\
& + \langle 0|P_\gamma^B(\mathbf{r}'')|k\rangle\langle k|P_\delta^{oB}(\mathbf{r}''')|m\rangle\langle m|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle (\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}\Delta_m^{-1}]\} \\
& \times P_{0\eta}^C(\mathbf{r}^{vi}) T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'') T_{\delta\lambda}(\mathbf{r}''',\mathbf{r}^v) T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi}). \qquad (67)
\end{aligned}
$$

Equation (67) can be recast in terms of the β hyperpolarizability densities of A and B, both taken at imaginary frequencies:

$$
\begin{aligned}
U_{disp} = \hbar/2\pi \int_0^\infty d\omega \int d\mathbf{r}' \cdots d\mathbf{r}^{vi}\, & \beta_{\lambda\beta\alpha}^A(\mathbf{r}^v,\mathbf{r}',\mathbf{r};i\omega,0) T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'') \\
& \times \beta_{\delta\gamma\varepsilon}^B(\mathbf{r}''',\mathbf{r}'',\mathbf{r}^{iv};i\omega,0) T_{\delta\lambda}(\mathbf{r}''',\mathbf{r}^v) T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi}) P_{0\eta}^C(\mathbf{r}^{vi}), \qquad (68)
\end{aligned}
$$

after use of the integral identity Eq. (31) and

$$\int_0^{\infty} dx\,[(a+ix)^{-1}(b+ix)^{-1}+(a-ix)^{-1}(b-ix)^{-1}]$$

$$\times[(c+ix)^{-1}(d+ix)^{-1}+(c-ix)^{-1}(d-ix)^{-1}]$$

$$=2\pi\,[(a+d)^{-1}(b+c)^{-1}(b+d)^{-1}+(a+c)^{-1}(a+d)^{-1}(b+c)^{-1}], \tag{69}$$

where a, b, c, d > 0.

Equation (68) for U_{disp} represents the effect of the perturbation of the *two-body* dispersion interactions between A and B due to the presence of the third body C; specifically, U_{disp} gives the change in the dispersion-induced polarization of A in the A$\cdots$B pair due to the lowest-order static field from C acting on B.

Next, the set of terms that contain the perturbation operators V_{AB}, V_{BC}, and V_{BC} are evaluated. A representative term of this set from Eq. (51) is $-\langle\Psi_0|P^A\,G\,V^o_{AB}\,G\,V^o_{BC}\,G\,V_{BC}|\Psi_0\rangle$. Substitution of Eq. (4) for G into this yields three nonzero terms

$$-\langle\Psi_0|P^A\,G\,V^o_{AB}\,G\,V^o_{BC}\,G\,V_{BC}|\Psi_0\rangle$$

$$=-\langle\Psi_0|P^A\,G^A\,\wp^B_0\,\wp^C_0\,V^o_{AB}\,G^B\,\wp^A_0\,\wp^C_0\,V^o_{BC}\,G^B\,\wp^A_0\,\wp^C_0\,V_{BC}|\Psi_0\rangle$$

$$-\langle\Psi_0|P^A\,G^A\,\wp^B_0\,\wp^C_0\,V^o_{AB}\,G^B\,\wp^A_0\,\wp^C_0\,V^o_{BC}\,G^C\,\wp^A_0\,\wp^B_0\,V_{BC}|\Psi_0\rangle$$

$$-\langle\Psi_0|P^A\,G^A\,\wp^B_0\,\wp^C_0\,V^o_{AB}\,G^B\,\wp^A_0\,\wp^C_0\,V^o_{BC}\,G^{B\oplus C}\,\wp^A_0\,V_{BC}|\Psi_0\rangle. \tag{70}$$

The full expansion in Eq. (51) gives 34 terms of this type. These can be grouped into four sets $W_1 - W_4$ so that

$$\left\langle P^A_\alpha(\mathbf{r})\right\rangle^{(3)}=W_1+W_2+W_3+W_4, \tag{71}$$

where the terms $W_1 - W_4$ are analyzed in Appendix D. The W_1 term is given by Eqs. (D2) and (D3),

$$W_1=2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\sum_{j,k,m}{}'\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\beta(\mathbf{r}')|0\rangle\langle 0|P^B_\delta(\mathbf{r}''')|k\rangle\langle k|P^B_\gamma(\mathbf{r}'')|0\rangle$$

$$\times P^B_{0\lambda}(\mathbf{r}^{vi})\langle 0|P^C_\phi(\mathbf{r}^{v})|m\rangle\langle m|P^C_\varepsilon(\mathbf{r}^{iv})|0\rangle[2\Delta_j^{-1}\Delta_m^{-1}(\Delta_k+\Delta_m)^{-1}$$

$$+2\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}]T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})T_{\phi\lambda}(\mathbf{r}^{v},\mathbf{r}^{vi}). \tag{72}$$

The W_1 terms reflect the linear polarization of molecule A due to the field from the permanent charge density of B via the polarization route $B \to C \to B \to A$; that is, the permanent charge density of B polarizes C, which then polarizes B, producing a change in the polarization in A. This effect is denoted by $W_{1,ind}$, which satisfies

$$\begin{aligned}
W_{1,ind} &= \int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\ \alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}')T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')\alpha^{B}_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''') \\
&\quad \times T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})\alpha^{C}_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v})T_{\phi\lambda}(\mathbf{r}^{v},\mathbf{r}^{vi})P^{B}_{0\lambda}(\mathbf{r}^{vi}) \\
&= 8\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,k,m}{}' \langle 0|P^{A}_{\alpha}(\mathbf{r})|j\rangle\langle j|P^{A}_{\beta}(\mathbf{r}')|0\rangle\langle 0|P^{B}_{\gamma}(\mathbf{r}'')|k\rangle\langle k|P^{B}_{\delta}(\mathbf{r}''')|0\rangle \\
&\qquad \times P^{B}_{0\lambda}(\mathbf{r}^{vi})\langle 0|P^{C}_{\varepsilon}(\mathbf{r}^{iv})|m\rangle\langle m|P^{C}_{\phi}(\mathbf{r}^{v})|0\rangle\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1} \\
&\qquad \times T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})T_{\phi\lambda}(\mathbf{r}^{v},\mathbf{r}^{vi}).
\end{aligned} \tag{73}$$

W_1 also contains one part of the dispersion contribution to the polarization; it is given by $W_1 - W_{1,ind}$.

Equations (D5)-(D11) give the W_2 term in the form:

$$\begin{aligned}
W_2 &= 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,k,m}{}' \langle 0|P^{A}_{\alpha}(\mathbf{r})|j\rangle\langle j|P^{A}_{\beta}(\mathbf{r}')|0\rangle \\
&\quad \times[2\langle 0|P^{B}_{\delta}(\mathbf{r}''')|k\rangle\langle k|P^{oB}_{\lambda}(\mathbf{r}^{vi})|m\rangle\langle m|P^{B}_{\gamma}(\mathbf{r}'')|0\rangle \\
&\qquad +\langle 0|P^{B}_{\delta}(\mathbf{r}''')|k\rangle\langle k|P^{oB}_{\gamma}(\mathbf{r}'')|m\rangle\langle m|P^{B}_{\lambda}(\mathbf{r}^{vi})|0\rangle]\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1} \\
&\qquad \times P^{C}_{0\varepsilon}(\mathbf{r}^{iv})P^{C}_{0\phi}(\mathbf{r}^{v})T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})T_{\phi\lambda}(\mathbf{r}^{v},\mathbf{r}^{vi}).
\end{aligned} \tag{74}$$

Equation (65) can be converted into an equivalent form in terms of the static polarizability density of A and the static β hyperpolarizability density of B,

$$\begin{aligned}
W_2 &= 1/2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\ \alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}')T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')\beta^{B}_{\gamma\delta\lambda}(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{vi}) \\
&\qquad \times T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})P^{C}_{0\varepsilon}(\mathbf{r}^{iv})T_{\lambda\phi}(\mathbf{r}^{vi},\mathbf{r}^{v})P^{C}_{0\phi}(\mathbf{r}^{v}).
\end{aligned} \tag{75}$$

The W_2 term represents the three-body component in the induced polarization in A due to the permanent charge density of C; specifically, the field from the permanent polarization of C hyperpolarizes B, and the induced polarization in B gives rise to a static field that polarizes A.

Terms that contain the matrix elements $P^B_{0\delta}(\mathbf{r}''')$, $P^B_{0\lambda}(\mathbf{r}^{vi})$, and $P^B_{0\gamma}(\mathbf{r}'')$ are grouped into W_3. These terms cancel out so that $W_3 = 0$, as shown in Appendix D.

The remaining dispersion terms are grouped into W_4, and it satisfies Eq. (D16). The dispersion contribution to the polarization W_{disp} is $W_4 + W_1 - W_{1,ind}$, given by

$$\begin{aligned}
W_{disp} = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,k,m,l}{}' \langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\beta(\mathbf{r}')|0\rangle \\
\times[2\langle 0|P^B_\delta(\mathbf{r}''')|k\rangle\langle k|P^{oB}_\lambda(\mathbf{r}^{vi})|m\rangle\langle m|P^B_\gamma(\mathbf{r}'')|0\rangle\Delta_j^{-1}\Delta_m^{-1}(\Delta_k+\Delta_l)^{-1} \\
+\langle 0|P^B_\delta(\mathbf{r}''')|k\rangle\langle k|P^{oB}_\gamma(\mathbf{r}'')|m\rangle\langle m|P^B_\lambda(\mathbf{r}^{vi})|0\rangle \\
\times\Delta_j^{-1}(\Delta_k+\Delta_l)^{-1}(\Delta_m+\Delta_l)^{-1}] \\
\times\langle 0|P^C_\phi(\mathbf{r}^v)|l\rangle\langle l|P^C_\varepsilon(\mathbf{r}^{iv})|0\rangle T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})T_{\phi\lambda}(\mathbf{r}^v,\mathbf{r}^{vi}). \quad (76)
\end{aligned}$$

Equation (76) is equivalent to

$$\begin{aligned}
W_{disp} = \hbar/2\pi\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\,\alpha^A_{\alpha\beta}(\mathbf{r},\mathbf{r}')\int_0^\infty d\omega\,\beta^B_{\delta\lambda\gamma}(\mathbf{r}''',\mathbf{r}^{vi},\mathbf{r}'';i\omega,0)\,\alpha^C_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^v;i\omega) \\
\times T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})T_{\phi\lambda}(\mathbf{r}^v,\mathbf{r}^{vi}); \quad (77)
\end{aligned}$$

W_{disp} gives the polarization induced in A due to the static field from the polarization induced in B by the *two-body* dispersion interactions between B and C.

Finally, the set of terms that contain the operators V_{AB}, V_{AB}, and V_{AC} are calculated. A representative term of this set from Eq. (51) is $-\langle\Psi_0|P^A\,G\,V^o_{AB}\,G\,V^o_{AB}\times G\,V_{AC}|\Psi_0\rangle$. Use of Eq. (4) for G yields

$$-\langle\Psi_0|P^A\,G\,V^o_{AB}\,G\,V^o_{AB}\,G\,V_{AC}|\Psi_0\rangle$$

$$=-\langle\Psi_0|P^A\,G^A\,\wp_0^B\,\wp_0^C\,V^o_{AB}\,G^A\,\wp_0^B\,\wp_0^C\,V^o_{AB}\,G^A\,\wp_0^B\,\wp_0^C\,V_{AC}|\Psi_0\rangle$$

$$-\langle\Psi_0|P^A\,G^A\,\wp_0^B\,\wp_0^C\,V^o_{AB}\,G^B\,\wp_0^A\,\wp_0^C\,V^o_{AB}\,G^A\,\wp_0^B\,\wp_0^C\,V_{AC}|\Psi_0\rangle$$

$$-\langle\Psi_0|P^A\,G^A\,\wp_0^B\,\wp_0^C\,V^o_{AB}\,G^{A\oplus B}\,\wp_0^C\,V^o_{AB}\,G^A\,\wp_0^B\,\wp_0^C\,V_{AC}|\Psi_0\rangle. \qquad (78)$$

The full expansion in Eq. (51) gives 33 terms of this type. These can be grouped into four sets $X_1 - X_4$, which are given explicitly in Appendix E, so that

$$\left\langle P_\alpha^A(\mathbf{r})\right\rangle^{(3)} = X_1 + X_2 + X_3 + X_4. \qquad (79)$$

The matrix element form of X_1 is given by Eq. (E2). It can be recast in terms of the static γ hyperpolarizability density of A

$$X_1 = 1/2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\,\gamma^A_{\alpha\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';0,0,0)\,T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})\,P^B_{0\lambda}(\mathbf{r}^{iv})$$

$$\times T_{\gamma\eta}(\mathbf{r}'',\mathbf{r}^{v})\,P^B_{0\eta}(\mathbf{r}^{v})\,T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi})\,P^C_{0\varepsilon}(\mathbf{r}^{vi}), \qquad (80)$$

assuming all the eigenstates can be taken as real. The γ hyperpolarizability density is defined by [3]

$$\gamma_{\alpha\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';-\omega_\sigma;\omega_1,\omega_2,0)$$

$$=[1+C(\omega_1\to-\omega_1,\omega_2\to-\omega_2,\omega_\sigma\to-\omega_\sigma)]$$

$$\times\{\langle 0|P_\alpha(\mathbf{r})G(\omega_\sigma)$$

$$\times\{P^o_\beta(\mathbf{r}')G(\omega_2)[P^o_\gamma(\mathbf{r}'')G(0)P_\delta(\mathbf{r}''')+P^o_\delta(\mathbf{r}''')G(\omega_2)P_\gamma(\mathbf{r}'')]$$

$$+P^o_\gamma(\mathbf{r}'')G(\omega_1)[P^o_\beta(\mathbf{r}')G(0)P_\delta(\mathbf{r}''')+P^o_\delta(\mathbf{r}''')G(\omega_1)P_\beta(\mathbf{r}')]$$

$$+P^o_\delta(\mathbf{r}''')G(\omega_\sigma)[P^o_\beta(\mathbf{r}')G(\omega_2)P_\gamma(\mathbf{r}'')+P^o_\gamma(\mathbf{r}'')G(\omega_1)P_\beta(\mathbf{r}')]\}|0\rangle$$

$$+\langle 0|P_\beta(\mathbf{r}')G^*(-\omega_1)P^o_\alpha(\mathbf{r})G(\omega_2)[P^o_\gamma(\mathbf{r}'')G(0)P_\delta(\mathbf{r}''')$$

$$+P^o_\delta(\mathbf{r}''')G(\omega_2)P_\gamma(\mathbf{r}'')]|0\rangle$$

$$+\langle 0|P_\gamma(\mathbf{r}'')G^*(-\omega_2)P^o_\alpha(\mathbf{r})G(\omega_1)[P^o_\beta(\mathbf{r}')G(0)P_\delta(\mathbf{r}''')$$

$$+P^o_\delta(\mathbf{r}''')G(\omega_1)P_\beta(\mathbf{r}')]|0\rangle$$

$$+\langle 0|P_\delta(\mathbf{r}''')G(0)P^o_\alpha(\mathbf{r})G(\omega_\sigma)[P^o_\beta(\mathbf{r}')G(\omega_2)P_\gamma(\mathbf{r}'')$$

$$+P^o_\gamma(\mathbf{r}'')G(\omega_1)P_\beta(\mathbf{r}')]|0\rangle$$

$$-\langle 0|P_\alpha(\mathbf{r})G(\omega_\sigma)G(\omega_1)P_\beta(\mathbf{r}')|0\rangle$$

$$\times[\langle 0|P_\gamma(\mathbf{r}'')G(0)P_\delta(\mathbf{r}''')|0\rangle+\langle 0|P_\delta(\mathbf{r}''')G(\omega_2)P_\gamma(\mathbf{r}'')|0\rangle]$$

$$-\langle 0|P_\alpha(\mathbf{r})G(\omega_\sigma)G(\omega_2)P_\gamma(\mathbf{r}'')|0\rangle$$

$$\times[\langle 0|P_\beta(\mathbf{r}')G(0)P_\delta(\mathbf{r}''')|0\rangle+\langle 0|P_\delta(\mathbf{r}''')G(\omega_1)P_\beta(\mathbf{r}')|0\rangle]$$

$$-\langle 0|P_\alpha(\mathbf{r})G(\omega_\sigma)G(0)P_\delta(\mathbf{r}''')|0\rangle$$

$$\times[\langle 0|P_\beta(\mathbf{r}')G(\omega_2)P_\gamma(\mathbf{r}'')|0\rangle+\langle 0|P_\gamma(\mathbf{r}'')G(\omega_1)P_\beta(\mathbf{r}')|0\rangle]$$

$$-\langle 0|P_\alpha(\mathbf{r})G(\omega_1)P_\beta(\mathbf{r}')|0\rangle$$

$$\times[\langle 0|P_\gamma(\mathbf{r}'')G^*(-\omega_2)G(0)P_\delta(\mathbf{r}''')|0\rangle+\langle 0|P_\delta(\mathbf{r}''')G(0)G(\omega_2)P_\gamma(\mathbf{r}'')|0\rangle]$$

$$-\langle 0|P_\alpha(\mathbf{r})G(\omega_2)P_\gamma(\mathbf{r}'')|0\rangle$$

$$\times[\langle 0|P_\beta(\mathbf{r}')G^*(-\omega_1)G(0)P_\delta(\mathbf{r}''')|0\rangle+\langle 0|P_\delta(\mathbf{r}''')G(0)G(\omega_1)P_\beta(\mathbf{r}')|0\rangle]$$

$$-\langle 0|P_\alpha(\mathbf{r})G(0)P_\delta(\mathbf{r}''')|0\rangle$$

$$\times[\langle 0|P_\beta(\mathbf{r}')G^*(-\omega_1)G(\omega_2)P_\gamma(\mathbf{r}'')|0\rangle+\langle 0|P_\gamma(\mathbf{r}'')G^*(-\omega_2)G(\omega_1)P_\beta(\mathbf{r}')|0\rangle]\},$$

(81)

where $\omega_\sigma \equiv \omega_1+\omega_2$, and $C(\omega_1 \to -\omega_1, \omega_2 \to -\omega_2, \omega_\sigma \to -\omega_\sigma)$ denotes the operator for complex conjugation and replacement of ω_1 by $-\omega_1$, ω_2 by $-\omega_2$, and ω_σ by $-\omega_\sigma$, and

$$G(\omega)=(1-\wp_0)(H-E_0-\hbar\omega)^{-1}(1-\wp_0). \tag{82}$$

Specializing to the case $\omega_1 = \omega_2 = 0$, Eq. (81) yields $\gamma_{\alpha\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';0,0,0)$.

The X_1 terms represent the hyperpolarization effects due to the fields from the permanent charge density of molecules B and C: The fields from the permanent polarization of molecule B and C hyperpolarize A to produce a change in the polarization of A via $\gamma^A_{\alpha\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';0,0,0)$; the field from $\mathbf{P}_0^B(\mathbf{r})$ acts twice at A, and the field from $\mathbf{P}_0^C(\mathbf{r})$ acts once at A.

The matrix element form of X_2 is given by Eq. (E4). In part, it reflects the hyperpolarization of molecule A due to the fields from the permanent polarization of A and C: The field from the polarization induced in B by the permanent charge density of A acting together with the field directly from the permanent polarization of C hyperpolarizes A to produce a polarization via $\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}''')$. This term is labeled by $X_{2,\text{ind}}$:

$$
\begin{aligned}
X_{2,\text{ind}} &= \int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, \beta^A_{\alpha\beta\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}''')\, T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})\, \alpha^B_{\lambda\eta}(\mathbf{r}^{iv},\mathbf{r}^{v}) \\
&\qquad \times T_{\eta\gamma}(\mathbf{r}^{v},\mathbf{r}'')\, P^A_{0\gamma}(\mathbf{r}'')\, T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi})\, P^C_{0\varepsilon}(\mathbf{r}^{vi}) \\
&= 4\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,n,k}{}' [\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\beta(\mathbf{r}')|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle \\
&\qquad + \langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\delta(\mathbf{r}''')|n\rangle\langle n|P^A_\beta(\mathbf{r}')|0\rangle \\
&\qquad + \langle 0|P^A_\beta(\mathbf{r}')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle] \\
&\qquad \times P^A_{0\gamma}(\mathbf{r}'')\langle 0|P^B_\lambda(\mathbf{r}^{iv})|k\rangle\langle k|P^B_\eta(\mathbf{r}^{v})|0\rangle \Delta_j^{-1}\Delta_n^{-1}\Delta_k^{-1} \\
&\qquad \times P^C_{0\varepsilon}(\mathbf{r}^{vi})\, T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})\, T_{\gamma\eta}(\mathbf{r}'',\mathbf{r}^{v})\, T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi}).
\end{aligned} \tag{83}
$$

X_2 also contains one part of the dispersion contribution to the polarization.

Terms containing the permanent polarization of molecule C alone are grouped into X_3. These terms reflect the linear polarization of molecule A due to the field from the permanent polarization of C: The permanent polarization of C polarizes A, which in turn polarizes B; the induced polarization in B gives rise to a field that polarizes A. This induction term is given by

$$X_{3,\mathrm{ind}} = \int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, \alpha^A_{\alpha\beta}(\mathbf{r},\mathbf{r}')T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})\alpha^B_{\lambda\eta}(\mathbf{r}^{iv},\mathbf{r}^{v})T_{\eta\gamma}(\mathbf{r}^{v},\mathbf{r}'')$$

$$\times \alpha^A_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi})P^C_{0\varepsilon}(\mathbf{r}^{vi})$$

$$= 8\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,n,k}{}' \langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\beta(\mathbf{r}')|0\rangle\langle 0|P^A_\gamma(\mathbf{r}'')|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle$$

$$\times\langle 0|P^B_\lambda(\mathbf{r}^{iv})|k\rangle\langle k|P^B_\eta(\mathbf{r}^{v})|0\rangle P^C_{0\varepsilon}(\mathbf{r}^{vi})\Delta_j^{-1}\Delta_n^{-1}\Delta_k^{-1}$$

$$\times T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})T_{\eta\gamma}(\mathbf{r}^{v},\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi}). \qquad (84)$$

The contribution to the dispersion term from X_3 is $X_3 - X_{3,\mathrm{ind}}$.

The remaining dispersion terms are contained in X_4. The matrix element form of X_4 satisfies Eq. (E7). The dispersion contribution to the polarization X_{disp} is given by $X_4 + X_2 - X_{2,\mathrm{ind}} + X_3 - X_{3,\mathrm{ind}}$. Regrouping the terms in X_{disp} yields

$$X_{\mathrm{disp}} = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,l,n,k}{}' \{\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\beta(\mathbf{r}')|l\rangle\langle l|P^{oA}_\gamma(\mathbf{r}'')|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle$$

$$\times\Delta_j^{-1}\Delta_n^{-1}(\Delta_l+\Delta_k)^{-1}$$

$$+\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\beta(\mathbf{r}')|l\rangle\langle l|P^{oA}_\delta(\mathbf{r}''')|n\rangle\langle n|P^A_\gamma(\mathbf{r}'')|0\rangle$$

$$\times\Delta_j^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_n+\Delta_k)^{-1}$$

$$+\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\delta(\mathbf{r}''')|l\rangle\langle l|P^{oA}_\beta(\mathbf{r}')|n\rangle\langle n|P^A_\gamma(\mathbf{r}'')|0\rangle$$

$$\times\Delta_j^{-1}\Delta_l^{-1}(\Delta_n+\Delta_k)^{-1}$$

$$+\langle 0|P^A_\beta(\mathbf{r}')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|l\rangle\langle l|P^{oA}_\delta(\mathbf{r}''')|n\rangle\langle n|P^A_\gamma(\mathbf{r}'')|0\rangle$$

$$\times(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_n+\Delta_k)^{-1}$$

$$+\langle 0|P^A_\beta(\mathbf{r}')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|l\rangle\langle l|P^{oA}_\gamma(\mathbf{r}'')|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle$$

$$\times\Delta_n^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}$$

$$+\langle 0|P_\delta^A(\mathbf{r}''')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\beta^{oA}(\mathbf{r}')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times\Delta_j^{-1}\Delta_l^{-1}(\Delta_n+\Delta_k)^{-1}$$

$$-\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\delta^A(\mathbf{r}''')|0\rangle\langle 0|P_\beta^A(\mathbf{r}')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times[\Delta_j^{-2}(\Delta_n+\Delta_k)^{-1}+\Delta_j^{-1}(\Delta_n+\Delta_k)^{-2}]$$

$$-\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle\langle 0|P_\gamma^A(\mathbf{r}'')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle$$

$$\times\Delta_j^{-1}\Delta_n^{-1}[(\Delta_n+\Delta_k)^{-1}+(\Delta_j+\Delta_k)^{-1}$$

$$+(\Delta_j+\Delta_k)^{-1}(\Delta_n+\Delta_k)^{-1}(\Delta_j+\Delta_n+\Delta_k)]\}$$

$$\times\langle 0|P_\lambda^B(\mathbf{r}^{iv})|k\rangle\langle k|P_\eta^B(\mathbf{r}^{v})|0\rangle P_{0\varepsilon}^C(\mathbf{r}^{vi})$$

$$\times T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})T_{\eta\gamma}(\mathbf{r}^{v},\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi}), \tag{85}$$

or equivalently,

$$X_{disp}=\hbar/2\pi\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\int_0^\infty d\omega\,\gamma_{\beta\gamma\delta\alpha}^A(\mathbf{r}',\mathbf{r}'',\mathbf{r}''',\mathbf{r};i\omega,0,0)\,T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})$$

$$\times\alpha_{\lambda\eta}^B(\mathbf{r}^{iv},\mathbf{r}^{v};i\omega)\,T_{\eta\gamma}(\mathbf{r}^{v},\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi})P_{0\varepsilon}^C(\mathbf{r}^{vi}), \tag{86}$$

where the following integral identities have been used

$$\int_0^\infty dx\,2a(a^2+x^2)^{-1}[(b-ix)^{-2}+(b+ix)^{-2}]=2\pi\,(a+b)^{-2}, \tag{87}$$

and

$$\int_0^\infty dx\,2a(a^2+x^2)^{-1}[(b-ix)^{-1}(c-ix)^{-1}(d-ix)^{-1}+(b+ix)^{-1}(c+ix)^{-1}(d+ix)^{-1}]$$

$$=2\pi\,(a+b)^{-1}(a+c)^{-1}(a+d)^{-1}, \tag{88}$$

and the γ hyperpolarizability density $\gamma_{\beta\gamma\delta\alpha}(\mathbf{r}',\mathbf{r}'',\mathbf{r}''',\mathbf{r};i\omega,0,0)$ is obtained from Eq. (81) with ω_1 replaced by $-i\omega$ and ω_2 replaced by $i\omega$.

The X_{disp} term represents the change in the dispersion-induced polarization of molecule A in the A$\cdots$B pair due to the presence of the third body C. Here C acts as the source of a static field that perturbs the dispersion interactions between A and B. Eq. (86) gives the lowest-order change in the dispersion polarization of A of the $A\cdots B$ pair due to the static field from C acting on A.

The total contribution from the "noncircuit" terms to the third-order polarization induced in A is

$$\left\langle P_{\alpha}^{A}(\mathbf{r})\right\rangle_{\text{noncir}}^{(3)} = (1+\wp^{BC})(U_1+U_2+U_3+W_1+W_2+W_4$$
$$+X_1+X_2+X_3+X_4), \tag{89}$$

and the full third-order polarization of A satisfies

$$P_{\alpha}^{A(3)}(\mathbf{r}) = \left\langle P_{\alpha}^{A}(\mathbf{r})\right\rangle_{\text{cir}}^{(3)} + \left\langle P_{\alpha}^{A}(\mathbf{r})\right\rangle_{\text{noncir}}^{(3)} \tag{90}$$

with $\left\langle P_{\alpha}^{A}(\mathbf{r})\right\rangle_{\text{cir}}^{(3)}$ given by Eq. (44).

The results from the perturbation analysis in this section are identical to the corresponding results obtained from the reaction field method in Sec. 6.4 of Chapter VI. This establishes the validity of the reaction-field results, subject to the assumptions of the perturbation analysis.

References

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[3] Equation (21) for $\beta_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';-\omega_\sigma;\omega_1,\omega_2)$ and equation (81) for $\gamma_{\alpha\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';-\omega_\sigma;\omega_1,\omega_2,0)$ are obtained by analogy with Eqs. (43b) and (43c) in Ref. 6.

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CHAPTER VIII

EFFECTS OF OVERLAP DAMPING ON THREE-BODY DISPERSION ENERGIES

8.1 Introduction

In Chapters VI and VII, both reaction-field methods and perturbation theory are used to analyze nonadditive three-body energies and dipoles. The analysis identifies different polarization mechanisms that contribute to three-body interactions. These include induction, dispersion, and combined induction-dispersion effects. Induction effects are classical, resulting from the polarization of a molecule by the fields from the permanent molecular charge distributions. For molecules interacting at long range, induction effects are determined simply by the permanent molecular multipole moments, the static polarizabilities, and the static hyperpolarizabilities. Dispersion interactions, however, are purely quantum mechanical in origin, stemming from correlations between the spontaneously fluctuating charge distributions. Dispersion effects are important, because they are present in a variety of interactions, including molecule-molecule, molecule-atom, atom-atom, and molecule-surface interactions [1-9]. Moreover, in such cases as interactions of three spherically symmetric atoms at long range, only the dispersion effects survive at third order. The three-body dispersion energy is the subject of this chapter.

The leading term in the three-body dispersion energy for S-state atoms A, B, and C interacting at long range was first derived by Axilrod and Teller [1], and independently by Muto [2]:

$$\Delta E_{LR}^{(3)}(1,1,1) = (3\cos\theta_A \cos\theta_B \cos\theta_C + 1)C_{111}(R_{AB} R_{BC} R_{CA})^{-3}, \quad (1)$$

where R_{AB} denotes the distance between atom A and atom B, θ_A is the angle between R_{AB} and R_{CA}, and C_{111} is a coefficient related to the first-order imaginary-frequency polarizabilities $\alpha_1(i\omega)$ of A, B, and C by

$$C_{111} = 3\hbar / \pi \int_0^\infty \alpha_1^A(i\omega)\alpha_1^B(i\omega)\alpha_1^C(i\omega)d\omega . \tag{2}$$

Eq. (1) is valid at long range when the multipole expansion of the interaction potential holds. At shorter range, the dispersion energy is damped due to modifications of charge-overlap effects. The damped dispersion energy can be derived within the nonlocal response theory that uses polarizability densities to describe the nonlocal response of a molecule to the fields from its interaction partners. The theory gives the three-body dispersion energy as an integral of imaginary-frequency polarizability densities of the interacting molecules [see Eq. (22) of Chapter VI]. The purpose of this chapter is to study how overlap modifies three-body dispersion energies. In Sec. 8.2, the damped three-body dispersion energy for interacting S-state atoms is analyzed. It is shown that at long-range the equations for damped dispersion energies reduce to a multipole series, in which the leading term is the triple-dipole energy from Eq. (1). Sec. 8.3 contains a numerical application to a model system, interacting ground-state hydrogen atoms. An analytical expression for the damped triple-dipole dispersion energy is derived, and the radial and angular dependence of the dispersion energy is investigated.

8.2. Dispersion Energy for Three Interacting S-state Atoms

In this section, the nonadditive three-body dispersion energy is calculated for interacting S-state atoms. The calculation includes the effects of direct charge-overlap on the dispersion energy, but not the effects due to intermolecular exchange or charge transfer.

In Chapter VI, a nonlocal response theory is used to derive an expression for the nonadditive three-body dispersion energy of interacting molecules A, B, and C. The theory yields a simple physical interpretation for the dispersion energy in terms of the induced polarization and the energy of polarization in a reaction field. The spontaneous, fluctuating polarization in molecule A polarizes B, which in turn polarizes C. The induced polarization in C produces a reaction field at A. This polarization route A→B→C→A gives one term in the energy shift of A, with the second term generated by A→C→B→A. Both terms depend upon the correlation in the polarization fluctuations at two points within A, which are related to the imaginary part of the nonlocal polarizability density of A via the fluctuation-dissipation theorem. Similar energy shifts occur on molecules B and C, giving the second and third terms in the total energy change of the three interacting molecules. The theory gives the nonadditive three-body dispersion energy

$$\Delta E_{\mathrm{disp}}^{(3)} = -\hbar/\pi \int_0^\infty d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{\mathrm{iv}}\, d\mathbf{r}^{\mathrm{v}}\, \alpha_{\alpha\beta}^{A}(\mathbf{r},\mathbf{r}^{\mathrm{v}};i\omega)\, T_{\beta\gamma}(\mathbf{r}^{\mathrm{v}},\mathbf{r}^{\mathrm{iv}})$$

$$\times\, \alpha_{\gamma\delta}^{C}(\mathbf{r}^{\mathrm{iv}},\mathbf{r}''';i\omega)\, T_{\delta\epsilon}(\mathbf{r}''',\mathbf{r}'')\, \alpha_{\epsilon\phi}^{B}(\mathbf{r}'',\mathbf{r}';i\omega)\, T_{\phi\alpha}(\mathbf{r}',\mathbf{r}), \qquad (3)$$

in terms of the tensor product of the imaginary-frequency nonlocal polarizability densities $\alpha_{\alpha\beta}^{X}(\mathbf{r},\mathbf{r}';i\omega)$ (X = A, B or C) and the dipole propagators $T_{\alpha\beta}(\mathbf{r},\mathbf{r}')$

$$T_{\alpha\beta}(\mathbf{r},\mathbf{r}') = T_{\alpha\beta}(\mathbf{r}-\mathbf{r}') = \nabla_\alpha \nabla_\beta (|\mathbf{r}-\mathbf{r}'|^{-1})$$

$$= [3(r_\alpha - r'_\alpha)(r_\beta - r'_\beta) - \delta_{\alpha\beta}|\mathbf{r}-\mathbf{r}'|^2]/(|\mathbf{r}-\mathbf{r}'|^5) - 4\pi/3\, \delta_{\alpha\beta}\, \delta(\mathbf{r}-\mathbf{r}') \qquad (4)$$

The Einstein convention of summation over repeated Greek subscripts has been used in Eq. (3) and below.

An expression equivalent to equation (3) can be obtained by first using the standard perturbation theory to find the interaction energy for three molecules A, B, and C at third order, then selecting terms that are purely of dispersion origin [see Sec. 7.1 of Chapter VII]. The result can be cast into the computationally useful form

$$\Delta E^{(3)}_{\text{disp}} = \hbar/(8\pi^7)\int_0^\infty d\omega \int d\mathbf{k}\exp(i\mathbf{k}\cdot\mathbf{R}_{AB})k^{-2}\int d\mathbf{k}'\exp(i\mathbf{k}'\cdot\mathbf{R}_{BC})(k')^{-2}$$
$$\times\int d\mathbf{k}''\exp(i\mathbf{k}''\cdot\mathbf{R}_{CA})(k'')^{-2}\chi^A(\mathbf{k},\mathbf{k}'';i\omega)\chi^B(\mathbf{k}',\mathbf{k};i\omega)\chi^C(\mathbf{k}'',\mathbf{k}';i\omega), \quad (5)$$

where $\mathbf{R}_{XY}$ is the vector from the origin in molecule X to the origin in Y (X, Y = A, B or C) and $\chi(\mathbf{k},\mathbf{k}';i\omega)$ is the imaginary-frequency charge-density susceptibility,

$$\chi(\mathbf{k},\mathbf{k}';i\omega) = 2/\hbar\sum_{n\neq 0}\omega_{n0}(\omega_{n0}^2+\omega^2)^{-1}\langle 0|\rho(-\mathbf{k})|n\rangle\langle n|\rho(\mathbf{k}')|0\rangle, \quad (6)$$

In Eq. (6), ω_{n0} is the transition frequency between the ground state $|0\rangle$ and the excited state $|n\rangle$, and $\rho(\mathbf{k})$ is the $\mathbf{k}$ Fourier component of the charge density operator:

$$\rho(\mathbf{k}) = \int d\mathbf{r}\exp(i\mathbf{k}\cdot\mathbf{r})\sum_j q_j\delta(\mathbf{r}-\mathbf{r}_j) = \sum_j q_j\exp(i\mathbf{k}\cdot\mathbf{r}_j) \quad (7)$$

with q_j the charge of particle j.

To evaluate the dispersion energy given by Eq. (5), the charge-density susceptibility $\chi(\mathbf{k},\mathbf{k}';\omega)$ is needed as a function of $\mathbf{k}$, $\mathbf{k}'$, and ω. Given an accurate ground state wavefunction, $\chi(\mathbf{k},\mathbf{k}';\omega)$ can be determined from Koide's method [10]. In this method, $\chi(\mathbf{k},\mathbf{k}';\omega)$ is expanded in terms of the spherical harmonics of the orientation angles of the vectors $\mathbf{k}$ and $\mathbf{k}'$ by substitution of Eq. (7) into (6) and use of the Rayleigh expansion for $\exp(i\,\mathbf{k}\cdot\mathbf{r}_j)$:

$$\chi(\mathbf{k},\mathbf{k}';\omega) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'} c_l\, c_{l'}^*\, Y_l^m(\theta,\phi)\, Y_{l'}^{m'}(\theta',\phi')^*\alpha_{ll'}^{mm'}(k,k';\omega), \quad (8)$$

where

$$c_l = (-i)^l 2^l l!/(2l)!\sqrt{4\pi/(2l+1)}, \quad (9)$$

and [10]

$$\alpha_{ll'}^{mm'}(k,k';\omega) = 2/\hbar\sum_{n\neq 0}\omega_{n0}(\omega_{n0}^2-\omega^2)^{-1}\langle 0|\rho_l^m(k)^*|n\rangle\langle n|\rho_{l'}^{m'}(k')|0\rangle \quad (10)$$

with the generalized multipole moment operator $\rho_l^m(k)$ given by

$$\rho_l^m(k) = \sum_j q_j \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_l^m(\theta_j, \phi_j) \frac{(2l+1)!}{2^l l!} j_l(kr_j), \tag{11}$$

where $j_l(kr_j)$ denotes the lth spherical Bessel function.

If the auxiliary functions $\Phi_l^m(k,\omega)$ are defined by [10]

$$\left|\Phi_l^m(k,\omega)\right\rangle = 1/\hbar \sum_{n\neq 0} (\omega_{n0} + \omega)^{-1} |n\rangle\langle n|\rho_l^m(k)|0\rangle, \tag{12}$$

then from Eq. (10),

$$\alpha_{ll'}^{mm'}(k,k';\omega) = \left\langle 0 \middle| \rho_l^m(k)^* \middle| \Phi_{l'}^{m'}(k',\omega) + \Phi_{l'}^{m'}(k',-\omega) \right\rangle. \tag{13}$$

$\Phi_l^m(k,\omega)$ can be approximated by the function Ψ which minimizes the functional [11, 12]

$$J_l^m(\Psi) = \langle\Psi|H_0 - E_0 + \hbar\omega|\Psi\rangle - \langle 0|\rho_l^m(k)^*|\Psi\rangle - \langle\Psi|\rho_l^m(k)|0\rangle \tag{14}$$

subject to the conditions $\langle 0|\Psi\rangle = 0$ and $\omega \geq 0$. In Eq. (14), H_0 is the Hamiltonian of the unperturbed molecule, and E_0 is the energy of its ground state.

For spherically symmetric atoms, $\alpha_{ll'}^{mm'}(k,k';\omega)$ takes a simple form [13]:

$$\alpha_{ll}^{mm'}(k,k';\omega) = \delta_{ll'}\,\delta_{mm'}\,\alpha_l(k,k';\omega) \tag{15}$$

Substitution of Eq. (8) into (5) and use of Eq. (15) yields

$$\begin{aligned}\Delta E_{disp}^{(3)} &= \hbar/8\pi^7 \int_0^\infty d\omega \int d\mathbf{k}\exp(i\mathbf{k}\cdot\mathbf{R}_{AB})k^{-2}\int d\mathbf{k}'\exp(i\mathbf{k}'\cdot\mathbf{R}_{BC})(k')^{-2}\\ &\times\int d\mathbf{k}''\exp(i\mathbf{k}''\cdot\mathbf{R}_{CA})(k'')^{-2}\sum_l\sum_m\sum_{l'}\sum_{m'}\sum_{l''}\sum_{m''}|c_l c_{l'} c_{l''}|^2\\ &\times Y_{l'}^{m'}(\theta,\phi)^* Y_l^m(\theta,\phi) Y_{l''}^{m''}(\theta',\phi')^* Y_{l'}^{m'}(\theta',\phi') Y_l^m(\theta'',\phi'')^* Y_{l''}^{m''}(\theta'',\phi'')\\ &\times \alpha_l^A(k,k'';i\omega)\alpha_{l'}^B(k',k;i\omega)\alpha_{l''}^C(k'',k';i\omega).\end{aligned} \tag{16}$$

The value of $\Delta E^{(3)}$ must be independent of the choice of the coordinate frame because it is a scalar. For convenience in the subsequent analysis, a coordinate (X, Y, Z) is used in which atom A is located at the origin, B on the positive Z-axis, and C in the X-Z half-plane with nonnegative X coordinate. Then use of the Rayleigh expansion for $\exp(i\mathbf{k}\cdot\mathbf{R})$ yields

$$\exp(i\mathbf{k}\cdot\mathbf{R}_{AB}) = \sum_{L}[4\pi(2L+1)]^{1/2}\, i^{L}\, Y_L^0(\theta,\phi)\, j_L(kR_{AB}), \tag{17}$$

$$\exp(i\mathbf{k}\cdot\mathbf{R}_{BC}) = \sum_{L'}\sum_{M'}(-i)^{L'}\, 4\pi\, Y_{L'}^{M'}(\theta',\phi')\, Y_{L'}^{M'}(\theta_B,\pi)^{*}\, j_{L'}(k'R_{BC}), \tag{18}$$

and

$$\exp(i\mathbf{k}\cdot\mathbf{R}_{CA}) = \sum_{L''}\sum_{M''}(-i)^{L''}\, 4\pi\, Y_{L''}^{M''}(\theta'',\phi'')\, Y_{L''}^{M''}(\theta_A,0)^{*}\, j_{L''}(k''R_{CA}), \tag{19}$$

where θ_A is the angle between $\mathbf{R}_{AB}$ and $\mathbf{R}_{CA}$, and θ_B is the angle between $\mathbf{R}_{AB}$ and $\mathbf{R}_{BC}$.

Inserting Eqs. (17)-(19) into (16) and integrating with respect to the polar angles (θ,ϕ), (θ',ϕ') and (θ'',ϕ'') gives the dispersion energy in the form:

$$\Delta E^{(3)} = \sum_{l}\sum_{l'}\sum_{l''}\Delta E^{(3)}(l,l',l''), \tag{20}$$

where

$$\Delta E^{(3)}(l,l',l'') = \hbar/(2\pi^6)\sum_{L}\sum_{L'}\sum_{L''} a_{LL'L''}^{l\,l'\,l''}\int_0^\infty d\omega\int_0^\infty dk\int_0^\infty dk'\int_0^\infty dk''\,\alpha_l^A(k,k'';i\omega)$$
$$\times\,\alpha_{l'}^B(k',k;i\omega)\,\alpha_{l''}^C(k'',k';i\omega)\, j_L(kR_{AB})\, j_{L'}(k'R_{BC})\, j_{L''}(k''R_{CA}) \tag{21}$$

with $a_{LL'L''}^{l\,l'\,l''}$ given by

$$a_{LL'L''}^{l\,l'\,l''} = i^{L}(-i)^{L'+L''}(2L+1)[(2L'+1)(2L''+1)]^{1/2}|c_l c_{l'} c_{l''}|^2\sum_{m}\sum_{m''}\sum_{M'} Y_{L'}^{-M'}(\theta_B,\pi)$$
$$\times Y_{L''}^{M'}(\theta_A,0)\langle L\,l\,0\,M|l'\,m\rangle\langle L\,l\,0\,0|l'\,0\rangle\langle L'\,l'\,M'\,m|l''\,m''\rangle$$
$$\times\langle L'\,l'\,0\,0|l''\,0\rangle\langle L''\,l''\,-M'\,m''|l\,m\rangle\,\langle L''\,l''\,0\,0|l\,0\rangle, \tag{22}$$

where $\langle l' l'' \, m' \, m'' | l \, m \rangle$ denotes a Clebsch-Gordan coefficient. In order to simplify the notation, the subscript "disp" is dropped in Eqs. (20) and (21) and below.

$\Delta E^{(3)}(l, l', l'')$ represents the energy of interactions among the 2^l-pole of A, the $2^{l'}$-pole of B, and the $2^{l''}$-pole of C, with the inclusion of the short-range overlap effects. This can be shown by examining the asymptotic behavior of Eq. (21) in the long-range limit. Use of the theorem on integrals involving spherical Bessel functions given in Appendix 1 of Ref. 10 gives

$$\int_0^\infty dk \int_0^\infty dk' \int_0^\infty dk'' \, \alpha_l^A(k, k''; i\omega) \, \alpha_{l'}^B(k', k; i\omega) \, \alpha_{l''}^C(k'', k'; i\omega)$$

$$\times j_L(kR_{AB}) j_{L'}(k'R_{BC}) j_{L''}(k''R_{CA})$$

$$= \pi^3 2^{-2(l+l'+l'')+3} (2l+2l')! \, (2l'+2l'')! \, (2l+2l'')! \, [(l+l')! \, (l'+l'')! \, (l+l'')!]^{-1}$$

$$\times \delta_{L \, l+l'} \, \delta_{L' \, l'+l''} \, \delta_{L'' \, l+l''} \, \alpha_l^A(i\omega) \alpha_{l'}^B(i\omega) \alpha_{l''}^C(i\omega) R_{AB}^{-(l+l'+1)} R_{BC}^{-(l'+l''+1)} R_{CA}^{-(l+l''+1)} \tag{23}$$

for $R_{AB} \to \infty$, $R_{BC} \to \infty$, and $R_{CA} \to \infty$. With this, Eq. (21) yields the three-body dispersion energy at long range in the form

$$\Delta E_{LR}^{(3)}(l, l', l'') = b_{l l' l''} \int_0^\infty d\omega \, \alpha_l^A(i\omega) \alpha_{l'}^B(i\omega) \alpha_{l''}^C(i\omega) R_{AB}^{-(l+l'+1)} R_{BC}^{-(l'+l''+1)} R_{CA}^{-(l+l''+1)}, \tag{24}$$

where

$$b_{l l' l''} = \hbar 2^{2(1-l-l'-l'')} a_{(l+l')(l'+l'')(l+l'')}^{l \, l' \, l''} (2l+2l')! \, (2l'+2l'')! \, (2l+2l'')!$$

$$\times [(l+l')! \, (l'+l'')! \, (l+l'')!]^{-1}. \tag{25}$$

In Eqs. (23) and (24), $\alpha_l(i\omega)$ is the imaginary-frequency multipole polarizability of order l, related to $\alpha_l(k, k'; i\omega)$ by

$$\alpha_l(i\omega) = lim_{k \to 0} \, lim_{k' \to 0} \, \alpha_l(k, k'; i\omega) \, k^{-l} \, (k')^{-l}. \tag{26}$$

Specializing to $l = l' = l'' = 1$, Eq. (24) recovers the long-range triple-dipole dispersion energy given by Eq. (1). The dipole-dipole-quadrupole dispersion term is obtained by setting $l = l' = 1$, and $l'' = 2$ in Eq. (24),

$$\Delta E_{LR}^{(3)}(1,1,2) = 3\hbar/(16\pi)\,\gamma_{112}(\theta_A,\theta_B,\theta_C)\int_0^\infty \alpha_1^A(i\omega)\alpha_1^B(i\omega)\alpha_2^C(i\omega)d\omega$$

$$\times R_{AB}^{-3}\,R_{CA}^{-3}\,R_{BC}^{-4} \tag{27}$$

where

$$\gamma_{112}(\theta_A,\theta_B,\theta_C) = 18\cos(\theta_A-\theta_B) - 9\cos(\theta_A+\theta_B) + 25\cos(3\theta_A+3\theta_B)$$

$$+15\cos(3\theta_A+\theta_B) + 15\cos(\theta_A+3\theta_B), \tag{28}$$

and similar expressions for $\Delta E_{LR}^{(3)}(1,2,1)$ and $\Delta E_{LR}^{(3)}(2,1,1)$.

8.3. Application to Interacting Hydrogen Atoms

Using a trial function of the form

$$|\Psi\rangle = \lambda(k,\omega)\sum_{n\neq 0} 1/\omega_{n0}\langle n|\rho_l^m|0\rangle|n\rangle \tag{29}$$

and then applying the variational principle (14) to find $\lambda(k,\omega)$, Koide [10] has determined $\alpha_l(k,k';\omega)$ for the hydrogen atom in the 1s state:

$$\alpha_l^H(k,k';\omega) = \frac{2a_l\omega_l}{\omega_l^2-\omega^2}f_l(k)f_l(k'), \tag{30}$$

where

$$\omega_l = \frac{l(l+1)(l+2)(2l+1)}{2l^4+11l^3+18l^2+10l+2}, \tag{31}$$

$$a_l = \frac{(2l)!(l+1)(l+2)^2(2l+1)^2}{2^{2l+1}(2l^4+11l^3+18l^2+10l+2)}, \tag{32}$$

and

$$f_l(k) = \frac{2l}{2l+1} k^l \left(\frac{4}{k^2+4}\right)^{l+2} \left(\frac{4}{k^2+4} + \frac{1}{2l}\right). \tag{33}$$

In Eq. (29), ρ_l^m is the usual spherical multipole operator. Atomic units are used in Eqs. (29)-(33) and below.

Substitution of Eq. (30) into (21) and integration with respect to the frequency ω yields

$$\Delta E^{(3)}(l,l',l'') = 2/\pi^5 \, a_l a_{l'} a_{l''} (\omega_l + \omega_{l'} + \omega_{l''})[(\omega_l + \omega_{l'})(\omega_{l'} + \omega_{l''})(\omega_l + \omega_{l''})]^{-1}$$
$$\times \sum_L \sum_{L'} \sum_{L''} a_{LL'L''}^{ll'l''} \int_0^\infty f_l(k) f_{l'}(k) j_L(kR_{AB}) dk \int_0^\infty f_{l'}(k') f_{l''}(k') j_{L'}(k'R_{BC}) dk'$$
$$\times \int_0^\infty f_l(k'') f_{l''}(k'') j_{L''}(k''R_{CA}) dk'', \tag{34}$$

where the integral identity

$$\int_0^\infty (a^2+\omega^2)^{-1}(b^2+\omega^2)^{-1}(c^2+\omega^2)^{-1} d\omega$$
$$= \pi/2 \, (a+b+c)[abc(a+b)(b+c)(a+c)]^{-1} \tag{35}$$

has been used for a, b, c > 0.

The integrals in Eq. (34) can be evaluated analytically using contour integration techniques. For example, from Eqs. (30)-(34) the damped triple-dipole dispersion energy ($l = l' = l'' = 1$ in Eq. (34)) has been obtained as an analytical function of the interatomic distances R_{AB}, R_{BC}, and R_{CA}:

$$\Delta E^{(3)}(1,1,1) = 2187/344 \, [f(R_{AB}) f(R_{BC}) f(R_{CA}) + (3\cos^2\theta_C - 1)$$
$$\times f(R_{AB}) g(R_{BC}) g(R_{CA}) + (3\cos^2\theta_A - 1) g(R_{AB}) f(R_{BC}) g(R_{CA})$$
$$+ (3\cos^2\theta_B - 1) g(R_{AB}) g(R_{BC}) f(R_{CA}) + (3\cos\theta_A \cos\theta_B \cos\theta_C + 1)$$
$$\times g(R_{AB}) g(R_{BC}) g(R_{CA})], \tag{36}$$

where the functions $f(x)$ and $g(x)$ are defined by

$$f(x) = e^{-2x}[89/1152 + (89/576)x + (119/864)x^2 + (5/72)x^3 + (11/540)x^4 + (1/324)x^5 + (1/5670)x^6], \quad (37)$$

$$g(x) = 3/(2x^3) - e^{-2x}[2 + 3/(2x^3) + 3/x^2 + 3/x + x + (1699/4320)x^2 + (259/2160)x^3 + (197/7560)x^4 + (19/5670)x^5 + (1/5670)x^6]. \quad (38)$$

For $R_{AB} \to \infty$, $R_{BC} \to \infty$, and $R_{CA} \to \infty$, Eq. (36) reduces to

$$\Delta E_{LR}^{(3)}(1,1,1) = c_{111}(3\cos\theta_A \cos\theta_B \cos\theta_C + 1) R_{AB}^{-3} R_{BC}^{-3} R_{CA}^{-3} \quad (39)$$

with the coefficient $c_{111} = 59049/2752 \cong 21.4568$, in good agreement with the accurate value 21.6425 [14].

To illustrate how overlap modifies the dispersion energy, the results from Eq. (36) are compared with those from Eq. (39). Figure 8.1 gives the dispersion energies as functions of R for the geometry of an equilateral triangle, where R denotes the separation between the hydrogen atoms. The damping function χ_{111} is plotted against R in Figure 8.2.; here χ_{111} is given by

$$\chi_{111} = \Delta E^{(3)}(1,1,1) / \Delta E_{LR}^{(3)}(1,1,1). \quad (40)$$

Figure 8.1 and Figure 8.2 show that including the charge-overlap effects appreciably reduces the rate of increase of the dispersion energy with decrease of the interatomic distance R. In fact, at vanishing R, Eq. (36) gives a finite value for the dispersion energy, while Eq. (39) goes to the limit of infinity. The same effects are present in two-body interactions, which have been studied extensively [10, 13, 15-21].

The inclusion of charge-overlap effects also modifies the angular dependence of the three-body dispersion energy. To illustrate this, three interacting ground-state hydrogen atoms in the geometry of an isosceles triangle are considered. In Figure 8.3, the damped and undamped dispersion energies are plotted as functions of the angle θ between the two equal sides (R) of the isosceles triangle, for fixed values of R. Two values R = 3, and R = 4 have been selected. For all values of R, the long-range three-body dispersion energy is repulsive for $\theta < 117.2$, while it is attractive for $\theta > 117.2$. With R = 4, the damped three-body dispersion energy from Eq. (36) is only attractive for $\theta > 156.7$, and it is repulsive for all values of θ when R = 3. These results agree qualitatively with those obtained by O'Shea and Meath, using a formal partial wave analysis and pseudo-state techniques [22, 23].

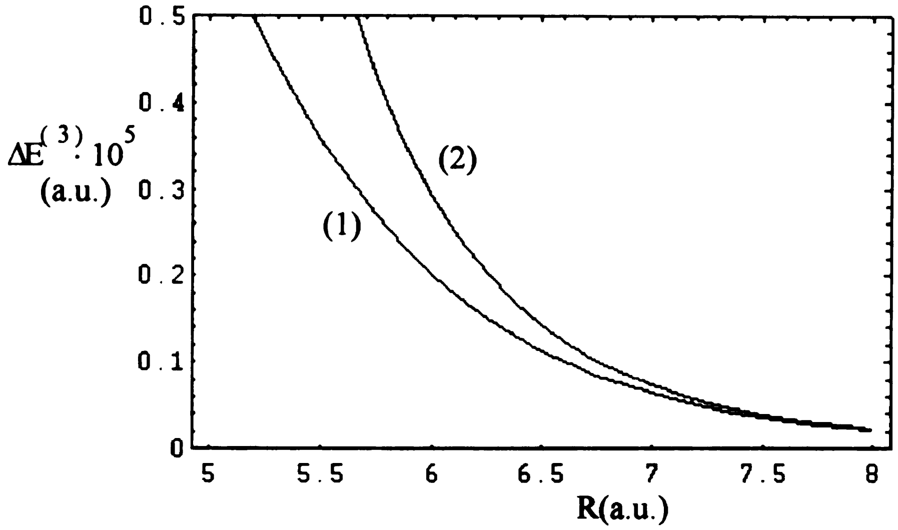

Figure 8.1 The triple-dipole dispersion energy of interacting ground-state hydrogen atoms in the geometry of an equilateral triangle with R the length of a side. (1) the damped dispersion energy from Eq. (36), and (2) the undamped form from Eq. (39).

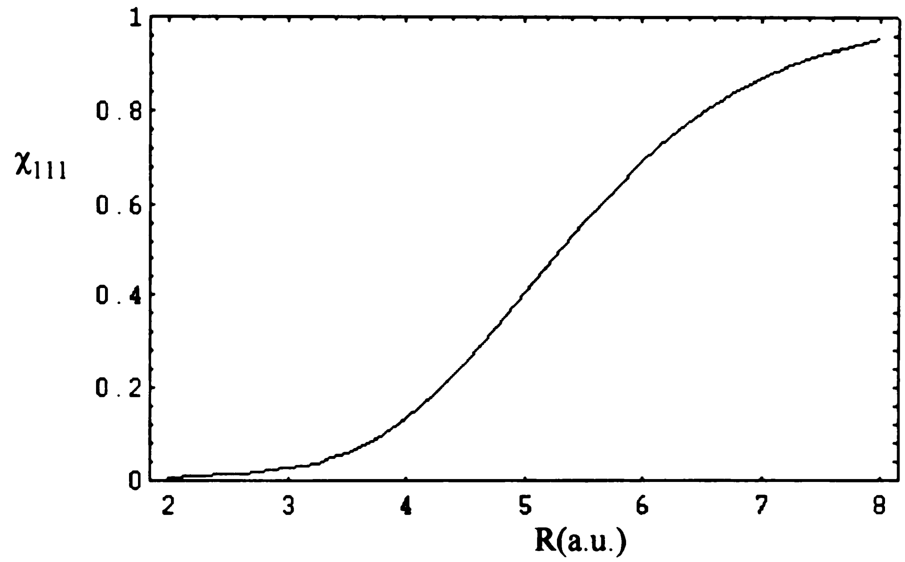

Figure 8.2 The damping function χ_{111} for the triple-dipole dispersion energy of interacting ground-state hydrogen atoms in the geometry of an equilateral triangle.

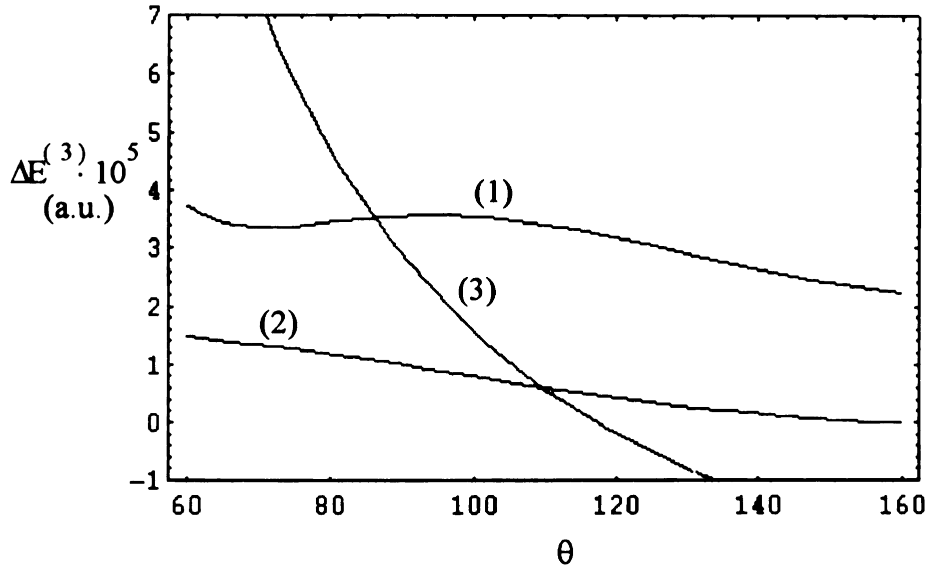

Figure 8.3 The triple-dipole dispersion energy for interacting ground-state hydrogen atoms in the geometry of an isosceles triangle, as a function of the angle θ between the two equal sides R. (1) $\Delta E^{(3)}(1,1,1)$ with R = 3, (2) $\Delta E^{(3)}(1,1,1)$ with R = 4, and (3) $\Delta E^{(3)}_{LR}(1,1,1)$ with R = 4 [24].

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Appendix A

By means of contour integration techniques, the functions $\mu_5(R)$, $\mu_7(R)$, and $\Theta_6(R)$ given by Eqs. (49), (50), and (51) of Chapter V, respectively, are evaluated analytically:

$$\mu_5(R) = \phi_1(R)e^{-2R} - \phi_2(R)e^{-4R}, \tag{A1}$$

$$\mu_7(R) = D_7 R^{-7} + \phi_3(R)e^{-2R} - \phi_4(R)e^{-4R}, \tag{A2}$$

and

$$\Theta_6(R) = M_6 R^{-6} + \phi_5(R)e^{-2R} - \phi_6(R)e^{-4R}. \tag{A3}$$

In Eqs. (A1)-(A3),

$$D_7 = -\frac{107571969}{258344}, \tag{A4}$$

$$M_6 = -\frac{40095}{688}, \tag{A5}$$

$$\phi_1(R) = \frac{124101}{110080} + \frac{28431}{44032}R^{-2} + \frac{28431}{22016}R^{-1} + \frac{29331}{55040}R + \frac{3267}{24080}R^2$$
$$+\frac{1923}{96320}R^3 + \frac{257}{144480}R^4 + \frac{1}{14448}R^5, \tag{A6}$$

$$\phi_2(R) = \frac{275283}{55040} + \frac{28431}{44032}R^{-2} + \frac{28431}{11008}R^{-1} + \frac{176070249}{28180480}R + \frac{279868959}{49315840}R^2$$
$$+\frac{1188219827}{295895040}R^3 + \frac{56994281}{24657920}R^4 + \frac{204673009}{184934400}R^5 + \frac{61303057}{138700800}R^6$$
$$+\frac{1812509111}{12483072000}R^7 + \frac{11949733}{312076800}R^8 + \frac{955321}{121363200}R^9 + \frac{4009973}{3276806400}R^{10}$$
$$+\frac{456077}{3276806400}R^{11} + \frac{143}{13003200}R^{12} + \frac{221}{409600800}R^{13} + \frac{1}{81920160}R^{14}, \tag{A7}$$

$$\phi_3(R) = \frac{11219260329}{578690560} + \frac{107571969}{129172}R^{-7} + \frac{107571969}{64586}R^{-6} + \frac{107571969}{64586}R^{-5}$$
$$+\frac{35857323}{32293}R^{-4} + \frac{35857323}{64586}R^{-3} + \frac{73127134197}{330680320}R^{-2} + \frac{11930636277}{165340160}R^{-1}$$
$$+\frac{153760947}{36168160}R + \frac{5402517}{7233632}R^2 + \frac{998061}{10333760}R^3 + \frac{808739}{108504480}R^4 + \frac{6163}{27126120}R^5, \tag{A8}$$

$$\phi_4(R) = \frac{311621667759}{231476224} + \frac{107571969}{258344} R^{-7} + \frac{1075719691}{64586} R^{-6} + \frac{107571969}{32293} R^{-5}$$
$$+ \frac{143429292}{32293} R^{-4} + \frac{143429292}{32293} R^{-3} + \frac{1174664096757}{330680320} R^{-2}$$
$$+ \frac{195520130037}{82670080} R^{-1} + \frac{296563134494651}{444434350080} R + \frac{32416131852059}{111108587520} R^{2}$$
$$+ \frac{63098078603249}{555542937600} R^{3} + \frac{16520765448167}{416657203200} R^{4} + \frac{3466717350289}{277771468800} R^{5}$$
$$+ \frac{148048034867}{41665720320} R^{6} + \frac{2999482556923}{3281175475200} R^{7} + \frac{346045385663}{1640587737600} R^{8}$$
$$+ \frac{84623425049}{1968705285120} R^{9} + \frac{18626834567}{2460881606400} R^{10} + \frac{7894399}{7031090304} R^{11}$$
$$+ \frac{1259893361}{9228306024000} R^{12} + \frac{2824919}{214611768000} R^{13} + \frac{4385431}{4614153012000} R^{14}$$
$$+ \frac{1217}{26826471000} R^{15} + \frac{1}{958088250} R^{16}, \qquad \text{(A9)}$$

$$\phi_5(R) = \frac{1414961361}{82670080} + \frac{40095}{344} R^{-6} + \frac{40095}{172} R^{-5} + \frac{40095}{172} R^{-4} + \frac{337949577}{2066752} R^{-3}$$
$$+ \frac{97058817}{1033376} R^{-2} + \frac{7485399441}{165340160} R^{-1} + \frac{268721181}{57869056} R + \frac{6273129}{7233632} R^{2}$$
$$+ \frac{4302887}{36168160} R^{3} + \frac{2495753}{180840800} R^{4} + \frac{1178543}{994624400} R^{5} + \frac{11271}{248656100} R^{6}, \qquad \text{(A10)}$$

and

$$\phi_6(R) = \frac{16944372081}{41335040} + \frac{40095}{688} R^{-6} + \frac{40095}{172} R^{-5} + \frac{40095}{86} R^{-4} + \frac{1301512617}{2066752} R^{-3}$$
$$+ \frac{337959577}{516688} R^{-2} + \frac{92616153201}{165340160} R^{-1} + \frac{150493937751}{578690560} R + \frac{15957391370551}{111108587520} R^{2}$$
$$+ \frac{1921075957543}{27777146880} R^{3} + \frac{8085289847027}{277771468800} R^{4} + \frac{24607739770651}{2291614617600} R^{5} + \frac{15948903098831}{4583229235200} R^{6}$$
$$+ \frac{1135044714739}{1145807308800} R^{7} + \frac{17828075669207}{72185860544400} R^{8} + \frac{4835951926759}{90232325568000} R^{9} + \frac{905293545841}{90232325568000} R^{10}$$
$$+ \frac{108448476469}{67674244176000} R^{11} + \frac{14581137517}{67674244176000} R^{12} + \frac{404737297}{16918561044000} R^{13} + \frac{1712983}{805645764000} R^{14}$$
$$+ \frac{12211}{85447278000} R^{15} + \frac{211}{32787909000} R^{16} + \frac{1}{7025980500} R^{17}. \qquad \text{(A11)}$$

Appendix B

Fully expanded, Eq. (51) gives 68 nonzero "circuit" terms. These terms can be grouped into four sets $T_1 - T_4$ according to the types of matrix elements appearing in each. T_1 is given by

$$
\begin{aligned}
T_1 = (1+C)\{-\langle\Psi_0|\, & P^A G^A \wp_0^B \wp_0^C \\
& \times [V_{AB}^o G^A \wp_0^B \wp_0^C (V_{BC}^o G^{A\oplus C} \wp_0^B V_{CA} + V_{CA}^o G^C \wp_0^A \wp_0^B V_{BC}) \\
& + V_{CA}^o G^{A\oplus C} \wp_0^B (V_{BC}^o G^A \wp_0^B \wp_0^C V_{AB} + V_{AB}^o G^C \wp_0^A \wp_0^B V_{BC}) \\
& + V_{BC}^o G^{A\oplus C} \wp_0^B (V_{CA}^o G^A \wp_0^B \wp_0^C V_{AB} + V_{AB}^o (G^C \wp_0^A \wp_0^B \\
& \qquad + G^{A\oplus C} \wp_0^B) V_{CA})] |\Psi_0\rangle \\
& - \langle\Psi_0| V_{AB} G^A \wp_0^B \wp_0^C P^{oA} G^A \wp_0^B \wp_0^C (V_{BC}^o G^{A\oplus C} \wp_0^B V_{CA} \\
& \qquad + V_{CA}^o G^C \wp_0^A \wp_0^B V_{BC}) |\Psi_0\rangle \\
& - \langle\Psi_0| V_{BC} G^C \wp_0^A \wp_0^B P^{oA} G^{A\oplus C} \wp_0^B (V_{CA}^o G^A \wp_0^B \wp_0^C V_{AB} \\
& \qquad + V_{AB}^o G^C \wp_0^A \wp_0^B V_{CA} + V_{AB}^o G^{A\oplus C} \wp_0^B V_{CA}) |\Psi_0\rangle \\
& - \langle\Psi_0| V_{CA} (G^C \wp_0^A \wp_0^B + G^{A\oplus C} \wp_0^B) P^{oA} G^{A\oplus C} \wp_0^B (V_{BC}^o G^A \wp_0^B \wp_0^C V_{AB} \\
& \qquad + V_{AB}^o G^C \wp_0^A \wp_0^B V_{BC}) |\Psi_0\rangle \\
& + \langle\Psi_0| P^A G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AB} |\Psi_0\rangle (1+C) \langle\Psi_0| V_{CA} G^C \wp_0^A \wp_0^B V_{BC} |\Psi_0\rangle \\
& + \langle\Psi_0| P^A G^A \wp_0^B \wp_0^C V_{AB} |\Psi_0\rangle (1+C) \langle\Psi_0| V_{BC} G^C \wp_0^A \wp_0^B G^C \wp_0^A \wp_0^B V_{CA} |\Psi_0\rangle \}.
\end{aligned}
\tag{B1}
$$

The T_1 terms reflect the hyperpolarization of A by the simultaneous action of the direct field from $\mathbf{P}_0^B(\mathbf{r})$ and the field from the polarization induced in C by $\mathbf{P}_0^B(\mathbf{r})$. The corresponding set of 20 fully expanded terms, with A hyperpolarized by $\mathbf{P}_0^{C}(\mathbf{r})$, is contained in T_2:

$$T_2 = \wp^{BC} T_1, \tag{B2}$$

where $\wp^{BC}$ permutes the labels A and B.

Terms containing the permanent polarization of A are grouped into T_3:

$$\begin{aligned}
T_3 = (1+C)(1+\wp^{BC})\{ & -\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C \\
& \times[V_{AB}^o G^B \wp_0^A \wp_0^C (V_{BC}^o G^C \wp_0^A \wp_0^B V_{CA} + V_{CA}^o G^{B\oplus C} \wp_0^A V_{BC}) \\
& + V_{BC}^o G^{A\oplus B\oplus C} V_{AB}^o G^C \wp_0^A \wp_0^B V_{CA}]|\Psi_0\rangle \\
& -\langle\Psi_0|V_{AB} G^{A\oplus B} \wp_0^C P^{oA} G^B \wp_0^A \wp_0^C (V_{BC}^o G^C \wp_0^A \wp_0^B V_{CA} \\
& + V_{CA}^o G^{B\oplus C} \wp_0^A V_{BC})|\Psi_0\rangle \\
& -\langle\Psi_0|V_{CA} G^C \wp_0^A \wp_0^B P^{oA} G^{A\oplus C} \wp_0^B (V_{BC}^o G^{A\oplus B} \wp_0^C V_{AB} \\
& + V_{AB}^o G^{B\oplus C} \wp_0^A V_{BC})|\Psi_0\rangle \\
& -\langle\Psi_0|V_{BC} G^{B\oplus C} \wp_0^A P^{oA} G^{A\oplus B\oplus C} V_{AB}^o G^C \wp_0^A \wp_0^B V_{CA}|\Psi_0\rangle\}.
\end{aligned} \tag{B3}$$

T_3 subsumes the static induction effects that involve sequential linear response. Specifically, the permanent polarization of A induces a polarization in B, which polarizes C, giving a reaction field back at A, thus polarizing A; and the same polarization mechanism applies with B and C interchanged. T_3 also contains one part of the dispersion contribution to the polarization. The remaining dispersion terms are contained in T_4:

$$\begin{aligned}
T_4 = (1+C)(1+\wp^{BC})\{ & -\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C \\
& \times[V_{CA}^o G^{A\oplus C} \wp_0^B (V_{BC}^o G^{A\oplus B} \wp_0^C V_{AB} + V_{AB}^o G^{B\oplus C} \wp_0^A V_{BC}) \\
& + V_{BC}^o G^{A\oplus B\oplus C} V_{CA}^o G^{A\oplus B} \wp_0^C V_{AB}]|\Psi_0\rangle
\end{aligned}$$

$$-\langle\Psi_0|V_{AB}G^{A\oplus B}\wp_0^C P^{oA} G^{A\oplus B}\wp_0^C(V_{BC}^o G^{A\oplus C}\wp_0^B V_{CA}$$

$$+V_{CA}^o G^{B\oplus C}\wp_0^A V_{BC})|\Psi_0\rangle$$

$$-\langle\Psi_0|V_{BC}G^{B\oplus C}\wp_0^A P^{oA} G^{A\oplus B\oplus C} V_{CA}^o G^{A\oplus B}\wp_0^C V_{AB}|\Psi_0\rangle\}. \tag{B4}$$

To analyze these contributions, $T_1 - T_4$ are converted into matrix element form. For T_1,

$$T_1 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\,[\sum_{j,l,m}{}'\{[\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^{oA}(\mathbf{r}')|l\rangle\langle l|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$+\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\gamma^A(\mathbf{r}'')|0\rangle]f_{1a}(\Delta_j,\Delta_l,\Delta_m)$$

$$+\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\gamma^A(\mathbf{r}'')|l\rangle\langle l|P_\beta^A(\mathbf{r}')|0\rangle f_{1b}(\Delta_j,\Delta_l,\Delta_m)\}$$

$$+\sum_{j,m}{}'\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle P_{0\gamma}^A(\mathbf{r}'')f_{1c}(\Delta_j,\Delta_m)]$$

$$\times P_{0\delta}^B(\mathbf{r}''')P_{0\varepsilon}^B(\mathbf{r}^{iv})\langle 0|P_\phi^C(\mathbf{r}^v)|m\rangle\langle m|P_\lambda^C(\mathbf{r}^{vi})|0\rangle$$

$$\times T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^v)T_{\gamma\lambda}(\mathbf{r}'',\mathbf{r}^{vi}) \tag{B5}$$

assuming all the molecular eigenstates can be taken as real. In Eq. (B5),

$$f_{1a}(\Delta_j,\Delta_l,\Delta_m) = \Delta_j^{-1}\Delta_l^{-1}(\Delta_l+\Delta_m)^{-1} + \Delta_j^{-1}\Delta_l^{-1}\Delta_m^{-1}$$

$$+\Delta_j^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_l+\Delta_m)^{-1} + \Delta_m^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_l+\Delta_m)^{-1}, \tag{B6}$$

$$f_{1b}(\Delta_j,\Delta_l,\Delta_m) = \Delta_j^{-1}\Delta_l^{-1}(\Delta_l+\Delta_m)^{-1} + \Delta_j^{-1}\Delta_m^{-1}(\Delta_l+\Delta_m)^{-1}$$

$$+\Delta_j^{-1}\Delta_l^{-1}(\Delta_j+\Delta_m)^{-1} + \Delta_l^{-1}\Delta_m^{-1}(\Delta_j+\Delta_m)^{-1}, \tag{B7}$$

and

$$f_{1c}(\Delta_j,\Delta_m) = \Delta_j^{-1}\Delta_m^{-1}(\Delta_j+\Delta_m)^{-1} + \Delta_j^{-1}\Delta_m^{-1}(\Delta_j+\Delta_m)^{-1} + \Delta_m^{-2}(\Delta_j+\Delta_m)^{-1}$$

$$+\Delta_m^{-2}(\Delta_j+\Delta_m)^{-1} - 2\Delta_j^{-2}\Delta_m^{-1} - 2\Delta_j^{-1}\Delta_m^{-2}. \tag{B8}$$

The energy denominators in Eq. (B5)-(B8) are given directly in the form generated by Eq. (B1); the expressions simplify to

$$f_{la}(\Delta_j, \Delta_l, \Delta_m) = f_{lb}(\Delta_j, \Delta_l, \Delta_m) = 2\Delta_j^{-1}\Delta_l^{-1}\Delta_m^{-1} \tag{B9}$$

and

$$f_{lc}(\Delta_j, \Delta_m) = -2\Delta_j^{-2}\Delta_m^{-1}. \tag{B10}$$

With this simplification, the T_1 terms yield Eq. (54) in Chapter VII. Similarly the T_2 terms, representing hyperpolarization by the permanent charge density of molecule C, can be obtained from Eqs. (B2) and (B5)-(B10). In matrix element form, the T_3 terms reduce to

$$T_3 = 2(1+\wp^{BC})\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,k,m}{}' \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle P_{0\gamma}^A(\mathbf{r}'')$$
$$\times\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle\langle 0|P_\phi^C(\mathbf{r}^v)|m\rangle\langle m|P_\lambda^C(\mathbf{r}^{vi})|0\rangle$$
$$\times f_3(\Delta_j, \Delta_k, \Delta_m) T_{\beta\delta}(\mathbf{r}', \mathbf{r}''') T_{\varepsilon\phi}(\mathbf{r}^{iv}, \mathbf{r}^v) T_{\gamma\lambda}(\mathbf{r}'', \mathbf{r}^{vi}) \tag{B11}$$

with

$$\begin{aligned}
f_3(\Delta_j, \Delta_k, \Delta_m) = {} & \Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1} + \Delta_j^{-1}\Delta_k^{-1}(\Delta_k+\Delta_m)^{-1} + \Delta_j^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k+\Delta_m)^{-1} \\
& + \Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1} + \Delta_k^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1} \\
& + \Delta_m^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_k+\Delta_m)^{-1} + \Delta_k^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_k+\Delta_m)^{-1} \\
& + \Delta_m^{-1}(\Delta_k+\Delta_m)^{-1}(\Delta_j+\Delta_k+\Delta_m)^{-1} \\
= {} & 2\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1} + \Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1} + \Delta_k^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1} \\
& + \Delta_m^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_k+\Delta_m)^{-1} + \Delta_k^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_k+\Delta_m)^{-1}.
\end{aligned} \tag{B12}$$

The T_4 terms are given by

$$T_4 = 2(1+\wp^{BC})\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,l,k,m}{}' [\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\gamma^A(\mathbf{r}'')|l\rangle\langle l|P_\beta^A(\mathbf{r}')|0\rangle$$
$$\times f_{4a}(\Delta_j, \Delta_l, \Delta_k, \Delta_m)$$

$$+\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times f_{4b}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)]$$

$$\times\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle\langle 0|P_\phi^C(\mathbf{r}^v)|m\rangle\langle m|P_\lambda^C(\mathbf{r}^{vi})|0\rangle$$

$$\times T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^v)T_{\gamma\lambda}(\mathbf{r}'',\mathbf{r}^{vi}), \qquad \text{(B13)}$$

where

$$f_{4a}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)=\Delta_j^{-1}(\Delta_l+\Delta_m)^{-1}(\Delta_l+\Delta_k)^{-1}+\Delta_j^{-1}(\Delta_l+\Delta_m)^{-1}(\Delta_k+\Delta_m)^{-1}$$

$$+\Delta_j^{-1}(\Delta_j+\Delta_k+\Delta_m)^{-1}(\Delta_l+\Delta_k)^{-1}+(\Delta_l+\Delta_k)^{-1}(\Delta_k+\Delta_m)^{-1}$$

$$\times(\Delta_j+\Delta_k+\Delta_m)^{-1}$$

$$=2\Delta_j^{-1}(\Delta_l+\Delta_k+\Delta_m)(\Delta_l+\Delta_k)^{-1}(\Delta_k+\Delta_m)^{-1}(\Delta_l+\Delta_m)^{-1},$$

$$\text{(B14)}$$

and

$$f_{4b}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)=(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_l+\Delta_m)^{-1}$$

$$+(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_k+\Delta_m)^{-1}. \qquad \text{(B15)}$$

The linear induction contribution to the polarization $P_\alpha^A(\mathbf{r})$ is denoted by $T_{3,ind}$. The quantity $T_{3,ind}$ is identical to the right side of Eq. (B11), except that $f_3(\Delta_j,\Delta_k,\Delta_m)$ is replaced by

$$f_{3,ind}(\Delta_j,\Delta_k,\Delta_m)=4\,\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}. \qquad \text{(B16)}$$

$T_{3,ind}$ is related to the nonlocal polarizability densities of molecules A, B, and C by Eq. (55) in Chapter VII. The dispersion contribution to the polarization $P_\alpha^A(\mathbf{r})$ is given by $T_{disp}=T_4+(T_3-T_{3,ind})$. The effect of adding $(T_3-T_{3,ind})$ to T_4 from Eq. (B13) is to replace $\langle j|P_\gamma^A(\mathbf{r}'')|l\rangle$ by $\langle j|P_\gamma^{oA}(\mathbf{r}'')|l\rangle$, because

$$f_3(\Delta_j,\Delta_k,\Delta_m)-4\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}=-f_{4a}(\Delta_j,\Delta_j,\Delta_k,\Delta_m). \tag{B17}$$

That is

$$\begin{aligned}
T_{disp} = 2(1+\wp^{BC})\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,l,k,m}{}' [&\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\gamma^{oA}(\mathbf{r}'')|l\rangle\langle l|P_\beta^A(\mathbf{r}')|0\rangle \\
&\times f_{4a}(\Delta_j,\Delta_l,\Delta_k,\Delta_m) \\
&+\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\gamma^A(\mathbf{r}'')|0\rangle \\
&\times f_{4b}(\Delta_j,\Delta_l,\Delta_k,\Delta_m)] \\
&\times\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle\langle 0|P_\phi^C(\mathbf{r}^{v})|m\rangle\langle m|P_\lambda^C(\mathbf{r}^{vi})|0\rangle \\
&\times T_{\beta\delta}(\mathbf{r}',\mathbf{r}''')\,T_{\varepsilon\phi}(\mathbf{r}^{iv},\mathbf{r}^{v})\,T_{\gamma\lambda}(\mathbf{r}'',\mathbf{r}^{vi}).
\end{aligned} \tag{B18}$$

After label changes $j\leftrightarrow l$, $k\leftrightarrow m$, $\beta\leftrightarrow\gamma$, $\varepsilon\leftrightarrow\phi$, $\delta\leftrightarrow\lambda$, $\mathbf{r}'\leftrightarrow\mathbf{r}''$, $\mathbf{r}'''\leftrightarrow\mathbf{r}^{iv}$, and $\mathbf{r}^{v}\leftrightarrow\mathbf{r}^{vi}$ in the term generated by $\wp^{BC}$ in Eq. (B18) and summation with the expression given explicitly in the same equation, Eq. (57) of Chapter VII is obtained.

Appendix C

The full expansion in Eq. (51) yields 27 terms of (V_{AB}, V_{AB}, V_{BC}) type. They can be grouped into three sets $U_1 - U_3$, according to the different types of matrix elements appearing in these terms. U_1 is given by

$$
\begin{aligned}
U_1 = (1+C)\{ & -\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C \\
& \times[V_{AB}^o G^B \wp_0^A \wp_0^C (V_{AB}^o G^B \wp_0^A \wp_0^C V_{BC} + V_{BC}^o G^B \wp_0^A \wp_0^C V_{AB}) \\
& \quad + V_{BC}^o G^{A\oplus B} \wp_0^C V_{AB}^o G^B \wp_0^A \wp_0^C V_{AB}]|\Psi_0\rangle \\
& -\langle\Psi_0|V_{AB}(G^B \wp_0^A \wp_0^C P^{oA} G^{A\oplus B} \wp_0^C + G^{A\oplus B} \wp_0^C P^{oA} G^B \wp_0^A \wp_0^C) \\
& \quad \times V_{AB}^o G^B \wp_0^A \wp_0^C V_{BC}|\Psi_0\rangle \\
& -\langle\Psi_0|V_{AB} G^B \wp_0^A \wp_0^C P^{oA} G^{A\oplus B} \wp_0^C V_{BC}^o (G^A \wp_0^B \wp_0^C \\
& \quad + G^{A\oplus B} \wp_0^C) V_{AB}|\Psi_0\rangle \\
& -\langle\Psi_0|(V_{AB} G^{A\oplus B} \wp_0^C P^{oA} G^B \wp_0^A \wp_0^C V_{BC}^o + V_{BC} G^B \wp_0^A \wp_0^C P^{oA} \\
& \quad \times G^{A\oplus B} \wp_0^C V_{AB}^o) G^B \wp_0^A \wp_0^C V_{AB}|\Psi_0\rangle \\
& +\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C V_{AB}|\Psi_0\rangle (1+C) \\
& \quad \times\langle\Psi_0|(V_{AB} G^B \wp_0^A \wp_0^C G^B \wp_0^A \wp_0^C V_{BC}|\Psi_0\rangle\}.
\end{aligned} \tag{C1}
$$

In matrix element form,

$$
\begin{aligned}
U_1 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,k,m}{}' & \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle P_{0\lambda}^A(\mathbf{r}^v) \\
& \times\{\langle 0|P_\gamma^B(\mathbf{r}'')|k\rangle\langle k|P_\delta^{oB}(\mathbf{r}''')|m\rangle\langle m|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle g_{1a}(\Delta_j,\Delta_k,\Delta_m) \\
& +\langle 0|P_\gamma^B(\mathbf{r}'')|k\rangle\langle k|P_\varepsilon^{oB}(\mathbf{r}^{iv})|m\rangle\langle m|P_\delta^B(\mathbf{r}''')|0\rangle g_{1b}(\Delta_j,\Delta_k,\Delta_m)
\end{aligned}
$$

$$+\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\gamma^{oB}(\mathbf{r}'')|m\rangle\langle m|P_\varepsilon^B(\mathbf{r}^{iv})|0\rangle g_{1a}(\Delta_j,\Delta_k,\Delta_m)\}$$

$$\times P_{0\eta}^C(\mathbf{r}^{vi})T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\lambda}(\mathbf{r}''',\mathbf{r}^{v})T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi}) \tag{C2}$$

with

$$g_{1a}(\Delta_j,\Delta_k,\Delta_m)=\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}+\Delta_k^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}, \tag{C3}$$

and

$$g_{1b}(\Delta_j,\Delta_k,\Delta_m)=\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}+\Delta_k^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}$$

$$+\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1}. \tag{C4}$$

In U_1 terms, the fields from the permanent polarization of molecules A and C hyperpolarize B; the induced polarization in B produces a static field at A to induce a polarization. U_1 also contains one part of the dispersion contribution to the polarization $\left\langle P_\alpha^A(\mathbf{r})\right\rangle^{(3)}$.

The U_2 terms satisfy

$$U_2=(1+C)\{-\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C$$

$$\times[V_{AB}^o G^A \wp_0^B \wp_0^C (V_{AB}^o G^B \wp_0^A \wp_0^C V_{BC}+V_{BC}^o G^{A\oplus B}\wp_0^C V_{AB})$$

$$+(V_{AB}^o G^{A\oplus B}\wp_0^C V_{BC}^o+V_{BC}^o G^{A\oplus B}\wp_0^C V_{AB}^o)G^A \wp_0^B \wp_0^C V_{AB}]|\Psi_0\rangle$$

$$-\langle\Psi_0|V_{AB} G^A \wp_0^B \wp_0^C P^{oA} G^A \wp_0^B \wp_0^C (V_{AB}^o G^B \wp_0^A \wp_0^C V_{BC}$$

$$+V_{BC}^o G^{A\oplus B}\wp_0^C V_{AB})|\Psi_0\rangle$$

$$-\langle\Psi_0|(V_{AB} G^{A\oplus B}\wp_0^C P^{oA} G^{A\oplus B}\wp_0^C V_{BC}^o+V_{BC} G^B \wp_0^A \wp_0^C$$

$$\times P^{oA} G^{A\oplus B}\wp_0^C V_{AB}^o)G^A \wp_0^B \wp_0^C V_{AB}|\Psi_0\rangle$$

$$+\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AB}|\Psi_0\rangle(1+C)$$

$$\times\langle\Psi_0|V_{AB} G^B \wp_0^A \wp_0^C V_{BC}|\Psi_0\rangle\}. \tag{C5}$$

The matrix form of U_2 is

$$U_2 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,l,k}{}' \{[\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\beta(\mathbf{r}')|l\rangle\langle l|P^A_\lambda(\mathbf{r}^v)|0\rangle$$

$$+\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\lambda(\mathbf{r}^v)|l\rangle\langle l|P^A_\beta(\mathbf{r}')|0\rangle]g_{2a}(\Delta_j,\Delta_l,\Delta_k)$$

$$+\langle 0|P^A_\beta(\mathbf{r}')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r}|l\rangle\langle l|P^A_\lambda(\mathbf{r}^v)|0\rangle g_{2b}(\Delta_j,\Delta_l,\Delta_k)$$

$$-\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\beta(\mathbf{r}')|0\rangle P^A_{\lambda 0}(\mathbf{r}^v) g_{2c}(\Delta_j,\Delta_k)\}$$

$$\times\langle 0|P^B_\delta(\mathbf{r}''')|k\rangle\langle k|P^B_\varepsilon(\mathbf{r}^{iv})|0\rangle P^B_{0\gamma}(\mathbf{r}'')P^C_{0\eta}(\mathbf{r}^{vi})$$

$$\times T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\lambda}(\mathbf{r}''',\mathbf{r}^v)T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi}) \qquad \text{(C6)}$$

with

$$g_{2a}(\Delta_j,\Delta_l,\Delta_k) = \Delta_j^{-1}\Delta_l^{-1}\Delta_k^{-1} + \Delta_j^{-1}\Delta_l^{-1}(\Delta_l+\Delta_k)^{-1}, \qquad \text{(C7)}$$

$$g_{2b}(\Delta_j,\Delta_l,\Delta_k) = \Delta_j^{-1}\Delta_l^{-1}\Delta_k^{-1} + \Delta_j^{-1}\Delta_l^{-1}(\Delta_l+\Delta_k)^{-1}$$

$$+\Delta_j^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}, \qquad \text{(C8)}$$

and

$$g_{2c}(\Delta_j,\Delta_k) = \Delta_j^{-1}\Delta_k^{-1}(\Delta_j+\Delta_k)^{-1}. \qquad \text{(C9)}$$

U_3 contains the remaining dispersion terms,

$$U_3 = (1+C)\{-\langle\Psi_0|P^A\, G^A\, \wp_0^B\, \wp_0^C$$

$$\times[V^o_{AB}\, G^{A\oplus B}\, \wp_0^C\,(V^o_{AB}\, G^B\, \wp_0^A\, \wp_0^C\, V_{BC} + V^o_{BC}\, G^{A\oplus B}\, \wp_0^C\, V_{AB})$$

$$+V^o_{BC}\, G^{A\oplus B}\, \wp_0^C\, V^o_{AB}\, G^{A\oplus B}\, \wp_0^C\, V_{AB}]|\Psi_0\rangle$$

$$-\langle\Psi_0|V_{AB}\, G^{A\oplus B}\, \wp_0^C\, P^{oA}\, G^{A\oplus B}\, \wp_0^C\,(V^o_{AB}\, G^B\, \wp_0^A\, \wp_0^C\, V_{BC}$$

$$+V^o_{BC}\, G^{A\oplus B}\, \wp_0^C\, V_{AB})|\Psi_0\rangle$$

$$-\langle\Psi_0|V_{BC}\, G^B\, \wp_0^A\, \wp_0^C\, P^{oA}\, G^{A\oplus B}\, \wp_0^C\, V^o_{AB}\, G^{A\oplus B}\, \wp_0^C\, V_{AB}|\Psi_0\rangle\}. \qquad \text{(C10)}$$

In matrix element form, the U_3 terms reduce to

$$
\begin{aligned}
U_3 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,l,k,m}{}' \{ & \langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\beta(\mathbf{r}')|l\rangle\langle l|P^A_\lambda(\mathbf{r}^v)|0\rangle \\
& \times[\langle 0|P^B_\gamma(\mathbf{r}'')|k\rangle\langle k|P^B_\delta(\mathbf{r}''')|m\rangle\langle m|P^B_\varepsilon(\mathbf{r}^{iv})|0\rangle \\
& \times\Delta_j^{-1}(\Delta_l+\Delta_k)^{-1}\Delta_m^{-1} \\
& +\langle 0|P^B_\gamma(\mathbf{r}'')|k\rangle\langle k|P^{oB}_\varepsilon(\mathbf{r}^{iv})|m\rangle\langle m|P^B_\delta(\mathbf{r}''')|0\rangle \\
& \times\Delta_j^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_l+\Delta_m)^{-1} \\
& +\langle 0|P^B_\delta(\mathbf{r}''')|k\rangle\langle k|P^B_\gamma(\mathbf{r}'')|m\rangle\langle m|P^B_\varepsilon(\mathbf{r}^{iv})|0\rangle \\
& \times\Delta_j^{-1}(\Delta_l+\Delta_k)^{-1}\Delta_m^{-1}] \\
& -\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\lambda(\mathbf{r}^v)|0\rangle\langle 0|P^B_\delta(\mathbf{r}''')|k\rangle\langle k|P^B_\varepsilon(\mathbf{r}^{iv})|0\rangle \\
& \times P^A_{\beta 0}(\mathbf{r}')P^B_{\gamma 0}(\mathbf{r}'')\Delta_k^{-1}(\Delta_j+\Delta_k)^{-2} \\
& +\langle 0|P^A_\beta(\mathbf{r}')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|l\rangle\langle l|P^A_\lambda(\mathbf{r}^v)|0\rangle \\
& \times[\langle 0|P^B_\gamma(\mathbf{r}'')|k\rangle\langle k|P^B_\delta(\mathbf{r}''')|m\rangle\langle m|P^B_\varepsilon(\mathbf{r}^{iv})|0\rangle \\
& \times(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}\Delta_m^{-1} \\
& +\langle 0|P^B_\gamma(\mathbf{r}'')|k\rangle\langle k|P^{oB}_\varepsilon(\mathbf{r}^{iv})|m\rangle\langle m|P^B_\delta(\mathbf{r}''')|0\rangle \\
& \times(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_l+\Delta_m)^{-1}]\} \\
& \times P^C_{0\eta}(\mathbf{r}^{vi})T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\lambda}(\mathbf{r}''',\mathbf{r}^v)T_{\varepsilon\eta}(\mathbf{r}^{iv},\mathbf{r}^{vi}). \qquad \text{(C11)}
\end{aligned}
$$

Adding $(U_1 - U_{1,ind})$ and $(U_2 - U_{2,ind})$ to U_3 from Eq. (C11), and using the fact that simultaneously interchanging the operators $P^A_\beta(\mathbf{r}')$ and $P^A_\lambda(\mathbf{r}^v)$, and $P^B_\gamma(\mathbf{r}'')$ and $P^B_\delta(\mathbf{r}''')$ does not affect the result, Eq. (67) of Chapter VII is obtained.

Appendix D

For (V_{AB}, V_{BC}, V_{BC}) terms, the full expansion of Eq. (51) generates four sets $W_1 - W_4$, according to the different types of matrix elements appearing in each of these. W_1 is given by

$$
\begin{aligned}
W_1 = (1+C)\{ & -\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C \\
& \times[V_{BC}^o G^{A\oplus C} \wp_0^B (V_{BC}^o G^{A\oplus B} \wp_0^C V_{AB} + V_{AB}^o G^{B\oplus C} \wp_0^A V_{BC}) \\
& \quad +(V_{BC}^o G^{A\oplus B\oplus C} V_{AB}^o + V_{AB}^o G^B \wp_0^A \wp_0^C V_{BC}) G^C \wp_0^A \wp_0^B V_{BC}]|\Psi_0\rangle \\
& -\langle\Psi_0|V_{BC} G^C \wp_0^A \wp_0^B P^{oA} G^{A\oplus C} \wp_0^B (V_{BC}^o G^{A\oplus B} \wp_0^C V_{AB} \\
& \quad + V_{AB}^o G^{B\oplus C} \wp_0^A V_{BC})|\Psi_0\rangle \\
& -\langle\Psi_0|(V_{AB} G^{A\oplus B} \wp_0^C P^{oA} G^B \wp_0^A \wp_0^C V_{BC}^o + V_{BC} G^{B\oplus C} \wp_0^A \\
& \quad \times P^{oA} G^{A\oplus B\oplus C} V_{AB}^o) G^C \wp_0^A \wp_0^B V_{BC}|\Psi_0\rangle\},
\end{aligned}
\tag{D1}
$$

or in matrix element form,

$$
\begin{aligned}
W_1 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} & \sum_{j,k,m}{}' \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\gamma^B(\mathbf{r}'')|0\rangle \\
& \times P_{0\lambda}^B(\mathbf{r}^{vi})\langle 0|P_\phi^C(\mathbf{r}^v)|m\rangle\langle m|P_\varepsilon^C(\mathbf{r}^{iv})|0\rangle\, h_1(\Delta_j,\Delta_k,\Delta_m) \\
& \times T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'') T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv}) T_{\phi\lambda}(\mathbf{r}^v,\mathbf{r}^{vi})
\end{aligned}
\tag{D2}
$$

with

$$
\begin{aligned}
h_1(\Delta_j,\Delta_k,\Delta_m) = {} & \Delta_j^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_j+\Delta_k)^{-1} + \Delta_j^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_k+\Delta_m)^{-1} \\
& + \Delta_j^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k+\Delta_m)^{-1} + \Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1} \\
& + \Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1} + \Delta_m^{-1}(\Delta_j+\Delta_m)^{-1}(\Delta_k+\Delta_m)^{-1} \\
& + \Delta_m^{-1}(\Delta_k+\Delta_m)^{-1}(\Delta_j+\Delta_k+\Delta_m)^{-1} + (\Delta_j+\Delta_k)^{-1}\Delta_k^{-1}\Delta_m^{-1} \\
= {} & 2\,\Delta_j^{-1}\Delta_m^{-1}(\Delta_k+\Delta_m)^{-1} + 2\,\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}.
\end{aligned}
\tag{D3}
$$

In the W_1 terms, the field from the permanent polarization of molecule B polarizes C, which then polarizes B, and produces a field that polarizes A.

W_2 is given by

$$W_2 = (1+C)\{-\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C$$

$$\times[V_{BC}^o G^{A\oplus B} \wp_0^C V_{BC}^o (G^A \wp_0^B \wp_0^C + G^{A\oplus B} \wp_0^C) V_{AB}$$

$$+(V_{BC}^o G^{A\oplus B} \wp_0^C V_{AB}^o + V_{AB}^o G^B \wp_0^A \wp_0^C V_{BC}^o) G^B \wp_0^A \wp_0^C V_{BC}]|\Psi_0\rangle$$

$$-\langle\Psi_0|V_{BC} G^B \wp_0^A \wp_0^C P^{oA} G^{A\oplus B} \wp_0^C V_{BC}^o (G^A \wp_0^B \wp_0^C$$

$$+G^{A\oplus B} \wp_0^C) V_{AB}|\Psi_0\rangle$$

$$-\langle\Psi_0|(V_{BC} G^B \wp_0^A \wp_0^C P^{oA} G^{A\oplus B} \wp_0^C V_{AB}^o + V_{AB} G^{A\oplus B} \wp_0^C$$

$$\times P^{oA} G^B \wp_0^A \wp_0^C V_{BC}^o) G^B \wp_0^A \wp_0^C V_{BC}|\Psi_0\rangle$$

$$+\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AB}|\Psi_0\rangle\langle\Psi_0|V_{BC} G^B \wp_0^A \wp_0^C V_{BC}|\Psi_0\rangle$$

$$+\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C V_{AB}|\Psi_0\rangle\langle\Psi_0|V_{BC} G^B \wp_0^A \wp_0^C G^B \wp_0^A \wp_0^C V_{BC}|\Psi_0\rangle. \tag{D4}$$

The matrix element form of the W_2 term satisfies

$$W_2 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,k,m}{}' \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle$$

$$\times[\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\lambda^{oB}(\mathbf{r}^{vi})|m\rangle\langle m|P_\gamma^B(\mathbf{r}'')|0\rangle h_{2a}(\Delta_j,\Delta_k,\Delta_m)$$

$$+\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\gamma^B(\mathbf{r}'')|m\rangle\langle m|P_\lambda^B(\mathbf{r}^{vi})|0\rangle h_{2b}(\Delta_j,\Delta_k,\Delta_m)$$

$$+\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\lambda^B(\mathbf{r}^{vi})|0\rangle P_{\gamma 0}^B(\mathbf{r}'') h_{2c}(\Delta_j,\Delta_k)] P_{0\varepsilon}^C(\mathbf{r}^{iv}) P_{0\phi}^C(\mathbf{r}^v)$$

$$\times T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'') T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv}) T_{\phi\lambda}(\mathbf{r}^v,\mathbf{r}^{vi}), \tag{D5}$$

where

$$h_{2a}(\Delta_j,\Delta_k,\Delta_m)=\Delta_j^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1}+\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}$$

$$+\Delta_k^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_j+\Delta_m)^{-1}+\Delta_k^{-1}\Delta_m^{-1}(\Delta_j+\Delta_m)^{-1}, \tag{D6}$$

$$h_{2b}(\Delta_j,\Delta_k,\Delta_m)=\Delta_j^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}+\Delta_k^{-1}\Delta_m^{-1}(\Delta_j+\Delta_k)^{-1}, \tag{D7}$$

and

$$h_{2c}(\Delta_j,\Delta_k)=\Delta_j^{-2}(\Delta_j+\Delta_k)^{-1}-\Delta_j^{-2}\Delta_k^{-1}+\Delta_j^{-1}\Delta_k^{-1}(\Delta_j+\Delta_k)^{-1}-\Delta_j^{-1}\Delta_k^{-2}. \tag{D8}$$

After algebraic simplification,

$$h_{2a}(\Delta_j,\Delta_k,\Delta_m)=2\,\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}, \tag{D9}$$

$$h_{2b}(\Delta_j,\Delta_k,\Delta_m)=\Delta_j^{-1}\Delta_k^{-1}\Delta_m^{-1}, \tag{D10}$$

and

$$h_{2c}(\Delta_j,\Delta_k)=-\Delta_j^{-1}\Delta_k^{-2}. \tag{D11}$$

With this simplification, Eq. (D5) yields Eq. (74) in Chapter VII.

Terms containing the matrix elements $P_{0\delta}^{B}(\mathbf{r}''')$, $P_{0\lambda}^{B}(\mathbf{r}^{vi})$, and $P_{0\gamma}^{B}(\mathbf{r}'')$ (with molecule B in the ground state) are grouped into W_3,

$$\begin{aligned}
W_3=(1+C)\{&-\langle\Psi_0|P^A\,G^A\,\wp_0^B\,\wp_0^C\,V_{BC}^{o}\,G^{A\oplus C}\,\wp_0^B\\
&\quad\times(V_{BC}^{o}\,G^A\,\wp_0^B\,\wp_0^C\,V_{AB}+V_{AB}^{o}\,G^C\,\wp_0^A\,\wp_0^B\,V_{BC})|\Psi_0\rangle\\
&+\langle\Psi_0|P^A\,G^A\,\wp_0^B\,\wp_0^C\,G^A\,\wp_0^B\,\wp_0^C\,V_{AB}|\Psi_0\rangle\\
&\quad\times\langle\Psi_0|V_{BC}\,G^C\,\wp_0^A\,\wp_0^B\,V_{BC}|\Psi_0\rangle\\
&-\langle\Psi_0|V_{BC}\,G^C\,\wp_0^A\,\wp_0^B\,P^{oA}\,G^{A\oplus C}\,\wp_0^B\\
&\quad\times(V_{BC}^{o}\,G^A\,\wp_0^B\,\wp_0^C\,V_{AB}+V_{AB}^{o}\,G^C\,\wp_0^A\,\wp_0^B\,V_{BC})|\Psi_0\rangle\\
&+\langle\Psi_0|P^A\,G^A\,\wp_0^B\,\wp_0^C\,V_{AB}|\Psi_0\rangle\langle\Psi_0|V_{BC}\,G^C\,\wp_0^A\,\wp_0^B\\
&\quad\times G^C\,\wp_0^A\,\wp_0^B\,V_{BC}|\Psi_0\rangle\}.
\end{aligned} \tag{D12}$$

or in matrix element form

$$W_3 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,m}{}' \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle P_{0\delta}^B(\mathbf{r}''')P_{0\lambda}^B(\mathbf{r}^{vi})P_{0\gamma}^B(\mathbf{r}'')$$

$$\times\langle 0|P_\phi^C(\mathbf{r}^v)|m\rangle\langle m|P_\varepsilon^C(\mathbf{r}^{iv})|0\rangle h_3(\Delta_j,\Delta_m)$$

$$\times T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})T_{\phi\lambda}(\mathbf{r}^v,\mathbf{r}^{vi}), \qquad \text{(D13)}$$

where

$$h_3(\Delta_j,\Delta_m) = \Delta_j^{-2}(\Delta_j+\Delta_m)^{-1} + \Delta_j^{-1}\Delta_m^{-1}(\Delta_j+\Delta_m)^{-1} - \Delta_j^{-2}\Delta_m^{-1}$$

$$+\Delta_m^{-2}(\Delta_j+\Delta_m)^{-1} + \Delta_j^{-1}\Delta_m^{-1}(\Delta_j+\Delta_m)^{-1} - \Delta_j^{-1}\Delta_m^{-2}. \qquad \text{(D14)}$$

The W_3 term vanishes because $h_3(\Delta_j,\Delta_m) = 0$.

W_4 contains the remaining dispersion terms,

$$W_4 = (1+C)\{-\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C$$

$$\times [V_{BC}^o G^{A\oplus B\oplus C} V_{BC}^o (G^A \wp_0^B \wp_0^C + G^{A\oplus B}\wp_0^C) V_{AB}$$

$$+(V_{BC}^o G^{A\oplus B\oplus C} V_{AB}^o + V_{AB}^o G^B \wp_0^A \wp_0^C V_{BC}^o) G^{B\oplus C}\wp_0^A V_{BC}]|\Psi_0\rangle$$

$$-\langle\Psi_0|V_{BC} G^{B\oplus C}\wp_0^A P^{oA} G^{A\oplus B\oplus C} V_{BC}^o (G^A \wp_0^B \wp_0^C + G^{A\oplus B}\wp_0^C) V_{AB}|\Psi_0\rangle$$

$$-\langle\Psi_0|(V_{BC} G^{B\oplus C}\wp_0^A P^{oA} G^{A\oplus B\oplus C} V_{AB}^o + V_{AB} G^{A\oplus B}\wp_0^C$$

$$\times P^{oA} G^B \wp_0^A \wp_0^C V_{BC}^o) G^{B\oplus C}\wp_0^A V_{BC}|\Psi_0\rangle$$

$$+\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AB}|\Psi_0\rangle\langle\Psi_0|V_{BC} G^{B\oplus C}\wp_0^A V_{BC}|\Psi_0\rangle$$

$$+\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C V_{AB}|\Psi_0\rangle\langle\Psi_0|V_{BC} G^{B\oplus C}\wp_0^A G^{B\oplus C}\wp_0^A V_{BC}|\Psi_0\rangle\}.$$

(D15)

The matrix element form of Eq. (D15) is

$$W_4 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,k,m,l}{}' \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle$$

$$\times[\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\lambda^B(\mathbf{r}^{vi})|m\rangle\langle m|P_\gamma^B(\mathbf{r}'')|0\rangle\, h_{4a}(\Delta_j,\Delta_k,\Delta_m,\Delta_l)$$

$$+\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\gamma^B(\mathbf{r}'')|m\rangle\langle m|P_\lambda^B(\mathbf{r}^{vi})|0\rangle h_{4b}(\Delta_j,\Delta_k,\Delta_m,\Delta_l)$$

$$+\langle 0|P_\delta^B(\mathbf{r}''')|k\rangle\langle k|P_\lambda^B(\mathbf{r}^{vi})|0\rangle P_{0\gamma}^B(\mathbf{r}'') h_{4c}(\Delta_j,\Delta_k,\Delta_l)]$$

$$\times\langle 0|P_\phi^C(\mathbf{r}^v)|l\rangle\langle l|P_\varepsilon^C(\mathbf{r}^{iv})|0\rangle T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{iv})T_{\phi\lambda}(\mathbf{r}^v,\mathbf{r}^{vi}), \quad \text{(D16)}$$

where the fact has been used that simultaneously interchanging the operators $P_\varepsilon^C(\mathbf{r}^{iv})$ and $P_\phi^C(\mathbf{r}^v)$, and $P_\delta^B(\mathbf{r}''')$ and $P_\lambda^B(\mathbf{r}^{vi})$ leaves the result unchanged, and

$$h_{4a}(\Delta_j,\Delta_k,\Delta_m,\Delta_l) = \Delta_j^{-1}(\Delta_j+\Delta_k+\Delta_l)^{-1}(\Delta_j+\Delta_m)^{-1} + \Delta_j^{-1}(\Delta_k+\Delta_l)^{-1}\Delta_m^{-1}$$

$$+(\Delta_j+\Delta_k+\Delta_l)^{-1}(\Delta_k+\Delta_l)^{-1}(\Delta_j+\Delta_m)^{-1}$$

$$+(\Delta_k+\Delta_l)^{-1}\Delta_m^{-1}(\Delta_j+\Delta_m)^{-1}$$

$$= 2\Delta_j^{-1}\Delta_m^{-1}(\Delta_k+\Delta_l)^{-1}, \quad \text{(D17)}$$

$$h_{4b}(\Delta_j,\Delta_k,\Delta_m,\Delta_l) = \Delta_j^{-1}(\Delta_j+\Delta_k+\Delta_l)^{-1}(\Delta_m+\Delta_l)^{-1}$$

$$+(\Delta_j+\Delta_k+\Delta_l)^{-1}(\Delta_k+\Delta_l)^{-1}(\Delta_m+\Delta_l)^{-1}$$

$$= \Delta_j^{-1}(\Delta_k+\Delta_l)^{-1}(\Delta_m+\Delta_l)^{-1}, \quad \text{(D18)}$$

and

$$h_{4c}(\Delta_j,\Delta_k,\Delta_l) = \Delta_j^{-2}(\Delta_j+\Delta_k+\Delta_l)^{-1} - \Delta_j^{-2}(\Delta_k+\Delta_l)^{-1}$$

$$+\Delta_j^{-1}(\Delta_j+\Delta_k+\Delta_l)^{-1}(\Delta_k+\Delta_l)^{-1} - \Delta_j^{-1}(\Delta_k+\Delta_l)^{-2}$$

$$= -\Delta_j^{-1}(\Delta_k+\Delta_l)^{-2}. \quad \text{(D19)}$$

Appendix E

The full expansion in Eq. (51) gives 33 terms of (V_{AB}, V_{AB}, V_{AC}) type. These can be split into four sets $X_1 - X_4$, according to the types of the matrix elements appearing in each. X_1 is given by

$$
\begin{aligned}
X_1 = (1+C)\{ & -\langle \Psi_0 | P^A G^A \wp_0^B \wp_0^C \\
& \quad \times [V_{AB}^o G^A \wp_0^B \wp_0^C (V_{AB}^o G^A \wp_0^B \wp_0^C V_{AC} + V_{AC}^o G^A \wp_0^B \wp_0^C V_{AB}) \\
& \qquad + V_{AC}^o G^A \wp_0^B \wp_0^C V_{AB}^o G^A \wp_0^B \wp_0^C V_{AB}] | \Psi_0 \rangle \\
& -\langle \Psi_0 | V_{AB} G^A \wp_0^B \wp_0^C P^{oA} G^A \wp_0^B \wp_0^C (V_{AB}^o G^A \wp_0^B \wp_0^C V_{AC} \\
& \qquad + V_{AC}^o G^A \wp_0^B \wp_0^C V_{AB}) | \Psi_0 \rangle \\
& -\langle \Psi_0 | V_{AC} G^A \wp_0^B \wp_0^C P^{oA} G^A \wp_0^B \wp_0^C V_{AB}^o G^A \wp_0^B \wp_0^C V_{AB} | \Psi_0 \rangle \\
& +\langle \Psi_0 | P^A G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AB} | \Psi_0 \rangle \\
& \qquad \times \langle \Psi_0 | (V_{AB} G^A \wp_0^B \wp_0^C V_{AC} + V_{AC} G^A \wp_0^B \wp_0^C V_{AB}) | \Psi_0 \rangle \\
& +\langle \Psi_0 | P^A G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AC} | \Psi_0 \rangle \langle \Psi_0 | V_{AB} G^A \wp_0^B \wp_0^C V_{AB} | \Psi_0 \rangle \\
& +\langle \Psi_0 | P^A G^A \wp_0^B \wp_0^C V_{AB} | \Psi_0 \rangle \langle \Psi_0 | (V_{AB} G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AC} \\
& \qquad + V_{AC} G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AB}) | \Psi_0 \rangle \\
& +\langle \Psi_0 | P^A G^A \wp_0^B \wp_0^C V_{AC} | \Psi_0 \rangle \langle \Psi_0 | V_{AB} G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AB} | \Psi_0 \rangle,
\end{aligned}
\tag{E1}
$$

or in matrix element form,

$$
\begin{aligned}
X_1 = 2 \int d\mathbf{r}' \cdots d\mathbf{r}^{vi} \sum_{j,l,n}{}' \{ [& \langle 0 | P_\alpha^A(\mathbf{r}) | j \rangle \langle j | P_\beta^{oA}(\mathbf{r}') | l \rangle \langle l | P_\gamma^{oA}(\mathbf{r}'') | n \rangle \langle n | P_\delta^A(\mathbf{r}''') | 0 \rangle \\
& + \langle 0 | P_\alpha^A(\mathbf{r}) | j \rangle \langle j | P_\beta^{oA}(\mathbf{r}') | l \rangle \langle l | P_\delta^{oA}(\mathbf{r}''') | n \rangle \langle n | P_\gamma^A(\mathbf{r}'') | 0 \rangle
\end{aligned}
$$

$$+\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\delta(\mathbf{r}''')|l\rangle\langle l|P^{oA}_\beta(\mathbf{r}')|n\rangle\langle n|P^A_\gamma(\mathbf{r}'')|0\rangle$$

$$+\langle 0|P^A_\gamma(\mathbf{r}'')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|l\rangle\langle l|P^{oA}_\beta(\mathbf{r}')|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle$$

$$+\langle 0|P^A_\beta(\mathbf{r}')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|l\rangle\langle l|P^{oA}_\delta(\mathbf{r}''')|n\rangle\langle n|P^A_\gamma(\mathbf{r}'')|0\rangle$$

$$+\langle 0|P^A_\delta(\mathbf{r}''')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|l\rangle\langle l|P^{oA}_\beta(\mathbf{r}')|n\rangle\langle n|P^A_\gamma(\mathbf{r}'')|0\rangle]\ \Delta_j^{-1}\Delta_l^{-1}\Delta_n^{-1}$$

$$-\sum_{j,n}{}'[2\ \langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\beta(\mathbf{r}')|0\rangle\langle 0|P^A_\gamma(\mathbf{r}'')|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle$$

$$+\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\delta(\mathbf{r}''')|0\rangle\langle 0|P^A_\beta(\mathbf{r}')|n\rangle\langle n|P^A_\gamma(\mathbf{r}'')|0\rangle]$$

$$\times P^B_{0\lambda}(\mathbf{r}^{iv})P^B_{0\eta}(\mathbf{r}^{v})P^C_{0\varepsilon}(\mathbf{r}^{vi})(\Delta_j^{-2}\Delta_n^{-1}+\Delta_j^{-1}\Delta_n^{-2})\}$$

$$\times T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})T_{\gamma\eta}(\mathbf{r}'',\mathbf{r}^{v})T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi}). \tag{E2}$$

The X_2 terms are given by

$$X_2=(1+C)\{-\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C$$

$$\times(V^o_{AB}G^{A\oplus B}\wp_0^C V^o_{AC}+V^o_{AC}G^A\wp_0^B\wp_0^C V^o_{AB})G^B\wp_0^A\wp_0^C V_{AB}|\Psi_0\rangle$$

$$-\langle\Psi_0|V_{AB}G^B\wp_0^A\wp_0^C P^{oA}G^{A\oplus B}\wp_0^C(V^o_{AB}G^A\wp_0^B\wp_0^C V_{AC}$$

$$+V^o_{AC}G^{A\oplus B}\wp_0^C V_{AB})|\Psi_0\rangle$$

$$-\langle\Psi_0|(V_{AC}G^A\wp_0^B\wp_0^C P^{oA}G^A\wp_0^B\wp_0^C V^o_{AB}+V_{AB}G^{A\oplus B}\wp_0^C$$

$$\times P^{oA}G^{A\oplus B}\wp_0^C V^o_{AC})G^B\wp_0^A\wp_0^C V_{AB}|\Psi_0\rangle\}, \tag{E3}$$

or in matrix element form

$$X_2=2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\,P^A_{0\gamma}(\mathbf{r}'')\sum_{j,n,k}{}'\{\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^A_\beta(\mathbf{r}')|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle$$

$$\times[\Delta_j^{-1}\Delta_k^{-1}(\Delta_n+\Delta_k)^{-1}+\Delta_n^{-1}\Delta_k^{-1}(\Delta_j+\Delta_k)^{-1}]$$

$$+[\langle 0|P^A_\alpha(\mathbf{r})|j\rangle\langle j|P^{oA}_\delta(\mathbf{r}''')|n\rangle\langle n|P^A_\beta(\mathbf{r}')|0\rangle$$

$$+\langle 0|P^A_\beta(\mathbf{r}')|j\rangle\langle j|P^{oA}_\alpha(\mathbf{r})|n\rangle\langle n|P^A_\delta(\mathbf{r}''')|0\rangle]$$

$$\times[\Delta_j^{-1}\Delta_n^{-1}\Delta_k^{-1} + \Delta_k^{-1}(\Delta_j + \Delta_k)^{-1}(\Delta_n + \Delta_k)^{-1}]\}$$

$$\times\langle 0|P_\lambda^B(\mathbf{r}^{iv})|k\rangle\langle k|P_\eta^B(\mathbf{r}^{v})|0\rangle P_{0\varepsilon}^C(\mathbf{r}^{vi})$$

$$\times T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv}) T_{\gamma\eta}(\mathbf{r}'',\mathbf{r}^{v}) T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi}). \tag{E4}$$

Terms containing the permanent polarization of molecule C alone are grouped into X_3:

$$X_3 = (1+C)\,[-\langle\Psi_0|(P^A G^A \wp_0^B \wp_0^C V_{AB}^o G^B \wp_0^A \wp_0^C + V_{AB}^o G^{A\oplus B} \wp_0^C$$

$$\times P^{oA} G^B \wp_0^A \wp_0^C)(V_{AB}^o G^A \wp_0^B \wp_0^C V_{AC} + V_{AC}^o G^{A\oplus B} \wp_0^C V_{AB})|\Psi_0\rangle]$$

$$= 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,n,k}{}' \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle\langle 0|P_\gamma^A(\mathbf{r}'')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle$$

$$\times\langle 0|P_\lambda^B(\mathbf{r}^{iv})|k\rangle\langle k|P_\eta^B(\mathbf{r}^{v})|0\rangle P_{0\varepsilon}^C(\mathbf{r}^{vi})$$

$$\times[\Delta_j^{-1}\Delta_n^{-1}\Delta_k^{-1} + \Delta_j^{-1}\Delta_k^{-1}(\Delta_n + \Delta_k)^{-1} + \Delta_n^{-1}\Delta_k^{-1}(\Delta_j + \Delta_k)^{-1}$$

$$+ \Delta_k^{-1}(\Delta_j + \Delta_k)^{-1}(\Delta_n + \Delta_k)^{-1}]$$

$$\times T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv}) T_{\gamma\eta}(\mathbf{r}'',\mathbf{r}^{v}) T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi}). \tag{E5}$$

X_4 contains the remaining dispersion terms,

$$X_4 = (1+C)\{-\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C$$

$$\times[V_{AB}^o G^{A\oplus B} \wp_0^C (V_{AB}^o G^A \wp_0^B \wp_0^C V_{AC} + V_{AC}^o G^{A\oplus B} \wp_0^C V_{AB})$$

$$+ V_{AC}^o G^A \wp_0^B \wp_0^C V_{AB}^o G^{A\oplus B} \wp_0^C V_{AB}]|\Psi_0\rangle$$

$$+\langle\Psi_0|P^A G^A \wp_0^B \wp_0^C G^A \wp_0^B \wp_0^C V_{AC}|\Psi_0\rangle$$

$$\times[\langle\Psi_0|V_{AB} G^B \wp_0^A \wp_0^C V_{AB}|\Psi_0\rangle + \langle\Psi_0|V_{AB} G^{A\oplus B} \wp_0^C V_{AB}|\Psi_0\rangle]$$

$$-\langle\Psi_0|V_{AB} G^{A\oplus B} \wp_0^C P^{oA} G^{A\oplus B} \wp_0^C (V_{AB}^o G^A \wp_0^B \wp_0^C V_{AC}$$

$$+ V_{AC}^o G^{A\oplus B} \wp_0^C V_{AB})|\Psi_0\rangle$$

$$-\langle \Psi_0 | V_{AB}\, G^{B}\, \wp_0^{A}\, \wp_0^{C}\, P^{oA}\, G^{A\oplus B}\, \wp_0^{C}\, V_{AC}^{o}\, G^{B}\, \wp_0^{A}\, \wp_0^{C}\, V_{AB} | \Psi_0 \rangle$$

$$-\langle \Psi_0 | V_{AC}\, G^{A}\, \wp_0^{B}\, \wp_0^{C}\, P^{oA}\, G^{A}\, \wp_0^{B}\, \wp_0^{C}\, V_{AB}^{o}\, G^{A\oplus B}\, \wp_0^{C}\, V_{AB} | \Psi_0 \rangle$$

$$+\langle \Psi_0 | P^{A}\, G^{A}\, \wp_0^{B}\, \wp_0^{C}\, V_{AC} | \Psi_0 \rangle\, [\langle \Psi_0 | V_{AB}\, G^{B}\, \wp_0^{A}\, \wp_0^{C}\, G^{B}\, \wp_0^{A}\, \wp_0^{C}\, V_{AB} | \Psi_0 \rangle$$

$$+\langle \Psi_0 | V_{AB}\, G^{A\oplus B}\, \wp_0^{C}\, G^{A\oplus B}\, \wp_0^{C}\, V_{AB} | \Psi_0 \rangle]\}, \qquad \text{(E6)}$$

or in matrix element form,

$$X_4 = 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi} \sum_{j,l,n,k}{}' \{\langle 0 | P_\alpha^A(\mathbf{r}) | j\rangle \langle j | P_\beta^A(\mathbf{r}') | l\rangle \langle l | P_\gamma^A(\mathbf{r}'') | n\rangle \langle n | P_\delta^A(\mathbf{r}''') | 0\rangle$$

$$\times \Delta_j^{-1} \Delta_n^{-1} (\Delta_l + \Delta_k)^{-1}$$

$$+\langle 0 | P_\alpha^A(\mathbf{r}) | j\rangle \langle j | P_\beta^A(\mathbf{r}') | l\rangle \langle l | P_\delta^{oA}(\mathbf{r}''') | n\rangle \langle n | P_\gamma^A(\mathbf{r}'') | 0\rangle$$

$$\times \Delta_j^{-1} (\Delta_l + \Delta_k)^{-1} (\Delta_n + \Delta_k)^{-1}$$

$$+\langle 0 | P_\alpha^A(\mathbf{r}) | j\rangle \langle j | P_\delta^{oA}(\mathbf{r}''') | l\rangle \langle l | P_\beta^A(\mathbf{r}') | n\rangle \langle n | P_\gamma^A(\mathbf{r}'') | 0\rangle$$

$$\times \Delta_j^{-1} \Delta_l^{-1} (\Delta_n + \Delta_k)^{-1}$$

$$+\langle 0 | P_\beta^A(\mathbf{r}') | j\rangle \langle j | P_\alpha^{oA}(\mathbf{r}) | l\rangle \langle l | P_\gamma^A(\mathbf{r}'') | n\rangle \langle n | P_\delta^A(\mathbf{r}''') | 0\rangle$$

$$\times \Delta_n^{-1} (\Delta_j + \Delta_k)^{-1} (\Delta_l + \Delta_k)^{-1}$$

$$+\langle 0 | P_\beta^A(\mathbf{r}') | j\rangle \langle j | P_\alpha^{oA}(\mathbf{r}) | l\rangle \langle l | P_\delta^{oA}(\mathbf{r}''') | n\rangle \langle n | P_\gamma^A(\mathbf{r}'') | 0\rangle$$

$$\times (\Delta_j + \Delta_k)^{-1} (\Delta_l + \Delta_k)^{-1} (\Delta_n + \Delta_k)^{-1}$$

$$+\langle 0 | P_\delta^A(\mathbf{r}''') | j\rangle \langle j | P_\alpha^{oA}(\mathbf{r}) | l\rangle \langle l | P_\beta^A(\mathbf{r}') | n\rangle \langle n | P_\gamma^A(\mathbf{r}'') | 0\rangle$$

$$\times \Delta_j^{-1} \Delta_l^{-1} (\Delta_n + \Delta_k)^{-1}$$

$$-\langle 0 | P_\alpha^A(\mathbf{r}) | j\rangle \langle j | P_\delta^A(\mathbf{r}''') | 0\rangle\, P_{0\beta}^A(\mathbf{r}')\, P_{0\gamma}^A(\mathbf{r}'')$$

$$\times [\Delta_j^{-2} \Delta_k^{-1} + \Delta_j^{-1} \Delta_k^{-2} - \Delta_k^{-2} (\Delta_j + \Delta_k)^{-1}]$$

$$-\langle 0 | P_\alpha^A(\mathbf{r}) | j\rangle \langle j | P_\delta^A(\mathbf{r}''') | 0\rangle \langle 0 | P_\beta^A(\mathbf{r}') | n\rangle \langle n | P_\gamma^A(\mathbf{r}'') | 0\rangle$$

$$\times[\Delta_j^{-2}(\Delta_n+\Delta_k)^{-1}+\Delta_j^{-1}(\Delta_n+\Delta_k)^{-2}]\}$$

$$\times\langle 0|P_\lambda^B(\mathbf{r}^{iv})|k\rangle\langle k|P_\eta^B(\mathbf{r}^{v})|0\rangle P_{0\varepsilon}^C(\mathbf{r}^{vi})$$

$$\times T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})T_{\eta\gamma}(\mathbf{r}^{v},\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi}). \quad \text{(E7)}$$

Adding $X_2 - X_{2,\text{ind}}$ and $X_3 - X_{3,\text{ind}}$ to X_4 and grouping the terms according to the types of the matrix elements yields

$$X_4 + X_2 - X_{2,\text{ind}} + X_3 - X_{3,\text{ind}}$$

$$= 2\int d\mathbf{r}'\cdots d\mathbf{r}^{vi}\, T_{\beta\lambda}(\mathbf{r}',\mathbf{r}^{iv})T_{\eta\gamma}(\mathbf{r}^{v},\mathbf{r}'')T_{\delta\varepsilon}(\mathbf{r}''',\mathbf{r}^{vi})$$

$$\times\sum_{j,l,n,k}{}'\langle 0|P_\lambda^B(\mathbf{r}^{iv})|k\rangle\langle k|P_\eta^B(\mathbf{r}^{v})|0\rangle P_{0\varepsilon}^C(\mathbf{r}^{vi})$$

$$\times[Y_1+Y_2+Y_3+Y_4+Y_5+Y_6+Y_7+Y_8], \quad \text{(E8)}$$

where

$$Y_1 = \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|l\rangle\langle l|P_\gamma^A(\mathbf{r}'')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle\Delta_j^{-1}\Delta_n^{-1}(\Delta_l+\Delta_k)^{-1}$$

$$-\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle P_{0\gamma}^A(\mathbf{r}'')\Delta_j^{-1}\Delta_n^{-1}(\Delta_n+\Delta_k)^{-1}$$

$$-\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\gamma^A(\mathbf{r}'')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle P_{0\beta}^A(\mathbf{r}')\Delta_j^{-1}\Delta_n^{-1}(\Delta_j+\Delta_k)^{-1}$$

$$+\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\delta^A(\mathbf{r}''')|0\rangle P_{0\beta}^A(\mathbf{r}')P_{0\gamma}^A(\mathbf{r}'')\,[\Delta_j^{-2}\Delta_k^{-1}-\Delta_j^{-1}\Delta_k^{-2}$$

$$+\Delta_k^{-2}(\Delta_j+\Delta_k)^{-1}]$$

$$= \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^{oA}(\mathbf{r}')|l\rangle\langle l|P_\gamma^{oA}(\mathbf{r}'')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle$$

$$\times\Delta_j^{-1}\Delta_n^{-1}(\Delta_l+\Delta_k)^{-1}, \quad \text{(E9)}$$

$$Y_2 = \langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|l\rangle\langle l|P_\delta^{oA}(\mathbf{r}''')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times\Delta_j^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_n+\Delta_k)^{-1}$$

$$-\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\delta^{oA}(\mathbf{r}''')|n\rangle\langle n|P_\beta^A(\mathbf{r}')|0\rangle P_{0\gamma}^A(\mathbf{r}'')$$

$$\times \Delta_j^{-1}\Delta_n^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_n+\Delta_k)^{-1}(\Delta_j+\Delta_n+\Delta_k)$$

$$=\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^{oA}(\mathbf{r}')|l\rangle\langle l|P_\delta^{oA}(\mathbf{r}''')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times \Delta_j^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_n+\Delta_k)^{-1}$$

$$-\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\delta^{oA}(\mathbf{r}''')|n\rangle\langle n|P_\beta^A(\mathbf{r}')|0\rangle P_{0\gamma}^A(\mathbf{r}'')$$

$$\times \Delta_j^{-1}\Delta_n^{-1}(\Delta_n+\Delta_k)^{-1}, \tag{E10}$$

$$Y_3=\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\delta^{oA}(\mathbf{r}''')|l\rangle\langle l|P_\beta^A(\mathbf{r}')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times \Delta_j^{-1}\Delta_l^{-1}(\Delta_n+\Delta_k)^{-1}, \tag{E11}$$

$$Y_4=\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\delta^{oA}(\mathbf{r}''')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}(\Delta_n+\Delta_k)^{-1}, \tag{E12}$$

$$Y_5=\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\gamma^A(\mathbf{r}'')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle$$

$$\times \Delta_n^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}$$

$$-\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle P_{0\gamma}^A(\mathbf{r}'')$$

$$\times \Delta_j^{-1}\Delta_n^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_n+\Delta_k)^{-1}(\Delta_j+\Delta_n+\Delta_k)$$

$$=\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\gamma^{oA}(\mathbf{r}'')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle$$

$$\times \Delta_n^{-1}(\Delta_j+\Delta_k)^{-1}(\Delta_l+\Delta_k)^{-1}$$

$$-\langle 0|P_\beta^A(\mathbf{r}')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle P_{0\gamma}^A(\mathbf{r}'')$$

$$\times \Delta_j^{-1}\Delta_n^{-1}(\Delta_j+\Delta_k)^{-1}, \tag{E13}$$

$$Y_6=\langle 0|P_\delta^A(\mathbf{r}''')|j\rangle\langle j|P_\alpha^{oA}(\mathbf{r})|l\rangle\langle l|P_\beta^A(\mathbf{r}')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times \Delta_j^{-1}\Delta_l^{-1}(\Delta_n+\Delta_k)^{-1}, \tag{E14}$$

$$Y_7 = -\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\delta^A(\mathbf{r}''')|0\rangle\langle 0|P_\beta^A(\mathbf{r}')|n\rangle\langle n|P_\gamma^A(\mathbf{r}'')|0\rangle$$

$$\times[\Delta_j^{-2}(\Delta_n+\Delta_k)^{-1}+\Delta_j^{-1}(\Delta_n+\Delta_k)^{-2}], \tag{E15}$$

and

$$Y_8 = -\langle 0|P_\alpha^A(\mathbf{r})|j\rangle\langle j|P_\beta^A(\mathbf{r}')|0\rangle\langle 0|P_\gamma^A(\mathbf{r}'')|n\rangle\langle n|P_\delta^A(\mathbf{r}''')|0\rangle$$

$$\times\Delta_j^{-1}\Delta_n^{-1}[(\Delta_n+\Delta_k)^{-1}+(\Delta_j+\Delta_k)^{-1}+(\Delta_j+\Delta_k)^{-1}$$

$$\times(\Delta_n+\Delta_k)^{-1}(\Delta_j+\Delta_n+\Delta_k)]. \tag{E16}$$

Adding the second term of Eq. (E10) to Eq. (E11), and adding the second term of Eq. (E13) to Eq. (E14) converts the matrix element $\langle l|P_\beta^A(\mathbf{r}')|n\rangle$ in Eqs. (E11) and (E14) to $\langle l|P_\beta^{oA}(\mathbf{r}')|n\rangle$. This transforms Eq. (E8) into Eq. (85) of Chapter VII.