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ON THE PROPERTIES OF PAIRS OF ATOMS AND MOLECULES AT LONG RANGE

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By

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ABSTRACT

FIELD-INDUCED FLUCTUATION CORRELATIONS AND THE EFFECTS OF VAN DER WAALS INTERACTIONS ON THE PROPERTIES OF PAIRS OF ATOMS AND MOLECULES AT LONG RANGE

By

James E. Bohr

One contribution to pair properties during molecular collisions comes from the van der Waals interactions between the fluctuating charge distributions of the collision partners. Application of an external field to a molecular pair changes the van der Waals interaction energy in two ways. First, the field alters the response of each molecule to the nonuniform, fluctuating field of its neighbor. Second, the applied field induces new correlations between the fluctuating charge moments on each molecular center. Such field-induced fluctuation correlations have not been included in earlier models of the van der Waals contribution to pair dipoles and pair polarizabilities. Using a reaction field model that includes these effects, general equations are derived for the van der Waals dipole and polarizability of a molecular pair interacting at long range, where overlap and exchange effects are negligible. The van der Waals dipole and polarizability each depend on an imaginary-frequency integral consisting of two or more terms; each

term involves the product of either a linear or nonlinear response tensor for one molecule and a nonlinear response tensor for the neighboring molecule. Symmetry-adapted expressions for the van der Waals contribution to the dipole moments of some specific systems are derived in this model. In particular, the long-range van der Waals dipole of a pair of dissimilar atoms, an atom-centrosymmetric linear molecule pair, and a pair of centrosymmetric linear molecules are investigated. The leading contributions vary as R^{-7} in the intermolecular separation R and depend upon products of the dipole polarizability $\alpha_{\alpha\beta}(i\omega)$ of one molecule with the dipole-quadrupole hyperpolarizability $B_{\alpha\beta,\gamma\delta}(0,i\omega)$ of the other, integrated over imaginary frequencies. Because the B tensor is not well known as a function of frequency, approximations are developed for the integrals in terms of the static $\alpha_{\alpha\beta}$ polarizability, the static $B_{\alpha\beta,\gamma\delta}$ hyperpolarizability, and the van der Waals energy coefficients C_6 and C_8 (both isotropic and anisotropic components for atom-molecule and molecule-molecule pairs). These approximations agree well with accurate perturbation results for the model systems $H...H_\zeta$ (where H_ζ is a hydrogen-like atom scaled by a factor ζ) and H...He. Applied to $He...H_2$, $He...N_2$, $H_2...H_2$, and $N_2...N_2$, the approximations provide the first direct results for the leading van der Waals contribution to the dipole moment of each of these systems. For some symmetry components of the long-range dipoles, van der Waals effects are greater than induction contributions; both need to be included in fitting collision-induced rototranslational spectra.

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CHAPTER 1. INTRODUCTION

A. Foundations of Molecular Interactions

Forces of attraction and repulsion are known to exist between molecular systems. These stem from electromagnetic interactions and, at small intermolecular separations, electron exchange effects. Although gravitational forces are also present, these are extremely weak and may be ignored. For the purposes of this dissertation, magnetic effects will be neglected, and the focus will be entirely on the electrical forces of interaction between molecules.

It is useful to separate the electrical forces of interaction into short-range and long-range contributions. When the distance between centers is small, overlap of the electronic wavefunctions of the individual molecules is significant. The interaction force in this region may be either attractive or repulsive, but at very small separations the force becomes entirely repulsive and behaves exponentially. Long-range forces vary as R^{-n} in the separation R, where n is a positive integer. Electron exchange is negligible at long range, so for the purposes of numerical calculation the electrons may be assigned exclusively to one or the other of the interacting molecules. This means that for calculation purposes the total system wavefunction does not need to be antisymmetrized with respect to exchange of electrons, and a perturbation scheme may be employed in which the unperturbed wavefunction is a simple product of the wavefunctions of the isolated molecules. At long range then, the forces between a pair of molecules can be related to the

properties of the individual molecules. At present no theory exists relating short-range interactions to individual molecular properties, because in this region electron exchange is significant, and the total wavefunction must be fully antisymmetrized at short range.

The long-range interaction energy of a molecular pair can be divided further into several contributing types. When the free molecules are in states $\psi_{n_1}^{(o)}$ and $\psi_{n_2}^{(o)}$, standard perturbation theory gives as the energy of the pair

$$\Delta E = E_{n_1}^{(o)} + E_{n_2}^{(o)} + \langle\psi_{n_1}^{(o)}\ \psi_{n_2}^{(o)}|H'|\psi_{n_1}^{(o)}\ \psi_{n_2}^{(o)}\rangle$$

$$- \quad \Sigma' \quad \frac{|\langle\psi_{n_1}^{(o)}\ \psi_{n_2}^{(o)}|H'|\psi_{j_1}^{(o)}\ \psi_{j_2}^{(o)}\rangle|^2}{(E_{j_1}^{(o)} - E_{n_1}^{(o)}) + (E_{j_2}^{(o)} - E_{n_2}^{(o)})} \quad + \quad . . . \qquad (1.1)$$

where H' is the perturbed part of the Hamiltonian and where Σ' indicates a summation over all states $\psi_{j_1}^{(o)}\ \psi_{j_2}^{(o)}$ except $\psi_{n_1}^{(o)}\ \psi_{n_2}^{(o)}$. The first-order term in Eq. (1.1) is the electrostatic energy ΔE^{el}, and results from the interaction between the permanent electric moments (charge, dipole, quadrupole, etc.) of both molecules. While it is true that the charge distribution of each molecule is modified by the presence of the other, this is <u>not</u> included in the electrostatic energy; only the permanent moments of the free molecules contribute to ΔE^{el}. The second-order term in Eq. (1.1) includes both the induction energy and the dispersion or van der

Waals energy. The induction energy ΔE^{ind} arises from the interaction between the induced electric moments of each molecule and the permanent moments of its partner. It is produced from the matrix elements of H' that are diagonal in n_1 or n_2:

$$\Delta E^{ind} = - \sum_{j_1 \neq n_1} \frac{|\langle \psi_{n_1}^{(o)} \ \psi_{n_2}^{(o)} | H' | \psi_{j_1}^{(o)} \ \psi_{n_2}^{(o)} \rangle|^2}{(E_{j_1}^{(o)} - E_{n_1}^{(o)})}$$

$$- \sum_{j_2 \neq n_2} \frac{|\langle \psi_{n_1}^{(o)} \ \psi_{n_2}^{(o)} | H' | \psi_{n_1}^{(o)} \ \psi_{j_2}^{(o)} \rangle|^2}{(E_{j_2}^{(o)} - E_{n_2}^{(o)})} \quad . \tag{1.2}$$

Both the electrostatic and induction effects can be explained through the use of classical electrodynamics. The remainder of the second-order term in Eq. (1.1) constitutes the van der Waals energy ΔE^{vdW}:

$$\Delta E^{vdW} = - \sum_{\substack{j_1 \neq n_1 \\ j_2 \neq n_2}} \frac{|\langle \psi_{n_1}^{(o)} \ \psi_{n_2}^{(o)} | H' | \psi_{j_1}^{(o)} \ \psi_{j_2}^{(o)} \rangle|^2}{(E_{j_1}^{(o)} - E_{n_1}^{(o)}) + (E_{j_2}^{(o)} - E_{n_2}^{(o)})} \quad . \tag{1.3}$$

ΔE^{vdW} results from the correlation in the fluctuating charge distributions of the interacting molecules. It is a purely quantum mechanical effect: A region of space at a particular temperature T is permeated with a quantized radiation field characteristic of that temperature. This photon field will interact with any molecule that is present, inducing instantaneous multipoles in the molecule. The

instantaneous multipoles arise from electron-photon interactions in which excited electronic states are mixed into the ground electronic state, with simultaneous changes in the state of the photon field. For sufficiently low temperatures, the photon field can be considered to be in a vacuum state in which virtual photons may be produced; for atoms and molecules, the electron-photon interaction at room temperature is essentially the same as the interaction at zero temperature. In other words, at ordinary temperatures the van der Waals interaction between molecular systems results when the electrons interact with virtual photons that are produced from the vacuum state; effects of the real photons are negligible, because their energy is too low to induce electronic transitions.

Using second-order quantum-mechanical perturbation theory, London was able to describe the attractive long-range van der Waals force between two atoms, showing that it arises from a correlation in the fluctuations of the electronic coordinates [1,2]. He based his theory on the assumption that an electron in a particular atom perceives the instantaneous rather than the average position of the electrons in a neighboring atom. Modeling the neighboring atom as an instantaneous dipole, London solved the Schrödinger equation to second order in the perturbation, expressing the energy reduction caused by two-electron correlations in terms of one-electron excitations.

The exact theoretical treatment of van der Waals interactions requires the quantization of both matter and electromagnetic fields. The coupled electron-photon system should thus be treated using quantum electrodynamics. Then the total Hamiltonian is comprised of

an electron contribution H_{el}, a photon contribution H_{ph}, and an electron-photon interaction H_{int}. The van der Waals energy between two molecules becomes a fourth-order perturbation, due to the interaction of two electrons with two photons (two electron-photon interactions on each center). Quantum electrodynamics gives directly the proper effects of retardation on the van der Waals pair energy at very large separations. The field of a fluctuating multipole requires a finite propagation time R/c (where R is the distance between molecules and c is the speed of light) before it reaches and polarizes a neighboring molecule. At very long range this propagation time is nonnegligible; this leads to weaker correlations and a smaller energy change. Both the retarded and nonretarded behaviors arise naturally from a quantum electrodynamic treatment of interacting molecules.

The nonrelativistic London formalism assumes a static Coulomb interaction potential between the electrons. It does not account for field propagation, and therefore cannot explain retardation effects at very large separations. Retardation can be incorporated by using time-dependent perturbation theory. Casimir and Polder used this approach in their investigation of retardation [3]. They introduced the randomly fluctuating vector potential of the electromagnetic radiation into the Schrödinger equation and calculated the energy of interaction between two atoms to fourth order in the perturbation. The interaction energy was found to vary as R^{-7} for very large separations R, instead of following the usual R^{-6} behavior.

Quantum electrodynamics replaces electrons and photons by quasi-particles. Following an analysis by Langbein [73], if one assumes the electron system to be essentially in its ground state and averaged over all instantaneous excitations, electric and magnetic susceptibilities may be defined and Maxwell's equations retrieved. This assumption not only reduces the quantum theoretical effort but also allows the van der Waals energy to be expressed in terms of the susceptibilities of the interacting molecules. Assuming instead that the photon system is essentially in its ground state, the electric and magnetic interaction potentials may be introduced and Schrödinger's equation for the interacting molecules retrieved.

In this dissertation, the first step away from the quantum electrodynamic procedure is taken, but not the second. The electrons are assumed to be essentially in the ground state; fluctuating multipoles arise from the absorption and emission of photons by the electrons. It is the correlation of these fluctuating multipoles that gives rise to the van der Waals interaction between molecules. The quantized photon field is not treated explicity here, but it should be understood that the fluctuations in the electronic charge distributions are due to electron-photon interactions.

How are the fluctuating multipoles correlated? The parameters that couple photons and molecules are the molecular susceptibilities. The susceptibilities are complex functions whose real parts describe the polarization of the molecule, and whose imaginary parts describe the energy dissipation from the molecule to

the photon field and from the photon field to the molecule. The fluctuation-dissipation theorem as derived by Callen and Welton [4] states that the correlation function of the fluctuating multipoles is proportional to the imaginary part of the susceptibility.

The model for molecular interactions that is formulated in this dissertation is essentially a reaction field model based on the concept of fluctuating molecular charge distributions. These fluctuations are due to the interaction of electrons with a photon field, and give rise to instantaneous multipole moments. The instantaneous moments of one molecule set up a field and field gradients which propagate to a second molecule, inducing multipoles in it. These induced moments produce a reaction field and reaction field gradients that act back at the first molecule, lowering its energy. This energy change is determined by taking a time average over the coupled fluctuations, as computed by use of the fluctuation-dissipation theorem. The same scenario holds for the second molecule as well, and the total van der Waals energy for the pair is obtained by adding the energy reductions for each molecule. Treatments of the van der Waals interaction energy which employ the reaction field model may be found in Refs. [71-73]. The intermolecular separation, though large enough that overlap and exchange can be ignored, is assumed to be small compared to the characteristic wavelengths of the radiation associated with the fields. Under these conditions a multipole expansion in the fluctuating and induced moments can be used in describing the fields and field gradients.

B. Collision-induced Properties

Collisions between molecules in compressed gases and liquids cause distortions in the charge distributions of the colliding partners, giving rise to changes in molecular dipole moments [5]. These transient dipoles are responsible for the collision induced absorption and emission spectra of such nondipolar species as H_2 [6], N_2 [6-9], O_2 [6-8], CH_4 [10], and SF_6 [11,12], and the absorption by mixtures of inert gases [13,14], H_2 with He [15-18], and H_2 with N_2 [19]. The spectra can provide information on the pair and cluster dynamics of these systems, if the interaction-induced dipoles are known as functions of intermolecular separation and relative orientation. High-resolution, gas-phase spectroscopic measurements have recently become accurate enough [16-18] that it is necessary to include the van der Waals contribution to collision-induced dipoles in order that theoretical and experimental results can reach agreement.

The polarizabilities of molecules in compressed gases and liquids are also affected by intermolecular interactions, as evidenced by the dielectric and optical properties of bulk samples. Dielectric virial coefficients [20-24], virial coefficients for the DC Kerr effect [25,26], birefringent response of fluids on the subpicosecond time scale [27,28], and intensities of collision-induced Rayleigh and Raman light scattering [29-41] all depend on the transient changes in polarizabilities that occur when molecules collide. Calculations of these changes are needed to evaluate local field factors or effective polarizabilities of molecules in dense

media [42-45]. Also, information about intermolecular dynamics in liquids can be obtained from line shape analyses of light scattering spectra, if the polarizabilities of the interacting molecules are known [46].

When the separation between a pair of molecules is large enough that overlap and exchange effects are negligible, the collision-induced dipole and polarizability come entirely from classical polarization (induction effects) and from van der Waals interactions. Previous reaction field models have attributed the van der Waals contribution to polarizabilities [47-51] and dipole moments [52-54] to hyperpolarization of each molecule by the field and field gradients arising from the fluctuating charge distribution of the other. The van der Waals dipole has also been evaluated by considering the changes in the reaction field at one molecule due to the application of an external field to the second molecule [55]. These changes result from the nonlinear polarization of the second molecule by the simultaneous action of the external field and the nonuniform field due to the fluctuating charge distribution of the first molecule.

Hunt and Bohr have shown that an additional physical effect contributes to van der Waals dipoles [56] and polarizabilities [57]. The external field not only combines with the fluctuating molecular field to produce nonlinear polarization, it also alters the correlations between the fluctuating moments of each molecule taken singly. For example, application of an external field to a centrosymmetric molecule introduces correlations between the fluctuating dipole and quadrupole moments that are absent in the media [42-45]. Also, information about intermolecular dynamics in liquids can be obtained from line shape analyses of light scattering spectra, if the polarizabilities of the interacting molecules are known [46].

When the separation between a pair of molecules is large enough that overlap and exchange effects are negligible, the collision-induced dipole and polarizability come entirely from classical polarization. [illegible]

[illegible]

unperturbed molecule. Such field-induced fluctuation correlations were not included in earlier models, though the effects are implicitly present in calculations of the van der Waals contribution to dipole moments using two-center, third-order perturbation theory [58-60] and to polarizabilities using two-center, fourth-order perturbation theory [61,62].

This dissertation will focus on the long-range van der Waals contribution to dipoles and polarizabilities as formulated in a reaction field model which includes field-induced fluctuation correlations. The van der Waals interaction energy for two nonoverlapping molecules in the presence of a uniform, static external field is derived and then differentiated once with respect to the field to determine the van der Waals dipole, and differentiated twice to give the van der Waals polarizability.

At short range, overlap and exchange contributions to pair dipoles and polarizabilities are significant [51,63-68], and the van der Waals contribution is damped by overlap [69,70]. The present model does not include these effects. The long-range induction and van der Waals contributions to dipoles and polarizabilities are additive to second order in the molecular interaction. To a first approximation, the van der Waals and overlap/exchange contributions to pair dipoles and polarizabilities may also be treated as additive.

C. Overview of Dissertation

Chapter 2 of the dissertation is devoted to the derivation of general equations for the van der Waals contribution to the long-range energy, dipole moment, and polarizability of a pair of molecules. In Chapter 3, the collision-induced dipole moment is examined in detail for a number of different interacting systems. For a pair of dissimilar S state atoms, the only source of a long-range dipole is the van der Waals interaction, giving a dipole which varies as R^{-7} in the interatomic separation R. When an atom interacts with a diatomic molecule, or when two diatomics interact, there is an induction contribution to the collision-induced dipole as well. Induction and van der Waals interactions are both studied in Chapter 3 for these systems. The resulting equations for the van der Waals contribution to the dipoles of all of these pairs depend on integrals over imaginary frequencies of products of certain susceptibility tensors for the individual atoms or molecules. Since these tensors are not readily known functions of frequency, an approximation technique is needed to find numerical results for real systems. A constant-ratio approximation is used in Chapter 4 to relate these integrals to static susceptibilities and the van der Waals energy coefficients C_n. Then, values are found for the collision-induced van der Waals dipole moment for the pairs $H...H_{\zeta}$, $H...He$, $He...H_2$, $He...N_2$, $H_2...H_2$ and $N_2...N_2$. For the latter four systems, the van der Waals effect is compared with the induction contribution to the total dipole. Finally, Chapter 5 provides a discussion of results with recommendations for further work.

In closing this introductory chapter, the question of systems of measurement should be addressed. The theoretician usually prefers to use atomic units, where $\hbar = m_e = e = 1$; atomic units are used in the calculated results of this dissertation. While this system simplifies computational work, it is not the one of choice for experimentalists. Table 1.1 provides values equivalent to atomic units for the SI system of measurement and for other commonly used units.

Table 1.1

UNITS OF MEASUREMENT

	Q.M. (a.u.)	Common	SI
Length	1 bohr (a_o)	0.529177 Å	0.529177×10^{-10} m
Mass	1 (m_e)	5.48580×10^{-4} unified amu (u)	9.10953×10^{-31} kg
Energy	1 hartree	219,474.64 cm^{-1}	4.359828×10^{-18} J
		~627.5 kcal/mol	$\sim 2.6 \times 10^{6}$ J/mol
Charge	1 (e)	4.80324×10^{-10} statcoul	$\sim 1.6 \times 10^{-19}$ C
Dipole	1 (ea_o)	~2.54 Debye (D)	$\sim 8.48 \times 10^{-30}$ Cm
Quadrupole	1 (ea_o^2)		$\sim 4.5 \times 10^{-40}$ Cm^2

CHAPTER 2. THE EFFECTS OF FIELD-INDUCED FLUCTUATION CORRELATIONS

As discussed in the Introduction, pair properties are induced and/or changed during collisions between molecules. When the intermolecular separation is large enough that overlap and exchange effects can be neglected, these collision-induced properties result entirely from classical polarization and van der Waals interactions. In previous models of pair dipoles [52-55] and pair polarizabilities [47-51], the van der Waals contribution has been attributed to the hyperpolarization of each molecule by an applied field and by the field and field gradients due to the fluctuating charge distributions of the other molecule.

In this chapter field-induced fluctuation correlations are shown to have an effect on van der Waals pair properties. These effects have not been included in earlier models. The derivations which follow are carried out under the assumption that the interacting molecules are well separated, so that overlap and exchange effects are negligible. This means that a multipole expansion can be used to characterize the molecular electric fields. Retardation effects are not considered in this work; the molecules are sufficiently close together that the signal propagation between them is essentially instantaneous.

A. van der Waals Interaction Energy

In this section, an expression for the van der Waals interaction energy ΔE^{AB} of two molecules A and B in the presence of a uniform, static applied electric field $\underline{F}$ will be developed. This interaction energy is attributable to correlations of the fluctuating charge distributions of the two molecules. The fluctuating field of one molecule polarizes the other; this induced polarization gives rise to a reaction field which acts back on the first molecule, resulting in an energy shift for the system. The effect of the external field is incorporated in the susceptibility tensors of each molecule. As the theory is developed and the dependence of these tensors on the external field is explicitly determined, the manner in which the field induces correlations in the molecular charge fluctuations will become apparent.

The fluctuating charge distribution of molecule A induces time dependent moments in molecule B. When the separation between the molecules is sufficiently large that the multipole expansion is valid, the ω-frequency component of the dipole moment induced in B by A (in the presence of the static applied field $\underline{F}$) is [74-76]

$$\begin{aligned}\underline{\mu}^{B}_{IND}(\omega) = {} & \underline{\underline{\alpha}}^{B}(\underline{F},\omega) \cdot \underline{F}^{B}(\omega) + \frac{1}{3} \underline{\underline{A}}^{B}(\underline{F},\omega) \vdots \underline{\underline{F}}'^{B}(\omega) \\ & + \frac{1}{15} \underline{\underline{E}}^{B}(\underline{F},\omega) \,\vdots\, \underline{\underline{F}}''^{B}(\omega) \\ & + \left(\frac{1}{\omega}\right) \underline{\underline{G}}'^{B}(\underline{F},\omega) \cdot \underline{\dot{B}}^{B}(\omega) + \left(\frac{1}{\omega}\right) \underline{\underline{S}}'^{B}(\underline{F},\omega) : \underline{\underline{\dot{B}}}'^{B}(\omega) + \cdots , \quad (2.1)\end{aligned}$$

where $\underline{F}^{B}(\omega)$ is the ω-frequency component of the field at B due to the fluctuating multipoles of A, $\underline{\underline{F}}'^{B}(\omega)$ is the field gradient, and

$\underline{\underline{F}}''^{B}(\omega)$ is the gradient of the field gradient. $\underline{\dot{B}}^{B}(\omega)$ is the ω-frequency component of the time derivative of the magnetic field at B due to A, and $\underline{\underline{\dot{B}}}'^{B}(\omega)$ is the gradient of $\underline{\dot{B}}^{B}(\omega)$. The susceptibility tensor $\underline{\underline{\alpha}}^{B}(\underline{F},\omega)$ is the dipole polarizability of B in the presence of the static applied field $\underline{F}$, $\underline{\underline{A}}^{B}(\underline{F},\omega)$ is the dipole-quadrupole polarizability, and $\underline{\underline{E}}^{B}(\underline{F},\omega)$ is the dipole-octopole polarizability. $\underline{\underline{G}}'^{B}(\underline{F},\omega)$ is a gyration polarizability that determines the optical rotation of an isotropic medium [74].

Similarly, the quadrupole induced in B by the fluctuating charge distribution of A is

$$\underline{\underline{\Theta}}^{B}_{IND}(\omega) = \underline{\underline{A}}^{B}(\underline{F},\omega) \cdot \underline{F}^{B}(\omega) + \underline{\underline{C}}^{B}(\underline{F},\omega) \vdots \underline{\underline{F}}'^{B}(\omega) - \left(\frac{1}{\omega}\right) \underline{\underline{D}}'^{B}(\underline{F},\omega) \cdot \underline{\dot{B}}^{B}(\omega) + \cdots . \tag{2.2}$$

In this equation $\underline{\underline{C}}^{B}(\underline{F},\omega)$ is the quadrupole polarizability of B in the presence of the static applied field $\underline{F}$.

The octopole induced in B by the fluctuating charge distribution of A is

$$\underline{\underline{\Omega}}^{B}_{IND}(\omega) = \underline{\underline{E}}^{B}(\underline{F},\omega) \cdot \underline{F}^{B}(\omega) + \cdots . \tag{2.3}$$

Provided that the intermolecular separation is small compared to the characteristic wavelengths of the radiation associated with $\underline{F}^{B}(\omega)$, the field and field gradients at B are related to the fluctuating dipole $\underline{\mu}^{A}_{FL}$, fluctuating quadrupole $\underline{\underline{\Theta}}^{A}_{FL}$, and fluctuating octopole $\underline{\underline{\Omega}}^{A}_{FL}$ of molecule A by

$$\underline{F}^{B}(\omega) = \underline{\underline{T}}^{(2)}(\underline{R}) \cdot \underline{\mu}^{A}_{FL}(\omega) + \frac{1}{3}\,\underline{\underline{T}}^{(3)}(\underline{R}) \,\vdots\, \underline{\underline{\Theta}}^{A}_{FL}(\omega) + \frac{1}{15}\,\underline{\underline{T}}^{(4)}(\underline{R}) \,\vdots\, \underline{\underline{\Omega}}^{A}_{FL}(\omega) + \cdots , \qquad (2.4)$$

$$\underline{\underline{F}}'^{B}(\omega) = -\,\underline{\underline{T}}^{(3)}(\underline{R}) \cdot \underline{\mu}^{A}_{FL}(\omega) - \frac{1}{3}\,\underline{\underline{T}}^{(4)}(\underline{R}) \,\vdots\, \underline{\underline{\Theta}}^{A}_{FL}(\omega) - \cdots , \qquad (2.5)$$

and

$$\underline{\underline{F}}''^{B}(\omega) = \underline{\underline{T}}^{(4)}(\underline{R}) \cdot \underline{\mu}^{A}_{FL}(\omega) + \cdots . \qquad (2.6)$$

In Eqs. (2.4) through (2.6), $\underline{R}$ is the vector from an origin in molecule B to an origin in molecule A; the propagator tensors are

$$T^{(2)}_{\alpha\beta}(\underline{R}) = \nabla_{\alpha}\,\nabla_{\beta}\,(R^{-1}) ,$$

$$T^{(3)}_{\alpha\beta\gamma}(\underline{R}) = \nabla_{\alpha}\,\nabla_{\beta}\,\nabla_{\gamma}\,(R^{-1}) ,$$

and

$$T^{(4)}_{\alpha\beta\gamma\delta}(\underline{R}) = \nabla_{\alpha}\,\nabla_{\beta}\,\nabla_{\gamma}\,\nabla_{\delta}\,(R^{-1}) ,$$

where Greek subscripts designate the vector or tensor components x, y, and z. At this level of approximation, $\dot{\underline{B}}^{B}(\omega)$ and its gradient vanish, simplifying Eqs. (2.1) and (2.2).

The moments induced in molecule B by molecule A give rise to a reaction field which acts on A:

$$\underline{F}^{A}(\omega) = \underline{\underline{T}}^{(2)}(\underline{R}) \cdot \underline{\mu}^{B}_{IND}(\omega) - \frac{1}{3}\,\underline{\underline{T}}^{(3)}(\underline{R}) \,\vdots\, \underline{\underline{\Theta}}^{B}_{IND}(\omega)$$

$$+ \frac{1}{15} \underline{\underline{T}}^{(4)}(\underline{R}) \vdots \underline{\underline{\Omega}}^{B}_{IND}(\omega) - \cdots , \tag{2.7}$$

a reaction field gradient:

$$\underline{\underline{F}}'^{A}(\omega) = \underline{\underline{T}}^{(3)}(\underline{R}) \cdot \underline{\mu}^{B}_{IND}(\omega) - \frac{1}{3} \underline{\underline{T}}^{(4)}(\underline{R}) \vdots \underline{\underline{\Theta}}^{B}_{IND}(\omega) + \cdots , \tag{2.8}$$

and a gradient of the reaction field gradient:

$$\underline{\underline{F}}''^{A}(\omega) = \underline{\underline{T}}^{(4)}(\underline{R}) \cdot \underline{\mu}^{B}_{IND}(\omega) + \cdots . \tag{2.9}$$

The resulting change in the energy of molecule A is found by averaging the instantaneous energy shift over the configurations of the charge distribution of A:

$$\Delta E^{A} = - \frac{1}{2} < \underline{\mu}^{A}_{FL}(t) \cdot \underline{F}^{A}(t) >_{s} - \frac{1}{6} < \underline{\underline{\Theta}}^{A}_{FL}(t) \vdots \underline{\underline{F}}'^{A}(t) >_{s}$$
$$- \frac{1}{30} < \underline{\underline{\Omega}}^{A}_{FL}(t) \vdots \underline{\underline{F}}''^{A}(t) >_{s} - \cdots , \tag{2.10}$$

where the subscript s on the angular brackets denotes the average of the symmetrized contracted product of the terms within. Substituting frequency Fourier representations for $\underline{F}^{A}(t)$, $\underline{\underline{F}}'^{A}(t)$, $\underline{\underline{F}}''^{A}(t)$, $\underline{\mu}^{A}_{FL}(t)$, $\underline{\underline{\Theta}}^{A}_{FL}(t)$ and $\underline{\underline{\Omega}}^{A}_{FL}(t)$, and using Eqs. (2.1) - (2.9) gives the shift in energy as a sum of terms

$$\Delta E^{A} = \sum_{n=6}^{\infty} \Delta E^{A}_{n} \tag{2.11}$$

where ΔE_n^A varies as R^{-n} in the intermolecular separation. The contributions through order R^{-8} are

$$
\begin{aligned}
\Delta E_6^A = &-\frac{1}{4}\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \exp\left[-i(\omega+\omega')t\right] \\
&\times \langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot[\underline{\underline{\alpha}}^B(\underline{F},\omega) + \underline{\underline{\alpha}}^B(\underline{F},\omega')]\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot\underline{\mu}_{FL}^A(\omega')\rangle \ ,
\end{aligned}
\tag{2.12}
$$

$$
\begin{aligned}
\Delta E_7^A = &-\frac{1}{6}\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \exp\left[-i(\omega+\omega')t\right] \\
&\times \left[\langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot[\underline{\underline{\alpha}}^B(\underline{F},\omega) + \underline{\underline{\alpha}}^B(\underline{F},\omega')]\cdot\underline{\underline{T}}^{(3)}(\underline{R})\colon\underline{\underline{\Theta}}_{FL}^A(\omega')\rangle_s\right. \\
&\left.- \langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot[\underline{\underline{A}}^B(\underline{F},\omega) + \underline{\underline{A}}^B(\underline{F},\omega')]\colon\underline{\underline{T}}^{(3)}(\underline{R})\cdot\underline{\mu}_{FL}^A(\omega')\rangle_s\right],
\end{aligned}
\tag{2.13}
$$

and

$$
\begin{aligned}
\Delta E_8^A = &-\frac{1}{6}\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \exp\left[-i(\omega+\omega')t\right] \\
&\times \Big[\frac{1}{2}\langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(3)}(\underline{R})\colon[\underline{\underline{C}}^B(\underline{F},\omega) + \underline{\underline{C}}^B(\underline{F},\omega')]\colon\underline{\underline{T}}^{(3)}(\underline{R})\cdot\underline{\mu}_{FL}^A(\omega')\rangle \\
&+ \frac{1}{5}\langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot[\underline{\underline{E}}^B(\underline{F},\omega) + \underline{\underline{E}}^B(\underline{F},\omega')]\vdots\underline{\underline{T}}^{(4)}(\underline{R})\cdot\underline{\mu}_{FL}^A(\omega')\rangle_s \\
&- \frac{1}{3}\langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(3)}(\underline{R})\colon[\underline{\underline{A}}^B(\underline{F},\omega) + \underline{\underline{A}}^B(\underline{F},\omega')]\cdot\underline{\underline{T}}^{(3)}(\underline{R})\colon\underline{\underline{\Theta}}_{FL}^A(\omega')\rangle_s \\
&- \frac{1}{3}\langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot[\underline{\underline{A}}^B(\underline{F},\omega) + \underline{\underline{A}}^B(\underline{F},\omega')]\colon\underline{\underline{T}}^{(4)}(\underline{R})\colon\underline{\underline{\Theta}}_{FL}^A(\omega')\rangle_s \\
&+ \frac{1}{5}\langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot[\underline{\underline{\alpha}}^B(\underline{F},\omega) + \underline{\underline{\alpha}}^B(\underline{F},\omega')]\cdot\underline{\underline{T}}^{(4)}(\underline{R})\vdots\underline{\underline{\Omega}}_{FL}^A(\omega')\rangle_s \\
&+ \frac{1}{6}\langle \underline{\underline{\Theta}}_{FL}^A(\omega)\colon\underline{\underline{T}}^{(3)}(\underline{R})\cdot[\underline{\underline{\alpha}}^B(\underline{F},\omega) + \underline{\underline{\alpha}}^B(\underline{F},\omega')]\cdot\underline{\underline{T}}^{(3)}(\underline{R})\colon\underline{\underline{\Theta}}_{FL}^A(\omega')\rangle\Big].
\end{aligned}
\tag{2.14}
$$

In Eqs. (2.13) and (2.14), the subscript s denotes the symmetrized contracted tensor product. For example,

$$
\begin{aligned}
&\langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot[\underline{\underline{\alpha}}^B(\underline{F},\omega) + \underline{\underline{\alpha}}^B(\underline{F},\omega')]\cdot\underline{\underline{T}}^{(3)}(\underline{R})\colon\underline{\underline{\Theta}}_{FL}^A(\omega')\rangle_s \\
&= \frac{1}{2}\langle \underline{\mu}_{FL}^A(\omega)\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot[\underline{\underline{\alpha}}^B(\underline{F},\omega) + \underline{\underline{\alpha}}^B(\underline{F},\omega')]\cdot\underline{\underline{T}}^{(3)}(\underline{R})\colon\underline{\underline{\Theta}}_{FL}^A(\omega')\rangle \\
&+ \frac{1}{2}\langle \underline{\underline{\Theta}}_{FL}^A(\omega')\colon\underline{\underline{T}}^{(3)}(\underline{R})\cdot[\underline{\underline{\alpha}}^B(\underline{F},\omega) + \underline{\underline{\alpha}}^B(\underline{F},\omega')]\cdot\underline{\underline{T}}^{(2)}(\underline{R})\cdot\underline{\mu}_{FL}^A(\omega)\rangle .
\end{aligned}
\tag{2.15}
$$

If the applied field is absent, and if molecule B is centrosymmetric, then $\underline{\underline{A}}^B(\underline{F}=0,\omega) = 0$ and the second term of Eq. (2.13) will vanish. If molecule A is centrosymmetric, the first term of Eq. (2.13) also vanishes in the absence of an applied field, because the fluctuating dipole moment of A is then uncorrelated with its fluctuating quadrupole moment.

If A and B are S state atoms, then in the absence of the applied field the only nonzero terms of Eq. (2.14) are the first and sixth terms. This is due to the fact that for isotropic systems both $\underline{\underline{E}}(\underline{F}=0,\omega)$ and $\underline{\underline{A}}(\underline{F}=0,\omega)$ vanish, eliminating terms two through four, and also because octopolar fluctuations are uncorrelated with dipolar fluctuations for isotropic systems, eliminating the fifth term.

Application of the external field $\underline{F}$ distorts the charge distributions of molecules A and B, introducing additional interaction effects. One effect arises from changes in the response of molecule B to the nonuniform local field of A. For example, the applied field alters the susceptibility tensors of B such that $\underline{\underline{A}}^B(\underline{F},\omega)$ is no longer equal to zero for a centrosymmetric molecule B. Thus the field gradient from the fluctuating dipole of A induces a dipole in B, and the field from the fluctuating dipole of A induces a quadrupole in B. Both of these induced moments produce reaction fields at A, with resulting energy shifts proportional to R^{-7} (see the second term of Eq. (2.13)). Earlier models of the van der Waals contributions to collision-induced dipoles [52-55] and polarizabilities [47-51] have included these types of effects as a

net hyperpolarization of molecule B by the simultaneous action of the applied field $\underline{F}$ and the fluctuating local field of molecule A.

In addition, the applied field modifies the correlations between the spontaneous quantum mechanical charge fluctuations on each center. By the fluctuation-dissipation theorem [4,77]

$$\frac{1}{2}\langle \mu^A_{\alpha,FL}(\omega)\,\mu^A_{\beta,FL}(\omega') + \mu^A_{\beta,FL}(\omega')\,\mu^A_{\alpha,FL}(\omega)\rangle = \frac{\hbar}{2\pi}\,\alpha^{A\,\prime\prime}_{\alpha\beta}(\underline{F},\omega)\,\coth\left[\frac{\hbar\omega}{2kT}\right]\delta(\omega+\omega')\ , \tag{2.16}$$

$$\frac{1}{2}\langle \mu^A_{\alpha,FL}(\omega)\,\Theta^A_{\beta\gamma,FL}(\omega') + \Theta^A_{\beta\gamma,FL}(\omega')\,\mu^A_{\alpha,FL}(\omega)\rangle = \frac{\hbar}{2\pi}\,A^{A\,\prime\prime}_{\alpha,\beta\gamma}(\underline{F},\omega)\,\coth\left[\frac{\hbar\omega}{2kT}\right]\delta(\omega+\omega')\ , \tag{2.17}$$

$$\frac{1}{2}\langle \Theta^A_{\alpha\beta,FL}(\omega)\,\Theta^A_{\gamma\delta,FL}(\omega') + \Theta^A_{\gamma\delta,FL}(\omega')\,\Theta^A_{\alpha\beta,FL}(\omega)\rangle = \frac{3\hbar}{2\pi}\,C^{A\,\prime\prime}_{\alpha\beta,\gamma\delta}(\underline{F},\omega)\,\coth\left[\frac{\hbar\omega}{2kT}\right]\delta(\omega+\omega')\ , \tag{2.18}$$

and

$$\frac{1}{2}\langle \mu^A_{\alpha,FL}(\omega)\,\Omega^A_{\beta\gamma\delta,FL}(\omega') + \Omega^A_{\beta\gamma\delta,FL}(\omega')\,\mu^A_{\alpha,FL}(\omega)\rangle = \frac{\hbar}{2\pi}\,E^{A\,\prime\prime}_{\alpha,\beta\gamma\delta}(\underline{F},\omega)\,\coth\left[\frac{\hbar\omega}{2kT}\right]\delta(\omega+\omega')\ , \tag{2.19}$$

where $\underline{\underline{\alpha}}^{A\,\prime\prime}(\underline{F},\omega)$ is the imaginary part of the dipole polarizability of A in the presence of the applied field $\underline{F}$, $\underline{\underline{A}}^{A\,\prime\prime}(\underline{F},\omega)$ is the imaginary part of the dipole-quadrupole polarizability of A, $\underline{\underline{C}}^{A\,\prime\prime}(\underline{F},\omega)$ is the imaginary part of the quadrupole polarizability, and $\underline{\underline{E}}^{A\,\prime\prime}(\underline{F},\omega)$ is the imaginary part of the dipole-octopole polarizability. Note that both sides of Eq. (2.17) will vanish in the absence of an applied field for a centrosymmetric molecule A, since in that case $\underline{\underline{A}}^{A}(\underline{F}=0,\omega) = 0$. If A is an S state atom and the external field is absent, then $\underline{\underline{E}}^{A}(\underline{F}=0,\omega) = 0$ also, and both sides of Eq. (2.19) will vanish. This

is the manner in which the applied field induces correlations in the fluctuating moments: it alters molecular susceptibilities, endowing nonzero values on response tensors which would ordinarily vanish in the absence of the field; $\underline{\underline{\alpha}}^A(\underline{F},\omega)$ and $\underline{\underline{C}}^A(\underline{F},\omega)$ also differ from their zero-field values.

The fluctuation-dissipation relations given in Eqs. (2.16) - (2.19) can be used to simplify Eqs. (2.12) - (2.14) for ΔE_6^A, ΔE_7^A, and ΔE_8^A. After integration over ω' we have

$$\Delta E_6^A = -\frac{\hbar}{8\pi}\int_{-\infty}^{\infty} d\omega \coth\left[\frac{\hbar\omega}{2kT}\right] \times T_{\alpha\beta}^{(2)}(\underline{R})\,[\alpha_{\beta\gamma}^B(\underline{F},\omega) + \alpha_{\beta\gamma}^B(\underline{F},-\omega)]\,T_{\gamma\delta}^{(2)}(\underline{R})\,\alpha_{\delta\alpha}^{A''}(\underline{F},\omega)\ , \tag{2.20}$$

$$\begin{aligned}\Delta E_7^A = -\frac{\hbar}{12\pi}\int_{-\infty}^{\infty} d\omega \coth\left[\frac{\hbar\omega}{2kT}\right] &\times [T_{\alpha\beta}^{(2)}(\underline{R})\,[\alpha_{\beta\gamma}^B(\underline{F},\omega) + \alpha_{\beta\gamma}^B(\underline{F},-\omega)]\,T_{\gamma\delta\varepsilon}^{(3)}(\underline{R})\,A_{\delta\varepsilon,\alpha}^{A''}(\underline{F},\omega)\\ &- T_{\alpha\beta}^{(2)}(\underline{R})\,[A_{\beta,\gamma\delta}^B(\underline{F},\omega) + A_{\beta,\gamma\delta}^B(\underline{F},-\omega)]\,T_{\gamma\delta\varepsilon}^{(3)}(\underline{R})\,\alpha_{\varepsilon\alpha}^{A''}(\underline{F},\omega)]\ ,\end{aligned} \tag{2.21}$$

and

$$\begin{aligned}\Delta E_8^A = &-\frac{\hbar}{12\pi}\int_{-\infty}^{\infty} d\omega \coth\left[\frac{\hbar\omega}{2kT}\right]\\ &\times [\tfrac{1}{2}\,T_{\alpha\beta\gamma}^{(3)}(\underline{R})\,[C_{\beta\gamma,\delta\varepsilon}^B(\underline{F},\omega) + C_{\beta\gamma,\delta\varepsilon}^B(\underline{F},-\omega)]\,T_{\delta\varepsilon\phi}^{(3)}(\underline{R})\,\alpha_{\phi\alpha}^{A''}(\underline{F},\omega)\\ &+ \tfrac{1}{5}\,T_{\alpha\beta}^{(2)}(\underline{R})\,[E_{\beta,\gamma\delta\varepsilon}^B(\underline{F},\omega) + E_{\beta,\gamma\delta\varepsilon}^B(\underline{F},-\omega)]\,T_{\gamma\delta\varepsilon\phi}^{(4)}(\underline{R})\,\alpha_{\phi\alpha}^{A''}(\underline{F},\omega)\\ &- \tfrac{1}{3}\,T_{\alpha\beta\gamma}^{(3)}(\underline{R})\,[A_{\beta\gamma,\delta}^B(\underline{F},\omega) + A_{\beta\gamma,\delta}^B(\underline{F},-\omega)]\,T_{\delta\varepsilon\phi}^{(3)}(\underline{R})\,A_{\varepsilon\phi,\alpha}^{A''}(\underline{F},\omega)\\ &- \tfrac{1}{3}\,T_{\alpha\beta}^{(2)}(\underline{R})\,[A_{\beta,\gamma\delta}^B(\underline{F},\omega) + A_{\beta,\gamma\delta}^B(\underline{F},-\omega)]\,T_{\gamma\delta\varepsilon\phi}^{(4)}(\underline{R})\,A_{\varepsilon\phi,\alpha}^{A''}(\underline{F},\omega)\\ &+ \tfrac{1}{5}\,T_{\alpha\beta}^{(2)}(\underline{R})\,[\alpha_{\beta\gamma}^B(\underline{F},\omega) + \alpha_{\beta\gamma}^B(\underline{F},-\omega)]\,T_{\gamma\delta\varepsilon\phi}^{(4)}(\underline{R})\,E_{\delta\varepsilon\phi,\alpha}^{A''}(\underline{F},\omega)\\ &+ \tfrac{1}{2}\,T_{\alpha\beta\gamma}^{(3)}(\underline{R})\,[\alpha_{\gamma\delta}^B(\underline{F},\omega) + \alpha_{\gamma\delta}^B(\underline{F},-\omega)]\,T_{\delta\varepsilon\phi}^{(3)}(\underline{R})\,C_{\varepsilon\phi,\alpha\beta}^{A''}(\underline{F},\omega)]\ .\end{aligned} \tag{2.22}$$

is the manner in which the applied field induces correlations in the fluctuating moments: it alters molecular susceptibilities, endowing nonzero values on response tensors which would ordinarily vanish in the absence of the field; $g^A(\underline{r},\omega)$ and $g^A(\underline{r},\omega)$ also differ from their zero-field values.

The fluctuation-dissipation relations given in Eqs. (2.16) - (2.19) can be used to s[illegible] Eqs. (2.1[illegible]) - (2.14) for [illegible], ΔE^A_7, and $\Delta E^A_{[illegible]}$. All [illegible] (a repeated Greek subscript α represents an implicit summation over α = x, y, and z). Since $\underline{\underline{\alpha}}^{A}{}''(\underline{F},\omega)$, $\underline{\underline{A}}^{A}{}''(\underline{F},\omega)$, $\underline{\underline{C}}^{A}{}''(\underline{F},\omega)$, and $\underline{\underline{E}}^{A}{}''(\underline{F},\omega)$ are all odd functions of ω, only the even, real parts $\underline{\underline{\alpha}}^{B}{}'(\underline{F},\omega)$, $\underline{\underline{A}}^{B}{}'(\underline{F},\omega)$, $\underline{\underline{C}}^{B}{}'(\underline{F},\omega)$, and $\underline{\underline{E}}^{B}{}'(\underline{F},\omega)$ of the B molecule polarizabilities can contribute to the integrals in Eqs. (2.20) - (2.22) [73].

Adding the energy shift ΔE^{B} of molecule B, noting that $\underline{\underline{T}}^{(2)}(-\underline{R}) = \underline{\underline{T}}^{(2)}(\underline{R})$ and $\underline{\underline{T}}^{(4)}(-\underline{R}) = \underline{\underline{T}}^{(4)}(\underline{R})$ but $\underline{\underline{T}}^{(3)}(-\underline{R}) = -\underline{\underline{T}}^{(3)}(\underline{R})$, and again noting that the real and imaginary parts of the susceptibilities are respectively even and odd functions of ω gives

$$\begin{aligned}
\Delta E^{AB} = {} & \frac{i\hbar}{4\pi} \int_{-\infty}^{\infty} d\omega \; T^{(2)}_{\alpha\beta}(\underline{R}) \; \alpha^{B}_{\beta\gamma}(\underline{F},\omega) \; T^{(2)}_{\gamma\delta}(\underline{R}) \; \alpha^{A}_{\delta\alpha}(\underline{F},\omega) \coth\left[\frac{\hbar\omega}{2kT}\right] \\
& - \frac{i\hbar}{6\pi} (1-P^{AB}) \int_{-\infty}^{\infty} d\omega \; T^{(2)}_{\alpha\beta}(\underline{R}) \; A^{B}_{\beta,\gamma\delta}(\underline{F},\omega) \; T^{(3)}_{\gamma\delta\varepsilon}(\underline{R}) \; \alpha^{A}_{\varepsilon\alpha}(\underline{F},\omega) \coth\left[\frac{\hbar\omega}{2kT}\right] \\
& + \frac{i\hbar}{12\pi} (1+P^{AB}) \int_{-\infty}^{\infty} d\omega \; \Big[T^{(3)}_{\alpha\beta\gamma}(\underline{R}) \; C^{B}_{\beta\gamma,\delta\varepsilon}(\underline{F},\omega) \; T^{(3)}_{\delta\varepsilon\phi}(\underline{R}) \; \alpha^{A}_{\phi\alpha}(\underline{F},\omega) \\
& \qquad + \frac{2}{5} T^{(2)}_{\alpha\beta}(\underline{R}) \; E^{B}_{\beta,\gamma\delta\varepsilon}(\underline{F},\omega) \; T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R}) \; \alpha^{A}_{\phi\alpha}(\underline{F},\omega) \\
& \qquad - \frac{1}{3} T^{(3)}_{\alpha\beta\gamma}(\underline{R}) \; A^{B}_{\beta\gamma,\delta}(\underline{F},\omega) \; T^{(3)}_{\delta\varepsilon\phi}(\underline{R}) \; A^{A}_{\varepsilon\phi,\alpha}(\underline{F},\omega) \\
& \qquad - \frac{1}{3} T^{(2)}_{\alpha\beta}(\underline{R}) \; A^{B}_{\beta,\gamma\delta}(\underline{F},\omega) \; T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R}) \; A^{A}_{\varepsilon\phi,\alpha}(\underline{F},\omega) \Big] \coth\left[\frac{\hbar\omega}{2kT}\right] \quad (2.23)
\end{aligned}$$

for the van der Waals energy shift of the AB pair through order R^{-8}. The permutation operator P^{AB} interchanges the molecule labels A and B, while leaving the sign of $\underline{R}$ unchanged.

ΔE^{AB} should be computed as the Cauchy principal value of the integrals in Eq. (2.23), since the field-dependent susceptibilities vanish at ω=0, and zero-frequency fluctuations cannot contribute to the van der Waals energy shift. The poles of the susceptibilities $\underline{\underline{\alpha}}(\underline{F},\omega)$, $\underline{\underline{A}}(\underline{F},\omega)$, $\underline{\underline{C}}(\underline{F},\omega)$ and $\underline{\underline{E}}(\underline{F},\omega)$ all lie in the lower half-plane in ω, by causality [73,77]. Therefore the integrands in Eq. (2.23) are

analytic functions of ω in the upper half-plane, except at the poles of $\coth[\frac{\hbar\omega}{2kT}]$ lying on the imaginary axis at $\omega_n = 2\pi inkT/\hbar$. Integrating along a contour running from $-R$ to $-\varepsilon$ on the negative real axis, around a small semicircle $r = \varepsilon\exp(i\Theta)$ in the upper half-plane to $+\varepsilon$, along the positive real axis to $+R$, and then around a large semicircle $r = R\exp(i\Theta)$ yields in the limits $R \to \infty$ and $\varepsilon \to 0$

$$\begin{aligned}
\Delta E^{AB} = &- kT\, \Sigma_n'\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(\underline{F},\omega_n)\, T^{(2)}_{\gamma\delta}(\underline{R})\, \alpha^A_{\delta\alpha}(\underline{F},\omega_n) \\
&+ \frac{2kT}{3}(1 - P^{AB})\, \Sigma_n'\, T^{(2)}_{\alpha\beta}(\underline{R})\, A^B_{\beta,\gamma\delta}(\underline{F},\omega_n)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(\underline{F},\omega_n) \\
&- \frac{kT}{3}(1 + P^{AB})\, \Sigma_n'\, [T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, C^B_{\beta\gamma,\delta\varepsilon}(\underline{F},\omega_n)\, T^{(3)}_{\delta\varepsilon\phi}(\underline{R})\, \alpha^A_{\phi\alpha}(\underline{F},\omega_n) \\
&\qquad + \frac{2}{5}\, T^{(2)}_{\alpha\beta}(\underline{R})\, E^B_{\beta,\gamma\delta\varepsilon}(\underline{F},\omega_n)\, T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R})\, \alpha^A_{\phi\alpha}(\underline{F},\omega_n) \\
&\qquad - \frac{1}{3}\, T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, A^B_{\beta\gamma,\delta}(\underline{F},\omega_n)\, T^{(3)}_{\delta\varepsilon\phi}(\underline{R})\, A^A_{\varepsilon\phi,\alpha}(\underline{F},\omega_n) \\
&\qquad - \frac{1}{3}\, T^{(2)}_{\alpha\beta}(\underline{R})\, A^B_{\beta,\gamma\delta}(\underline{F},\omega_n)\, T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R})\, A^A_{\varepsilon\phi,\alpha}(\underline{F},\omega_n)]\ , \qquad (2.24)
\end{aligned}$$

where the sum over n runs from 0 to ∞, with the prime on the summation indicating that the $n = 0$ term is multiplied by $\frac{1}{2}$.

The sum in Eq. (2.24) can be used directly to compute the van der Waals energies of interacting rigid rotors or oscillators. If the spacing between the poles ω_n is small relative to the frequency range over which the susceptibilities change appreciably for imaginary ω, then the infinite summations in the above equation can be converted to integrals [73]. This requirement is fulfilled for atomic and molecular systems at ordinary temperatures, and Eq. (2.24) becomes

$$\Delta E^{AB} = -\frac{\hbar}{2\pi}\int_0^\infty d\omega\; T^{(2)}_{\alpha\beta}(\underline{R})\; \alpha^{B}_{\beta\gamma}(\underline{F},i\omega)\; T^{(2)}_{\gamma\delta}(\underline{R})\; \alpha^{A}_{\delta\alpha}(\underline{F},i\omega)$$
$$+ \frac{\hbar}{3\pi}(1 - P^{AB})\int_0^\infty d\omega\; T^{(2)}_{\alpha\beta}(\underline{R})\; A^{B}_{\beta,\gamma\delta}(\underline{F},i\omega)\; T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\; \alpha^{A}_{\varepsilon\alpha}(\underline{F},i\omega)$$
$$- \frac{\hbar}{6\pi}(1 + P^{AB})\int_0^\infty d\omega\; [T^{(3)}_{\alpha\beta\gamma}(\underline{R})\; C^{B}_{\beta\gamma,\delta\varepsilon}(\underline{F},i\omega)\; T^{(3)}_{\delta\varepsilon\phi}(\underline{R})\; \alpha^{A}_{\phi\alpha}(\underline{F},i\omega)$$
$$+ \frac{2}{5}\, T^{(2)}_{\alpha\beta}(\underline{R})\; E^{B}_{\beta,\gamma\delta\varepsilon}(\underline{F},i\omega)\; T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R})\; \alpha^{A}_{\phi\alpha}(\underline{F},i\omega)$$
$$- \frac{1}{3}\, T^{(3)}_{\alpha\beta\gamma}(\underline{R})\; A^{B}_{\beta\gamma,\delta}(\underline{F},i\omega)\; T^{(3)}_{\delta\varepsilon\phi}(\underline{R})\; A^{A}_{\varepsilon\phi,\alpha}(\underline{F},i\omega)$$
$$- \frac{1}{3}\, T^{(2)}_{\alpha\beta}(\underline{R})\; A^{B}_{\beta,\gamma\delta}(\underline{F},i\omega)\; T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R})\; A^{A}_{\varepsilon\phi,\alpha}(\underline{F},i\omega)] \;. \tag{2.25}$$

Application of the external field $\underline{F}$ shifts the poles of the susceptibilities from their zero-field locations, causing large changes in them near resonant frequencies. Along the imaginary ω axis the changes are smaller and $\underline{\underline{\alpha}}(\underline{F},i\omega)$, $\underline{\underline{A}}(\underline{F},i\omega)$, $\underline{\underline{C}}(\underline{F},i\omega)$, and $\underline{\underline{E}}(\underline{F},i\omega)$ may be expanded in Taylor series [74]. Specializing to centrosymmetric systems, these expansions are

$$\alpha_{\alpha\beta}(\underline{F},i\omega) = \alpha_{\alpha\beta}(i\omega) + \frac{1}{2}\,\gamma_{\alpha\beta\gamma\delta}(i\omega,0,0)\; F_\gamma\, F_\delta + \ldots\,, \tag{2.26}$$

$$A_{\alpha,\beta\gamma}(\underline{F},i\omega) = B_{\alpha\delta,\beta\gamma}(0,i\omega)\; F_\delta + \ldots\,, \tag{2.27}$$

$$C_{\alpha\beta,\gamma\delta}(\underline{F},i\omega) = C_{\alpha\beta,\gamma\delta}(i\omega) + \frac{1}{2}\,P_{\varepsilon\phi,\alpha\beta,\gamma\delta}(0,0,i\omega)\; F_\varepsilon F_\phi + \ldots\,, \tag{2.28}$$

and

$$E_{\alpha,\beta\gamma\delta}(\underline{F},i\omega) = E_{\alpha,\beta\gamma\delta}(i\omega) + \frac{1}{2}\,Q_{\alpha\varepsilon\phi,\beta\gamma\delta}(0,0,i\omega)\; F_\varepsilon F_\phi + \ldots\,, \tag{2.29}$$

to second-order in the applied field $\underline{F}$. The expressions on the right-hand sides of Eqs. (2.26) - (2.29) are given in terms of the response tensors in the absence of the applied field. In Eq.

(2.26), the dipole indices γ and δ are associated with the static field ($\omega = 0$) and the index β with the frequency $i\omega$; in Eq. (2.27), the dipole index δ is associated with the static field and the quadrupole indices $\beta\gamma$ with the frequency $i\omega$; in Eq. (2.28), the dipole indices ε and ϕ are associated with the static field and the quadrupole indices $\gamma\delta$ with the frequency $i\omega$; and in Eq. (2.29), the dipole indices ε and ϕ are associated with the static field and the octopole indices $\beta\gamma\delta$ with the frequency $i\omega$. When the Taylor series are substituted into Eq. (2.25), the van der Waals energy for a pair of centrosymmetric molecules A and B interacting at long range in the presence of a static applied field is

$$
\begin{aligned}
\Delta E^{AB} = &-\frac{\hbar}{2\pi}\int_0^\infty d\omega\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(2)}_{\gamma\delta}(\underline{R})\, \alpha^A_{\delta\alpha}(i\omega) \\
&-\frac{\hbar}{4\pi}(1+P^{AB})\int_0^\infty d\omega\, T^{(2)}_{\alpha\beta}(\underline{R})\, \gamma^B_{\beta\gamma\varepsilon\phi}(i\omega,0,0)\, T^{(2)}_{\gamma\delta}(\underline{R})\, \alpha^A_{\delta\alpha}(i\omega)\, F_\varepsilon\, F_\phi \\
&+\frac{\hbar}{3\pi}(1-P^{AB})\int_0^\infty d\omega\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^B_{\beta\phi,\gamma\delta}(0,i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(i\omega)\, F_\phi \\
&-\frac{\hbar}{6\pi}(1+P^{AB})\int_0^\infty d\omega\, \Big[T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, C^B_{\beta\gamma,\delta\varepsilon}(i\omega)\, T^{(3)}_{\delta\varepsilon\phi}(\underline{R})\, \alpha^A_{\phi\alpha}(i\omega) \\
&\qquad + \frac{2}{5}\, T^{(2)}_{\alpha\beta}(\underline{R})\, E^B_{\beta,\gamma\delta\varepsilon}(i\omega)\, T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R})\, \alpha^A_{\phi\alpha}(i\omega)\Big] \\
&-\frac{\hbar}{6\pi}(1+P^{AB})\int_0^\infty d\omega\, \Big[\frac{1}{2}\, T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, P^B_{\eta\lambda,\beta\gamma,\delta\varepsilon}(0,0,i\omega)\, T^{(3)}_{\delta\varepsilon\phi}(\underline{R})\, \alpha^A_{\phi\alpha}(i\omega) \\
&\qquad + \frac{1}{2}\, T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, C^B_{\beta\gamma,\delta\varepsilon}(i\omega)\, T^{(3)}_{\delta\varepsilon\phi}(\underline{R})\, \gamma^A_{\phi\alpha\eta\lambda}(i\omega,0,0) \\
&\qquad + \frac{1}{5}\, T^{(2)}_{\alpha\beta}(\underline{R})\, Q^B_{\beta\eta\lambda,\gamma\delta\varepsilon}(0,0,i\omega)\, T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R})\, \alpha^A_{\phi\alpha}(i\omega) \\
&\qquad + \frac{1}{5}\, T^{(2)}_{\alpha\beta}(\underline{R})\, E^B_{\beta,\gamma\delta\varepsilon}(i\omega)\, T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R})\, \gamma^A_{\phi\alpha\eta\lambda}(i\omega,0,0) \\
&\qquad - \frac{1}{3}\, T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, B^B_{\delta\eta,\beta\gamma}(0,i\omega)\, T^{(3)}_{\delta\varepsilon\phi}(\underline{R})\, B^A_{\alpha\lambda,\varepsilon\phi}(0,i\omega) \\
&\qquad - \frac{1}{3}\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^B_{\beta\eta,\gamma\delta}(0,i\omega)\, T^{(4)}_{\gamma\delta\varepsilon\phi}(\underline{R})\, B^A_{\alpha\lambda,\varepsilon\phi}(0,i\omega)\Big]\, F_\eta\, F_\lambda\ , \qquad (2.30)
\end{aligned}
$$

to second-order in $\underline{F}$ and to order R^{-8} in the intermolecular separation R.

(2.26), the dipole indices γ and δ are associated with the static field ($\omega = 0$) and the index ϵ with the frequency $i\omega$; in Eq. (2.27), the dipole index δ is associated with the static field and the quadrupole indices $\epsilon\gamma$ with the frequency $i\omega$; in Eq. (2.28), the dipole indices ϵ and ζ are associated with the static field and the quadrupole indices $\gamma\delta$ with the frequency $i\omega$; and in Eq. (2.29), the dipole indices ϵ and ϕ are associated with the static field and the octopole indices [illegible]

are subscripted [illegible]

The results of this section will be used in the next sections in determining expressions for the pair dipole and pair polarizability of interacting molecules.

B. van der Waals Pair Dipole

The van der Waals contribution to the dipole induced by the interaction of two molecules A and B is

$$\underline{\mu}^{AB}_{vdW} = - \frac{\partial \Delta E^{AB}}{\partial \underline{F}} \Bigg|_{\underline{F} = 0} \tag{2.31}$$

where ΔE^{AB} is the van der Waals interaction energy for the AB pair in the presence of a static, uniform, externally applied electric field $\underline{F}$. This energy was derived in the previous section and given by Eq. (2.25) for interacting molecules of unspecified symmetry; our attention will be restricted to the first two terms of that equation, which gives the van der Waals energy through order R^{-7}.

As in Section A, $\alpha_{\alpha\beta}(\underline{F},i\omega)$ and $A_{\alpha,\beta\gamma}(\underline{F},i\omega)$ can be expanded in Taylor series. To first-order in the applied field $\underline{F}$ these expansions for general noncentrosymmetric molecules are

$$\alpha_{\alpha\beta}(\underline{F},i\omega) = \alpha_{\alpha\beta}(i\omega) + \beta_{\alpha\beta\gamma}(i\omega,0)\, F_\gamma + \ldots \tag{2.32}$$

and

$$A_{\alpha,\beta\gamma}(\underline{F},i\omega) = A_{\alpha,\beta\gamma}(i\omega) + B_{\alpha\delta,\beta\gamma}(0,i\omega)\, F_\delta + \ldots , \tag{2.33}$$

where $\underline{\underline{\alpha}}(i\omega)$, $\underline{\underline{\beta}}(i\omega,0)$, $\underline{\underline{A}}(i\omega)$, and $\underline{\underline{B}}(0,i\omega)$ are the molecular response tensors in the absence of the applied field. These expansions differ from Eqs. (2.26) and (2.27) in that the latter equations are

specialized to centrosymmetric systems, for which $\underline{\underline{\beta}}$ and $\underline{\underline{A}}$ vanish. In Eq. (2.32), the dipole index γ is associated with the $(\omega = 0)$ static field and the index β with the frequency $i\omega$; in Eq. (2.33), the dipole index δ is associated with the static field and the quadrupole indices $\beta\gamma$ with the frequency $i\omega$. When these expansions are substituted into the first two terms of Eq. (2.25), application of Eq. (2.31) results in

$$\begin{aligned}\mu^{AB}_{\phi,\mathrm{vdW}} = \frac{\hbar}{2\pi} \int_0^\infty d\omega \, \Big[& T^{(2)}_{\alpha\beta}(\underline{R})\, \beta^B_{\beta\gamma\phi}(i\omega,0)\, T^{(2)}_{\gamma\delta}(\underline{R})\, \alpha^A_{\delta\alpha}(i\omega) \\ & + T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(2)}_{\gamma\delta}(\underline{R})\, \beta^A_{\delta\alpha\phi}(i\omega,0) \\ & - \frac{2}{3} T^{(2)}_{\alpha\beta}(\underline{R})\, B^B_{\beta\phi,\gamma\delta}(0,i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(i\omega) \\ & - \frac{2}{3} T^{(2)}_{\alpha\beta}(\underline{R})\, A^B_{\beta,\gamma\delta}(i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, \beta^A_{\varepsilon\alpha\phi}(i\omega,0) \\ & + \frac{2}{3} T^{(2)}_{\alpha\beta}(\underline{R})\, \beta^B_{\beta\gamma\phi}(i\omega,0)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, A^A_{\delta\varepsilon,\alpha}(i\omega) \\ & + \frac{2}{3} T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, B^A_{\alpha\phi,\delta\varepsilon}(0,i\omega) \Big] \end{aligned} \tag{2.34}$$

for the van der Waals contribution to the collision-induced dipole through order R^{-7}. This equation holds for any pair of molecules of arbitrary symmetry interacting at long range.

The molecular systems investigated in this dissertation possess centrosymmetric or greater symmetry. Then the tensors $\underline{\underline{A}}$ and $\underline{\underline{\beta}}$ vanish, and Eq. (2.34) simplifies to

$$\begin{aligned}\mu^{AB}_{\phi,\mathrm{vdW}} = \frac{\hbar}{3\pi} \int_0^\infty d\omega \, \Big[& T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, B^A_{\alpha\phi,\delta\varepsilon}(0,i\omega) \\ & - T^{(2)}_{\alpha\beta}(\underline{R})\, B^B_{\beta\phi,\gamma\delta}(0,i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(i\omega) \Big] \; . \end{aligned} \tag{2.35}$$

This equation provides the starting point for the anlayses in Chapter 3, where the van der Waals pair dipoles of some specific systems are studied.

C. van der Waals Pair Polarizability

The van der Waals contribution to the collision-induced polarizability of two molecules A and B interacting at long range is given by

$$\Delta\alpha^{AB}_{\alpha\beta,vdW} = - \left. \frac{\partial^2 \Delta E^{AB}}{\partial F_\alpha \partial F_\beta} \right|_{\underline{F} = 0} \tag{2.36}$$

where ΔE^{AB} is the van der Waals interaction energy for the AB pair in the presence of a static, uniform, externally applied electric field $\underline{F}$. Using Eq. (2.30) derived in Section A for ΔE^{AB} in Eq. (2.36) yields for the van der Waals polarizability of a pair of centrosymmetric molecules

$$\begin{aligned}
\Delta\alpha^{AB}_{\eta\lambda,vdW} = \frac{\hbar}{2\pi} (1 + P^{AB}) \int_0^\infty d\omega \, \Big[& T^{(2)}_{\alpha\beta}(\underline{R}) \, \gamma^{B}_{\beta\gamma\eta\lambda}(i\omega,0,0) \, T^{(2)}_{\gamma\delta}(\underline{R}) \, \alpha^{A}_{\delta\alpha}(i\omega) \\
& + \frac{1}{3} T^{(3)}_{\alpha\beta\gamma}(\underline{R}) \, P^{B}_{\eta\lambda,\beta\gamma,\delta\epsilon}(0,0,i\omega) \, T^{(3)}_{\delta\epsilon\phi}(\underline{R}) \, \alpha^{A}_{\phi\alpha}(i\omega) \\
& + \frac{1}{3} T^{(3)}_{\alpha\beta\gamma}(\underline{R}) \, C^{B}_{\beta\gamma,\delta\epsilon}(i\omega) \, T^{(3)}_{\delta\epsilon\phi}(\underline{R}) \, \gamma^{A}_{\phi\alpha\eta\lambda}(i\omega,0,0) \\
& + \frac{2}{15} T^{(2)}_{\alpha\beta}(\underline{R}) \, Q^{B}_{\beta\eta\lambda,\gamma\delta\epsilon}(0,0,i\omega) \, T^{(4)}_{\gamma\delta\epsilon\phi}(\underline{R}) \, \alpha^{A}_{\phi\alpha}(i\omega) \\
& + \frac{2}{15} T^{(2)}_{\alpha\beta}(\underline{R}) \, E^{B}_{\beta,\gamma\delta\epsilon}(i\omega) \, T^{(4)}_{\gamma\delta\epsilon\phi}(\underline{R}) \, \gamma^{A}_{\phi\alpha\eta\lambda}(i\omega,0,0) \\
& - \frac{2}{9} T^{(3)}_{\alpha\beta\gamma}(\underline{R}) \, B^{B}_{\delta\eta,\beta\gamma}(0,i\omega) \, T^{(3)}_{\delta\epsilon\phi}(\underline{R}) \, B^{A}_{\alpha\lambda,\epsilon\phi}(0,i\omega) \\
& - \frac{2}{9} T^{(2)}_{\alpha\beta}(\underline{R}) \, B^{B}_{\beta\eta,\gamma\delta}(0,i\omega) \, T^{(4)}_{\gamma\delta\epsilon\phi}(\underline{R}) \, B^{A}_{\alpha\lambda,\epsilon\phi}(0,i\omega) \Big] \; .
\end{aligned} \tag{2.37}$$

If A and B are both S state atoms, then the response tensors appearing in Eq. (2.37) are isotropic and can be expressed as weighted sums of Kronecker-delta products that satisfy the symmetry constraints for index contraction or interchange. Thus

$$\alpha_{\alpha\beta}(i\omega) = \alpha(i\omega)\,\delta_{\alpha\beta} \quad . \tag{2.38}$$

The quadrupole polarizability $C_{\alpha\beta,\gamma\delta}(i\omega)$ is unaffected by interchange of α with β or γ with δ, and $C_{\alpha\alpha,\gamma\delta}(i\omega) = C_{\alpha\beta,\gamma\gamma}(i\omega) = 0$; therefore

$$C_{\alpha\beta,\gamma\delta}(i\omega) = \frac{1}{6}\,C(i\omega)\left[3\,(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) - 2\,\delta_{\alpha\beta}\,\delta_{\gamma\delta}\right] . \tag{2.39}$$

The hyperpolarizability $B_{\alpha\beta,\gamma\delta}(0,i\omega)$ is unaffected by interchange of the quadrupole indices γ and δ, and $B_{\alpha\beta,\gamma\gamma}(0,i\omega) = 0$:

$$B_{\alpha\beta,\gamma\delta}(0,i\omega) = \frac{1}{4}\,B(0,i\omega)\left[3\,(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) - 2\,\delta_{\alpha\beta}\,\delta_{\gamma\delta}\right] . \tag{2.40}$$

The dipole-octopole polarizability $\underline{\underline{E}}$ vanishes for isotropic systems. The hyperpolarizability $\gamma_{\alpha\beta\gamma\delta}(i\omega,0,0)$ is symmetric upon interchange of α with β or γ with δ, but it is <u>not</u> symmetric under exchange of α with γ, α with δ, β with γ, or β with δ, <u>unless</u> the frequencies associated with these indices are also exchanged. This means that two independent constants are necessary to specify $\underline{\underline{\gamma}}(i\omega,0,0)$, when only one constant is needed to fix the static hyperpolarizability $\underline{\underline{\gamma}}(0,0,0)$. Thus

$$\begin{aligned}\gamma_{\alpha\beta\gamma\delta}(i\omega,0,0) &= \gamma_{xxzz}(i\omega,0,0)\,\delta_{\alpha\beta}\,\delta_{\gamma\delta} \\ &\quad + \frac{1}{2}\left[\gamma_{zzzz}(i\omega,0,0) - \gamma_{xxzz}(i\omega,0,0)\right](\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) \quad . \end{aligned} \tag{2.41}$$

The tensor $P_{\alpha\beta,\gamma\delta,\epsilon\phi}(0,0,i\omega)$ is symmetric with respect to interchange of α with β, γ with δ, ϵ with ϕ, and the pairs $\gamma\delta$ with $\epsilon\phi$. These constraints together with the contractions $P_{\alpha\beta,\gamma\gamma,\epsilon\phi}(0,0,i\omega) = P_{\alpha\beta,\gamma\delta,\epsilon\epsilon}(0,0,i\omega) = 0$ and the relation $P_{xx,yy,zz}(0,0,i\omega) = \frac{2}{9} P_{xx,yz,yz}(0,0,i\omega)$ imply

$$
\begin{aligned}
P_{\alpha\beta,\gamma\delta,\epsilon\phi}(0,0,i\omega) = \frac{2}{11} P(0,0,i\omega) \Big[& \frac{1}{6} \delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\phi} \\
& + \frac{3}{4} (\delta_{\alpha\beta} \delta_{\gamma\epsilon} \delta_{\delta\phi} + \delta_{\alpha\beta} \delta_{\gamma\phi} \delta_{\delta\epsilon}) \\
& - (\delta_{\alpha\gamma} \delta_{\beta\delta} \delta_{\epsilon\phi} + \delta_{\alpha\delta} \delta_{\beta\gamma} \delta_{\epsilon\phi} \\
& + \delta_{\alpha\epsilon} \delta_{\beta\phi} \delta_{\gamma\delta} + \delta_{\alpha\phi} \delta_{\beta\epsilon} \delta_{\gamma\delta}) \\
& + \frac{3}{4} (\delta_{\alpha\gamma} \delta_{\beta\epsilon} \delta_{\delta\phi} + \delta_{\alpha\gamma} \delta_{\beta\phi} \delta_{\delta\epsilon} \\
& + \delta_{\alpha\delta} \delta_{\beta\epsilon} \delta_{\gamma\phi} + \delta_{\alpha\delta} \delta_{\beta\phi} \delta_{\gamma\epsilon} \\
& + \delta_{\alpha\epsilon} \delta_{\beta\gamma} \delta_{\delta\phi} + \delta_{\alpha\epsilon} \delta_{\beta\delta} \delta_{\gamma\phi} \\
& + \delta_{\alpha\phi} \delta_{\beta\gamma} \delta_{\delta\epsilon} + \delta_{\alpha\phi} \delta_{\beta\delta} \delta_{\gamma\epsilon}) \Big] . \qquad (2.42)
\end{aligned}
$$

Lastly, $Q_{\alpha\beta\gamma,\delta\epsilon\phi}(0,0,i\omega)$ is unaffected by interchange of β with γ, or by exchange of δ, ϵ, and ϕ with each other. The tensor vanishes upon contraction of any pair of indices from the group δ, ϵ, and ϕ; therefore

$$
\begin{aligned}
Q_{\alpha\beta\gamma,\delta\epsilon\phi}(0,0,i\omega) = \frac{1}{12} Q(0,0,i\omega) \Big[& - 2 (\delta_{\alpha\beta} \delta_{\gamma\delta} \delta_{\epsilon\phi} \\
& + \delta_{\alpha\beta} \delta_{\gamma\epsilon} \delta_{\delta\phi} + \delta_{\alpha\beta} \delta_{\gamma\phi} \delta_{\delta\epsilon} \\
& + \delta_{\alpha\gamma} \delta_{\beta\delta} \delta_{\epsilon\phi} + \delta_{\alpha\gamma} \delta_{\beta\epsilon} \delta_{\delta\phi} \\
& + \delta_{\alpha\gamma} \delta_{\beta\phi} \delta_{\delta\epsilon} + \delta_{\alpha\delta} \delta_{\beta\gamma} \delta_{\epsilon\phi} \\
& + \delta_{\alpha\epsilon} \delta_{\beta\gamma} \delta_{\delta\phi} + \delta_{\alpha\phi} \delta_{\beta\gamma} \delta_{\delta\epsilon}) \\
& + 5 (\delta_{\alpha\delta} \delta_{\beta\epsilon} \delta_{\gamma\phi} + \delta_{\alpha\delta} \delta_{\beta\phi} \delta_{\gamma\epsilon} \\
& + \delta_{\alpha\epsilon} \delta_{\beta\delta} \delta_{\gamma\phi} + \delta_{\alpha\epsilon} \delta_{\beta\phi} \delta_{\gamma\delta}
\end{aligned}
$$

$$+ \delta_{\alpha\phi} \delta_{\beta\delta} \delta_{\gamma\epsilon} + \delta_{\alpha\phi} \delta_{\beta\epsilon} \delta_{\gamma\delta})] . \tag{2.43}$$

When Eqs. (2.38) - (2.43) are used in Eq. (2.37), together with the propagator products

$$T^{(2)}_{\alpha\beta} T^{(2)}_{\alpha\gamma} = (3 R_\beta R_\gamma + \delta_{\beta\gamma} R^2) R^{-8} , \tag{2.44}$$

$$T^{(3)}_{\alpha\beta\gamma} T^{(3)}_{\alpha\beta\delta} = (36 R_\gamma R_\delta + 18 \delta_{\gamma\delta} R^2) R^{-10} , \tag{2.45}$$

and

$$T^{(2)}_{\alpha\beta} T^{(4)}_{\alpha\beta\gamma\delta} = (108 R_\gamma R_\delta - 36 \delta_{\gamma\delta} R^2) R^{-10} , \tag{2.46}$$

the van der Waals contributions to the xx and zz components of the pair polarizability for a pair of S state atoms separated along the z axis by a distance R become

$$\begin{aligned}\Delta\alpha^{AB}_{xx,vdW} = {} & \frac{\hbar}{2\pi} (1+P^{AB})R^{-6} \int_0^\infty d\omega \, [5\gamma^B_{xxzz}(i\omega,0,0)+\gamma^B_{zzzz}(i\omega,0,0)] \, \alpha^A(i\omega) \\ & + \frac{\hbar}{\pi} (1+P^{AB})R^{-8} \int_0^\infty d\omega \, [[12\gamma^B_{xxzz}(i\omega,0,0)+3\gamma^B_{zzzz}(i\omega,0,0)] \, C^A(i\omega) \\ & \quad + \frac{81}{11} P^B(0,0,i\omega) \, \alpha^A(i\omega) - 6 \, \alpha^B(i\omega) \, Q^A(0,0,i\omega) \\ & \quad + \frac{9}{2} B^B(0,i\omega) \, B^A(0,i\omega)] , \end{aligned} \tag{2.47}$$

and

$$\Delta\alpha^{AB}_{zz,vdW} = \frac{\hbar}{2\pi}(1+P^{AB})R^{-6}\int_0^\infty d\omega\,[2\gamma^B_{xxzz}(i\omega,0,0)+4\gamma^B_{zzzz}(i\omega,0,0)]\,\alpha^A(i\omega)$$
$$+\frac{\hbar}{\pi}(1+P^{AB})R^{-8}\int_0^\infty d\omega\,\Big[[6\gamma^B_{xxzz}(i\omega,0,0)+9\gamma^B_{zzzz}(i\omega,0,0)]\,C^A(i\omega)$$
$$+\frac{153}{11}P^B(0,0,i\omega)\,\alpha^A(i\omega)+12\,\alpha^B(i\omega)\,Q^A(0,0,i\omega)$$
$$-\frac{63}{2}B^B(0,i\omega)\,B^A(0,i\omega)\Big]\;. \qquad (2.48)$$

These equations are identical through order R^{-6} to the expressions derived by Hunt, Zilles, and Bohr [49]. Eqs. (2.47) and (2.48) are thus equivalent to the results of two-center, fourth-order perturbation theory for $\Delta\alpha_{vdW}$ through order R^{-6} [62]. Although a proof has not yet been formulated, indications are that the R^{-8} terms are equivalent to the perturbation theory results as well.

The effects of field-induced fluctuation correlations are present at order R^{-6} in Eqs. (2.47) and (2.48), but become particularly clear at order R^{-8}. Specifically, the terms involving products of the dipole-quadrupole susceptibilities $B^A(0,i\omega)$ and $B^B(0,i\omega)$ cannot be interpreted as changes in the polarizability of atom A or atom B, nor can they be explained by earlier hyperpolarization models. These terms represent the concerted effect of the external field acting at the two centers. The external field induces a correlation between the fluctuating dipole and quadrupole of one atom, and combines with the fluctuating field of that atom to produce a net nonlinear polarization of the other atom.

CHAPTER 3. COLLISION-INDUCED VAN DER WAALS DIPOLES FOR SPECIFIC SYSTEMS

In Chapter 2, an expression was derived for the long-range van der Waals contribution to the dipole moment of two interacting molecules, using a new reaction field model which includes field-induced fluctuation correlations. This expression, specialized to molecules of centrosymmetric or greater symmetry, is given by Eq. (2.35). In the present chapter, Eq. (2.35) will be examined in detail for some specific systems. First, in Section A we consider the long-range van der Waals dipole for a pair of dissimilar S state atoms. Then, in Section B, the case of an S state atom interacting with a centrosymmetric linear molecule will be investigated. Section C covers the interaction of two centrosymmetric linear molecules. For the latter two systems, long-range induction also contributes to the collision-induced dipole, because a centrosymmetric linear molecule possesses nonzero permanent quadrupole and hexadecapole moments. These induction effects are also presented in Sections B and C.

A. van der Waals Dipole for a Heteroatom Pair

Consider two dissimilar S state atoms labeled A and B, separated by a distance R, with the vector $\underline{R}$ pointing from atom B to atom A. The dipole polarizability $\underline{\underline{\alpha}}(i\omega)$ and the dipole-quadrupole hyperpolarizability $\underline{\underline{B}}(0,i\omega)$ of an S state atom are isotropic tensors given by

$$\alpha_{\alpha\beta}(i\omega) = \alpha(i\omega)\,\delta_{\alpha\beta}\,, \tag{3.1}$$

and

$$B_{\alpha\beta,\gamma\delta}(0,i\omega) = B(0,i\omega)\left[\tfrac{3}{4}\left(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\right) - \tfrac{1}{2}\,\delta_{\alpha\beta}\delta_{\gamma\delta}\right] . \tag{3.2}$$

Substitution of Eqs. (3.1) and (3.2) into Eq. (2.35) leads to

$$\begin{aligned}\mu^{AB}_{\phi,\mathrm{vdW}} = \frac{\hbar}{2\pi}\int_0^\infty d\omega\,\Big[&T^{(2)}_{\alpha\gamma}(\underline{R})\;\alpha^B(i\omega)\;T^{(3)}_{\alpha\gamma\phi}(\underline{R})\;B^A(0,i\omega)\\ &- T^{(2)}_{\alpha\beta}(\underline{R})\;B^B(0,i\omega)\;T^{(3)}_{\alpha\beta\phi}(\underline{R})\;\alpha^A(i\omega)\Big] .\end{aligned} \tag{3.3}$$

The propagator products in the expression above take the form

$$T^{(2)}_{\alpha\beta}(\underline{R})\;T^{(3)}_{\alpha\beta\gamma}(\underline{R}) = -\,18\,R_\gamma\,R^{-8} . \tag{3.4}$$

Using Eq. (3.4) in Eq. (3.3), and specifying the interatomic separation R to be along the z axis ($R = R_z$ and $R_x = R_y = 0$) gives to order R^{-7}

$$\mu^{AB}_{z,\mathrm{vdW}} = \frac{9\hbar}{\pi}\,R^{-7}\int_0^\infty d\omega\,\left[\alpha^A(i\omega)\;B^B(0,i\omega) - B^A(0,i\omega)\;\alpha^B(i\omega)\right] . \tag{3.5}$$

This expression is shown in Appendix A to be equivalent to the results of Craig and Thirunamachandran [60] from two-center, third-order perturbation theory. From Eq. (3.5) the dipole moment coefficient D_7 is

$$D^{AB}_7 = \frac{9\hbar}{\pi}\int_0^\infty d\omega\,\left[\alpha^A(i\omega)\;B^B(0,i\omega) - B^A(0,i\omega)\;\alpha^B(i\omega)\right] . \tag{3.6}$$

B. van der Waals Dipole for an Atom and a Centrosymmetric Linear Molecule

Consider an S state atom A interacting at long range with a centrosymmetric linear molecule B. Define a vector $\underline{r}$ that lies along the symmetry axis of the molecule B (taken to be the z axis of a body fixed frame), and a vector $\underline{R}$ originating from the midpoint of molecule B and pointing to the nucleus of atom A; $\hat{r}$ and $\hat{R}$ are the corresponding unit vectors.

The dipole polarizability $\underline{\underline{\alpha}}(i\omega)$ of molecule B can be expressed in terms of the orientation of its symmetry axis with respect to the laboratory frame as [74]

$$\alpha_{\alpha\beta}(i\omega) = \alpha_{\perp}(i\omega)\,\delta_{\alpha\beta} + \left[\alpha_{\parallel}(i\omega) - \alpha_{\perp}(i\omega)\right]\hat{r}_{\alpha}\,\hat{r}_{\beta}\ , \qquad (3.7)$$

where $\hat{r}_{\alpha}$ is the direction cosine between the α axis of the laboratory frame and the symmetry axis of the molecular frame, and where the subscripts $_{\parallel}$ and $_{\perp}$ denote components along and at right angles to the symmetry axis:

$$\alpha_{\parallel}(i\omega) = \alpha_{zz}(i\omega)\ , \qquad (3.8)$$

and

$$\alpha_{\perp}(i\omega) = \alpha_{xx}(i\omega) = \alpha_{yy}(i\omega)\ . \qquad (3.9)$$

Similarly, the dipole-quadrupole hyperpolarizability $\underline{\underline{B}}(0,i\omega)$ of molecule B is

$$\begin{aligned}
B_{\alpha\beta,\gamma\delta}(0,i\omega) = \bar{B}(0,i\omega)\ &[\tfrac{3}{4}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) - \tfrac{1}{2}\delta_{\alpha\beta}\delta_{\gamma\delta}] \\
&+ B_{2a}(0,i\omega)\ (3\ \hat{r}_\alpha\hat{r}_\beta - \delta_{\alpha\beta})\ \delta_{\gamma\delta} \\
&+ B_{2b}(0,i\omega)\ (3\ \hat{r}_\gamma\hat{r}_\delta - \delta_{\gamma\delta})\ \delta_{\alpha\beta} \\
&+ B_{2c}(0,i\omega)\ [3\ \hat{r}_\alpha\hat{r}_\gamma - \delta_{\alpha\gamma})\ \delta_{\beta\delta} + (3\ \hat{r}_\alpha\hat{r}_\delta - \delta_{\alpha\delta})\ \delta_{\beta\gamma}] \\
&+ B_{2d}(0,i\omega)\ [3\ \hat{r}_\beta\hat{r}_\gamma - \delta_{\beta\gamma})\ \delta_{\alpha\delta} + (3\ \hat{r}_\beta\hat{r}_\delta - \delta_{\beta\delta})\ \delta_{\alpha\gamma}] \\
&+ B_4(0,i\omega)\ [35\ \hat{r}_\alpha\hat{r}_\beta\hat{r}_\gamma\hat{r}_\delta - 5\ (\hat{r}_\alpha\hat{r}_\beta\ \delta_{\gamma\delta} + \hat{r}_\alpha\hat{r}_\gamma\ \delta_{\beta\delta} \\
&\quad + \hat{r}_\alpha\hat{r}_\delta\ \delta_{\beta\gamma} + \hat{r}_\beta\hat{r}_\gamma\ \delta_{\alpha\delta} + \hat{r}_\beta\hat{r}_\delta\ \delta_{\alpha\gamma} \\
&\quad + \hat{r}_\gamma\hat{r}_\delta\ \delta_{\alpha\beta}) + \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}]\ ,
\end{aligned} \qquad (3.10)$$

where $\bar{B}$, B_{2a-d}, and B_4 are linear combinations of the five independent components of $\underline{\underline{B}}(0,i\omega)$ for molecule B:

$$\bar{B}(0,i\omega) = \frac{2}{15}\ (B_{zz,zz}+2B_{xz,xz}+2B_{zx,xz}+B_{xx,zz}+4B_{xx,xx})\ , \qquad (3.11)$$

$$B_{2a}(0,i\omega) = -\frac{2}{21}\ (B_{zz,zz}+B_{xz,xz}+B_{zx,xz}-3B_{xx,zz}-4B_{xx,xx})\ , \qquad (3.12)$$

$$B_{2b}(0,i\omega) = \frac{1}{42}\ (3B_{zz,zz}-4B_{xz,xz}-4B_{zx,xz}+26B_{xx,zz}+16B_{xx,xx})\ , \qquad (3.13)$$

$$B_{2c}(0,i\omega) = \frac{1}{42}\ (3B_{zz,zz}-4B_{xz,xz}+10B_{zx,xz}-9B_{xx,zz}-12B_{xx,xx})\ , \qquad (3.14)$$

$$B_{2d}(0,i\omega) = \frac{1}{42}\ (3B_{zz,zz}+10B_{xz,xz}-4B_{zx,xz}-9B_{xx,zz}-12B_{xx,xx})\ , \qquad (3.15)$$

and

$$B_4(0,i\omega) = \frac{1}{70} (3B_{zz,zz} - 4B_{xz,xz} - 4B_{zx,xz} - 2B_{xx,zz} + 2B_{xx,xx}) \; . \qquad (3.16)$$

Each tensor component $B_{\alpha\beta,\gamma\delta}$ on the right-hand side of Eqs. (3.11) - (3.16) is understood to represent $B_{\alpha\beta,\gamma\delta}(0,i\omega)$. The frequency-dependent B tensor lacks the symmetry of the static B tensor with respect to interchange of the two dipole indices, and so differs in form from the B tensor as given in Ref. [74]; it has one additional independent component. Appendix B provides a detailed analysis of the frequency-dependent B tensor for a linear molecule.

Use of Eqs. (3.1) and (3.2) for atom A and Eqs. (3.7) and (3.10) for molecule B in Eq. (2.35), together with the propagator products

$$T^{(2)}_{\alpha\beta}(\underline{R})\, T^{(3)}_{\alpha\beta\gamma}(\underline{R}) = -\,18\, R_\gamma\, R^{-8} \qquad (3.17)$$

and

$$\begin{aligned} T^{(2)}_{\alpha\beta}(\underline{R})\, T^{(3)}_{\alpha\gamma\delta}(\underline{R}) &= -\,12\, R_\beta R_\gamma R_\delta\, R^{-10} \\ &\quad + [6\, R_\beta \delta_{\gamma\delta} - 3\, R_\gamma \delta_{\beta\delta} - 3\, R_\delta \delta_{\beta\gamma}]\, R^{-8} \; , \end{aligned} \qquad (3.18)$$

and noting that $\hat{r}_\alpha \hat{r}_\alpha = 1$ leads to

$$\begin{aligned} \mu^{AB}_{\phi,\mathrm{vdW}} = \frac{\hbar}{\pi} \int_0^\infty d\omega\, [&-9\, \alpha^B_\perp(i\omega)\, B^A(0,i\omega)\, R_\phi\, R^{-8} \\ &- 2\, [\alpha^B_\parallel(i\omega) - \alpha^B_\perp(i\omega)]\, B^A(0,i\omega)\, \hat{r}_\alpha\, \hat{r}_\beta\, R_\alpha\, R_\beta\, R_\phi\, R^{-10} \\ &+ \frac{3}{2}\, [\alpha^B_\parallel(i\omega) - \alpha^B_\perp(i\omega)]\, B^A(0,i\omega)\, \hat{r}_\alpha\, \hat{r}_\phi\, R_\alpha\, R^{-8} \\ &- \frac{3}{2}\, [\alpha^B_\parallel(i\omega) - \alpha^B_\perp(i\omega)]\, B^A(0,i\omega)\, R_\phi\, R^{-8} \\ &+ 9\, \bar{B}^B(0,i\omega)\, \alpha^A(i\omega)\, R_\phi\, R^{-8} \end{aligned}$$

$$
\begin{aligned}
&+ 4\, B_{2b}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, (3\, \hat{r}_{\alpha}\, \hat{r}_{\beta} - \delta_{\alpha\beta})\, R_{\alpha}\, R_{\beta}\, R_{\phi}\, R^{-10} \\
&+ 2\, B_{2b}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, (3\, \hat{r}_{\alpha}\, \hat{r}_{\phi} - \delta_{\alpha\phi})\, R_{\alpha}\, R^{-8} \\
&+ 8\, B_{2c}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, (3\, \hat{r}_{\alpha}\, \hat{r}_{\beta} - \delta_{\alpha\beta})\, R_{\alpha}\, R_{\beta}\, R_{\phi}\, R^{-10} \\
&- 2\, B_{2c}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, (3\, \hat{r}_{\alpha}\, \hat{r}_{\phi} - \delta_{\alpha\phi})\, R_{\alpha}\, R^{-8} \\
&+ 12\, B_{2d}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, (3\, \hat{r}_{\alpha}\, \hat{r}_{\phi} - \delta_{\alpha\phi})\, R_{\alpha}\, R^{-8} \\
&+ 140\, B_{4}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, \hat{r}_{\alpha}\, \hat{r}_{\beta}\, \hat{r}_{\gamma}\, \hat{r}_{\phi}\, R_{\alpha}\, R_{\beta}\, R_{\gamma}\, R^{-10} \\
&- 60\, B_{4}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, \hat{r}_{\alpha}\, \hat{r}_{\beta}\, R_{\alpha}\, R_{\beta}\, R_{\phi}\, R^{-10} \\
&- 60\, B_{4}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, \hat{r}_{\alpha}\, \hat{r}_{\phi}\, R_{\alpha}\, R^{-8} \\
&+ 12\, B_{4}^{B}(0,i\omega)\, \alpha^{A}(i\omega)\, R_{\phi}\, R^{-8}] \qquad (3.19)
\end{aligned}
$$

for the van der Waals dipole moment to order R^{-7}.

The form of Eq. (3.19) is not convenient for analysis. Alternatively, the pair dipole for the interaction of an atom and a centrosymmetric linear molecule may be written as a first-rank spherical tensor by coupling spherical harmonic functions of $\hat{r}$ and $\hat{R}$ in the following way [9,16,78]:

$$
\mu_{M}(\underline{r},\underline{R}) = \frac{4\pi}{(3)^{1/2}} \sum_{\lambda,L,m} D_{\lambda L}(r,R)\, Y_{\lambda}^{m}(\hat{r})\, Y_{L}^{M-m}(\hat{R})\, C(\lambda L1;m,M-m) \;, \qquad (3.20)
$$

where $\underline{r}$ is the vector connecting the atoms of the diatomic molecule and $\underline{R}$ is the vector from the center of the diatomic to the atom, with $\hat{r}$ and $\hat{R}$ the corresponding unit vectors. The functions $D_{\lambda L}(r,R)$ are expansion coefficients which must be determined and $C(\lambda L1;m,M-m)$ is a Clebsch-Gordan coefficient; M is the spherical tensor index of $\underline{\mu}$ in the laboratory frame, and can take the values M = - 1, 0, 1 (the laboratory z axis corresponds to M = 0). Spectroscopic

lineshape analyses [16-18] for collision-induced absorption generally employ functions $\underline{\mu}$ of the form in Eq. (3.20).

We now wish to determine the van der Waals contribution to the $D_{\lambda L}$ coefficients. In so doing the focus will be on the dependence of these functions on the separation R, with r held fixed at its equilibrium or vibrationally averaged value. Let VDW_z designate the entire right hand side of Eq. (3.19) with $\phi = z$. Specifying the undetermined coefficients to be the long-range van der Waals contribution to the AB interaction dipole, and equating VDW_z to Eq. (3.20) with M = 0 we have

$$\frac{4\pi}{(3)^{1/2}} \sum_{\lambda,L,m} D^{vdW}_{\lambda L}(r,R)\; Y^m_\lambda(\hat{r})\; Y^{-m}_L(\hat{R})\; C(\lambda L1;m,-m) = VDW_z \tag{3.21}$$

or

$$\frac{4\pi}{(3)^{1/2}} D^{vdW}_{\lambda L}(r,R)\; C(\lambda L1;m,-m)$$
$$= \int d\Omega_r \int d\Omega_R \; VDW_z \left[Y^m_\lambda(\hat{r})\; Y^{-m}_L(\hat{R})\right]^* . \tag{3.22}$$

The factors that depend on $\hat{r}$ and $\hat{R}$ in VDW_z can be expanded in spherical harmonics; Appendix C presents the method. When these expansions are used in Eq. (3.22) the $D^{vdW}_{\lambda L}$ coefficients that survive are

$$D^{vdW}_{01} = 9\,\frac{\hbar}{\pi}\,R^{-7} \int_0^\infty d\omega\,\left[\alpha^A(i\omega)\;\bar{B}^B(0,i\omega) - B^A(0,i\omega)\;\bar{\alpha}^B(i\omega)\right] , \tag{3.23}$$

$$D^{vdW}_{21} = -\,\frac{3}{5(2)^{1/2}}\,\frac{\hbar}{\pi}\,R^{-7} \int_0^\infty d\omega$$

$$\times \left[4\, \alpha^A(i\omega)\, [3B^B_{2b}(0,i\omega) + B^B_{2c}(0,i\omega) + 10B^B_{2d}(0,i\omega)] - B^A(0,i\omega)\, [\alpha^B_{\parallel}(i\omega) - \alpha^B_{\perp}(i\omega)]\right] , \tag{3.24}$$

$$D^{vdW}_{23} = \frac{4(3)^{1/2}}{5} \frac{\hbar}{\pi} R^{-7} \int_0^\infty d\omega \left[2\, \alpha^A(i\omega)\, [B^B_{2b}(0,i\omega) + 2B^B_{2c}(0,i\omega)] - B^A(0,i\omega)\, [\alpha^B_{\parallel}(i\omega) - \alpha^B_{\perp}(i\omega)]\right] , \tag{3.25}$$

and

$$D^{vdW}_{43} = -\, 16 \frac{\hbar}{\pi} R^{-7} \int_0^\infty d\omega\, \alpha^A(i\omega)\, B^B_4(0,i\omega) . \tag{3.26}$$

In Eq. (3.23) we have introduced for the first time the isotropically averaged part of the molecular dipole polarizability, given by

$$\bar{\alpha}(i\omega) = \frac{1}{3} \left[\alpha_{\parallel}(i\omega) + 2\alpha_{\perp}(i\omega)\right] . \tag{3.27}$$

Because the molecule B has nonvanishing permanent quadrupole and hexadecapole moments, induction effects also contribute to the long-range dipole of the AB pair. The permanent multipoles of B produce a field that polarizes A, and the moments induced in A give rise to a static reaction field that acts back at B (back-induction). The induction dipole that results from these effects can be expressed to order R^{-7} as

$$\mu^{AB}_{\alpha,ind} = -\, \frac{1}{3}\, \alpha^A\, T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, \Theta^B_{\beta\gamma} - \frac{1}{105}\, \alpha^A\, T^{(5)}_{\alpha\beta\gamma\delta\varepsilon}(\underline{R})\, \Phi^B_{\beta\gamma\delta\varepsilon}$$

$$- \frac{1}{3} \alpha_{\perp}^{B} T_{\alpha\beta}^{(2)}(\underline{R}) \alpha^{A} T_{\beta\gamma\delta}^{(3)}(\underline{R}) \Theta_{\gamma\delta}^{B}$$
$$- \frac{1}{3} [\alpha_{//}^{B} - \alpha_{\perp}^{B}] T_{\beta\gamma}^{(2)}(\underline{R}) \alpha^{A} T_{\gamma\delta\varepsilon}^{(3)}(\underline{R}) \Theta_{\delta\varepsilon}^{B} \hat{r}_{\alpha} \hat{r}_{\beta} . \qquad (3.28)$$

The quadrupole and hexadecapole moments of B appearing in Eq. (3.28) can be written as [74]

$$\Theta_{\alpha\beta} = \frac{1}{2} \Theta (3 \hat{r}_{\alpha} \hat{r}_{\beta} - \delta_{\alpha\beta}) , \qquad (3.29)$$

and

$$\begin{aligned} \Phi_{\alpha\beta\gamma\delta} = \frac{1}{24} \Phi \big[& 105 \hat{r}_{\alpha} \hat{r}_{\beta} \hat{r}_{\gamma} \hat{r}_{\delta} \\ & - 15 (\hat{r}_{\alpha} \hat{r}_{\beta} \delta_{\gamma\delta} + \hat{r}_{\alpha} \hat{r}_{\gamma} \delta_{\beta\delta} + \hat{r}_{\alpha} \hat{r}_{\delta} \delta_{\beta\gamma} \\ & + \hat{r}_{\beta} \hat{r}_{\gamma} \delta_{\alpha\delta} + \hat{r}_{\beta} \hat{r}_{\delta} \delta_{\alpha\gamma} + \hat{r}_{\gamma} \hat{r}_{\delta} \delta_{\alpha\beta}) \\ & + 3 (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \big] , \end{aligned} \qquad (3.30)$$

where the center of symmetry of the B molecule is taken as the origin for the charge moments, with $\Theta = \Theta_{zz}$ and $\Phi = \Phi_{zzzz}$.

Using Eqs. (3.29) and (3.30) in Eq. (3.28) gives

$$\begin{aligned} \mu_{\alpha,ind}^{AB} = & - \frac{1}{2} \alpha^{A} T_{\alpha\beta\gamma}^{(3)}(\underline{R}) \Theta^{B} \hat{r}_{\beta} \hat{r}_{\gamma} \\ & - \frac{1}{24} \alpha^{A} T_{\alpha\beta\gamma\delta\varepsilon}^{(5)}(\underline{R}) \Phi^{B} \hat{r}_{\beta} \hat{r}_{\gamma} \hat{r}_{\delta} \hat{r}_{\varepsilon} \\ & - \frac{1}{2} \alpha_{\perp}^{B} T_{\alpha\beta}^{(2)}(\underline{R}) \alpha^{A} T_{\beta\gamma\delta}^{(3)}(\underline{R}) \Theta^{B} \hat{r}_{\gamma} \hat{r}_{\delta} \\ & - \frac{1}{2} [\alpha_{\parallel}^{B} - \alpha_{\perp}^{B}] T_{\beta\gamma}^{(2)}(\underline{R}) \alpha^{A} T_{\gamma\delta\varepsilon}^{(3)}(\underline{R}) \Theta^{B} \hat{r}_{\alpha} \hat{r}_{\beta} \hat{r}_{\delta} \hat{r}_{\varepsilon} . \end{aligned} \qquad (3.31)$$

The propagator tensors and tensor products appearing in the above equation are given by

$$T^{(3)}_{\alpha\beta\gamma}(\underline{R}) = [- 15\ R_\alpha R_\beta R_\gamma$$
$$+ 3\ (R_\alpha\ \delta_{\beta\gamma} + R_\beta\ \delta_{\alpha\gamma} + R_\gamma\ \delta_{\alpha\beta})\ R^2]\ R^{-7}\ , \qquad (3.32)$$

$$T^{(5)}_{\alpha\beta\gamma\delta\varepsilon}(\underline{R}) = [- 945\ R_\alpha R_\beta R_\gamma R_\delta R_\varepsilon$$
$$+ 105\ (R_\alpha R_\beta R_\gamma\ \delta_{\delta\varepsilon} + R_\alpha R_\beta R_\delta\ \delta_{\gamma\varepsilon} + R_\alpha R_\beta R_\varepsilon\ \delta_{\gamma\delta}$$
$$+ R_\alpha R_\gamma R_\delta\ \delta_{\beta\varepsilon} + R_\alpha R_\gamma R_\varepsilon\ \delta_{\beta\delta} + R_\alpha R_\delta R_\varepsilon\ \delta_{\beta\gamma}$$
$$+ R_\beta R_\gamma R_\delta\ \delta_{\alpha\varepsilon} + R_\beta R_\gamma R_\varepsilon\ \delta_{\alpha\delta} + R_\beta R_\delta R_\varepsilon\ \delta_{\alpha\gamma}$$
$$+ R_\gamma R_\delta R_\varepsilon\ \delta_{\alpha\beta})\ R^2$$
$$- 15\ (R_\alpha\ \delta_{\beta\gamma}\ \delta_{\delta\varepsilon} + R_\alpha\ \delta_{\beta\delta}\ \delta_{\gamma\varepsilon} + R_\alpha\ \delta_{\beta\varepsilon}\ \delta_{\gamma\delta}$$
$$+ R_\beta\ \delta_{\alpha\gamma}\ \delta_{\delta\varepsilon} + R_\beta\ \delta_{\alpha\delta}\ \delta_{\gamma\varepsilon} + R_\beta\ \delta_{\alpha\varepsilon}\ \delta_{\gamma\delta}$$
$$+ R_\gamma\ \delta_{\alpha\beta}\ \delta_{\delta\varepsilon} + R_\gamma\ \delta_{\alpha\delta}\ \delta_{\beta\varepsilon} + R_\gamma\ \delta_{\alpha\varepsilon}\ \delta_{\beta\delta}$$
$$+ R_\delta\ \delta_{\alpha\beta}\ \delta_{\gamma\varepsilon} + R_\delta\ \delta_{\alpha\gamma}\ \delta_{\beta\varepsilon} + R_\delta\ \delta_{\alpha\varepsilon}\ \delta_{\beta\gamma}$$
$$+ R_\varepsilon\ \delta_{\alpha\beta}\ \delta_{\gamma\delta} + R_\varepsilon\ \delta_{\alpha\gamma}\ \delta_{\beta\delta} + R_\varepsilon\ \delta_{\alpha\delta}\ \delta_{\beta\gamma})\ R^4]\ R^{-11}\ , \qquad (3.33)$$

and

$$T^{(2)}_{\alpha\beta}(\underline{R})\ T^{(3)}_{\beta\gamma\delta}(\underline{R}) = [- 12\ R_\alpha R_\gamma R_\delta$$
$$+ (6\ R_\alpha\ \delta_{\gamma\delta} - 3\ R_\gamma\ \delta_{\alpha\delta} - 3\ R_\delta\ \delta_{\alpha\gamma})\ R^2]\ R^{-10}\ . \qquad (3.34)$$

Substitution of Eqs. (3.32) - (3.34) into Eq. (3.31) leads to

$$\mu^{AB}_{\alpha,\mathrm{ind}} = \frac{15}{2}\ \alpha^A\ \Theta^B\ \hat{r}_\beta\ \hat{r}_\gamma\ R_\alpha\ R_\beta\ R_\gamma\ R^{-7}$$
$$- 3\ \alpha^A\ \Theta^B\ \hat{r}_\alpha\ \hat{r}_\beta\ R_\beta\ R^{-5}$$
$$- \frac{3}{2}\ \alpha^A\ \Theta^B\ R_\alpha\ R^{-5}$$
$$+ \frac{315}{8}\ \alpha^A\ \Phi^B\ \hat{r}_\beta\ \hat{r}_\gamma\ \hat{r}_\delta\ \hat{r}_\varepsilon\ R_\alpha\ R_\beta\ R_\gamma\ R_\delta\ R_\varepsilon\ R^{-11}$$
$$- \frac{35}{2}\ \alpha^A\ \Phi^B\ \hat{r}_\alpha\ \hat{r}_\beta\ \hat{r}_\gamma\ \hat{r}_\delta\ R_\beta\ R_\gamma\ R_\delta\ R^{-9}$$
$$- \frac{105}{4}\ \alpha^A\ \Phi^B\ \hat{r}_\beta\ \hat{r}_\gamma\ R_\alpha\ R_\beta\ R_\gamma\ R^{-9}$$

$$+ \frac{15}{2} \alpha^A \Phi^B \hat{r}_\alpha \hat{r}_\beta R_\beta R^{-7}$$
$$+ \frac{15}{8} \alpha^A \Phi^B R_\alpha R^{-7}$$
$$+ 6 \alpha_\perp^B \alpha^A \Theta^B \hat{r}_\beta \hat{r}_\gamma R_\alpha R_\beta R_\gamma R^{-10}$$
$$+ 3 \alpha_\perp^B \alpha^A \Theta^B \hat{r}_\alpha \hat{r}_\beta R_\beta R^{-8}$$
$$- 3 \alpha_\perp^B \alpha^A \Theta^B R_\alpha R^{-8}$$
$$+ 6 [\alpha_{||}^B - \alpha_\perp^B] \alpha^A \Theta^B \hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma \hat{r}_\delta R_\beta R_\gamma R_\delta R^{-10} \qquad (3.35)$$

for the induction contribution to the dipole moment to order R^{-7}.

The induction contribution can also be expressed in terms of spherical harmonics, as in Eq. (3.20). Let IND_z denote the right-hand side of Eq. (3.35) with $\alpha = z$. In direct analogy with Eq. (3.22) we can write

$$\frac{4\pi}{(3)^{1/2}} D_{\lambda L}^{ind}(r,R)\ C(\lambda L1;m,-m)$$
$$= \int d\Omega_r \int d\Omega_R\ IND_z \left[Y_\lambda^m(\hat{r})\ Y_L^{-m}(\hat{R})\right]^* , \qquad (3.36)$$

where the $D_{\lambda L}^{ind}$ coefficients need to be determined. When IND_z is expanded in spherical harmonics (see Appendix C), use of Eq. (3.36) gives for the induction coefficients to order R^{-7}:

$$D_{01}^{ind} = \frac{6}{5} [\alpha_{||}^B - \alpha_\perp^B] \alpha^A \Theta^B R^{-7} , \qquad (3.37)$$

$$D_{21}^{ind} = - \frac{3}{5} (2)^{1/2} [2\alpha_{||}^B + \alpha_\perp^B] \alpha^A \Theta^B R^{-7} , \qquad (3.38)$$

$$D_{23}^{ind} = (3)^{1/2} \alpha^A \Theta^B R^{-4} + \frac{4}{35} (3)^{1/2} [3\alpha_{||}^B + 4\alpha_\perp^B] \alpha^A \Theta^B R^{-7} , \qquad (3.39)$$

$$D_{43}^{ind} = -\frac{24}{35}\,[\alpha_{||}^{B} - \alpha_{\perp}^{B}]\,\alpha^{A}\,\Theta^{B}\,R^{-7}\,, \qquad (3.40)$$

and

$$D_{45}^{ind} = (5)^{1/2}\,\alpha^{A}\,\Phi^{B}\,R^{-6}\,. \qquad (3.41)$$

The polarizabilities α^{A}, $\alpha_{||}^{B}$, and $\alpha_{\perp}^{B}$ in Eqs. (3.37) - (3.41) refer to the static, zero-frequency values. Adding the van der Waals coefficients in Eqs. (3.23) - (3.26) to the corresponding induction coefficients from Eqs. (3.37) - (3.41) gives the exact long-range dipole coefficients through order R^{-7} for an S state atom interacting with a centrosymmetric linear molecule in a fixed configuration.

C. van der Waals Dipole for a Pair of Centrosymmetric Linear Molecules

Consider the interaction between two centrosymmetric linear molecules A and B. Let $\underline{r}_1$ denote the vector that lies along the symmetry axis of molecule A, and let $\underline{r}_2$ be the vector that lies along the symmetry axis of the B molecule. Let $\underline{R}$ be the vector from the midpoint of B to the midpoint of A. The dipole polarizability $\underline{\underline{\alpha}}$ and the dipole-quadrupole hyperpolarizability $\underline{\underline{B}}$ for a centrosymmetric linear molecule have been given in Section B by Eqs. (3.7) and (3.10). First using Eq. (3.10) for both A and B in Eq. (2.35) results in

$$
\begin{aligned}
\mu^{AB}_{\phi,vdW} = \frac{\hbar}{3\pi}\int_0^\infty d\omega\, \Big[& \frac{3}{2}\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\alpha\gamma\phi}(\underline{R})\, \bar{B}^A(0,i\omega) \\
& + T^{(2)}_{\beta\phi}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, B^A_{2b}(0,i\omega)\, (3\,\hat{r}_{1\delta}\,\hat{r}_{1\varepsilon} - \delta_{\delta\varepsilon}) \\
& + 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\gamma\delta\phi}(\underline{R})\, B^A_{2c}(0,i\omega)\, (3\,\hat{r}_{1\alpha}\,\hat{r}_{1\delta} - \delta_{\alpha\delta}) \\
& + 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\alpha\gamma\delta}(\underline{R})\, B^A_{2d}(0,i\omega)\, (3\,\hat{r}_{1\delta}\,\hat{r}_{1\phi} - \delta_{\delta\phi}) \\
& + 35\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, B^A_4(0,i\omega)\, \hat{r}_{1\alpha}\,\hat{r}_{1\delta}\,\hat{r}_{1\varepsilon}\,\hat{r}_{1\phi} \\
& - 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\gamma\delta\phi}(\underline{R})\, B^A_4(0,i\omega)\, \hat{r}_{1\alpha}\,\hat{r}_{1\delta} \\
& - 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\alpha\gamma\delta}(\underline{R})\, B^A_4(0,i\omega)\, \hat{r}_{1\delta}\,\hat{r}_{1\phi} \\
& - 5\, T^{(2)}_{\beta\phi}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, B^A_4(0,i\omega)\, \hat{r}_{1\delta}\,\hat{r}_{1\varepsilon} \\
& + 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^B_{\beta\gamma}(i\omega)\, T^{(3)}_{\alpha\gamma\phi}(\underline{R})\, B^A_4(0,i\omega) \\
& - \frac{3}{2}\, T^{(2)}_{\alpha\beta}(\underline{R})\, \bar{B}^B(0,i\omega)\, T^{(3)}_{\beta\varepsilon\phi}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(i\omega) \\
& - T^{(2)}_{\alpha\phi}(\underline{R})\, B^B_{2b}(0,i\omega)\, (3\,\hat{r}_{2\gamma}\,\hat{r}_{2\delta} - \delta_{\gamma\delta})\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(i\omega) \\
& - 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^B_{2c}(0,i\omega)\, (3\,\hat{r}_{2\beta}\,\hat{r}_{2\gamma} - \delta_{\beta\gamma})\, T^{(3)}_{\gamma\varepsilon\phi}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(i\omega) \\
& - 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^B_{2d}(0,i\omega)\, (3\,\hat{r}_{2\phi}\,\hat{r}_{2\gamma} - \delta_{\phi\gamma})\, T^{(3)}_{\beta\gamma\varepsilon}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(i\omega) \\
& - 35\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^B_4(0,i\omega)\, \hat{r}_{2\beta}\,\hat{r}_{2\gamma}\,\hat{r}_{2\delta}\,\hat{r}_{2\phi}\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, \alpha^A_{\varepsilon\alpha}(i\omega)
\end{aligned}
$$

$$+ 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\beta}\, \hat{r}_{2\gamma}\, T^{(3)}_{\gamma\varepsilon\phi}(\underline{R})\, \alpha^{A}_{\varepsilon\alpha}(i\omega)$$
$$+ 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\gamma}\, \hat{r}_{2\phi}\, T^{(3)}_{\beta\gamma\varepsilon}(\underline{R})\, \alpha^{A}_{\varepsilon\alpha}(i\omega)$$
$$+ 5\, T^{(2)}_{\alpha\phi}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\gamma}\, \hat{r}_{2\delta}\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, \alpha^{A}_{\varepsilon\alpha}(i\omega)$$
$$- 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, T^{(3)}_{\beta\varepsilon\phi}(\underline{R})\, \alpha^{A}_{\varepsilon\alpha}(i\omega)] \;. \qquad (3.42)$$

Next, using Eq. (3.7) in Eq. (3.42) leads to

$$\mu^{AB}_{\phi,\mathrm{vdW}} = \frac{\hbar}{3\pi} \int_0^\infty d\omega\, [\frac{3}{2}\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\alpha\beta\phi}(\underline{R})\, \bar{B}^{A}(0,i\omega)$$
$$+ \frac{3}{2}\, T^{(2)}_{\alpha\beta}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\alpha\gamma\phi}(\underline{R})\, \bar{B}^{A}(0,i\omega)\, \hat{r}_{2\beta}\hat{r}_{2\gamma}$$
$$+ T^{(2)}_{\beta\phi}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\beta\delta\varepsilon}(\underline{R})\, B^{A}_{2b}(0,i\omega)\, (3\, \hat{r}_{1\delta}\hat{r}_{1\varepsilon} - \delta_{\delta\varepsilon})$$
$$+ T^{(2)}_{\beta\phi}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, B^{A}_{2b}(0,i\omega)$$
$$\times (3\, \hat{r}_{1\delta}\hat{r}_{1\varepsilon} - \delta_{\delta\varepsilon})\, \hat{r}_{2\beta}\hat{r}_{2\gamma}$$
$$+ 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\beta\delta\phi}(\underline{R})\, B^{A}_{2c}(0,i\omega)\, (3\, \hat{r}_{1\alpha}\hat{r}_{1\delta} - \delta_{\alpha\delta})$$
$$+ 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\gamma\delta\phi}(\underline{R})\, B^{A}_{2c}(0,i\omega)$$
$$\times (3\, \hat{r}_{1\alpha}\hat{r}_{1\delta} - \delta_{\alpha\delta})\, \hat{r}_{2\beta}\hat{r}_{2\gamma}$$
$$+ 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\alpha\beta\delta}(\underline{R})\, B^{A}_{2d}(0,i\omega)\, (3\, \hat{r}_{1\delta}\hat{r}_{1\phi} - \delta_{\delta\phi})$$
$$+ 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\alpha\gamma\delta}(\underline{R})\, B^{A}_{2d}(0,i\omega)$$
$$\times (3\, \hat{r}_{1\delta}\hat{r}_{1\phi} - \delta_{\delta\phi})\, \hat{r}_{2\beta}\hat{r}_{2\gamma}$$
$$+ 35\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\beta\delta\varepsilon}(\underline{R})\, B^{A}_{4}(0,i\omega)\, \hat{r}_{1\alpha}\hat{r}_{1\delta}\hat{r}_{1\varepsilon}\hat{r}_{1\phi}$$
$$+ 35\, T^{(2)}_{\alpha\beta}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, B^{A}_{4}(0,i\omega)$$
$$\times \hat{r}_{1\alpha}\hat{r}_{1\delta}\hat{r}_{1\varepsilon}\hat{r}_{1\phi}\hat{r}_{2\beta}\hat{r}_{2\gamma}$$
$$- 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\beta\delta\phi}(\underline{R})\, B^{A}_{4}(0,i\omega)\, \hat{r}_{1\alpha}\hat{r}_{1\delta}$$
$$- 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\gamma\delta\phi}(\underline{R})\, B^{A}_{4}(0,i\omega)\, \hat{r}_{1\alpha}\hat{r}_{1\delta}\hat{r}_{2\beta}\hat{r}_{2\gamma}$$
$$- 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\alpha\beta\delta}(\underline{R})\, B^{A}_{4}(0,i\omega)\, \hat{r}_{1\delta}\hat{r}_{1\phi}$$
$$- 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\alpha\gamma\delta}(\underline{R})\, B^{A}_{4}(0,i\omega)\, \hat{r}_{1\delta}\hat{r}_{1\phi}\hat{r}_{2\beta}\hat{r}_{2\gamma}$$
$$- 5\, T^{(2)}_{\beta\phi}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\beta\delta\varepsilon}(\underline{R})\, B^{A}_{4}(0,i\omega)\, \hat{r}_{1\delta}\hat{r}_{1\varepsilon}$$
$$- 5\, T^{(2)}_{\beta\phi}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R})\, B^{A}_{4}(0,i\omega)\, \hat{r}_{1\delta}\hat{r}_{1\varepsilon}\hat{r}_{2\beta}\hat{r}_{2\gamma}$$

$$
\begin{aligned}
&+ 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, \alpha^{B}_{\perp}(i\omega)\, T^{(3)}_{\alpha\beta\phi}(\underline{R})\, B^{A}_{4}(0,i\omega) \\
&+ 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, [\alpha^{B}_{\parallel}(i\omega) - \alpha^{B}_{\perp}(i\omega)]\, T^{(3)}_{\alpha\gamma\phi}(\underline{R})\, B^{A}_{4}(0,i\omega)\, \hat{r}_{2\beta}\hat{r}_{2\gamma} \\
&- \frac{3}{2}\, T^{(2)}_{\alpha\beta}(\underline{R})\, \bar{B}^{B}(0,i\omega)\, T^{(3)}_{\alpha\beta\phi}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&- \frac{3}{2}\, T^{(2)}_{\alpha\beta}(\underline{R})\, \bar{B}^{B}(0,i\omega)\, T^{(3)}_{\beta\epsilon\phi}(\underline{R})\, [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon} \\
&- T^{(2)}_{\alpha\phi}(\underline{R})\, B^{B}_{2b}(0,i\omega)\, (3\, \hat{r}_{2\gamma}\hat{r}_{2\delta} - \delta_{\gamma\delta})\, T^{(3)}_{\alpha\gamma\delta}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&- T^{(2)}_{\alpha\phi}(\underline{R})\, B^{B}_{2b}(0,i\omega)\, (3\, \hat{r}_{2\gamma}\hat{r}_{2\delta} - \delta_{\gamma\delta})\, T^{(3)}_{\gamma\delta\epsilon}(\underline{R}) \\
&\qquad \times [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon} \\
&- 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{2c}(0,i\omega)\, (3\, \hat{r}_{2\beta}\hat{r}_{2\gamma} - \delta_{\beta\gamma})\, T^{(3)}_{\alpha\gamma\phi}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&- 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{2c}(0,i\omega)\, (3\, \hat{r}_{2\beta}\hat{r}_{2\gamma} - \delta_{\beta\gamma})\, T^{(3)}_{\gamma\epsilon\phi}(\underline{R}) \\
&\qquad \times [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon} \\
&- 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{2d}(0,i\omega)\, (3\, \hat{r}_{2\phi}\hat{r}_{2\gamma} - \delta_{\phi\gamma})\, T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&- 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{2d}(0,i\omega)\, (3\, \hat{r}_{2\phi}\hat{r}_{2\gamma} - \delta_{\phi\gamma})\, T^{(3)}_{\beta\gamma\epsilon}(\underline{R}) \\
&\qquad \times [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon} \\
&- 35\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{2\phi}\, T^{(3)}_{\alpha\gamma\delta}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&- 35\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{2\phi}\, T^{(3)}_{\gamma\delta\epsilon}(\underline{R}) \\
&\qquad \times [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon} \\
&+ 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\beta}\hat{r}_{2\gamma}\, T^{(3)}_{\alpha\gamma\phi}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&+ 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\beta}\hat{r}_{2\gamma}\, T^{(3)}_{\gamma\epsilon\phi}(\underline{R})\, [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon} \\
&+ 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\gamma}\hat{r}_{2\phi}\, T^{(3)}_{\alpha\beta\gamma}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&+ 10\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\gamma}\hat{r}_{2\phi}\, T^{(3)}_{\beta\gamma\epsilon}(\underline{R})\, [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon} \\
&+ 5\, T^{(2)}_{\alpha\phi}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\gamma}\hat{r}_{2\delta}\, T^{(3)}_{\alpha\gamma\delta}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&+ 5\, T^{(2)}_{\alpha\phi}(\underline{R})\, B^{B}_{4}(0,i\omega)\, \hat{r}_{2\gamma}\hat{r}_{2\delta}\, T^{(3)}_{\gamma\delta\epsilon}(\underline{R})\, [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon} \\
&- 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, T^{(3)}_{\alpha\beta\phi}(\underline{R})\, \alpha^{A}_{\perp}(i\omega) \\
&- 2\, T^{(2)}_{\alpha\beta}(\underline{R})\, B^{B}_{4}(0,i\omega)\, T^{(3)}_{\beta\epsilon\phi}(\underline{R})\, [\alpha^{A}_{\parallel}(i\omega) - \alpha^{A}_{\perp}(i\omega)]\, \hat{r}_{1\alpha}\hat{r}_{1\epsilon}\Big] \ . \qquad (3.43)
\end{aligned}
$$

The propagator products in the above expression take the forms:

$$T^{(2)}_{\alpha\beta}(\underline{R})\, T^{(3)}_{\alpha\beta\gamma}(\underline{R}) = -\,18\, R_\gamma\, R^{-8} \,, \tag{3.44}$$

$$\begin{aligned} T^{(2)}_{\alpha\beta}(\underline{R})\, T^{(3)}_{\alpha\gamma\delta}(\underline{R}) &= -\,12\, R_\beta\, R_\gamma\, R_\delta\, R^{-10} \\ &\quad + [6\, R_\beta\, \delta_{\gamma\delta} - 3\, R_\gamma\, \delta_{\beta\delta} - 3\, R_\delta\, \delta_{\beta\gamma}]\, R^{-8} \,, \end{aligned} \tag{3.45}$$

and

$$\begin{aligned} T^{(2)}_{\alpha\beta}(R)\, T^{(3)}_{\gamma\delta\varepsilon}(\underline{R}) &= -\,45\, R_\alpha\, R_\beta\, R_\gamma\, R_\delta\, R_\varepsilon\, R^{-12} \\ &\quad + [15\, R_\gamma\, R_\delta\, R_\varepsilon\, \delta_{\alpha\beta} + 9\, R_\alpha\, R_\beta\, R_\gamma\, \delta_{\delta\varepsilon} \\ &\qquad + 9\, R_\alpha\, R_\beta\, R_\delta\, \delta_{\gamma\varepsilon} + 9\, R_\alpha\, R_\beta\, R_\varepsilon\, \delta_{\gamma\delta}]\, R^{-10} \\ &\quad - [3\, R_\gamma\, \delta_{\alpha\beta}\delta_{\delta\varepsilon} + 3\, R_\delta\, \delta_{\alpha\beta}\delta_{\gamma\varepsilon} + 3\, R_\varepsilon\, \delta_{\alpha\beta}\delta_{\gamma\delta}]\, R^{-8} \,. \end{aligned} \tag{3.46}$$

Using Eqs. (3.44) - (3.46) in Eq. (3.43) and noting that $\hat{r}_{1\alpha}\hat{r}_{1\alpha} = \hat{r}_{2\alpha}\hat{r}_{2\alpha} = 1$ gives as the van der Waals dipole for this system

$$\begin{aligned} \mu^{AB}_{\phi,\mathrm{vdW}} &= \frac{\hbar}{\pi} \int_0^\infty d\omega\, [6\, \{\alpha^B_\perp B^A_{2b} + \bar{\alpha}^B\, B^A_{2c}\}\, R_\phi\, R^{-8} \\ &\quad - [\alpha^B_{\parallel} + 5\alpha^B_\perp]\, [\tfrac{3}{2}\, \bar{B}^A - 2\, B^A_{2d} + 2\, B^A_4]\, R_\phi\, R^{-8} \\ &\quad - 6\, \{B^B_{2b}\, \alpha^A_\perp + B^B_{2c}\, \bar{\alpha}^A\}\, R_\phi\, R^{-8} \\ &\quad + [\tfrac{3}{2}\, \bar{B}^B - 2\, B^B_{2d} + 2\, B^B_4]\, [\alpha^A_{\parallel} + 5\alpha^A_\perp]\, R_\phi\, R^{-8} \\ &\quad - 6\, \alpha^B_\perp\, [B^A_{2b} - B^A_{2c}]\, \hat{r}_{1\alpha}\hat{r}_{1\phi} R_\alpha\, R^{-8} \\ &\quad - 2\, [\alpha^B_{\parallel} + 5\alpha^B_\perp]\, [3\, B^A_{2d} - 5\, B^A_4]\, \hat{r}_{1\alpha}\hat{r}_{1\phi} R_\alpha\, R^{-8} \\ &\quad + [\alpha^B_{\parallel} - \alpha^B_\perp]\, [\tfrac{3}{2}\, \bar{B}^A - 3\, B^A_{2b} - 2\, B^A_{2c} - 2\, B^A_{2d} + 7\, B^A_4] \\ &\qquad \times \hat{r}_{2\alpha}\hat{r}_{2\phi} R_\alpha\, R^{-8} \\ &\quad - [\tfrac{3}{2}\, \bar{B}^B - 3\, B^B_{2b} - 2\, B^B_{2c} - 2\, B^B_{2d} + 7\, B^B_4]\, [\alpha^A_{\parallel} - \alpha^A_\perp] \\ &\qquad \times \hat{r}_{1\alpha}\hat{r}_{1\phi} R_\alpha\, R^{-8} \\ &\quad + 6\, [B^B_{2b} - B^B_{2c}]\, \alpha^A_\perp\, \hat{r}_{2\alpha}\hat{r}_{2\phi} R_\alpha\, R^{-8} \\ &\quad + 2\, [3\, B^B_{2d} - 5\, B^B_4]\, [\alpha^A_{\parallel} + 5\alpha^A_\perp]\, \hat{r}_{2\alpha}\hat{r}_{2\phi} R_\alpha\, R^{-8} \end{aligned}$$

$$- 2\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,[3\,B^A_{2b} + 3\,B^A_{2c} - 10\,B^A_4]\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\alpha}\hat{r}_{2\phi}R_\beta\;R^{-8}$$

$$- [\alpha^B_{\parallel} - \alpha^B_{\perp}]\,[6\,B^A_{2c} - 6\,B^A_{2d} + 35\,B^A_4]\,\hat{r}_{1\alpha}\hat{r}_{1\phi}\hat{r}_{2\alpha}\hat{r}_{2\beta}R_\beta\;R^{-8}$$

$$- 2\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,[3\,B^A_{2c} - 5\,B^A_4]\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\alpha}\hat{r}_{2\beta}R_\phi\;R^{-8}$$

$$+ 2\,[3\,B^B_{2b} + 3\,B^B_{2c} - 10\,B^B_4]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\hat{r}_{1\alpha}\hat{r}_{1\phi}\hat{r}_{2\alpha}\hat{r}_{2\beta}R_\beta\;R^{-8}$$

$$+ [6\,B^B_{2c} - 6\,B^B_{2d} + 35\,B^B_4]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\alpha}\hat{r}_{2\phi}R_\beta\;R^{-8}$$

$$+ 2\,[3\,B^B_{2c} - 5\,B^B_4]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\alpha}\hat{r}_{2\beta}R_\phi\;R^{-8}$$

$$- 70\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,B^A_4\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\phi}\hat{r}_{2\alpha}\hat{r}_{2\beta}R_\gamma\;R^{-8}$$

$$+ 70\,B^B_4\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\phi}R_\gamma\;R^{-8}$$

$$- 12\,\alpha^B_{\perp}\,[B^A_{2b} + 2\,B^A_{2c} - 5\,B^A_4]\,\hat{r}_{1\alpha}\hat{r}_{1\beta}R_\alpha R_\beta R_\phi\;R^{-10}$$

$$- [\alpha^B_{\parallel} - \alpha^B_{\perp}]\,[6\,\bar{B}^A - 9\,B^A_{2b} - 8\,B^A_{2c} - 8\,B^A_{2d} + 23\,B^A_4]$$

$$\times\,\hat{r}_{2\alpha}\hat{r}_{2\beta}R_\alpha R_\beta R_\phi\;R^{-10}$$

$$+ [6\,\bar{B}^B - 9\,B^B_{2b} - 8\,B^B_{2c} - 8\,B^B_{2d} + 23\,B^B_4]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]$$

$$\times\,\hat{r}_{1\alpha}\hat{r}_{1\beta}R_\alpha R_\beta R_\phi\;R^{-10}$$

$$+ 12\,[B^B_{2b} + 2\,B^B_{2c} - 5\,B^B_4]\,\alpha^A_{\perp}\,\hat{r}_{2\alpha}\hat{r}_{2\beta}R_\alpha R_\beta R_\phi\;R^{-10}$$

$$+ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\,[18\,B^A_{2c} - 24\,B^A_{2d} + 115\,B^A_4]$$

$$\times\,\hat{r}_{1\alpha}\hat{r}_{1\phi}\hat{r}_{2\beta}\hat{r}_{2\gamma}R_\alpha R_\beta R_\gamma\;R^{-10}$$

$$+ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\,[15\,B^A_{2b} + 18\,B^A_{2c} - 55\,B^A_4]$$

$$\times\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\gamma}\hat{r}_{2\phi}R_\alpha R_\beta R_\gamma\;R^{-10}$$

$$+ 2\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,[9\,B^A_{2b} + 24\,B^A_{2c} - 55\,B^A_4]$$

$$\times\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\alpha}\hat{r}_{2\gamma}R_\beta R_\gamma R_\phi\;R^{-10}$$

$$- [15\,B^B_{2b} + 18\,B^B_{2c} - 55\,B^B_4]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]$$

$$\times\,\hat{r}_{1\alpha}\hat{r}_{1\phi}\hat{r}_{2\beta}\hat{r}_{2\gamma}R_\alpha R_\beta R_\gamma\;R^{-10}$$

$$- [18\,B^B_{2c} - 24\,B^B_{2d} + 115\,B^B_4]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]$$

$$\times\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\gamma}\hat{r}_{2\phi}R_\alpha R_\beta R_\gamma\;R^{-10}$$

$$- 2\,[9\,B^B_{2b} + 24\,B^B_{2c} - 55\,B^B_4]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]$$

$$\times\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\alpha}\hat{r}_{2\gamma}R_\beta R_\gamma R_\phi\;R^{-10}$$

$$- 140\,\alpha^B_{\perp}\,B^A_4\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\phi}R_\alpha R_\beta R_\gamma\;R^{-10}$$

$$+ 140\ B_4^B\ \alpha_\perp^A\ \hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\phi}R_\alpha R_\beta R_\gamma\ R^{-10}$$
$$+ 385\ [\alpha_{/\!/}^B - \alpha_\perp^B]\ B_4^A\ \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\phi}\hat{r}_{2\alpha}\hat{r}_{2\delta}R_\beta R_\gamma R_\delta\ R^{-10}$$
$$- 385\ B_4^B\ [\alpha_{/\!/}^A - \alpha_\perp^A]\ \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\alpha}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{2\phi}R_\beta R_\gamma R_\delta\ R^{-10}$$
$$- 45\ [\alpha_{/\!/}^B - \alpha_\perp^B]\ [B_{2b}^A + 2\ B_{2c}^A - 5\ B_4^A]$$
$$\times\ \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}R_\alpha R_\beta R_\gamma R_\delta R_\phi\ R^{-12}$$
$$+ 45\ [B_{2b}^B + 2\ B_{2c}^B - 5\ B_4^B]\ [\alpha_{/\!/}^A - \alpha_\perp^A]$$
$$\times\ \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}R_\alpha R_\beta R_\gamma R_\delta R_\phi\ R^{-12}$$
$$- 525\ [\alpha_{/\!/}^B - \alpha_\perp^B]\ B_4^A\ \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\phi}\hat{r}_{2\delta}\hat{r}_{2\varepsilon}R_\alpha R_\beta R_\gamma R_\delta R_\varepsilon\ R^{-12}$$
$$+ 525\ B_4^B\ [\alpha_{/\!/}^A - \alpha_\perp^A]\ \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{2\varepsilon}\hat{r}_{2\phi}R_\alpha R_\beta R_\gamma R_\delta R_\varepsilon\ R^{-12}] \qquad (3.47)$$

to order R^{-7}. The frequency dependence of the α and B tensor components on the right-hand side of Eq. (3.47) is to be understood.

The dipole moment for a pair of linear molecules may also be expressed in terms of spherical harmonics as

$$\mu_M(\underline{r}_1,\underline{r}_2,\underline{R}) = \frac{(4\pi)^{3/2}}{(3)^{1/2}}\ \Sigma\ D_{\lambda_1\lambda_2\lambda L}(r_1,r_2,R)\ Y_{\lambda_1}^{m_1}(\hat{r}_1)\ Y_{\lambda_2}^{m_2}(\hat{r}_2)\ Y_L^{M-m}(\hat{R})$$
$$\times\ C(\lambda_1\lambda_2\lambda;m_1m_2m)\ C(\lambda L1;m,M-m)\ , \qquad (3.48)$$

where the summation is carried out over the indices λ_1, λ_2, λ, L, m_1, m_2, and m. The vectors $\underline{r}_1$, $\underline{r}_2$, and $\underline{R}$ are as previously defined, $C(\lambda_1\lambda_2\lambda;m_1m_2m)$ and $C(\lambda L1;m,M-m)$ are Clebsch-Gordan coefficients, and M is the spherical tensor index of $\underline{\mu}$ in the lab-fixed frame. The functions $D_{\lambda_1\lambda_2\lambda L}(r_1,r_2,R)$ are undetermined expansion coefficients; they will be found from Eq. (3.47).

Fixing r_1 and r_2 at their equilibrium or vibrationally averaged values allows us to focus on the R dependence of the $D_{\lambda_1\lambda_2\lambda L}$

coefficients. Designate by VDW_z the right hand side of Eq. (3.47) with ϕ = z. Equating VDW_z to the M = 0 instance of Eq. (3.48) gives

$$\frac{(4\pi)^{3/2}}{(3)^{1/2}} \sum_{\lambda} D^{vdW}_{\lambda_1\lambda_2\lambda L}(r_1,r_2,R)\ C(\lambda_1\lambda_2\lambda;m_1m_2m)\ C(\lambda L1;m,-m)$$

$$= \int d\Omega_{r_1} \int d\Omega_{r_2} \int d\Omega_R\ VDW_z\ [Y^{m_1}_{\lambda_1}(\hat{r}_1)\ Y^{m_2}_{\lambda_2}(\hat{r}_2)\ Y^{-m}_L(\hat{R})]^* , \qquad (3.49)$$

where the coefficients have been specialized to the van der Waals contribution to the interaction dipole.

For a pair of interacting centrosymmetric linear molecules, the $D_{\lambda_1\lambda_2\lambda L}$ coefficients possess the following symmetry relation upon interchange of the indices λ_1 and λ_2:

$$D_{\lambda_2\lambda_1\lambda L} = (-1)^{\lambda+1}\ P^{AB}\ D_{\lambda_1\lambda_2\lambda L} , \qquad (3.50)$$

where P^{AB} interchanges the molecule labels A and B. When VDW_z is expressed in terms of spherical harmonics (see Appendix C) and substituted into Eq. (3.49), the following coefficients result:

$$D^{vdW}_{0001} = 9\,\frac{\hbar}{\pi} \int_0^\infty d\omega\ [\bar{B}^B\ \bar{\alpha}^A - \bar{B}^A\ \bar{\alpha}^B]\ R^{-7} , \qquad (3.51)$$

$$D^{vdW}_{2021} = \frac{3}{10}\,(2)^{1/2}\,\frac{\hbar}{\pi} \int_0^\infty d\omega\ \Big[4\,(3B^A_{2b} + B^A_{2c} + 10B^A_{2d})\ \bar{\alpha}^B - (\alpha^A_{\parallel} - \alpha^A_{\perp})\ \bar{B}^B\Big]\ R^{-7} , \qquad (3.52)$$

$$D^{vdW}_{2201} = \frac{4}{5}\,(\frac{1}{5})^{1/2}\,\frac{\hbar}{\pi} \int_0^\infty d\omega\ \Big[(\alpha^A_{\parallel} - \alpha^A_{\perp})\ (B^B_{2c} + B^B_{2d})$$

$$- (B_{2c}^A + B_{2d}^A)\ (\alpha_{\parallel}^B - \alpha_{\perp}^B)]\ R^{-7}\ , \tag{3.53}$$

$$D_{2211}^{vdW} = \frac{6}{5}\ (\frac{1}{5})^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ [(\alpha_{\parallel}^A - \alpha_{\perp}^A)\ B_{2d}^B + B_{2d}^A\ (\alpha_{\parallel}^B - \alpha_{\perp}^B)]\ R^{-7}\ , \tag{3.54}$$

$$D_{2221}^{vdW} = \frac{2}{5}\ (\frac{1}{35})^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ [(\alpha_{\parallel}^A - \alpha_{\perp}^A)\ (6B_{2b}^B - 2B_{2c}^B + 7B_{2d}^B) - (6B_{2b}^A - 2B_{2c}^A + 7B_{2d}^A)\ (\alpha_{\parallel}^B - \alpha_{\perp}^B)]\ R^{-7}\ , \tag{3.55}$$

$$D_{4221}^{vdW} = \frac{8}{5}\ (\frac{1}{7})^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ B_4^A\ (\alpha_{\parallel}^B - \alpha_{\perp}^B)\ R^{-7}\ , \tag{3.56}$$

$$D_{2023}^{vdW} = \frac{4}{5}\ (3)^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ [(\alpha_{\parallel}^A - \alpha_{\perp}^A)\ \bar{B}^B - 2\ (B_{2b}^A + 2B_{2c}^A)\ \bar{\alpha}^B]\ R^{-7}\ , \tag{3.57}$$

$$D_{2223}^{vdW} = \frac{8}{5}\ (\frac{2}{105})^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ [(B_{2b}^A - 2B_{2c}^A + 2B_{2d}^A)\ (\alpha_{\parallel}^B - \alpha_{\perp}^B) - (\alpha_{\parallel}^A - \alpha_{\perp}^A)\ (B_{2b}^B - 2B_{2c}^B + 2_{2d}^B)]\ R^{-7}\ , \tag{3.58}$$

$$D_{2233}^{vdW} = -\ \frac{2}{5}\ (\frac{2}{15})^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ [(5B_{2b}^A + 8B_{2d}^A)\ (\alpha_{\parallel}^B - \alpha_{\perp}^B) + (\alpha_{\parallel}^A - \alpha_{\perp}^A)\ (5B_{2b}^B + 8B_{2d}^B)]\ R^{-7}\ , \tag{3.59}$$

$$D_{2243}^{vdW} = \frac{2}{5}\ (\frac{2}{35})^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ [(5B_{2b}^A + 4B_{2c}^A + 24B_{2d}^A)\ (\alpha_{\parallel}^B - \alpha_{\perp}^B) - (\alpha_{\parallel}^A - \alpha_{\perp}^A)\ (5B_{2b}^B + 4B_{2c}^B + 24B_{2d}^B)]\ R^{-7}\ , \tag{3.60}$$

$$D_{4043}^{vdW} = 16\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ B_4^A\ \bar{\alpha}^B\ R^{-7}\ , \tag{3.61}$$

$$D_{4223}^{vdW} = \frac{4}{15}\ (\frac{2}{21})^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ B_4^A\ (\alpha_{\parallel}^B - \alpha_{\perp}^B)\ R^{-7}\ , \tag{3.62}$$

$$D_{4233}^{vdW} = -\ \frac{2}{3}\ (\frac{1}{3})^{1/2}\ \frac{\hbar}{\pi} \int_o^\infty d\omega\ B_4^A\ (\alpha_{\parallel}^B - \alpha_{\perp}^B)\ R^{-7}\ , \tag{3.63}$$

$$D^{vdW}_{4243} = \frac{2}{3} \left(\frac{11}{7}\right)^{1/2} \frac{\hbar}{\pi} \int_0^\infty d\omega \; B^A_4 \left(\alpha^B_{\parallel} - \alpha^B_{\perp}\right) R^{-7} \; , \tag{3.64}$$

$$D^{vdW}_{2245} = 4 \left(\frac{2}{7}\right)^{1/2} \frac{\hbar}{\pi} \int_0^\infty d\omega \; \left[\left(\alpha^A_{\parallel} - \alpha^A_{\perp}\right) \left(B^B_{2b} + 2B^B_{2c}\right) - \left(B^A_{2b} + 2B^A_{2c}\right) \left(\alpha^B_{\parallel} - \alpha^B_{\perp}\right)\right] R^{-7} \; , \tag{3.65}$$

$$D^{vdW}_{4245} = \frac{8}{3} \left(\frac{5}{77}\right)^{1/2} \frac{\hbar}{\pi} \int_0^\infty d\omega \; B^A_4 \left(\alpha^B_{\parallel} - \alpha^B_{\perp}\right) R^{-7} \; , \tag{3.66}$$

$$D^{vdW}_{4255} = -\frac{8}{3} \left(\frac{5}{3}\right)^{1/2} \frac{\hbar}{\pi} \int_0^\infty d\omega \; B^A_4 \left(\alpha^B_{\parallel} - \alpha^B_{\perp}\right) R^{-7} \; , \tag{3.67}$$

and

$$D^{vdW}_{4265} = \frac{40}{3} \left(\frac{26}{33}\right)^{1/2} \frac{\hbar}{\pi} \int_0^\infty d\omega \; B^A_4 \left(\alpha^B_{\parallel} - \alpha^B_{\perp}\right) R^{-7} \; . \tag{3.68}$$

Again, the frequency dependence of the α and B tensor components in Eqs. (3.51) - (3.68) is to be understood.

Induction effects also contribute to the long-range dipole moment of a pair of centrosymmetric linear molecules. The permanent quadrupole and hexadecapole moments of each molecule produce fields which polarize the other molecule. Additionally, the permanent quadrupole of each molecule sets up a gradient of a field gradient that polarizes its partner. The moments that are induced in the molecules from these fields and field gradients themselves give rise to static reaction fields which produce back-induction effects at each center. The combination of all these effects results in an induction dipole that may be written as

$$\mu^{AB}_{\alpha,ind} = -\frac{1}{3} \alpha^A_{\alpha\beta} \, T^{(3)}_{\beta\gamma\delta}(\underline{R}) \, \Theta^B_{\gamma\delta}$$

$$+ \frac{1}{3} \alpha^{B}_{\alpha\beta} \; T^{(3)}_{\beta\gamma\delta}(\underline{R}) \; \Theta^{A}_{\gamma\delta}$$
$$- \frac{1}{105} \alpha^{A}_{\alpha\beta} \; T^{(5)}_{\beta\gamma\delta\epsilon\phi}(\underline{R}) \; \Phi^{B}_{\gamma\delta\epsilon\phi}$$
$$+ \frac{1}{105} \alpha^{B}_{\alpha\beta} \; T^{(5)}_{\beta\gamma\delta\epsilon\phi}(\underline{R}) \; \Phi^{A}_{\gamma\delta\epsilon\phi}$$
$$- \frac{1}{45} E^{A}_{\alpha,\beta\gamma\delta} \; T^{(5)}_{\beta\gamma\delta\epsilon\phi}(\underline{R}) \; \Theta^{B}_{\epsilon\phi}$$
$$+ \frac{1}{45} E^{B}_{\alpha,\beta\gamma\delta} \; T^{(5)}_{\beta\gamma\delta\epsilon\phi}(\underline{R}) \; \Theta^{A}_{\epsilon\phi}$$
$$+ \frac{1}{3} \alpha^{A}_{\alpha\beta} \; T^{(2)}_{\beta\gamma}(\underline{R}) \; \alpha^{B}_{\gamma\delta} \; T^{(3)}_{\delta\epsilon\phi}(\underline{R}) \; \Theta^{A}_{\epsilon\phi}$$
$$- \frac{1}{3} \alpha^{B}_{\alpha\beta} \; T^{(2)}_{\beta\gamma}(\underline{R}) \; \alpha^{A}_{\gamma\delta} \; T^{(3)}_{\delta\epsilon\phi}(\underline{R}) \; \Theta^{B}_{\epsilon\phi} \; , \qquad (3.69)$$

through order R^{-7}. Expressions for the dipole polarizability, the quadrupole moment and the hexadecapole moment have been given by Eqs. (3.7), (3.29) and (3.30) of the previous section; the propagator tensors and tensor products that occur in the above equation were also given in that section by Eqs. (3.32) - (3.34). A quantity that appears for the first time in Eq. (3.69) is the dipole-octopole polarizability $E_{\alpha,\beta\gamma\delta}(i\omega)$. For a linear molecule, the E tensor has two independent components and can be written (see Appendix B)

$$\begin{aligned}
E_{\alpha,\beta\gamma\delta}(i\omega) = {} & \frac{1}{14} \left[E_{z,zzz}(i\omega) + 2\, E_{x,xxx}(i\omega)\right] \left[35\, \hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma \hat{r}_\delta \right. \\
& - 5\, (\hat{r}_\alpha \hat{r}_\beta\, \delta_{\gamma\delta} + \hat{r}_\alpha \hat{r}_\gamma\, \delta_{\beta\delta} + \hat{r}_\alpha \hat{r}_\delta\, \delta_{\beta\gamma} \\
& \quad + \hat{r}_\beta \hat{r}_\gamma\, \delta_{\alpha\delta} + \hat{r}_\beta \hat{r}_\delta\, \delta_{\alpha\gamma} + \hat{r}_\gamma \hat{r}_\delta\, \delta_{\alpha\beta}) \\
& \left. + \delta_{\alpha\beta}\, \delta_{\gamma\delta} + \delta_{\alpha\gamma}\, \delta_{\beta\delta} + \delta_{\alpha\delta}\, \delta_{\beta\gamma}\right] \\
& - \frac{1}{63} \left[3\, E_{z,zzz}(i\omega) - 8\, E_{x,xxx}(i\omega)\right] \left[(3\, \hat{r}_\alpha \hat{r}_\beta - \delta_{\alpha\beta})\, \delta_{\gamma\delta} \right. \\
& \quad \left. + (3\, \hat{r}_\alpha \hat{r}_\gamma - \delta_{\alpha\gamma})\, \delta_{\beta\delta} + (3\, \hat{r}_\alpha \hat{r}_\delta - \delta_{\alpha\delta})\, \delta_{\beta\gamma}\right] \\
& + \frac{5}{126} \left[3\, E_{z,zzz}(i\omega) - 8\, E_{x,xxx}(i\omega)\right] \left[(3\, \hat{r}_\beta \hat{r}_\gamma - \delta_{\beta\gamma})\, \delta_{\alpha\delta} \right. \\
& \quad \left. + (3\, \hat{r}_\beta \hat{r}_\delta - \delta_{\beta\delta})\, \delta_{\alpha\gamma} + (3\, \hat{r}_\gamma \hat{r}_\delta - \delta_{\gamma\delta})\, \delta_{\alpha\beta}\right] . \qquad (3.70)
\end{aligned}$$

Making use of Eqs. (3.7), (3.29), (3.30), (3.32) - (3.34), and (3.70) in Eq. (3.69) leads ultimately to

$$
\begin{aligned}
\mu^{AB}_{\alpha,ind} = \tfrac{1}{2}\, [&6\, \alpha^A_\perp \alpha^B_\perp \Theta^A R^{-8} - 6\, \alpha^B_\perp \alpha^A_\perp \Theta^B R^{-8} \\
&+ 5\, E^B_{x,xxx}\, \Theta^A R^{-7} - 5\, E^A_{x,xxx}\, \Theta^B R^{-7} \\
&+ \tfrac{15}{4}\, \alpha^A_\perp \Phi^B R^{-7} - \tfrac{15}{4}\, \alpha^B_\perp \Phi^A R^{-7} \\
&- 3\, \alpha^A_\perp \Theta^B R^{-5} + 3\, \alpha^B_\perp \Theta^A R^{-5}]\, R_\alpha \\
+ [3\, \alpha^B_\perp \Theta^A R^{-5} &- \tfrac{3}{2}\, [\alpha^A_{\parallel} - \alpha^A_\perp]\, \Theta^B R^{-5} \\
&- \tfrac{15}{2}\, \alpha^B_\perp \Phi^A R^{-7} + \tfrac{15}{8}\, [\alpha^A_{\parallel} - \alpha^A_\perp]\, \Phi^B R^{-7} \\
&+ \tfrac{5}{4}\, [2\, E^A_{x,xxx} + 3\, E^A_{z,zzz}]\, \Theta^B R^{-7} + 5\, E^B_{x,xxx}\, \Theta^A R^{-7} \\
&- 3\, \alpha^A_\perp \alpha^B_\perp \Theta^A R^{-8} + \tfrac{3}{2}\, \alpha^B_\perp [\alpha^A_{\parallel} - \alpha^A_\perp]\, \Theta^B R^{-8}]\, \hat{r}_{1\alpha} \hat{r}_{1\beta} R_\beta \\
- [3\, \alpha^A_\perp \Theta^B R^{-5} &- \tfrac{3}{2}\, [\alpha^B_{\parallel} - \alpha^B_\perp]\, \Theta^A R^{-5} \\
&- \tfrac{15}{2}\, \alpha^A_\perp \Phi^B R^{-7} + \tfrac{15}{8}\, [\alpha^B_{\parallel} - \alpha^B_\perp]\, \Phi^A R^{-7} \\
&+ 5\, E^A_{x,xxx}\, \Theta^B R^{-7} + \tfrac{5}{4}\, [2\, E^B_{x,xxx} + 3\, E^B_{z,zzz}]\, \Theta^A R^{-7} \\
&- 3\, \alpha^B_\perp \alpha^A_\perp \Theta^B R^{-8} + \tfrac{3}{2}\, \alpha^A_\perp [\alpha^B_{\parallel} - \alpha^B_\perp]\, \Theta^A R^{-8}]\, \hat{r}_{2\alpha} \hat{r}_{2\beta} R_\beta \\
- [\tfrac{15}{2}\, \alpha^B_\perp \Theta^A R^{-7} &- \tfrac{105}{4}\, \alpha^B_\perp \Phi^A R^{-9} \\
&- \tfrac{35}{2}\, E^A_{x,xxx}\, \Theta^B R^{-9} + \tfrac{35}{2}\, E^B_{x,xxx}\, \Theta^A R^{-9} \\
&+ 6\, \alpha^A_\perp \alpha^B_\perp \Theta^A R^{-10} + \tfrac{9}{2}\, \alpha^B_\perp [\alpha^A_{\parallel} - \alpha^A_\perp]\, \Theta^B R^{-10}] \\
&\quad \times \hat{r}_{1\beta} \hat{r}_{1\gamma} R_\alpha R_\beta R_\gamma \\
+ [\tfrac{15}{2}\, \alpha^A_\perp \Theta^B R^{-7} &- \tfrac{105}{4}\, \alpha^A_\perp \Phi^B R^{-9} \\
&+ \tfrac{35}{2}\, E^A_{x,xxx}\, \Theta^B R^{-9} - \tfrac{35}{2}\, E^B_{x,xxx}\, \Theta^A R^{-9} \\
&+ 6\, \alpha^B_\perp \alpha^A_\perp \Theta^B R^{-10} + \tfrac{9}{2}\, \alpha^A_\perp [\alpha^B_{\parallel} - \alpha^B_\perp]\, \Theta^A R^{-10}] \\
&\quad \times \hat{r}_{2\beta} \hat{r}_{2\gamma} R_\alpha R_\beta R_\gamma \\
- [3\, [\alpha^A_{\parallel} - \alpha^A_\perp]\, \Theta^B R^{-5} &- \tfrac{15}{2}\, [\alpha^A_{\parallel} - \alpha^A_\perp]\, \Phi^B R^{-7} \\
&- \tfrac{5}{2}\, [2\, E^A_{x,xxx} + 3\, E^A_{z,zzz}]\, \Theta^B R^{-7} - 10\, E^B_{x,xxx}\, \Theta^A R^{-7} \\
&- 3\, \alpha^B_\perp [\alpha^A_{\parallel} - \alpha^A_\perp]\, \Theta^B R^{-8} \\
&+ \tfrac{3}{2}\, [\alpha^A_{\parallel} - \alpha^A_\perp]\, [\alpha^B_{\parallel} - \alpha^B_\perp]\, \Theta^A R^{-8}]\, \hat{r}_{1\alpha} \hat{r}_{1\beta} \hat{r}_{2\beta} \hat{r}_{2\gamma} R_\gamma
\end{aligned}
$$

$$+ [3\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A\ R^{-5} - \frac{15}{2}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Phi^A\ R^{-7}$$

$$- 10\ E^A_{x,xxx}\ \Theta^B\ R^{-7} - \frac{5}{2}\ [2\ E^B_{x,xxx} + 3\ E^B_{z,zzz}]\ \Theta^A\ R^{-7}$$

$$- 3\ \alpha^A_{\perp}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A\ R^{-8}$$

$$+ \frac{3}{2}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\ R^{-8}]\ \hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{1\beta}\hat{r}_{1\gamma}R_{\gamma}$$

$$- 5\ [E^A_{x,xxx}\ \Theta^B\ R^{-7} - E^B_{x,xxx}\ \Theta^A\ R^{-7}]\ \hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{2\beta}\hat{r}_{2\gamma}R_{\alpha}$$

$$+ [\frac{15}{2}\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\ R^{-7} - \frac{105}{4}\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Phi^B\ R^{-9}$$

$$- \frac{35}{4}\ [2\ E^A_{x,xxx} + 3\ E^A_{z,zzz}]\ \Theta^B\ R^{-9} - 35\ E^B_{x,xxx}\ \Theta^A\ R^{-9}$$

$$- \frac{15}{2}\ \alpha^B_{\perp}\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\ R^{-10}$$

$$+ \frac{9}{2}\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A\ R^{-10}]$$

$$\times\ \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}R_{\beta}R_{\gamma}R_{\delta}$$

$$- [\frac{15}{2}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A\ R^{-7} - \frac{105}{4}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Phi^A\ R^{-9}$$

$$- 35\ E^A_{x,xxx}\ \Theta^B\ R^{-9} - \frac{35}{4}\ [2\ E^B_{x,xxx} + 3\ E^B_{z,zzz}]\ \Theta^A\ R^{-9}$$

$$- \frac{15}{2}\ \alpha^A_{\perp}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A\ R^{-10}$$

$$+ \frac{9}{2}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\ R^{-10}]$$

$$\times\ \hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{1\gamma}\hat{r}_{1\delta}R_{\beta}R_{\gamma}R_{\delta}$$

$$+ [70\ E^A_{x,xxx}\ \Theta^B\ R^{-9} - 70\ E^B_{x,xxx}\ \Theta^A\ R^{-9}$$

$$+ 9\ \alpha^A_{\perp}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A\ R^{-10} - 9\ \alpha^B_{\perp}\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\ R^{-10}]$$

$$\times\ \hat{r}_{1\beta}\hat{r}_{1\delta}\hat{r}_{2\gamma}\hat{r}_{2\delta}R_{\alpha}R_{\beta}R_{\gamma}$$

$$- \frac{45}{2}\ [\alpha^A_{\perp}\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A\ R^{-12} - \alpha^B_{\perp}\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\ R^{-12}$$

$$+ 7\ E^A_{x,xxx}\ \Theta^B\ R^{-11} - 7\ E^B_{x,xxx}\ \Theta^A\ R^{-11}]$$

$$\times\ \hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{2\delta}\hat{r}_{2\varepsilon}R_{\alpha}R_{\beta}R_{\gamma}R_{\delta}R_{\varepsilon}$$

$$- [\frac{7}{4}\ [10\ E^A_{x,xxx} + 5\ E^A_{z,zzz}]\ \Theta^B\ R^{-9}$$

$$- \frac{35}{2}\ \alpha^B_{\perp}\ \Phi^A\ R^{-9} + 6\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \alpha^B_{\perp}\ \Theta^A\ R^{-10}]$$

$$\times\ \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\delta}R_{\beta}R_{\gamma}R_{\delta}$$

$$+ [\frac{7}{4}\ [10\ E^B_{x,xxx} + 5\ E^B_{z,zzz}]\ \Theta^A\ R^{-9}$$

$$- \frac{35}{2}\ \alpha^A_{\perp}\ \Phi^B\ R^{-9} + 6\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \alpha^A_{\perp}\ \Theta^B\ R^{-10}]$$

$$\times\ \hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}R_{\beta}R_{\gamma}R_{\delta}$$

$$
\begin{aligned}
&+ \Big[\tfrac{3}{2}\,[10\,E^{A}_{x,xxx} + 5\,E^{A}_{z,zzz}]\,\Theta^{B}\,R^{-7} \\
&\qquad - 3\,[\alpha^{A}_{\parallel} - \alpha^{A}_{\perp}]\,[\alpha^{B}_{\parallel} - \alpha^{B}_{\perp}]\,\Theta^{A}\,R^{-8}\Big] \\
&\qquad\qquad \times \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\delta}\hat{r}_{2\gamma}\hat{r}_{2\delta}R_{\beta} \\
&- \Big[\tfrac{3}{2}\,[10\,E^{B}_{x,xxx} + 5\,E^{B}_{z,zzz}]\,\Theta^{A}\,R^{-7} \\
&\qquad - 3\,[\alpha^{B}_{\parallel} - \alpha^{B}_{\perp}]\,[\alpha^{A}_{\parallel} - \alpha^{A}_{\perp}]\,\Theta^{B}\,R^{-8}\Big] \\
&\qquad\qquad \times \hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{1\gamma}\hat{r}_{1\delta}R_{\beta} \\
&- \Big[\tfrac{21}{2}\,[10\,E^{A}_{x,xxx} + 5\,E^{A}_{z,zzz}]\,\Theta^{B}\,R^{-9} \\
&\qquad - \tfrac{33}{2}\,[\alpha^{A}_{\parallel} - \alpha^{A}_{\perp}]\,[\alpha^{B}_{\parallel} - \alpha^{B}_{\perp}]\,\Theta^{A}\,R^{-10}\Big] \\
&\qquad\qquad \times \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\varepsilon}\hat{r}_{2\delta}\hat{r}_{2\varepsilon}R_{\beta}R_{\gamma}R_{\delta} \\
&+ \Big[\tfrac{21}{2}\,[10\,E^{B}_{x,xxx} + 5\,E^{B}_{z,zzz}]\,\Theta^{A}\,R^{-9} \\
&\qquad - \tfrac{33}{2}\,[\alpha^{B}_{\parallel} - \alpha^{B}_{\perp}]\,[\alpha^{A}_{\parallel} - \alpha^{A}_{\perp}]\,\Theta^{B}\,R^{-10}\Big] \\
&\qquad\qquad \times \hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\varepsilon}\hat{r}_{1\delta}\hat{r}_{1\varepsilon}R_{\beta}R_{\gamma}R_{\delta} \\
&+ \Big[\tfrac{63}{4}\,[10\,E^{A}_{x,xxx} + 5\,E^{A}_{z,zzz}]\,\Theta^{B}\,R^{-11} \\
&\qquad - \tfrac{45}{2}\,[\alpha^{A}_{\parallel} - \alpha^{A}_{\perp}]\,[\alpha^{B}_{\parallel} - \alpha^{B}_{\perp}]\,\Theta^{A}\,R^{-12}\Big] \\
&\qquad\qquad \times \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\delta}\hat{r}_{2\varepsilon}\hat{r}_{2\phi}R_{\beta}R_{\gamma}R_{\delta}R_{\varepsilon}R_{\phi} \\
&- \Big[\tfrac{63}{4}\,[10\,E^{B}_{x,xxx} + 5\,E^{B}_{z,zzz}]\,\Theta^{A}\,R^{-11} \\
&\qquad - \tfrac{45}{2}\,[\alpha^{B}_{\parallel} - \alpha^{B}_{\perp}]\,[\alpha^{A}_{\parallel} - \alpha^{A}_{\perp}]\,\Theta^{B}\,R^{-12}\Big] \\
&\qquad\qquad \times \hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{1\varepsilon}\hat{r}_{1\phi}R_{\beta}R_{\gamma}R_{\delta}R_{\varepsilon}R_{\phi} \\
&- \tfrac{35}{2}\,[\alpha^{A}_{\parallel} - \alpha^{A}_{\perp}]\,\Phi^{B}\,R^{-9}\,\hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{2\varepsilon}R_{\gamma}R_{\delta}R_{\varepsilon} \\
&+ \tfrac{35}{2}\,[\alpha^{B}_{\parallel} - \alpha^{B}_{\perp}]\,\Phi^{A}\,R^{-9}\,\hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\delta}\hat{r}_{1\varepsilon}R_{\gamma}R_{\delta}R_{\varepsilon} \\
&- \tfrac{315}{8}\,\alpha^{B}_{\perp}\,\Phi^{A}\,R^{-11}\,\hat{r}_{1\beta}\hat{r}_{1\gamma}\hat{r}_{1\delta}\hat{r}_{1\varepsilon}R_{\alpha}R_{\beta}R_{\gamma}R_{\delta}R_{\varepsilon} \\
&+ \tfrac{315}{8}\,\alpha^{A}_{\perp}\,\Phi^{B}\,R^{-11}\,\hat{r}_{2\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{2\varepsilon}R_{\alpha}R_{\beta}R_{\gamma}R_{\delta}R_{\varepsilon} \\
&+ \tfrac{315}{8}\,[\alpha^{A}_{\parallel} - \alpha^{A}_{\perp}]\,\Phi^{B}\,R^{-11} \\
&\qquad\qquad \times \hat{r}_{1\alpha}\hat{r}_{1\beta}\hat{r}_{2\gamma}\hat{r}_{2\delta}\hat{r}_{2\varepsilon}\hat{r}_{2\phi}R_{\beta}R_{\gamma}R_{\delta}R_{\varepsilon}R_{\phi} \\
&- \tfrac{315}{8}\,[\alpha^{B}_{\parallel} - \alpha^{B}_{\perp}]\,\Phi^{A}\,R^{-11} \\
&\qquad\qquad \times \hat{r}_{2\alpha}\hat{r}_{2\beta}\hat{r}_{1\gamma}\hat{r}_{1\delta}\hat{r}_{1\varepsilon}\hat{r}_{1\phi}R_{\beta}R_{\gamma}R_{\delta}R_{\varepsilon}R_{\phi}
\end{aligned}
\tag{3.71}
$$

for the induction contribution to the long-range dipole moment to order R^{-7}.

The induction dipole can also be expressed in terms of spherical harmonics, as in Eq. (3.48). Letting IND_z denote the right-hand side of Eq. (3.71) with $\alpha = z$, we can write in direct analogy with Eq. (3.49)

$$\frac{(4\pi)^{3/2}}{(3)^{1/2}} \sum_{\lambda} D^{ind}_{\lambda_1\lambda_2\lambda L}(r_1,r_2,R)\ C(\lambda_1\lambda_2\lambda;m_1m_2m)\ C(\lambda L1;m,-m)$$
$$= \int d\Omega_{r_1} \int d\Omega_{r_2} \int d\Omega_R\ IND_z \left[Y^{m_1}_{\lambda_1}(\hat{r}_1)\ Y^{m_2}_{\lambda_2}(\hat{r}_2)\ Y^{-m}_L(\hat{R})\right]^* , \qquad (3.72)$$

where the coefficients have now been specialized to the induction contribution to the long-range dipole moment. Expressing IND_z in terms of spherical harmonics (see Appendix C) and substituting into Eq. (3.72) results in

$$D^{ind}_{0001} = -\frac{6}{5}\left[[\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \bar{\alpha}^B\ \Theta^A - [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \bar{\alpha}^A\ \Theta^B\right] R^{-7} , \qquad (3.73)$$

$$D^{ind}_{2021} = \frac{1}{5}\,(2)^{1/2}\left[3\ [2\alpha^A_{\parallel} + \alpha^A_{\perp}]\ \bar{\alpha}^B\ \Theta^A - \frac{1}{5}\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\right] R^{-7} , \qquad (3.74)$$

$$D^{ind}_{2201} = -\frac{4}{35}\left(\frac{1}{5}\right)^{1/2}\left[[\alpha^A_{\parallel} - \alpha^A_{\perp}]\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A - [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\right] R^{-7} , \qquad (3.75)$$

$$D^{ind}_{2211} = \frac{3}{35}\left(\frac{1}{5}\right)^{1/2}\left[[\alpha^A_{\parallel} - \alpha^A_{\perp}]\ [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ \Theta^A + [\alpha^B_{\parallel} - \alpha^B_{\perp}]\ [\alpha^A_{\parallel} - \alpha^A_{\perp}]\ \Theta^B\right] R^{-7} , \qquad (3.76)$$

$$D^{ind}_{2221} = -\frac{1}{35}\left(\frac{1}{35}\right)^{1/2}\Big[[11\alpha^A_{\parallel} + 31\alpha^A_{\perp}]\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A - [11\alpha^B_{\parallel} + 31\alpha^B_{\perp}]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\Theta^B\Big]\,R^{-7}\ , \tag{3.77}$$

$$D^{ind}_{4221} = \frac{12}{175}\left(\frac{1}{7}\right)^{1/2}[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-7}\ , \tag{3.78}$$

$$D^{ind}_{2023} = -(3)^{1/2}\Big[\bar{\alpha}^B\,\Theta^A\,R^{-4} + \frac{4}{35}[3\alpha^A_{\parallel} + 4\alpha^A_{\perp}]\,\bar{\alpha}^B\,\Theta^A\,R^{-7} - \frac{8}{75}[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\Theta^B\,R^{-7}\Big]\ , \tag{3.79}$$

$$D^{ind}_{2223} = -\frac{2}{3}\left(\frac{3}{70}\right)^{1/2}\Big[[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\Theta^B\,R^{-4} - [\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-4} - \frac{4}{35}[\alpha^A_{\parallel} + 6\alpha^A_{\perp}]\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-7} + \frac{4}{35}[\alpha^B_{\parallel} + 6\alpha^B_{\perp}]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\Theta^B\,R^{-7}\Big]\ , \tag{3.80}$$

$$D^{ind}_{2233} = \frac{2}{3}\left(\frac{3}{10}\right)^{1/2}\Big[[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\Theta^B\,R^{-4} + [\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-4} - \frac{1}{35}[13\alpha^A_{\parallel} + 22\alpha^A_{\perp}]\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-7} - \frac{1}{35}[13\alpha^B_{\parallel} + 22\alpha^B_{\perp}]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\Theta^B\,R^{-7}\Big]\ , \tag{3.81}$$

$$D^{ind}_{2243} = -\frac{2}{5}\left(\frac{5}{14}\right)^{1/2}\Big[3\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\Theta^B\,R^{-4} - 3\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-4} - \frac{1}{35}[33\alpha^A_{\parallel} + 2\alpha^A_{\perp}]\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-7} + \frac{1}{35}[33\alpha^B_{\parallel} + 2\alpha^B_{\perp}]\,[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\Theta^B\,R^{-7}\Big]\ , \tag{3.82}$$

$$D^{ind}_{4043} = \frac{24}{35}[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,\bar{\alpha}^B\,\Theta^A\,R^{-7}\ , \tag{3.83}$$

$$D^{ind}_{4223} = \frac{2}{175}\left(\frac{2}{21}\right)^{1/2}[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-7}\ , \tag{3.84}$$

$$D^{ind}_{4233} = -\frac{1}{35}\left(\frac{1}{3}\right)^{1/2}[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-7}\ , \tag{3.85}$$

$$D^{ind}_{4243} = \frac{1}{35}\left(\frac{11}{7}\right)^{1/2}[\alpha^A_{\parallel} - \alpha^A_{\perp}]\,[\alpha^B_{\parallel} - \alpha^B_{\perp}]\,\Theta^A\,R^{-7}\ , \tag{3.86}$$

$$D^{ind}_{2245} = (\tfrac{2}{7})^{1/2} [[3E^A_{z,zzz} - 8E^A_{x,xxx}] \Theta^B R^{-6}$$
$$- [3E^B_{z,zzz} - 8E^B_{x,xxx}] \Theta^A R^{-6}$$
$$- \tfrac{2}{7} [3\alpha^A_{\parallel} + 4\alpha^A_{\perp}] [\alpha^B_{\parallel} - \alpha^B_{\perp}] \Theta^A R^{-7}$$
$$+ \tfrac{2}{7} [3\alpha^B_{\parallel} + 4\alpha^B_{\perp}] [\alpha^A_{\parallel} - \alpha^A_{\perp}] \Theta^B R^{-7}] , \qquad (3.87)$$

$$D^{ind}_{4045} = -(5)^{1/2} \Phi^A \bar{\alpha}^B R^{-6} , \qquad (3.88)$$

$$D^{ind}_{4245} = 2 (\tfrac{7}{55})^{1/2} [\tfrac{1}{3} \Phi^A [\alpha^B_{\parallel} - \alpha^B_{\perp}] R^{-6}$$
$$- \tfrac{1}{7} [E^A_{z,zzz} + 2E^A_{x,xxx}] \Theta^B R^{-6}$$
$$+ \tfrac{2}{49} [\alpha^A_{\parallel} - \alpha^A_{\perp}] [\alpha^B_{\parallel} - \alpha^B_{\perp}] \Theta^A R^{-7}] , \qquad (3.89)$$

$$D^{ind}_{4255} = \tfrac{2}{3} (\tfrac{3}{5})^{1/2} [\Phi^A [\alpha^B_{\parallel} - \alpha^B_{\perp}] R^{-6}$$
$$+ [E^A_{z,zzz} + 2E^A_{x,xxx}] \Theta^B R^{-6}$$
$$- \tfrac{2}{7} [\alpha^A_{\parallel} - \alpha^A_{\perp}] [\alpha^B_{\parallel} - \alpha^B_{\perp}] \Theta^A R^{-7}] , \qquad (3.90)$$

and

$$D^{ind}_{4265} = 2 (\tfrac{13}{66})^{1/2} [\Phi^A [\alpha^B_{\parallel} - \alpha^B_{\perp}] R^{-6}$$
$$- 2 [E^A_{z,zzz} + 2E^A_{x,xxx}] \Theta^B R^{-6}$$
$$+ \tfrac{4}{7} [\alpha^A_{\parallel} - \alpha^A_{\perp}] [\alpha^B_{\parallel} - \alpha^B_{\perp}] \Theta^A R^{-7}] . \qquad (3.91)$$

In Eqs. (3.73) - (3.91), the α and E susceptibility tensor components take their static values. The exact long-range dipole coefficients through order R^{-7} for the interaction of two centrosymmetric linear molecules are obtained by adding the van der Waals coefficients given by Eqs. (3.51) - (3.68) to the corresponding induction coefficients from Eqs. (3.73) - (3.91).

CHAPTER 4. APPLICATION OF A CONSTANT-RATIO APPROXIMATION

In order to determine dipole coefficients directly from the equations derived in Chapter 3, it is necessary to have accurate values of the B tensors as functions of imaginary frequencies. Calculations of $\underline{\underline{B}}(0,i\omega)$ are now practicable, but results are not yet available. In this chapter, simple approximation methods are described which provide estimates of the van der Waals effects in Eqs. (3.6), (3.23) - (3.26), and (3.51) - (3.68). Numerical results are found in Section A for the atom-atom systems $H...H_\zeta$ and $H...He$, in Section B for the atom-diatom systems $He...H_2$ and $He...N_2$, and in Section C for the diatom-diatom systems $H_2...H_2$ and $N_2...N_2$. The estimates for the van der Waals dipole coefficients of the latter four systems are also compared with accurate values of their induction coefficients in Sections B and C.

A. van der Waals Dipoles of $H...H_\zeta$ and $H...He$

The dipole coefficient D_7 for two interacting S state atoms is given by Eq. (3.6). If the ratio $B^x(0,i\omega)/\alpha^x(i\omega)$ is approximated by a frequency-independent quantity I^x, then Eq. (3.6) can be expressed in terms of the C_6 van der Waals energy coefficient [79]

$$C_6 = 3\,\frac{\hbar}{\pi}\int_0^\infty d\omega\;\alpha^A(i\omega)\;\alpha^B(i\omega) \tag{4.1}$$

as

$$D_7 \cong 3\, C_6 \left[I^B - I^A \right] . \qquad (4.2)$$

As a first approximation, we choose for I^X the ratio of the integrals of $B^X(0,i\omega)$ and $\alpha^X(i\omega)$ over all frequencies:

$$I^X = \int_0^\infty d\omega\, B^X(0,i\omega) \Big/ \int_0^\infty d\omega\, \alpha^X(i\omega) . \qquad (4.3)$$

We assume that I^X has the same relation to the static α and B values as in the Unsöld approximation. For an atom or centrosymmetric molecule in the ground state, the Unsöld approximation gives

$$\alpha_{\alpha\beta}(i\omega) = \frac{2}{\hbar} \langle 0|\mu_\alpha\mu_\beta|0\rangle\, \Omega/(\Omega^2 + \omega^2) \qquad (4.4)$$

and

$$B_{\alpha\beta,\gamma\delta}(0,i\omega) = \frac{2}{\hbar^2}\, (3\Omega^2 + \omega^2)/(\Omega^2 + \omega^2)^2 \left[\langle 0|\mu_\alpha\mu_\beta\Theta_{\gamma\delta}|0\rangle - \langle 0|\mu_\alpha\mu_\beta|0\rangle \langle 0|\Theta_{\gamma\delta}|0\rangle \right] , \qquad (4.5)$$

where Ω is the average excitation frequency of the species. Using these expressions in Eq. (4.3) and carrying out the integrations leads to

$$I^X = 2B^X/3\alpha^X , \qquad (4.6)$$

where B^X and α^X are respectively the static dipole-quadrupole hyperpolarizability and static dipole polarizability of X. Using Eq. (4.6) in Eq. (4.2) yields

$$D_7 = 2\, C_6 \left[B^B/\alpha^B - B^A/\alpha^A \right] , \tag{4.7}$$

in agreement with the earlier result of Galatry and Gharbi [53,54].

Accurate values for both D_7 and the B tensor are not available for many systems. In a series of large-basis perturbation calculations, Byers Brown and Whisnant evaluated D_7 for a model system consisting of a hydrogren atom A and an atom B with a hydrogenic wavefunction scaled by a factor ζ [58]. The wavefunctions of these two systems can be expressed in atomic units as

$$\psi_A = \left(\frac{1}{\pi}\right)^{1/2} \exp\,[-r] , \tag{4.8}$$

and

$$\psi_B = \left(\frac{\zeta^3}{\pi}\right)^{1/2} \exp\,[-\zeta r] . \tag{4.9}$$

The accurate results for D_7 are listed in Table 4.1 for comparison with the approximations. The polarizability α_ζ and hyperpolarizability B_ζ of the scaled atom H_ζ are related to α and B of the hydrogen atom by

$$\alpha_\zeta = \zeta^{-4}\, \alpha \tag{4.10}$$

and

$$B_\zeta = \zeta^{-8} B . \tag{4.11}$$

Eq. (4.7) thus becomes

$$D_7 = 2 C_6 B (\zeta^{-4} - 1) / \alpha . \tag{4.12}$$

For the hydrogen atom, $\alpha = \frac{9}{2}$ and $B = -\frac{213}{2}$ in atomic units. Values of D_7 as computed using Eq. (4.12) are given in Table 4.1 for $\zeta = 1.0 - 2.0$; the error in this approximation ranges from 15% for small ζ to 12% for large ζ. For large ζ, Eq. (4.12) gives a slight improvement over the Unsöld approximation of Byers Brown and Whisnant [58].

The approximation of I^X in Eq. (4.3) does not take into account the frequency-dependent weighting of B tensor values for one atom by the α polarizability of the other, as found in the exact expression of Eq. (3.6). This suggests that I^X might be estimated more closely by the Unsöld approximation for the ratio

$$I^A = \int_0^\infty d\omega\, B^A(0,i\omega)\, \alpha^B(i\omega) \Big/ \int_0^\infty d\omega\, \alpha^A(i\omega)\, \alpha^B(i\omega) . \tag{4.13}$$

Employing the Unsöld approximations given by Eqs. (4.4) and (4.5) in Eq. (4.13) and carrying out the integrations leads to

$$I^A = \frac{1}{3} \frac{B^A}{\alpha^A} \left[2 + \frac{\Omega_A}{(\Omega_A + \Omega_B)}\right] , \tag{4.14}$$

with a similar result for I^B. Using I^A and I^B together in Eq. (4.2) yields

$$D_7 = C_6 \left[\frac{B^B}{\alpha^B}\left[2 + \frac{1}{(1 + \Omega_A/\Omega_B)}\right] - \frac{B^A}{\alpha^A}\left[2 + \frac{1}{(1 + \Omega_B/\Omega_A)}\right]\right] . \qquad (4.15)$$

Specializing to the pair $H...H_\zeta$, Eq. (4.15) becomes

$$D_7 = C_6\, B\, (\zeta^{-4} - 1)\, [2 + \zeta^2(1 + \zeta^2)^{-2}] \,/\, \alpha . \qquad (4.16)$$

As Table 4.1 shows, Eq. (4.16) provides good estimates for D_7, underestimating the accurate results by only 4.3 - 4.5% over the entire range of ζ values.

As a second test of the approximations, consider the interaction of hydrogen with helium. The accurate value of D_7 is 120 a.u. for H^+He^- [59]. With the values (all in a.u.) $\alpha^{He} = 1.383$ [80], $B^{He} = -6.587$ [81], and $C_6(H...He) = 2.82 \pm 0.01$ [82], Eq. (4.7) yields $D_7 = 107$ a.u., while a direct Unsöld approximation gives $D_7 = 108$ a.u. [59]. An improved estimate may be based on Eq. (4.15). Substituting the ratio of ionization potentials $I_H/I_{He} = 0.553$ for Ω_H/Ω_{He} in Eq. (4.15) yields $D_7 = 122$ a.u. (~2% error).

Table 4.1

The long-range dipole coefficients D_7 for a hydrogen atom interacting with a hydrogen-like atom scaled by a factor ζ. The system is polarized $H^+H_\zeta^-$.

ζ	C_6 [58]	D_7			
		Perturbation results [58]	Unsöld approx. [58]	Eq. (4.12)	Eq. (4.16)
1.0	6.499027	0	0	0	0
1.1	4.862103	85.65	72.84	72.95	81.99
1.2	3.703157	106.29	90.31	90.75	101.73
1.3	2.865143	102.87	87.29	88.13	98.43
1.4	2.247960	91.48	77.51	78.71	87.51
1.5	1.785978	78.49	66.39	67.84	75.06
1.6	1.435108	66.29	55.97	57.56	63.38
1.7	1.165113	55.64	46.90	48.55	53.18
1.8	0.9548598	46.65	39.25	40.89	44.58
1.9	0.7893366	39.17	32.91	34.50	37.42
2.0	0.6577167	33.00	27.68	29.19	31.52

B. van der Waals Dipoles of He...H_2 and He...N_2

As in the atom-atom case, a constant-ratio approximation may be used to connect the $D_{\lambda L}^{vdW}$ coefficients given by Eqs. (3.23) - (3.26) to van der Waals energy coefficients for the interaction of an S state atom with a centrosymmetric linear molecule. For such a system the van der Waals energy can be expanded to order R^{-8} as

$$\Delta E^{vdW}(R,\Theta_r) = - [C_6^o + C_6^2 P_2(\cos\Theta_r)] R^{-6} - [C_8^o + C_8^2 P_2(\cos\Theta_r) + C_8^4 P_4(\cos\Theta_r)] R^{-8} , \quad (4.17)$$

where $\underline{R}$ is the vector from the midpoint of the molecule to the atom, Θ_r is the angle between this vector and the molecular symmetry axis ($\cos\Theta_r = \hat{r} \cdot \hat{R}$), and P_ℓ is the ℓ^{th} Legendre polynomial. The energy coefficients C_6^0, C_6^2, C_8^0, C_8^2, and C_8^4 are expressed in terms of the susceptibilities of the separated species as

$$C_6^0 = 3 \frac{\hbar}{\pi} \int_0^\infty d\omega \, \alpha^A(i\omega) \, \bar{\alpha}^B(i\omega) , \quad (4.18)$$

$$C_6^2 = \frac{\hbar}{\pi} \int_0^\infty d\omega \, \alpha^A(i\omega) \, [\alpha_{\parallel}^B(i\omega) - \alpha_{\perp}^B(i\omega)] , \quad (4.19)$$

$$C_8^0 = 15 \frac{\hbar}{\pi} \int_0^\infty d\omega \, [C^A(i\omega) \, \bar{\alpha}^B(i\omega) + \bar{C}^B(i\omega) \, \alpha^A(i\omega)] , \quad (4.20)$$

$$C_8^2 = \frac{4}{7} \frac{\hbar}{\pi} \int_0^\infty d\omega \, [7 \, C^A(i\omega) \, [\alpha_{\parallel}^B(i\omega) - \alpha_{\perp}^B(i\omega)] + 3 \, [5C_{zz,zz}^B(i\omega) + 4C_{xz,xz}^B(i\omega) - 8C_{xx,xx}^B(i\omega)] \, \alpha^A(i\omega) + 3 \, [3E_{z,zzz}^B(i\omega) - 8E_{x,xxx}^B(i\omega)] \, \alpha^A(i\omega)] , \quad (4.21)$$

and

$$C_8^4 = \frac{4}{7}\frac{\hbar}{\pi}\int_0^\infty d\omega\,\left[3\,[2C^B_{zz,zz}(i\omega) - 4C^B_{xz,xz}(i\omega) + C^B_{xx,xx}(i\omega)]\,\alpha^A(i\omega) + 5\,[E^B_{z,zzz}(i\omega) + 2E^B_{x,xxx}(i\omega)]\,\alpha^A(i\omega)\right] . \qquad (4.22)$$

A susceptibility that appears for the first time in these expressions is the quadrupole polarizability $C_{\alpha\beta,\gamma\delta}(i\omega)$. For the atom A

$$C^A_{\alpha\beta,\gamma\delta}(i\omega) = C^A(i\omega)\,\left[\frac{1}{2}\,(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) - \frac{1}{3}\,\delta_{\alpha\beta}\,\delta_{\gamma\delta}\right] . \qquad (4.23)$$

For the molecule B

$$\bar{C}^B(i\omega) = \frac{1}{10}\,[C^B_{zz,zz}(i\omega) + 8C^B_{xz,xz}(i\omega) + 8C^B_{xx,xx}(i\omega)] , \qquad (4.24)$$

with the full C tensor given by Buckingham [74].

In order to construct approximations to the $D^{vdW}_{\lambda L}$ coefficients which are analogous to the atom-atom case, the Unsöld approximations for the C and E tensors are required. For centrosymmetric molecules these are

$$C_{\alpha\beta,\gamma\delta}(i\omega) = \frac{2}{3\hbar}\,[\langle 0|\Theta_{\alpha\beta}\Theta_{\gamma\delta}|0\rangle - \langle 0|\Theta_{\alpha\beta}|0\rangle\langle 0|\Theta_{\gamma\delta}|0\rangle]\,\frac{\Omega}{(\Omega^2 + \omega^2)} , \qquad (4.25)$$

and

$$E_{\alpha,\beta\gamma\delta}(i\omega) = \frac{2}{\hbar}\,\langle 0|\mu_\alpha\Omega_{\beta\gamma\delta}|0\rangle\,\frac{\Omega}{(\Omega^2 + \omega^2)} . \qquad (4.26)$$

We assume that the component of the B hyperpolarizability that transforms as a spherical tensor of rank ℓ will be best approximated in terms of components of $\underline{\underline{\alpha}}$, $\underline{\underline{C}}$, and $\underline{\underline{E}}$ of the same spherical tensor rank. If $D_{\lambda L}^{vdW}$ can be approximated in terms of either C_6^{λ} or C_8^{λ}, the former is preferred, because more reliable values of the C_6^{λ} energy coefficients are available. The resulting approximations are

$$D_{01}^{vdW} \cong 2\, C_6^{o}\, R^{-7} \left[\frac{\bar{B}^B}{\bar{\alpha}^B} - \frac{B^A}{\alpha^A}\right] , \tag{4.27}$$

$$D_{21}^{vdW} \cong \frac{1}{5} (2)^{1/2}\, C_6^{2}\, R^{-7} \left[\frac{B^A}{\alpha^A} - 4\,\frac{(3B_{2b}^B + B_{2c}^B + 10B_{2d}^B)}{(\alpha_{\parallel}^B - \alpha_{\perp}^B)}\right] , \tag{4.28}$$

$$D_{23}^{vdW} \cong \frac{8}{15} (3)^{1/2}\, C_6^{2}\, R^{-7} \left[2\,\frac{(B_{2b}^B + 2B_{2c}^B)}{(\alpha_{\parallel}^B - \alpha_{\perp}^B)} - \frac{B^A}{\alpha^A}\right] , \tag{4.29}$$

and

$$D_{43}^{vdW} \cong -\frac{56}{3}\, C_8^{4}\, R^{-7}\, B_4^B \times \left[3\,(2C_{zz,zz}^B - 4C_{xz,xz}^B + C_{xx,xx}^B) + 5\,(E_{z,zzz}^B + 2E_{x,xxx}^B)\right]^{-1} . \tag{4.30}$$

All susceptibilities appearing in Eqs. (4.27) - (4.30) take their static values; at zero frequency $B_{xz,xz}^B = B_{zx,xz}^B$.

The susceptibilities and van der Waals energy coefficients are known for the He...H_2 system and are given in Table 4.2, so we can determine the $D_{\lambda L}^{vdW}$ coefficients from Eqs. (4.27) - (4.30). Fixing

the internuclear distance in the H_2 molecule at its equilibrium value of 1.4 a.u., the van der Waals dipole coefficients are

$$D_{01}^{vdW} = -\ 71.00\ R^{-7}, \tag{4.31}$$

$$D_{21}^{vdW} = 10.53\ R^{-7}, \tag{4.32}$$

$$D_{23}^{vdW} = -\ 1.46\ R^{-7}, \tag{4.33}$$

and

$$D_{43}^{vdW} = 0.01\ R^{-7}. \tag{4.34}$$

A positive value for the net dipole moment corresponds to the polarity $He^{+}H_2^{-}$.

For comparison, the long-range induction dipole coefficients for the $He...H_2$ system are

$$D_{01}^{ind} = 1.37\ R^{-7}, \tag{4.35}$$

$$D_{21}^{ind} = -\ 9.29\ R^{-7}, \tag{4.36}$$

$$D_{23}^{ind} = 1.094\ R^{-4} + 4.68\ R^{-7}, \qquad (4.33)$$

$$D_{43}^{ind} = -\ 0.78\ R^{-7}, \tag{4.38}$$

and

$$D_{45}^{ind} = 0.87\ R^{-6}\ . \tag{4.39}$$

These dipole coefficients are expected to increase by ~ 10% if the internuclear separation in the H_2 molecule is increased to its ground-state vibrational average of 1.449 a.u.; an exception is D_{45}^{ind}, which increases 25% when the vibrationally averaged value of the hexadecapole is used in place of the value in Table 4.2.

The constant-ratio approximations suggest that van der Waals interactions affect D_{01} and D_{21} significantly for He...H_2 at long range. In fact, D_{01}^{vdW} is roughly fifty times D_{01}^{ind} in magnitude. The D_{23} coefficient is dominated by the quadrupole-induced dipole, which is proportional to R^{-4}. The van der Waals contribution to D_{43} is very small compared with the induction contribution, though both vary as R^{-7} at lowest order. Dispersion effects on the total collision-induced dipole moment are small relative to induction effects, but still appreciable. When the intermolecular vector $\hat{R}$ points along the z axis of the H_2 molecule, the long-range van der Waals term in the dipole μ_z is 13% of the induction term for collinear He...H_2 at R = 7 a.u., and is 19% of the induction term for the T-shaped geometry at this distance. At R = 5 a.u., the van der Waals contribution increases to 33% of the induction term in μ_z for the collinear configuration and 50% for the T-shape. However, overlap damping of both the induction and dispersion dipoles reduces $D_{\lambda L}^{vdW}$ and $D_{\lambda L}^{ind}$ below their asymptotic forms at this intermolecular distance, and short-range exchange effects predominate in the *ab initio* collision-induced dipole for R less than the collision diameter of 5.7 a.u. [68,90]. We may conclude that van der Waals

effects on the dipole moment of this system are most significant when the D_{01} term can be distinguished from the D_{23} term, as in spectroscopic lineshape studies. Selection rules for transitions of the atom-diatom complex differ for the D_{01} and D_{23} terms [16].

Given the accuracy of the approximations in Section A to the D_7 coefficient for H...H_ζ and H...He pairs, together with the accuracy of a similar approximation for the van der Waals contributions to the pair polarizabilities of H and He atoms [49], the error in $D_{01}^{(7)}$ (the coefficient of R^{-7} in D_{01}) is expected to fall between 15% and 25%. The value $D_{01}^{(7)} \cong -71$ a.u. determined here agrees with the result of a valence-bond calculation by Berns et al. [90] within this error margin. The valence-bond result, $D_{01}^{(7)} \cong -62$ a.u., was obtained from a numerical fit of the calculated dispersion dipole between R = 7 a.u. and 10 a.u. For comparison, we may assume that the van der Waals dipole of He...H_2 corresponds to a shift in the center of the electronic charge distribution of each system by a distance $\delta = \frac{\mu}{2e}$. Then, if δ is determined by balancing the dispersion energy gain vs. the energy required for polarization, the computed dispersion dipole coefficient for He...H_2 is $D_{01}^{(7)} = -48.5$ a.u. [17,18], or -44.5 a.u. using the molecular properties from Table 4.2. Meyer and Frommhold fit the collision-induced roto-translational absorption spectra of He...H_2, yielding an effective value of $D_{01}^{(7)} = -81$ a.u. [17,18]; but their fitting procedure incorporates not only the leading R^{-7} terms, but also all higher-order induction and dispersion effects in the range R = 7 a.u. to 10 a.u. A direct ab initio calculation of D_{01}^{vdW} based on Eq. (3.23)

would be valuable both in assessing the different numerical results and in providing a test of approximations analogous to Eq. (4.27).

The estimates of D_{21}^{vdW}, D_{23}^{vdW}, and D_{43}^{vdW} in terms of the anisotropic C_6^{λ} and C_8^{λ} energy coefficients are probably susceptible to larger errors than the isotropically averaged D_{01}^{vdW}. However, the charge shift model described above gives $D_{21}^{(7)}$ = 8 a.u. [17,18] or 9.9 a.u. using the properties in Table 4.2, in good agreement with the value of 10.53 a.u. from Eq. (4.32). Experimental results for these coefficients are not available; numerical noise prevented the recovery of an effective value of $D_{21}^{(7)}$ from the most recent fit of the collision-induced absorption spectra [17,18], and the fit of D_{23} reflects the quadrupole-induced dipole predominantly.

The susceptibilities and van der Waals energy coefficients are known for the He...N_2 system as well and are given in Table 4.3, so we can also determine the $D_{\lambda L}$ coefficients for this pair. However, as can be seen from the table, a discrepancy in both sign and order of magnitude occurs for the susceptibility component B_4 as computed using the ab initio results of Jameson and Fowler [87] and of Dykstra [86]. It is therefore pointless to compute D_{43}^{vdW} (its contribution is small in any case). The remaining $D_{\lambda L}^{vdW}$ coefficients are, in the constant-ratio approximation,

$$D_{01}^{vdW} = -\ 130.0\ (-\ 113.96)\ R^{-7}\ , \qquad (4.40)$$

$$D_{21}^{vdW} = 17.41\ (28.28)\ R^{-7}\ , \qquad (4.41)$$

and

would be valuable both in assessing the different numerical results and in providing a test of approximations analogous to Eq. (4.29).

The estimates of D_{21}^{vdW}, D_{23}^{vdW}, and D_{43}^{vdW} in terms of the anisotropic $C_6^{\perp}$ and $C_6^{\parallel}$ energy coefficients are probably susceptible to larger errors than the isotropically averaged C_6^{vdW}. However, the charge shift model described above gives $D_2^{(7)} = 8$ a.u. [17,18] or

$$D_{23}^{vdW} = -\ 0.17\ (-\ 2.28)\ R^{-7}, \tag{4.42}$$

where the parenthetical results were found using the B tensor values from Ref. [86] given in Table 4.3. A positive value for the net dipole moment corresponds to the polarity $He^{+}N_2^{-}$.

For comparison, the long-range induction dipole coefficients for the $He...N_2$ system are

$$D_{01}^{ind} = -\ 8.42\ R^{-7}, \tag{4.43}$$

$$D_{21}^{ind} = 50.53\ R^{-7}, \tag{4.44}$$

$$D_{23}^{ind} = -\ 2.61\ R^{-4} - 25.19\ R^{-7}, \tag{4.45}$$

$$D_{43}^{ind} = 4.81\ R^{-7}, \tag{4.46}$$

and

$$D_{45}^{ind} = -\ 23.10\ R^{-6}. \tag{4.47}$$

The approximation results show a significant contribution from the van der Waals interaction to the coefficients D_{01} and D_{21} for $He...N_2$ at long range; D_{01}^{vdW} is about fifteen times D_{01}^{ind} in magnitude. Again, the D_{23} coefficient is dominated by the quadrupole-induced dipole, which is proportional to R^{-4}. We note that here the van der Waals and induction contributions to each dipole coefficient enter with the same sign and so enhance one

another, while these contributions were of opposite sign in the $He...H_2$ system.

As with the earlier approximations, the error in $D_{01}^{(7)}$ should fall between 15% and 25% if the static B tensor is accurately known. However, the two calculations of D_{01}^{vdW} using values from Refs. [86] and [87] for the B tensor components give results that differ by nearly 15%, and this increases the likely error. The difference between the two results for D_{21}^{vdW} is greater, but the values should indicate the magnitude of this coefficient. The two results for D_{23}^{vdW} differ so much that the usefulness of the estimate is questionable. More reliable values of the static B tensor components would improve the estimates based on Eqs. (4.27) - (4.30) for $He...N_2$; direct ab initio calculations based on Eqs. (3.23) - (3.26) would be even more valuable.

Table 4.2

Molecular properties and van der Waals energy coefficients used in calculating $D_{\lambda L}$ for the He...H_2 system. The internuclear distance in the H_2 molecule is held fixed at its equilibrium value of 1.4 a.u. All values are given in atomic units.

	Property	Value		Property	Value
He	α	1.383[a]	H_2	$C_{zz,zz}$	5.927[g]
	B	-6.587[b]		$C_{xz,xz}$	4.242[g]
				$C_{xx,xx}$	4.944[g]
H_2	Θ	0.4568[c]		$E_{z,zzz}$	3.93[h]
	Φ	0.2826[d]		$E_{x,xxx}$	1.76[h]
	$\alpha_{\parallel}$	6.380[e]			
	$\alpha_{\perp}$	4.578[e]	He...H_2	C_6^0	3.904[g]
	$B_{zz,zz}$	-92.12[f]		C_6^2	0.445[i]
	$B_{xz,xz}$	-56.92[f]		C_8^4	0.308[i]
	$B_{xx,zz}$	30.54[f]			
	$B_{xx,xx}$	-62.24[f]			

a) Ref. 80; b) Ref. 81; c) Ref. 83; d) Ref. 84; e) Ref. 85;

f) Refs. 86 and 87; g) Ref. 88; h) Ref. 89; i) Computed using isotropic C_n coefficients from Ref. 88 and anisotropy factors from Ref. 89.

Table 4.3

Molecular properties and van der Waals energy coefficients used in calculating $D_{\lambda L}$ for the He...N_2 system. The internuclear distance in the N_2 molecule is held fixed at its vibrationally averaged value of 2.07 a.u. All values are given in atomic units.

	Property	Value			Property	Value
He	α	1.383[a]		N_2	$E_{z,zzz}$	22.04[h]
	B	-6.587[b]			$E_{x,xxx}$	16.67[h]
N_2	Θ	-1.09[c]		He...N_2	C_6^0	9.795[h]
	Φ	-7.47[d]			C_6^2	1.103[h]
	$\alpha_{\parallel}$	14.718[e]				
	$\alpha_{\perp}$	10.065[e]				
	$B_{zz,zz}$	-174[f]	(-170.55[g])			
	$B_{xz,xz}$	-102[f]	(-105.35[g])			
	$B_{xx,zz}$	67[f]	(61.23[g])			
	$B_{xx,xx}$	-119.5[f]	(-97.76[g])			
	$\bar{B}$	-132.4[f]	(-122.90[g])			
	B_{2b}	2.95[f]	(8.54[g])			
	B_{2c}	-7.21[f]	(-12.42[g])			
	B_{2d}	-7.21[f]	(-12.42[g])			
	B_4	-1.13[f]	(0.187[g])			

a) Ref. 80; b) Ref. 81; c) Ref. 94; d) Ref. 95; e) Ref. 96; f) Ref. 87; g) Ref. 86; h) Ref. 93.

C. van der Waals Dipoles of $H_2 \ldots H_2$ and $N_2 \ldots N_2$

We now apply the constant-ratio approximation technique to the $D^{vdW}_{\lambda_1\lambda_2\lambda L}$ coefficients given by Eqs. (3.51) - (3.68) for the interaction of two centrosymmetric linear molecules. The dipole coefficients will be connected to the van der Waals energy coefficients for this system; the energy can be expanded as

$$\Delta E_n^{vdW}(R,\Theta_1,\phi_1,\Theta_2,\phi_2) = - R^{-n} \sum C_n^{\lambda_1\lambda_2 m} P^m_{\lambda_1}(\cos\Theta_1)\, P^m_{\lambda_2}(\cos\Theta_2) \times \cos[m(\phi_1-\phi_2)] \ , \qquad (4.48)$$

where the summation is over λ_1, λ_2, and m. The particular energy coefficients to be used in the approximation are

$$C_6^{000} = 3\,\frac{\hbar}{\pi} \int_0^\infty d\omega\, \bar{\alpha}^A(i\omega)\, \bar{\alpha}^B(i\omega) \ , \qquad (4.49)$$

$$C_6^{200} = \frac{\hbar}{\pi} \int_0^\infty d\omega\, [\alpha^A_{\parallel}(i\omega) - \alpha^A_{\perp}(i\omega)]\, \bar{\alpha}^B(i\omega) \ , \qquad (4.50)$$

$$C_6^{220} = \frac{\hbar}{\pi} \int_0^\infty d\omega\, [\alpha^A_{\parallel}(i\omega) - \alpha^A_{\perp}(i\omega)]\, [\alpha^B_{\parallel}(i\omega) - \alpha^B_{\perp}(i\omega)] \ , \qquad (4.51)$$

$$C_8^{400} = \frac{4}{7}\frac{\hbar}{\pi} \int_0^\infty d\omega\, \Big[3\,[2C^A_{zz,zz}(i\omega) - 4C^A_{xz,xz}(i\omega) + C^A_{xx,xx}(i\omega)] + 5\,[E^A_{z,zzz}(i\omega) + 2E^A_{x,xxx}(i\omega)]\Big]\, \bar{\alpha}^B(i\omega) \ , \qquad (4.52)$$

and

$$C_8^{420} = \frac{4}{105}\frac{\hbar}{\pi}\int_0^\infty d\omega\ \left[66\ [2C^A_{zz,zz}(i\omega) - 4C^A_{xz,xz}(i\omega) + C^A_{xx,xx}(i\omega)]\right.$$
$$\left. + 95\ [E^A_{z,zzz}(i\omega) + 2E^A_{x,xxx}(i\omega)]\right]\ [\alpha^B_{\parallel}(i\omega) - \alpha^B_{\perp}(i\omega)]\ . \quad (4.53)$$

The Unsöld approximations for the α, B, C, and E tensors were given earlier by Eqs. (4.4), (4.5), (4.25), and (4.26). Using these equations together with Eqs. (4.49) - (4.53) results in the approximations

$$D^{vdW}_{0001} \cong 2\ C_6^{000}\ R^{-7}\ [\frac{\bar{B}^B}{\bar{\alpha}^B} - \frac{\bar{B}^A}{\bar{\alpha}^A}]\ , \quad (4.54)$$

$$D^{vdW}_{2021} \cong \frac{1}{5}\ (2)^{1/2}\ C_6^{200}\ R^{-7}\ [4\ \frac{(3B^A_{2b} + B^A_{2c} + 10B^A_{2d})}{(\alpha^A_{\parallel} - \alpha^A_{\perp})} - \frac{\bar{B}^B}{\bar{\alpha}^B}]\ , \quad (4.55)$$

$$D^{vdW}_{2201} \cong \frac{8}{15}\ (\frac{1}{5})^{1/2}\ C_6^{220}\ R^{-7}\ [\frac{(B^B_{2c} + B^B_{2d})}{(\alpha^B_{\parallel} - \alpha^B_{\perp})} - \frac{(B^A_{2c} + B^A_{2d})}{(\alpha^A_{\parallel} - \alpha^A_{\perp})}]\ , \quad (4.56)$$

$$D^{vdW}_{2211} \cong \frac{4}{5}\ (\frac{1}{5})^{1/2}\ C_6^{220}\ R^{-7}\ [\frac{B^B_{2d}}{(\alpha^B_{\parallel} - \alpha^B_{\perp})} + \frac{B^A_{2d}}{(\alpha^A_{\parallel} - \alpha^A_{\perp})}]\ , \quad (4.57)$$

$$D^{vdW}_{2221} \cong \frac{4}{15}\ (\frac{1}{35})^{1/2}\ C_6^{220}\ R^{-7}\ [\frac{(6B^B_{2b} - 2B^B_{2c} + 7B^B_{2d})}{(\alpha^B_{\parallel} - \alpha^B_{\perp})}$$
$$- \frac{(6B^A_{2b} - 2B^A_{2c} + 7B^A_{2d})}{(\alpha^A_{\parallel} - \alpha^A_{\perp})}]\ , \quad (4.58)$$

$$D^{vdW}_{4221} \cong 4\ (7)^{1/2}\ C_8^{420}\ R^{-7}\ B^A_4$$
$$\times \left[66\ (2C^A_{zz,zz} - 4C^A_{xz,xz} + C^A_{xx,xx}) + 95\ (E^A_{z,zzz} + 2E^A_{x,xxx})\right]^{-1}\ ,$$
$$(4.59)$$

$$D^{vdW}_{2023} \cong \frac{8}{15}\,(3)^{1/2}\; C_6^{200}\; R^{-7}\; \left[\frac{\bar{B}^B}{\bar{\alpha}^B} - 2\,\frac{(B^A_{2b} + 2B^A_{2c})}{(\alpha^A_{\parallel} - \alpha^A_{\perp})}\right] , \tag{4.60}$$

$$D^{vdW}_{2223} \cong \frac{16}{15}\,\left(\frac{2}{105}\right)^{1/2}\; C_6^{220}\; R^{-7}\; \left[\frac{(B^A_{2b} - 2B^A_{2c} + 2B^A_{2d})}{(\alpha^A_{\parallel} - \alpha^A_{\perp})} - \frac{(B^B_{2b} - 2B^B_{2c} + 2B^B_{2d})}{(\alpha^B_{\parallel} - \alpha^B_{\perp})}\right] , \tag{4.61}$$

$$D^{vdW}_{2233} \cong -\frac{4}{15}\,\left(\frac{2}{15}\right)^{1/2}\; C_6^{220}\; R^{-7}\; \left[\frac{(5B^A_{2b} + 8B^A_{2d})}{(\alpha^A_{\parallel} - \alpha^A_{\perp})} + \frac{(5B^B_{2b} + 8B^B_{2d})}{(\alpha^B_{\parallel} - \alpha^B_{\perp})}\right] , \tag{4.62}$$

$$D^{vdW}_{2243} \cong \frac{4}{15}\,\left(\frac{2}{35}\right)^{1/2}\; C_6^{220}\; R^{-7}\; \left[\frac{(5B^A_{2b} + 4B^A_{2c} + 24B^A_{2d})}{(\alpha^A_{\parallel} - \alpha^A_{\perp})} - \frac{(5B^B_{2b} + 4B^B_{2c} + 24B^B_{2d})}{(\alpha^B_{\parallel} - \alpha^B_{\perp})}\right] , \tag{4.63}$$

$$D^{vdW}_{4043} \cong \frac{56}{3}\; C_8^{400}\; R^{-7}\; B^A_4 \times \left[3\,(2C^A_{zz,zz} - 4C^A_{xz,xz} + C^A_{xx,xx}) + 5\,(E^A_{z,zzz} + 2E^A_{x,xxx})\right]^{-1} , \tag{4.64}$$

$$D^{vdW}_{4223} \cong \frac{2}{3}\,\left(\frac{14}{3}\right)^{1/2}\; C_8^{420}\; R^{-7}\; B^A_4 \times \left[66\,(2C^A_{zz,zz} - 4C^A_{xz,xz} + C^A_{xx,xx}) + 95\,(E^A_{z,zzz} + 2E^A_{x,xxx})\right]^{-1} , \tag{4.65}$$

$$D^{vdW}_{4233} \cong -\frac{35}{3}\left(\frac{1}{3}\right)^{1/2} C^{420}_{8} R^{-7} B^{A}_{4}$$
$$\times \left[66\,(2C^{A}_{zz,zz} - 4C^{A}_{xz,xz} + C^{A}_{xx,xx}) + 95\,(E^{A}_{z,zzz} + 2E^{A}_{x,xxx})\right]^{-1} , \tag{4.66}$$

$$D^{vdW}_{4243} \cong \frac{5}{3}\,(77)^{1/2} C^{420}_{8} R^{-7} B^{A}_{4}$$
$$\times \left[66\,(2C^{A}_{zz,zz} - 4C^{A}_{xz,xz} + C^{A}_{xx,xx}) + 95\,(E^{A}_{z,zzz} + 2E^{A}_{x,xxx})\right]^{-1} , \tag{4.67}$$

$$D^{vdW}_{2245} \cong \frac{8}{3}\left(\frac{2}{7}\right)^{1/2} C^{220}_{6} R^{-7} \left[\frac{(B^{B}_{2b} + 2B^{B}_{2c})}{(\alpha^{B}_{\parallel} - \alpha^{B}_{\perp})} - \frac{(B^{A}_{2b} + 2B^{A}_{2c})}{(\alpha^{A}_{\parallel} - \alpha^{A}_{\perp})}\right] , \tag{4.68}$$

$$D^{vdW}_{4245} \cong \frac{20}{3}\left(\frac{35}{11}\right)^{1/2} C^{420}_{8} R^{-7} B^{A}_{4}$$
$$\times \left[66\,(2C^{A}_{zz,zz} - 4C^{A}_{xz,xz} + C^{A}_{xx,xx}) + 95\,(E^{A}_{z,zzz} + 2E^{A}_{x,xxx})\right]^{-1} , \tag{4.69}$$

$$D^{vdW}_{4255} \cong -\frac{140}{3}\left(\frac{5}{3}\right)^{1/2} C^{420}_{8} R^{-7} B^{A}_{4}$$
$$\times \left[66\,(2C^{A}_{zz,zz} - 4C^{A}_{xz,xz} + C^{A}_{xx,xx}) + 95\,(E^{A}_{z,zzz} + 2E^{A}_{x,xxx})\right]^{-1} , \tag{4.70}$$

and

$$D^{vdW}_{4265} \cong \frac{700}{3}\left(\frac{26}{33}\right)^{1/2} C^{420}_{8} R^{-7} B^{A}_{4}$$
$$\times \left[66\,(2C^{A}_{zz,zz} - 4C^{A}_{xz,xz} + C^{A}_{xx,xx}) + 95\,(E^{A}_{z,zzz} + 2E^{A}_{x,xxx})\right]^{-1} . \tag{4.71}$$

The susceptibilities that appear in Eqs. (4.54) - (4.71) are evaluated at zero frequency, where $B^{B}_{xz,xz} = B^{B}_{zx,xz}$.

Susceptibilities and van der Waals energy coefficients are given in Table 4.4 for the $H_2 \ldots H_2$ system, so the dipole coefficients can be determined from Eqs. (4.54) - (4.71). We use the vibrationally averaged separation $\langle r \rangle = 1.449$ a.u. in the ground state as the representative value for the internuclear distance in the H_2 molecule; the values in Table 4.4 are given for this distance. The B tensor components were interpolated graphically to $r = \langle r \rangle$ from the data of Dykstra [86], who gives values over a range of internuclear separations. Values for the E tensor components are unavailable at the vibrationally averaged distance, but since they only affect terms of $\lambda = 4$ symmetry (which are small), they may be estimated from their values at the equilibrium separation without introducing significant error. The change in the B and C tensor components upon increasing r from r_{eq} to $\langle r \rangle$ averages to 7.05%. Using this as a correction factor to the Mulder *et al.* values [89] gives $E_{z,zzz} = 4.21$ and $E_{x,xxx} = 1.88$.

Results for the van der Waals dipole coefficients are compared with the induction coefficients in Table 4.5 for $H_2 \ldots H_2$. The van der Waals contribution to D_{2211} is four times the induction contribution; D_{2021}^{vdW} is about 60% of D_{2021}^{ind}. Van der Waals effects are very slight for the remaining coefficients. The induction coefficients show an appreciable contribution from back-induction, even though these enter only at order R^{-7} (to lowest order). Interpretations of collision-induced spectra typically include only the effects of quadrupole and hexadecapole induced dipole moments; addition of back-induction terms may improve the agreement between theory and experiment.

In Table 4.6 are listed the susceptibilities and van der Waals energy coefficients for the $N_2 \ldots N_2$ system. As discussed in Section B of this chapter, the large discrepancy in the B_4 values from Refs. [86] and [87] precludes computation of the dipole coefficients that depend on them. The remaining van der Waals dipole coefficients are listed in Table 4.7 (values in parentheses were determined using the results from Ref. [86] for the B tensor components), along with all of the induction dipole coefficients. Inclusion of back-induction effects is again seen to make an appreciable contribution.

Lastly, using the values in Table 4.4 for H_2 and in Table 4.6 for N_2, along with the result $C_6^{000}(H_2 \ldots N_2) = 29.28$ a.u. [93], we may determine D_{0001}^{vdW} for the $H_2 \ldots N_2$ system from Eq. (4.54). We find

$$D_{0001}^{vdW} = 169.4 \; (217.3) \; R^{-7} \; , \tag{4.72}$$

where the result in parentheses is based on the B tensor values from Ref. [86]. For comparison, the induction dipole coefficient is

$$D_{0001}^{ind} = - \, 46.20 \; R^{-7} \; . \tag{4.73}$$

From these results it is clear the the van der Waals contribution to the D_{0001} dipole coefficient is much greater than the induction contribution.

In Table 4.6 are listed the compressibilities and van der Waals energy coefficients for the N_2--X_2 system. As discussed in Section 6 of this chapter, the large discrepancy

(66) and [67] precludes

depend on

lies

Table 4.4

Molecular properties and van der Waals energy coefficients used in calculating $D_{\lambda_1\lambda_2\lambda L}$ for the $H_2 \ldots H_2$ system. The internuclear distance in each H_2 molecule is held fixed at its ground-state vibrationally averaged value of 1.449 a.u. All values are given in atomic units.

	Property	Value		Property	Value
H_2	Θ	0.4847[a]	H_2	$C_{zz,zz}$	6.357[e]
	Φ	0.3530[b]		$C_{xz,xz}$	4.512[e]
	$\alpha_{\parallel}$	6.713[c]		$C_{xx,xx}$	5.227[e]
	$\alpha_{\perp}$	4.736[c]		$E_{z,zzz}$	4.21[f]
	$B_{zz,zz}$	-100.31[d]		$E_{x,xxx}$	1.88[f]
	$B_{xz,xz}$	-61.44[d]			
	$B_{xx,zz}$	32.63[d]	$H_2 \ldots H_2$	C_6^{000}	12.078[g]
	$B_{xx,xx}$	-66.20[d]		C_6^{200}	1.233[h]
	$\bar{B}$	-77.10[d]		C_6^{220}	0.398[h]
	B_{2b}	-0.482[d]		C_8^{400}	1.38[h]
	B_{2c}	-4.02[d]		C_8^{420}	0.57[h]
	B_{2d}	-4.02[d]			
	B_4	-0.101[d]			

a) Ref. 83; b) Ref. 84; c) Ref. 91;
d) interpolated for r = <r> from data in Ref. 86; e) Ref. 88;
f) estimated for r = <r> from values in Ref. 89 (see text);
g) Ref. 92; h) Ref. 93.

Table 4.5

Comparison of van der Waals and induction contributions to the $D_{\lambda_1\lambda_2\lambda L}$ coefficients for the $H_2...H_2$ system. The internuclear distance in each H_2 molecule is held fixed at its vibrationally average value of 1.449 a.u. All values are given in atomic units.

λ_1	λ_2	λ	L	$D^{vdW}_{\lambda_1\lambda_2\lambda L}$	$D^{ind}_{\lambda_1\lambda_2\lambda L}$
2	0	2	1	$- 27.24\ R^{-7}$	$40.192\ R^{-7}$
2	2	1	1	$- 0.58\ R^{-7}$	$0.145\ R^{-7}$
4	2	2	1	$- 8.12 \times 10^{-4}\ R^{-7}$	$0.049\ R^{-7}$
2	0	2	3	$- 6.46\ R^{-7}$	$- 4.529\ R^{-4} - 19.88\ R^{-7}$
2	2	3	3	$1.36\ R^{-7}$	$0.700\ R^{-4} - 3.828\ R^{-7}$
4	0	4	3	$- 0.07\ R^{-7}$	$3.545\ R^{-7}$
4	2	2	3	$- 1.11 \times 10^{-4}\ R^{-7}$	$0.007\ R^{-7}$
4	2	3	3	$5.17 \times 10^{-4}\ R^{-7}$	$- 0.031\ R^{-7}$
4	2	4	3	$- 1.12 \times 10^{-3}\ R^{-7}$	$0.068\ R^{-7}$
4	0	4	5	0	$- 4.258\ R^{-6}$
4	2	4	5	$- 9.13 \times 10^{-4}\ R^{-7}$	$- 0.23\ R^{-6} + 0.055\ R^{-7}$
4	2	5	5	$4.62 \times 10^{-3}\ R^{-7}$	$2.36\ R^{-6} - 0.280\ R^{-7}$
4	2	6	5	$- 0.02\ R^{-7}$	$- 6.24\ R^{-6} + 0.961\ R^{-7}$

Table 4.6

Molecular properties and van der Waals energy coefficients used in calculating $D_{\lambda_1\lambda_2\lambda L}$ for the $N_2 \ldots N_2$ system. The internuclear distance in each N_2 molecule is held fixed at its vibrationally averaged value of 2.07 a.u. All values are given in atomic units.

	Property	Value			Property	Value
N_2	Θ	-1.09[a]		$N_2 \ldots N_2$	C_6^{000}	73.8[g]
	Φ	-7.47[b]			C_6^{200}	7.82[g]
	$\alpha_{\parallel}$	14.718[c]			C_6^{220}	2.67[g]
	$\alpha_{\perp}$	10.065[c]				
	$B_{zz,zz}$	-174[d]	(-170.55[e])			
	$B_{xz,xz}$	-102[d]	(-105.35[e])			
	$B_{xx,zz}$	67[d]	(61.23[e])			
	$B_{xx,xx}$	-119.5[d]	(-97.76[e])			
	$\bar{B}$	-132.4[d]	(-122.90[e])			
	B_{2b}	2.95[d]	(8.54[e])			
	B_{2c}	-7.21[d]	(-12.42[e])			
	B_{2d}	-7.21[d]	(-12.42[e])			
	B_4	-1.13[d]	(0.187[e])			
	$E_{z,zzz}$	22.04[f]				
	$E_{x,xxx}$	16.67[f]				

a) Ref. 94; b) Ref. 95; c) Ref. 96; d) Ref. 87; e) Ref. 86; f) Ref. 93; g) Ref. 97.

Table 4.7

Comparison of van der Waals and induction contributions to the $D_{\lambda_1\lambda_2\lambda L}$ coefficients for the $N_2 \ldots N_2$ system. The internuclear distance in each N_2 molecule is held fixed at its vibrationally averaged value of 2.07 a.u. All values are given in atomic units.

λ_1	λ_2	λ	L	$D^{vdW}_{\lambda_1\lambda_2\lambda L}$	$D^{ind}_{\lambda_1\lambda_2\lambda L}$
2	0	2	1	$-108.73\ (-187.61)\ R^{-7}$	$-423.05\ R^{-7}$
2	2	1	1	$-2.96\ (-5.10)\ R^{-7}$	$-1.81\ R^{-7}$
4	2	2	1	-	$-0.61\ R^{-7}$
2	0	2	3	$-46.73\ (-25.83)\ R^{-7}$	$21.93\ R^{-4} + 207.21\ R^{-7}$
2	2	3	3	$4.80\ (6.33)\ R^{-7}$	$-3.70\ R^{-4} + 43.69\ R^{-7}$
4	0	4	3	-	$-40.41\ R^{-7}$
4	2	2	3	-	$-0.08\ R^{-7}$
4	2	3	3	-	$0.39\ R^{-7}$
4	2	4	3	-	$-0.85\ R^{-7}$
4	0	4	5	0	$194.03\ R^{-6}$
4	2	4	5	-	$-2.12\ R^{-6} - 0.69\ R^{-7}$
4	2	5	5	-	$-49.12\ R^{-6} + 3.48\ R^{-7}$
4	2	6	5	-	$76.30\ R^{-6} - 11.97\ R^{-7}$

Table 4.7

Comparison of van der Waals and

$D_{\lambda_1\lambda_2\lambda L}$ coefficients

distance in

averaged

CHAPTER 5. DISCUSSION AND CONCLUSIONS

One contribution to the collision-induced changes in the energy, dipole moment, and polarizability of a molecular pair comes from the van der Waals interactions between the colliding partners. The van der Waals interaction arises from the correlations in the fluctuating charge distributions of the two molecules, which at long range can be characterized by a multipole expansion. The correlations are then connected to the susceptibilities of the individual molecules by use of the fluctuation-dissipation theorem.

Application of an external static field alters the response of each molecule to the fluctuating field of its neighbor, and induces new correlations between the fluctuating charge distributions on each molecule. A reaction field model incorporating these effects was developed in Chapter 2, and expressions for the long-range van der Waals dipole and polarizability of a molecular pair were derived. Field-induced fluctuation correlations have not been included in earlier models of the van der Waals contribution to pair dipoles and pair polarizabilities.

Previous methods of calculating dispersion dipoles [53-55] have been based on use of the fluctuation-dissipation theorem. One method [55] accounts for the polarization of molecule A bilinear in the field due to the fluctuating multipoles of molecule B and the external field $\underline{F}$. The polarization of A sets up a reaction field at B, producing a shift in energy that depends on the magnitude and direction of $\underline{F}$. The energy shift at A is found similarly, and the van der Waals dipole is obtained by differentiation of the total

interaction energy, as in Eq. (2.31). However, in calculating the energy shift, the external field is restricted to a region around molecule A and vanishes at molecule B. Thus the field-induced fluctuation correlations included in this dissertation are not present in the method of Ref. [55]. In a second method [53-55], the van der Waals dipole induced in each molecule is computed directly from its nonlinear polarization by the nonuniform field of the fluctuating multipoles of the neighboring molecule, in the absence of any external field. For a pair of S state atoms A and B, the dipole induced in A is expressed in terms of an integral over the frequency ω of the product $\alpha^{B}(\omega)\ B^{A}(\omega,-\omega)$. But the hyperpolarizability $B^{A}(\omega,-\omega)$ has poles in both the upper and lower ω half planes, which prevents a straightforward application of the residue theorem to evaluate the integral (see Eqs. (2.23) - (2.25)). This problem is avoided here, because the model gives an expression for the interaction energy that depends upon the linear response of each molecule, as modified by the presence of the external field.

For a pair of S state atoms, the van der Waals dipole given in Refs. [53-55] is equivalent to Eq. (3.5) of the dissertation, but the derivations differ in physical content. Symmetry-adapted equations were derived in Sections B and C of Chapter 3 for the leading induced dipole coefficients of collision systems comprising an atom and a centrosymmetric linear molecule or a pair of centrosymmetric linear molecules. These results are new, and provide a basis for comparison of the van der Waals and induction contributions to collision-induced dipole moments. Application of an approximation technique, in which the dipole coefficients are

expressed in terms of static susceptibilities and van der Waals energy coefficients, was carried out in Chapter 4. Results for the model systems $H...H_\zeta$ and H...He show this approximation method gives agreement with accurate perturbation calculations to within 15%. Analogous approximations give numerical estimates to the van der Waals dipole for the systems $He...H_2$, $He...N_2$, $H_2...H_2$, $H_2...N_2$, and $N_2...N_2$. When compared with the induction dipole, the dispersion contribution is seen to be significant for certain symmetry components, particularly D_{01} (for $He...H_2$) and D_{0001} (for $H_2...N_2$). Given the high accuracy now possible in measurements of the roto-translational absorption spectra of atom-diatom and diatom-diatom complexes, it is necessary to account for van der Waals effects in order to obtain agreement between theoretical and experimental lineshape analyses.

This dissertation opens many avenues for future studies. The van der Waals dipole moments of more systems may also be estimated, as values for their susceptibility tensors and van der Waals energies become available. Improved approximations could also be developed, possibly using Pade approximants for the susceptibilities, or combination rules to estimate the dipole of a system based on the values for related systems. Ideally, direct ab initio calculations based on the integral equations would give the best results.

Eq. (2.37) gives results for the van der Waals contribution to the polarizability of a pair of centrosymmetric molecules; Eqs. (2.47) and (2.48) specialize this to an atom pair. The same techniques that were used in deriving the van der Waals dipoles of

atom-diatom and diatom-diatom complexes can also be used to find the polarizabilities of these systems. Then, a constant-ratio approximation could be carried out to yield numerical values for specific collision pairs.

atom-diatom and diatom-diatom complexes can also be used to find the polarizabilities of these systems. Then, a consistent [illegible] approximation could be carried out to yield specific collision pairs.

APPENDICES

Appendix A. Equivalence of Reaction Field and Perturbation Results for Long-range Dipole Moment of Two S State Atoms

Craig and Thirunamachandran [60] have shown directly from two-center, third-order perturbation theory that the van der Waals dipole of interacting S state atoms A and B at long range is

$$\mu_{vdW}^{AB} = \frac{6}{5}\frac{\hat{R}}{\pi} R^{-7} \int_0^\infty d\omega \, [\tilde{B}^{B}_{\alpha\beta,\alpha\beta}(i\omega)\, \alpha^{A}_{\gamma\gamma}(i\omega) - \tilde{B}^{A}_{\alpha\beta,\alpha\beta}(i\omega)\, \alpha^{B}_{\gamma\gamma}(i\omega)] \quad (A.1)$$

in atomic units ($\hbar = 1$). The dipole-quadrupole hyperpolarizability $\tilde{\underline{\underline{B}}}(i\omega)$ is defined as

$$\tilde{B}_{\alpha\beta,\gamma\delta}(i\omega) = \sum_{m,n} \Bigg[\frac{\tilde{Q}^{0m}_{\alpha\beta}\, \mu^{mn}_{\gamma}\, \mu^{no}_{\delta}}{E_{n0}(E_{m0} - i\hbar\omega)} + \Bigg[\frac{\tilde{Q}^{0m}_{\alpha\beta}\, \mu^{mn}_{\gamma}\, \mu^{no}_{\delta}}{E_{n0}(E_{m0} + i\hbar\omega)}$$

$$+ \frac{\tilde{Q}^{0m}_{\alpha\beta}\, \mu^{mn}_{\delta}\, \mu^{n0}_{\gamma}}{(E_{n0} - i\hbar\omega)(E_{m0} - i\hbar\omega)}$$

$$+ \frac{\tilde{Q}^{0m}_{\alpha\beta}\, \mu^{mn}_{\delta}\, \mu^{n0}_{\gamma}}{(E_{n0} + i\hbar\omega)(E_{m0} + i\hbar\omega)}$$

$$+ \frac{\mu^{0m}_{\delta}\, \tilde{Q}^{mn}_{\alpha\beta}\, \mu^{n0}_{\gamma}}{(E_{n0} - i\hbar\omega)E_{m0}} + \frac{\mu^{0m}_{\delta}\, \tilde{Q}^{mn}_{\alpha\beta}\, \mu^{n0}_{\gamma}}{(E_{n0} + i\hbar\omega)E_{m0}}\Bigg] . \quad (A.2)$$

The matrix element $\tilde{Q}^{mn}_{\alpha\beta}$ is [58-60]

$$\tilde{Q}^{mn}_{\alpha\beta} = \langle \psi_m \,|\, -\frac{1}{2} \sum_{j=1}^{n_e} (r_{j\alpha} r_{j\beta} - \frac{1}{3}\delta_{\alpha\beta} r_j^2) \,|\, \psi_n \rangle \quad (A.3)$$

for an atom with n_e electrons. Matrix elements of the quadrupole operator $\Theta^{mn}_{\alpha\beta}$ used in this dissertation are three times $\tilde{Q}^{mn}_{\alpha\beta}$. Ignoring damping, which is negligible at imaginary frequencies, $B_{\alpha\beta,\gamma\delta}(0,i\omega)$ is [98-100]

$$B_{\alpha\beta,\gamma\delta}(0,i\omega) = 3\,\tilde{B}_{\gamma\delta,\alpha\beta}(i\omega)\ . \tag{A.4}$$

Then from the relations

$$B_{\alpha\beta,\alpha\beta}(0,i\omega) = \frac{15}{2}\,B(0,i\omega) \tag{A.5}$$

and

$$\alpha_{\gamma\gamma}(i\omega) = 3\,\alpha(i\omega)\ , \tag{A.6}$$

it follows that Eq. (A.1) is equivalent to Eq. (3.5).

Appendix B. Frequency-dependent B and E Tensors for Linear Molecules

We seek expressions for the frequency-dependent B and E tensors for a linear molecule, in terms of the orientation of the molecule with respect to the laboratory frame of reference. Beginning with the B tensor, we can in general write

$$B_{\alpha\beta,\gamma\delta}(0,i\omega) = a_{\alpha i}\, a_{\beta j}\, a_{\gamma k}\, a_{\delta l}\, B_{ij,kl}(0,i\omega)\ , \qquad \text{(B.1)}$$

where α, β, γ, and δ are the space-fixed laboratory axes, and i, j, k, and l are molecular axes; the $a_{\alpha i}$ are direction cosines between the two frames.

$\underline{\underline{B}}$ is a fourth-rank tensor with 81 cartesian components (for simplicity only the subscripts ij,kl are written):

xx,xx xx,xy xx,xz xx,yx xx,yy xx,yz xx,zx xx,zy xx,zz

xy,xx xy,xy xy,xz xy,yx xy,yy xy,yz xy,zx xy,zy xy,zz

xz,xx xz,xy xz,xz xz,yx xz,yy xz,yz xz,zx xz,zy xz,zz

yx,xx yx,xy yx,xz yx,yx yx,yy yx,yz yx,zx yx,zy yx,zz

yy,xx yy,xy yy,xz yy,yx yy,yy yy,yz yy,zx yy,zy yy,zz

yz,xx yz,xy yz,xz yz,yx yz,yy yz,yz yz,zx yz,zy yz,zz

zx,xx zx,xy zx,xz zx,yx zx,yy zx,yz zx,zx zx,zy zx,zz

zy,xx zy,xy zy,xz zy,yx zy,yy zy,yz zy,zx zy,zy zy,zz

zz,xx zz,xy zz,xz zz,yx zz,yy zz,yz zz,zx zz,zy zz,zz

For an axially symmetric molecule, components with a single x, y, or z vanish, leaving

xx,xx xx,yy xx,zz

xy,xy xy,yx

xz,xz xz,zx

yx,xy yx,yx

yy,xx yy,yy yy,zz

yz,yz yz,zy

zx,xz zx,zx

zy,yz zy,zy

zz,xx zz,yy zz,zz

The B tensor is symmetric with respect to interchange of quadrupole indices, so

$$xy,xy = xy,yx \ , \ yx,xy = yx,yx \ ,$$
$$xz,xz = xz,zx \ , \ zx,xz = zx,zx \ , \qquad (B.2)$$
$$yz,yz = yz,zy \ , \ zy,yz = zy,zy \ ,$$

leaving the following representative components:

xx,xx yy,xx zz,xx xy,xy yx,xy xz,xz zx,xz

xx,yy yy,yy zz,yy yz,yz zy,yz

xx,zz yy,zz zz,zz

Because the molecule is symmetric about its z axis, rotating the x axis onto the y axis and the y axis onto the -x axis leaves $\underline{\underline{B}}$ unchanged. Thus

$$xy,xy = yx,yx \ , \ xx,xx = yy,yy \ ,$$
$$xz,xz = yz,yz \ , \ zx,xz = zy,yz \ ,$$
$$yy,xx = xx,yy \ , \ zz,xx = zz,yy \ , \qquad (B.3)$$
$$xx,zz = yy,zz \ ,$$

leaving the following representative components:

xx,xx (= yy,yy)

zz,xx (= zz,yy)

xy,xy (= xy,yx = yx,xy = yx,yx)

xx,yy (= yy,xx)

xz,xz (= xz,zx = yz,zy = yz,yz)

zx,xz (= zx,zx = zy,zy = zy,yz)

xx,zz (= yy,zz)

zz,zz

We note that $B_{\alpha\beta,\gamma\gamma} = 0$. So

$$zz,xx + zz,yy + zz,zz = 0 \Rightarrow zz,xx = -\frac{1}{2}\, zz,zz \ , \qquad (B.4)$$

and

$$xx,xx + xx,yy + xx,zz = 0 \Rightarrow xx,yy = -\, xx,xx - xx,zz \ . \qquad (B.5)$$

We consider now an arbitrary rotation of the x and y axes about the z axis. The unit vectors in the new primed coordinate system can be expressed as

$$x' = x \cos\phi + y \sin\phi$$

$$y' = -\, x \sin\phi + y \cos\phi$$

$$z' = z$$

where ϕ is the rotation angle. We have from Eq. (B.1)

xy,xy = xx' yx' xx' yx' x'x',x'x'

+ xx' yx' xx' yy' x'x',x'y'

+ xx' yx' xy' yx' x'x',y'x'

+ xx' yx' xy' yy' x'x',y'y'

+ xx' yy' xx' yx' x'y',x'x'

+ xx' yy' xx' yy' x'y',x'y'

+ xx' yy' xy' yx' x'y',y'x'

+ xx' yy' xy' yy' x'y',y'y'

+ xy' yx' xx' yx' y'x',x'x'

+ xy' yx' xx' yy' y'x',x'y'

+ xy' yx' xy' yx' y'x',y'x'

$$+\ xy'\ yx'\ xy'\ yy'\ y'x',y'y'$$

$$+\ xy'\ yy'\ xx'\ yx'\ y'y',x'x'$$

$$+\ xy'\ yy'\ xx'\ yy'\ y'y',x'y'$$

$$+\ xy'\ yy'\ xy'\ yx'\ y'y',y'x'$$

$$+\ xy'\ yy'\ xy'\ yy'\ y'y',y'y'\ .$$

Just as in the unprimed system, those components with a single x' or y' vanish, leaving

$$xy,xy = xx'\ yx'\ xx'\ yx'\ x'x',x'x'$$

$$+\ xx'\ yx'\ xy'\ yy'\ x'x',y'y'$$

$$+\ xx'\ yy'\ xx'\ yy'\ x'y',x'y'$$

$$+\ xx'\ yy'\ xy'\ yx'\ x'y',y'x'$$

$$+\ xy'\ yx'\ xx'\ yy'\ y'x',x'y'$$

$$+\ xy'\ yx'\ xy'\ yx'\ y'x',y'x'$$

$$+\ xy'\ yy'\ xx'\ yx'\ y'y',x'x'$$

$$+\ xy'\ yy'\ xy'\ yy'\ y'y',y'y'\ .$$

The same rotation and index interchange properties hold, so we have

$$xy,xy = [xx'\ yx'\ xx'\ yx' + xy'\ yy'\ xy'\ yy']\ x'x',x'x'$$

$$+\ [xx'\ yx'\ xy'\ yy' + xy'\ yy'\ xx'\ yx']\ x'x',y'y'$$

$$+\ [xx'\ yy'\ xx'\ yy' + xx'\ yy'\ xy'\ yx'$$

$$+\ xy'\ yx'\ xx'\ yy' + xy'\ yx'\ xy'\ yx']\ x'y',x'y'\ .$$

Now the direction cosines are

$$xx' = \cos\phi\ ,\quad xy' = -\sin\phi\ ,$$

$$yx' = \sin\phi\ ,\quad yy' = \cos\phi\ .$$

Thus

$$xy,xy = [2\cos^2\phi\ \sin^2\phi]\ x'x',x'x' - [2\cos^2\phi\ \sin^2\phi]\ x'x',y'y'$$

$$+\ [\cos^4\phi - 2\cos^2\phi\ \sin^2\phi + \sin^4\phi]\ x'y',x'y'\ .$$

Setting $\phi = 45°$ (any value of ϕ leads to the same result, as it must) gives

$$xy,xy = \frac{1}{2}\, x'x',x'x' - \frac{1}{2}\, x'x',y'y'$$

$$= x'x',x'x' + \frac{1}{2}\, x'x',z'z'$$

$$= xx,xx + \frac{1}{2}\, xx,zz \ . \qquad (B.6)$$

Using the 21 nonzero components in Eq. (B.1) gives

$$\begin{aligned}
\alpha\beta,\gamma\delta = {} & \alpha x\ \beta x\ \gamma x\ \delta x\ xx,xx + \alpha y\ \beta y\ \gamma x\ \delta x\ yy,xx + \alpha z\ \beta z\ \gamma x\ \delta x\ zz,xx \\
& + \alpha x\ \beta y\ \gamma x\ \delta y\ xy,xy + \alpha y\ \beta x\ \gamma x\ \delta y\ yx,xy \\
& + \alpha x\ \beta z\ \gamma x\ \delta z\ xz,xz + \alpha z\ \beta x\ \gamma x\ \delta z\ zx,xz \\
& + \alpha x\ \beta y\ \gamma y\ \delta x\ xy,yx + \alpha y\ \beta x\ \gamma y\ \delta x\ yx,yx \\
& + \alpha x\ \beta x\ \gamma y\ \delta y\ xx,yy + \alpha y\ \beta y\ \gamma y\ \delta y\ yy,yy + \alpha z\ \beta z\ \gamma y\ \delta y\ zz,yy \\
& + \alpha y\ \beta z\ \gamma y\ \delta z\ yz,yz + \alpha z\ \beta y\ \gamma y\ \delta z\ zy,yz \\
& + \alpha x\ \beta z\ \gamma z\ \delta x\ xz,zx + \alpha z\ \beta x\ \gamma z\ \delta x\ zx,zx \\
& + \alpha y\ \beta z\ \gamma z\ \delta y\ yz,zy + \alpha z\ \beta y\ \gamma z\ \delta y\ zy,zy \\
& + \alpha x\ \beta x\ \gamma z\ \delta z\ xx,zz + \alpha y\ \beta y\ \gamma z\ \delta z\ yy,zz + \alpha z\ \beta z\ \gamma z\ \delta z\ zz,zz \ .
\end{aligned}$$

Making use of Eqs. (B.2) through (B.6) gives

$$\begin{aligned}
\alpha\beta,\gamma\delta = {} & \alpha x\ \beta x\ \gamma x\ \delta x\ xx,xx - \alpha y\ \beta y\ \gamma x\ \delta x\ (xx,xx + xx,zz) \\
& - \frac{1}{2}\, \alpha z\ \beta z\ \gamma x\ \delta x\ zz,zz \\
& + \alpha x\ \beta y\ \gamma x\ \delta y\ (xx,xx + \frac{1}{2}\, xx,zz) \\
& + \alpha y\ \beta x\ \gamma x\ \delta y\ (xx,xx + \frac{1}{2}\, xx,zz) \\
& + \alpha x\ \beta z\ \gamma x\ \delta z\ xz,xz + \alpha z\ \beta x\ \gamma x\ \delta z\ zx,xz \\
& + \alpha x\ \beta y\ \gamma y\ \delta x\ (xx,xx + \frac{1}{2}\, xx,zz) \\
& + \alpha y\ \beta x\ \gamma y\ \delta x\ (xx,xx + \frac{1}{2}\, xx,zz) \\
& - \alpha x\ \beta x\ \gamma y\ \delta y\ (xx,xx + xx,zz) + \alpha y\ \beta y\ \gamma y\ \delta y\ xx,xx \\
& - \frac{1}{2}\, \alpha z\ \beta z\ \gamma y\ \delta y\ zz,zz \\
& + \alpha y\ \beta z\ \gamma y\ \delta z\ xz,xz + \alpha z\ \beta y\ \gamma y\ \delta z\ zx,xz \\
& + \alpha x\ \beta z\ \gamma z\ \delta x\ xz,xz + \alpha z\ \beta x\ \gamma z\ \delta x\ zx,xz
\end{aligned}$$

$$+ \alpha y\ \beta z\ \gamma z\ \delta y\ xz,xz + \alpha z\ \beta y\ \gamma z\ \delta y\ zx,xz$$

$$+ \alpha x\ \beta x\ \gamma z\ \delta z\ xx,zz + \alpha y\ \beta y\ \gamma z\ \delta z\ xx,zz$$

$$+ \alpha z\ \beta z\ \gamma z\ \delta z\ zz,zz$$

$$= xx,xx\ [\alpha x\ \beta x\ \gamma x\ \delta x - \alpha y\ \beta y\ \gamma x\ \delta x - \alpha x\ \beta x\ \gamma y\ \delta y + \alpha y\ \beta y\ \gamma y\ \delta y$$

$$+ \alpha x\ \beta y\ \gamma x\ \delta y + \alpha y\ \beta x\ \gamma x\ \delta y + \alpha x\ \beta y\ \gamma y\ \delta x + \alpha y\ \beta x\ \gamma y\ \delta x]$$

$$+ xx,zz\ [\alpha x\ \beta x\ \gamma z\ \delta z + \alpha y\ \beta y\ \gamma z\ \delta z - \alpha y\ \beta y\ \gamma x\ \delta x - \alpha x\ \beta x\ \gamma y\ \delta y$$

$$+ \frac{1}{2}\ (\alpha x\ \beta y\ \gamma x\ \delta y + \alpha y\ \beta x\ \gamma x\ \delta y + \alpha x\ \beta y\ \gamma y\ \delta x + \alpha y\ \beta x\ \gamma y\ \delta x)]$$

$$+ xz,xz\ [\alpha x\ \beta z\ \gamma x\ \delta z + \alpha y\ \beta z\ \gamma y\ \delta z + \alpha x\ \beta z\ \gamma z\ \delta x + \alpha y\ \beta z\ \gamma z\ \delta y]$$

$$+ zx,xz\ [\alpha z\ \beta x\ \gamma x\ \delta z + \alpha z\ \beta y\ \gamma y\ \delta z + \alpha z\ \beta x\ \gamma z\ \delta x + \alpha z\ \beta y\ \gamma z\ \delta y]$$

$$+ zz,zz\ [\alpha z\ \beta z\ \gamma z\ \delta z - \frac{1}{2}\ \alpha z\ \beta z\ \gamma x\ \delta x - \frac{1}{2}\ \alpha z\ \beta z\ \gamma y\ \delta y]\ . \quad (B.7)$$

We must now cast this equation into the same form as Buckingham [74]. Working in reverse from Buckingham's expression for $B_{\alpha\beta,\gamma\delta}$ one can easily verify that the terms involving the components xx,xx and xx,zz and zz,zz are in agreement. (Note that $\alpha z = \hat{r}_\alpha$ etc.) Thus Buckingham's equation remains unchanged for those components. The affected components are xz,xz and zx,xz. In the static case these are equal to each other; in the frequency dependent case they are not. Looking at the xz,xz term of Eq. (B.7), we can write

$$xz,xz\ [\beta z\ \gamma z\ (\alpha x\ \delta x + \alpha y\ \delta y) + \beta z\ \delta z\ (\alpha x\ \gamma x + \alpha y\ \gamma y)]$$

$$= xz,xz\ [-\ 2\ \alpha z\ \beta z\ \gamma z\ \delta z$$

$$+ \beta z\ \gamma z\ (\alpha x\ \delta x + \alpha y\ \delta y + \alpha z\ \delta z)$$

$$+ \beta z\ \delta z\ (\alpha x\ \gamma x + \alpha y\ \gamma y + \alpha z\ \gamma z)]$$

$$= xz,xz\ [-\ 2\ \alpha z\ \beta z\ \gamma z\ \delta z + \beta z\ \gamma z\ \delta_{\alpha\delta} + \beta z\ \delta z\ \delta_{\alpha\gamma}]$$

$$= xz,xz\ [\frac{1}{5}\ (\delta_{\alpha\gamma}\ \delta_{\beta\delta} + \delta_{\alpha\delta}\ \delta_{\beta\gamma}) - \frac{2}{15}\ \delta_{\alpha\beta}\ \delta_{\gamma\delta}$$

$$- \frac{2}{21}\ [(3\ \alpha z\ \beta z - \delta_{\alpha\beta})\ \delta_{\gamma\delta} + (3\ \gamma z\ \delta z - \delta_{\gamma\delta})\ \delta_{\alpha\beta}]$$

$$- \frac{2}{21}\ [(3\ \alpha z\ \gamma z - \delta_{\alpha\gamma})\ \delta_{\beta\delta} + (3\ \alpha z\ \delta z - \delta_{\alpha\delta})\ \delta_{\beta\gamma}]$$

$$+ \frac{5}{21}\ [(3\ \beta z\ \gamma z - \delta_{\beta\gamma})\ \delta_{\alpha\delta} + (3\ \beta z\ \delta z - \delta_{\beta\delta})\ \delta_{\alpha\gamma}]$$

$$- 2\,\alpha z\,\beta z\,\gamma z\,\delta z$$

$$+ \frac{2}{7}(\alpha z\,\beta z\,\delta_{\gamma\delta} + \alpha z\,\gamma z\,\delta_{\beta\delta} + \alpha z\,\delta z\,\delta_{\beta\gamma}$$

$$+ \beta z\,\gamma z\,\delta_{\alpha\delta} + \beta z\,\delta z\,\delta_{\alpha\gamma} + \gamma z\,\delta z\,\delta_{\alpha\beta})$$

$$- \frac{2}{35}(\delta_{\alpha\beta}\,\delta_{\gamma\delta} + \delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma})] \;.$$

Similarly the zx,xz term can be expressed as

$$zx,xz\,[\alpha z\,\gamma z\,(\beta x\,\delta x + \beta y\,\delta y) + \alpha z\,\delta z\,(\beta x\,\gamma x + \beta y\,\gamma y)]$$

$$= zx,xz\,[\,- 2\,\alpha z\,\beta z\,\gamma z\,\delta z$$

$$+ \alpha z\,\gamma z\,(\beta x\,\delta x + \beta y\,\delta y + \beta z\,\delta z)$$

$$+ \alpha z\,\delta z\,(\beta x\,\gamma x + \beta y\,\gamma y + \beta z\,\gamma z)]$$

$$= zx,xz\,[\,- 2\,\alpha z\,\beta z\,\gamma z\,\delta z + \alpha z\,\gamma z\,\delta_{\beta\delta} + \alpha z\,\delta z\,\delta_{\beta\gamma}]$$

$$= zx,xz\,[\frac{1}{5}(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) - \frac{2}{15}\delta_{\alpha\beta}\,\delta_{\gamma\delta}$$

$$- \frac{2}{21}[(3\,\alpha z\,\beta z - \delta_{\alpha\beta})\,\delta_{\gamma\delta} + (3\,\gamma z\,\delta z - \delta_{\gamma\delta})\,\delta_{\alpha\beta}]$$

$$+ \frac{5}{21}[(3\,\alpha z\,\gamma z - \delta_{\alpha\gamma})\,\delta_{\beta\delta} + (3\,\alpha z\,\delta z - \delta_{\alpha\delta})\,\delta_{\beta\gamma}]$$

$$- \frac{2}{21}[(3\,\beta z\,\gamma z - \delta_{\beta\gamma})\,\delta_{\alpha\delta} + (3\,\beta z\,\delta z - \delta_{\beta\delta})\,\delta_{\alpha\gamma}]$$

$$- 2\,\alpha z\,\beta z\,\gamma z\,\delta z$$

$$+ \frac{2}{7}(\alpha z\,\beta z\,\delta_{\gamma\delta} + \alpha z\,\gamma z\,\delta_{\beta\delta} + \alpha z\,\delta z\,\delta_{\beta\gamma}$$

$$+ \beta z\,\gamma z\,\delta_{\alpha\delta} + \beta z\,\delta z\,\delta_{\alpha\gamma} + \gamma z\,\delta z\,\delta_{\alpha\beta})$$

$$- \frac{2}{35}(\delta_{\alpha\beta}\,\delta_{\gamma\delta} + \delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma})] \;.$$

Putting these results together gives finally the following equation for the frequency-dependent B tensor of a linear molecule:

$$B_{\alpha\beta,\beta\delta}(0,i\omega) = \frac{2}{15}(B_{zz,zz} + 2B_{xz,xz} + 2B_{zx,xz} + B_{xx,zz} + 4B_{xx,xx})$$

$$\times [\frac{3}{4}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) - \frac{1}{2}\delta_{\alpha\beta}\delta_{\gamma\delta}]$$

$$- \frac{2}{21}(B_{zz,zz} + B_{xz,xz} + B_{zx,xz} - 3B_{xx,zz} - 4B_{xx,xx})$$

$$\times (3\,\hat{r}_\alpha\,\hat{r}_\beta - \delta_{\alpha\beta})\,\delta_{\gamma\delta}$$

$$+ \frac{1}{42}(3B_{zz,zz} - 4B_{xz,xz} - 4B_{zx,xz} + 26B_{xx,zz} + 16B_{xx,xx})$$

$$\times (3\,\hat{r}_\gamma\,\hat{r}_\delta - \delta_{\gamma\delta})\,\delta_{\alpha\beta}$$

$$+ \frac{1}{42}(3B_{zz,zz} - 4B_{xz,xz} + 10B_{zx,xz} - 9B_{xx,zz} - 12B_{xx,xx})$$

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

$$+ \frac{1}{42}\,(3B_{zz,zz} + 10B_{xz,xz} - 4B_{zx,xz} - 9B_{xx,zz} - 12B_{xx,xx})$$

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

$$+ \frac{1}{70}\,(3B_{zz,zz} - 4B_{xz,xz} - 4B_{zx,xz} - 2B_{xx,zz} + 2B_{xx,xx})$$

$$\times \left[35\,\hat{r}_\alpha\,\hat{r}_\beta\,\hat{r}_\gamma\,\hat{r}_\delta - 5\,(\hat{r}_\alpha\,\hat{r}_\beta\,\delta_{\gamma\delta} + \hat{r}_\alpha\,\hat{r}_\gamma\,\delta_{\beta\delta} \right.$$

$$+ \hat{r}_\alpha\,\hat{r}_\delta\,\delta_{\beta\gamma} + \hat{r}_\beta\,\hat{r}_\gamma\,\delta_{\alpha\delta} + \hat{r}_\beta\,\hat{r}_\delta\,\delta_{\alpha\gamma}$$

$$\left. + \hat{r}_\gamma\,\hat{r}_\delta\,\delta_{\alpha\beta}) + \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} \right] , \qquad \text{(B.8)}$$

where the frequency dependence of each B component on the right side of the equation is understood.

We now consider the E tensor. Just as in Eq. (B.1) we can write

$$E_{\alpha,\beta\gamma\delta}(i\omega) = a_{\alpha i}\ a_{\beta j}\ a_{\gamma k}\ a_{\delta l}\ E_{i,jkl}(i\omega) \ . \qquad \text{(B.9)}$$

$\underline{\underline{E}}$ is also a fourth-rank tensor with 81 cartesian components. For an axially symmetric molecule, components with a single x, y, or z vanish, leaving

x,xxx x,xyy x,xzz

x,yxy x,yyx

x,zxz x,zzx

y,xxy y,xyx

y,yxx y,yyy y,yzz

y,zyz y,zzy

z,xxz z,xzx

z,yyz z,yzy

z,zxx z,zyy z,zzz

The E tensor is symmetric with respect to interchange of any two octopole indices, so

$$x,xyy = x,yxy = x,yyx ,$$
$$x,xzz = x,zxz = x,zzx ,$$
$$y,xxy = y,xyx = y,yxx , \quad (B.10)$$
$$y,yzz = y,zyz = y,zzy ,$$
$$z,xxz = z,xzx = z,zxx ,$$
$$z,yyz = z,yzy = z,zyy ,$$

leaving the following representative components:

$$x,xxx \quad x,xyy \quad x,xzz$$
$$y,xxy \quad y,yyy \quad y,yzz$$
$$z,xxz \quad z,yyz \quad z,zzz$$

Because the molecule is symmetric about its z axis, rotating the x axis onto the y axis and the y axis onto the -x axis leaves $\underline{\underline{E}}$ unchanged. Thus

$$x,xxx = y,yyy ,$$
$$x,xyy = y,yxx \; (= y,xxy) , \quad (B.11)$$
$$x,xzz = y,yzz ,$$
$$z,xxz = z,yyz ,$$

leaving the following representative components:

$$x,xxx \; (= y,yyy)$$
$$x,xyy \; (= x,yxy = x,yyx = y,xxy = y,xyx = y,yxx)$$
$$x,xzz \; (= x,zxz = x,zzx = y,zzy = y,zyz = y,yzz)$$
$$z,xxz \; (= z,xzx = z,zxx = z,zyy = z,yzy = z,yyz)$$
$$z,zzz$$

We now consider an arbitrary rotation of the x and y axes about the z axis. The unit vectors in the new, primed coordinate system can be written

$$x' = x \cos\phi + y \sin\phi$$

$$y' = -x \sin\phi + y \cos\phi$$

$$z' = z$$

where ϕ is the angle of rotation. Using Eq. (B.9), and noting that components with a single x', y' or z' vanish just as in the unprimed system, we have

$$\begin{aligned}
x,xyy = {} & xx'\ xx'\ yx'\ yx'\ x',x'x'x' \\
& + xx'\ xx'\ yy'\ yy'\ x',x'y'y' \\
& + xx'\ xx'\ yz'\ yz'\ x',x'z'z' \\
& + xx'\ xy'\ yx'\ yy'\ x',y'x'y' \\
& + xx'\ xy'\ yy'\ yx'\ x',y'y'x' \\
& + xx'\ xz'\ yx'\ yz'\ x',z'x'z' \\
& + xx'\ xz'\ yz'\ yx'\ x',z'z'x' \\
& + xy'\ xx'\ yx'\ yy'\ y',x'x'y' \\
& + xy'\ xx'\ yy'\ yx'\ y',x'y'x' \\
& + xy'\ xy'\ yx'\ yx'\ y',y'x'x' \\
& + xy'\ xy'\ yy'\ yy'\ y',y'y'y' \\
& + xy'\ xy'\ yz'\ yz'\ y',y'z'z' \\
& + xy'\ xz'\ yy'\ yz'\ y',z'y'z' \\
& + xy'\ xz'\ yz'\ yy'\ y',z'z'y' \\
& + xz'\ xx'\ yx'\ yz'\ z',x'x'z' \\
& + xz'\ xx'\ yz'\ yx'\ z',x'z'x' \\
& + xz'\ xy'\ yy'\ yz'\ z',y'y'z' \\
& + xz'\ xy'\ yz'\ yy'\ z',y'z'y' \\
& + xz'\ xz'\ yx'\ yx'\ z',z'x'x' \\
& + xz'\ xz'\ yy'\ yy'\ z',z'y'y' \\
& + xz'\ xz'\ yz'\ yz'\ z',z'z'z' \ .
\end{aligned}$$

We notice that $xz' = yz' = 0$. The above reduces to

$$x,xyy = xx'\ xx'\ yx'\ yx'\ x',x'x'x'$$
$$+ xx'\ xx'\ yy'\ yy'\ x',x'y'y'$$
$$+ xx'\ xy'\ yx'\ yy'\ x',y'x'y'$$
$$+ xx'\ xy'\ yy'\ yx'\ x',y'y'x'$$
$$+ xy'\ xx'\ yx'\ yy'\ y',x'x'y'$$
$$+ xy'\ xx'\ yy'\ yx'\ y',x'y'x'$$
$$+ xy'\ xy'\ yx'\ yx'\ y',y'x'x'$$
$$+ xy'\ xy'\ yy'\ yy'\ y',y'y'y'$$

$$x,xyy = [xx'\ xx'\ yx'\ yx' + xy'\ xy'\ yy'\ yy']\ x',x'x'x'$$
$$+ [xx'\ xx'\ yy'\ yy' + xx'\ xy'\ yx'\ yy'$$
$$+ xx'\ xy'\ yy'\ yx' + xy'\ xx'\ yx'\ yy'$$
$$+ xy'\ xx'\ yy'\ yx' + xy'\ xy'\ yx'\ yx']\ x',x'y'y' .$$

The direction cosines are

$$xx' = \cos\phi\ ,\ xy' = -\sin\phi\ ,$$
$$yx' = \sin\phi\ ,\ yy'\ \cos\phi\ .$$

Thus

$$x,xyy = 2\cos^2\phi\ \sin^2\phi\ x',x'x'x'$$
$$+ [\cos^4\phi - 4\cos^2\phi\ \sin^2\phi + \sin^4\phi]\ x',x'y'y' .$$

Letting $\phi = 45°$, we have

$$x,xyy = \frac{1}{2}\ x',x'x'x' - \frac{1}{2}\ x',x'y'y'$$

or

$$x,xyy = \frac{1}{3}\ x,xxx, \tag{B.12}$$

leaving as representative components:

$$x,xxx\ (= y,yyy = 3\ x,xyy = 3\ x,yxy = 3\ x,yyx$$
$$= 3\ y,xxy = 3\ y,xyx = 3\ y,yxx)$$
$$x,xzz\ (= x,zxz = x,zzx = y,zzy = y,zyz = y,yzz)$$
$$z,xxz\ (= z,xzx = z,zxx = z,zyy = z,yzy = z,yyz)$$

z,zzz

Now, $E_{\alpha,\beta\gamma\gamma} = 0$. So

$$z,xxz + z,yyz + z,zzz = 0 \Rightarrow z,xxz = -\frac{1}{2}\, z,zzz \ , \tag{B.13}$$

and

$$x,xxx + x,xyy + x,xzz = 0 \Rightarrow x,xzz = -\frac{4}{3}\, x,xxx \ . \tag{B.14}$$

Using the 21 nonzero components in Eq. (B.9) gives

$$\begin{aligned}
\alpha,\beta\gamma\delta = {} & \alpha x\ \beta x\ \gamma x\ \delta x\ x,xxx + \alpha x\ \beta x\ \gamma y\ \delta y\ x,xyy + \alpha x\ \beta x\ \gamma z\ \delta z\ x,xzz \\
& + \alpha x\ \beta y\ \gamma x\ \delta y\ x,yxy + \alpha x\ \beta y\ \gamma y\ \delta x\ x,yyx \\
& + \alpha x\ \beta z\ \gamma x\ \delta z\ x,zxz + \alpha x\ \beta z\ \gamma z\ \delta x\ x,zzx \\
& + \alpha y\ \beta x\ \gamma x\ \delta y\ y,xxy + \alpha y\ \beta x\ \gamma y\ \delta x\ y,xyx \\
& + \alpha y\ \beta y\ \gamma x\ \delta x\ y,yxx + \alpha y\ \beta y\ \gamma y\ \delta y\ y,yyy + \alpha y\ \beta y\ \gamma z\ \delta z\ y,yzz \\
& + \alpha y\ \beta z\ \gamma y\ \delta z\ y,zyz + \alpha y\ \beta z\ \gamma z\ \delta y\ y,zzy \\
& + \alpha z\ \beta x\ \gamma x\ \delta z\ z,xxz + \alpha z\ \beta x\ \gamma z\ \delta x\ z,xzx \\
& + \alpha z\ \beta y\ \gamma y\ \delta z\ z,yyz + \alpha z\ \beta y\ \gamma z\ \delta y\ z,yzy \\
& + \alpha z\ \beta z\ \gamma x\ \delta x\ z,zxx + \alpha z\ \beta z\ \gamma y\ \delta y\ z,zyy + \alpha z\ \beta z\ \gamma z\ \delta z\ z,zzz \ .
\end{aligned}$$

Making use of Eqs. (B.10) - (B.14) gives

$$\begin{aligned}
\alpha,\beta\gamma\delta = {} & \alpha x\ \beta x\ \gamma x\ \delta x\ x,xxx + \frac{1}{3}\alpha x\ \beta x\ \gamma y\ \delta y\ x,xxx - \frac{4}{3}\alpha x\ \beta x\ \gamma z\ \delta z \\
& \qquad x,xxx \\
& + \frac{1}{3}\alpha x\ \beta y\ \gamma x\ \delta y\ x,xxx + \frac{1}{3}\alpha x\ \beta y\ \gamma y\ \delta x\ x,xxx \\
& - \frac{4}{3}\alpha x\ \beta z\ \gamma x\ \delta z\ x,xxx - \frac{4}{3}\alpha x\ \beta z\ \gamma z\ \delta x\ x,xxx \\
& + \frac{1}{3}\alpha y\ \beta x\ \gamma x\ \delta y\ x,xxx + \frac{1}{3}\alpha y\ \beta x\ \gamma y\ \delta x\ x,xxx \\
& + \frac{1}{3}\alpha y\ \beta y\ \gamma x\ \delta x\ x,xxx + \alpha y\ \beta y\ \gamma y\ \delta y\ x,xxx - \frac{4}{3}\alpha y\ \beta y\ \gamma z\ \delta z\ x,xxx \\
& - \frac{4}{3}\alpha y\ \beta z\ \gamma y\ \delta z\ x,xxx - \frac{4}{3}\alpha y\ \beta z\ \gamma z\ \delta y\ x,xxx \\
& - \frac{1}{2}\alpha z\ \beta x\ \gamma x\ \delta z\ z,zzz - \frac{1}{2}\alpha z\ \beta x\ \gamma z\ \delta x\ z,zzz \\
& - \frac{1}{2}\alpha z\ \beta y\ \gamma y\ \delta z\ z,zzz - \frac{1}{2}\alpha z\ \beta y\ \gamma z\ \delta y\ z,zzz \\
& - \frac{1}{2}\alpha z\ \beta z\ \gamma x\ \delta x\ z,zzz - \frac{1}{2}\alpha z\ \beta z\ \gamma y\ \delta y\ z,zzz + \alpha z\ \beta z\ \gamma z\ \delta z\ z,zzz
\end{aligned}$$

$$
\begin{aligned}
\alpha,\beta\gamma\delta = x,xxx\, \Big[& \alpha x\ \beta x\ \gamma x\ \delta x + \frac{1}{3}\,(\alpha x\ \beta x\ \gamma y\ \delta y + \alpha x\ \beta y\ \gamma x\ \delta y + \alpha x\ \beta y\ \gamma y\ \delta x \\
& + \alpha y\ \beta x\ \gamma x\ \delta y + \alpha y\ \beta x\ \gamma y\ \delta x + \alpha y\ \beta y\ \gamma x\ \delta x) \\
& - \frac{4}{3}\,(\alpha x\ \beta x\ \gamma z\ \delta z + \alpha x\ \beta z\ \gamma x\ \delta z + \alpha x\ \beta z\ \gamma z\ \delta x \\
& + \alpha y\ \beta y\ \gamma z\ \delta z + \alpha y\ \beta z\ \gamma y\ \delta z + \alpha y\ \beta z\ \gamma z\ \delta y) + \alpha y\ \beta y\ \gamma y\ \delta y \Big] \\
+ z,zzz\, \Big[& \alpha z\ \beta z\ \gamma z\ \delta z - \frac{1}{2}\,(\alpha z\ \beta x\ \gamma x\ \delta z + \alpha z\ \beta x\ \gamma z\ \delta x + \alpha z\ \beta y\ \gamma y\ \delta z \\
& + \alpha z\ \beta y\ \gamma z\ \delta y + \alpha z\ \beta z\ \gamma x\ \delta x + \alpha z\ \beta z\ \gamma y\ \delta y) \Big] \,.
\end{aligned} \tag{B.15}
$$

This equation must now be expressed in terms of the orientation of the molecular symmetry z axis with respect to the lab frame. Note that $\hat{r}\alpha = \alpha z$, etc. Looking first at the z,zzz term in Eq. (B.15), we have

$$
\begin{aligned}
& z,zzz\, \Big[\alpha z\ \beta z\ \gamma z\ \delta z - \frac{1}{2}\,(\alpha z\ \beta x\ \gamma x\ \delta z + \alpha z\ \beta x\ \gamma z\ \delta x + \alpha z\ \beta y\ \gamma y\ \delta z \\
& \qquad + \alpha z\ \beta y\ \gamma z\ \delta y + \alpha z\ \beta z\ \gamma x\ \delta x + \alpha z\ \beta z\ \gamma y\ \delta y) \Big] \\
& = z,zzz\, \Big[\frac{5}{2}\,\alpha z\ \beta z\ \gamma z\ \delta z - \frac{1}{2}\,(\alpha z\ \beta x\ \gamma x\ \delta z + \alpha z\ \beta y\ \gamma y\ \delta z + \alpha z\ \beta z\ \gamma z\ \delta z) \\
& \qquad - \frac{1}{2}\,(\alpha z\ \beta x\ \gamma z\ \delta x + \alpha z\ \beta y\ \gamma z\ \delta y + \alpha z\ \beta z\ \gamma z\ \delta z) \\
& \qquad - \frac{1}{2}\,(\alpha z\ \beta z\ \gamma x\ \delta x + \alpha z\ \beta z\ \gamma y\ \delta y + \alpha z\ \beta z\ \gamma z\ \delta z) \Big] \\
& = z,zzz\, \Big[\frac{5}{2}\,\hat{r}\alpha\ \hat{r}\beta\ \hat{r}\gamma\ \hat{r}\delta - \frac{1}{2}\,\hat{r}\alpha\ \hat{r}\beta\ \delta_{\gamma\delta} - \frac{1}{2}\,\hat{r}\alpha\ \hat{r}\gamma\ \delta_{\beta\delta} - \frac{1}{2}\,\hat{r}\alpha\ \hat{r}\delta\ \delta_{\beta\gamma} \Big] \,.
\end{aligned} \tag{B.16}
$$

Next, the x,xxx term of Eq. (B.15) is

$$
\begin{aligned}
x,xxx\, \Big[& \alpha x\ \beta x\ \gamma x\ \delta x + \frac{1}{3}\,(\alpha x\ \beta x\ \gamma y\ \delta y + \alpha x\ \beta y\ \gamma x\ \delta y + \alpha x\ \beta y\ \gamma y\ \delta x \\
& + \alpha y\ \beta x\ \gamma x\ \delta y + \alpha y\ \beta x\ \gamma y\ \delta x + \alpha y\ \beta y\ \gamma x\ \delta x) \\
& - \frac{4}{3}\,(\alpha x\ \beta x\ \gamma z\ \delta z + \alpha x\ \beta z\ \gamma x\ \delta z + \alpha x\ \beta z\ \gamma z\ \delta x \\
& + \alpha y\ \beta y\ \gamma z\ \delta z + \alpha y\ \beta z\ \gamma y\ \delta z + \alpha y\ \beta z\ \gamma z\ \delta y) + \alpha y\ \beta y\ \gamma y\ \delta y \Big]
\end{aligned}
$$

$$= x,xxx \left[\frac{1}{3} (\alpha x\ \beta x\ \gamma x\ \delta x + \alpha x\ \beta x\ \gamma y\ \delta y + \alpha x\ \beta x\ \gamma z\ \delta z)\right.$$
$$+ \frac{1}{3} (\alpha x\ \beta x\ \gamma x\ \delta x + \alpha x\ \beta y\ \gamma x\ \delta y + \alpha x\ \beta z\ \gamma x\ \delta z)$$
$$+ \frac{1}{3} (\alpha x\ \beta x\ \gamma x\ \delta x + \alpha x\ \beta y\ \gamma y\ \delta x + \alpha x\ \beta z\ \gamma z\ \delta x)$$
$$+ \frac{1}{3} (\alpha y\ \beta x\ \gamma x\ \delta y + \alpha y\ \beta y\ \gamma y\ \delta y + \alpha y\ \beta z\ \gamma z\ \delta y)$$
$$+ \frac{1}{3} (\alpha y\ \beta x\ \gamma y\ \delta x + \alpha y\ \beta y\ \gamma y\ \delta y + \alpha y\ \beta z\ \gamma y\ \delta z)$$
$$+ \frac{1}{3} (\alpha y\ \beta y\ \gamma x\ \delta x + \alpha y\ \beta y\ \gamma y\ \delta y + \alpha y\ \beta y\ \gamma z\ \delta z)$$
$$- \frac{5}{3} (\alpha x\ \beta x\ \gamma z\ \delta z + \alpha y\ \beta y\ \gamma z\ \delta z + \alpha z\ \beta z\ \gamma z\ \delta z)$$
$$- \frac{5}{3} (\alpha x\ \beta z\ \gamma x\ \delta z + \alpha y\ \beta z\ \gamma y\ \delta z + \alpha z\ \beta z\ \gamma z\ \delta z)$$
$$- \frac{5}{3} (\alpha x\ \beta z\ \gamma z\ \delta x + \alpha y\ \beta z\ \gamma z\ \delta y + \alpha z\ \beta z\ \gamma z\ \delta z)$$
$$\left. + 5\ \alpha z\ \beta z\ \gamma z\ \delta z\right]$$

$$= x,xxx \left[\frac{1}{3} \alpha x\ \beta x\ \delta_{\gamma\delta} + \frac{1}{3} \alpha x\ \gamma x\ \delta_{\beta\delta} + \frac{1}{3} \alpha x\ \delta x\ \delta_{\beta\gamma}\right.$$
$$+ \frac{1}{3} \alpha y\ \delta y\ \delta_{\beta\gamma} + \frac{1}{3} \alpha y\ \gamma y\ \delta_{\beta\delta} + \frac{1}{3} \alpha y\ \beta y\ \delta_{\gamma\delta}$$
$$- \frac{5}{3} \gamma z\ \delta z\ \delta_{\alpha\beta} - \frac{5}{3} \beta z\ \delta z\ \delta_{\alpha\gamma} - \frac{5}{3} \beta z\ \gamma z\ \delta_{\alpha\delta}$$
$$\left. + 5\ \alpha z\ \beta z\ \gamma z\ \delta z\right]$$

$$= x,xxx \left[\frac{1}{3} \delta_{\alpha\beta}\ \delta_{\gamma\delta} + \frac{1}{3} \delta_{\alpha\delta}\ \delta_{\beta\delta} + \frac{1}{3} \delta_{\alpha\delta}\ \delta_{\beta\gamma}\right.$$
$$- \frac{5}{3} \gamma z\ \delta z\ \delta_{\alpha\beta} - \frac{5}{3} \beta z\ \delta z\ \delta_{\alpha\gamma} - \frac{5}{3} \beta z\ \gamma z\ \delta_{\alpha\delta}$$
$$- \frac{1}{3} \alpha z\ \delta z\ \delta_{\beta\gamma} - \frac{1}{3} \alpha z\ \gamma z\ \delta_{\beta\delta} - \frac{1}{3} \alpha z\ \beta z\ \delta_{\gamma\delta}$$
$$\left. + 5\ \alpha z\ \beta z\ \gamma z\ \delta z\right]$$

$$= x,xxx \left[\frac{1}{3} \delta_{\alpha\beta}\ \delta_{\gamma\delta} + \frac{1}{3} \delta_{\alpha\gamma}\ \delta_{\beta\delta} + \frac{1}{3} \delta_{\alpha\delta}\ \delta_{\beta\gamma}\right.$$
$$- \frac{5}{3} \hat{r}\gamma\ \hat{r}\delta\ \delta_{\alpha\beta} - \frac{5}{3} \hat{r}\beta\ \hat{r}\delta\ \delta_{\alpha\gamma} - \frac{5}{3} \hat{r}\beta\ \hat{r}\gamma\ \delta_{\alpha\delta}$$
$$- \frac{1}{3} \hat{r}\alpha\ \hat{r}\delta\ \delta_{\beta\gamma} - \frac{1}{3} \hat{r}\alpha\ \hat{r}\gamma\ \delta_{\beta\delta} - \frac{1}{3} \hat{r}\alpha\ \hat{r}\beta\ \delta_{\gamma\delta}$$
$$\left. + 5\ \hat{r}\alpha\ \hat{r}\beta\ \hat{r}\gamma\ \hat{r}\delta\right] . \qquad \text{(B.17)}$$

Finally, we can express the frequency-dependent E tensor for a linear molecule in terms of the orientations of its symmetry axis as

$$E_{\alpha,\beta\gamma\delta}(i\omega) = \frac{1}{3} E_{x,xxx}(i\omega) \left[15\ \hat{r}\alpha\ \hat{r}\beta\ \hat{r}\gamma\ \hat{r}\delta\right.$$

$$- \hat{r}_\alpha \hat{r}_\beta \delta_{\gamma\delta} - \hat{r}_\alpha \hat{r}_\gamma \delta_{\beta\delta} - \hat{r}_\alpha \hat{r}_\delta \delta_{\beta\gamma}$$
$$- 5 \hat{r}_\beta \hat{r}_\gamma \delta_{\alpha\delta} - 5 \hat{r}_\beta \hat{r}_\delta \delta_{\alpha\gamma} - 5 \hat{r}_\gamma \hat{r}_\delta \delta_{\alpha\beta}$$
$$+ \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}]$$
$$+ \frac{1}{2} E_{z,zzz}(i\omega) [5 \hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma \hat{r}_\delta$$
$$- \hat{r}_\alpha \hat{r}_\beta \delta_{\gamma\delta} - \hat{r}_\alpha \hat{r}_\gamma \delta_{\beta\delta} - \hat{r}_\alpha \hat{r}_\delta \delta_{\beta\gamma}]$$

or, in a symmetry-adapted form,

$$\begin{aligned}
E_{\alpha,\beta\gamma\delta}(i\omega) = \frac{1}{14} & [E_{z,zzz}(i\omega) + 2 E_{x,xxx}(i\omega)] [35 \hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma \hat{r}_\delta \\
& - 5 (\hat{r}_\alpha \hat{r}_\beta \delta_{\gamma\delta} + \hat{r}_\alpha \hat{r}_\gamma \delta_{\beta\delta} + \hat{r}_\alpha \hat{r}_\delta \delta_{\beta\gamma} \\
& \quad + \hat{r}_\beta \hat{r}_\gamma \delta_{\alpha\delta} + \hat{r}_\beta \hat{r}_\delta \delta_{\alpha\gamma} + \hat{r}_\gamma \hat{r}_\delta \delta_{\alpha\beta}) \\
& + \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}] \\
- \frac{1}{63} & [3 E_{z,zzz}(i\omega) - 8 E_{x,xxx}(i\omega)] [(3 \hat{r}_\alpha \hat{r}_\beta - \delta_{\alpha\beta}) \delta_{\gamma\delta} \\
& + (3 \hat{r}_\alpha \hat{r}_\gamma - \delta_{\alpha\gamma}) \delta_{\beta\delta} + (3 \hat{r}_\alpha \hat{r}_\delta - \delta_{\alpha\delta}) \delta_{\beta\gamma}] \\
+ \frac{5}{126} & [3 E_{z,zzz}(i\omega) - 8 E_{x,xxx}(i\omega)] [(3 \hat{r}_\beta \hat{r}_\gamma - \delta_{\beta\gamma}) \delta_{\alpha\delta} \\
& + (3 \hat{r}_\beta \hat{r}_\delta - \delta_{\beta\delta}) \delta_{\alpha\gamma} + (3 \hat{r}_\gamma \hat{r}_\delta - \delta_{\gamma\delta}) \delta_{\alpha\beta}] . \qquad \text{(B.18)}
\end{aligned}$$

Appendix C. Expanding a Function in Spherical Harmonics

We want to determine the symmetry-adapted expressions for the dipole coefficients using the Cartesian expansions in Eqs. (3.19) and (3.47) for VDW_z, and in Eqs. (3.35) and (3.71) for IND_z. These depend upon several different types of products of the unit vectors $\hat{r}$ and $\hat{R}$. This appendix will show a method to express these factors in terms of spherical harmonics; we then can easily find $D^{vdW}_{\lambda L}$ and $D^{ind}_{\lambda L}$ from Eqs. (3.22) and (3.36), and $D^{vdW}_{\lambda_1\lambda_2\lambda L}$ and $D^{ind}_{\lambda_1\lambda_2\lambda L}$ from Eqs. (3.49) and (3.72). One type of Cartesian term is simply R_z. We can write

$$R_z = R \cos\Theta_R ,$$

where Θ_R is the angle that the vector $\underline{R}$ makes with the space-fixed z axis. Now

$$Y^0_0(\hat{r}) = (4\pi)^{-1/2}$$

and

$$Y^0_1(\hat{R}) = (\tfrac{3}{4\pi})^{1/2} \cos\Theta_R ,$$

so

$$R_z = \frac{4\pi}{(3)^{1/2}} R\, Y^0_0(\hat{r})\, Y^0_1(\hat{R}) . \qquad \text{(C.1)}$$

Appendix C. Expanding a Function in Spherical Harmonics

We want to determine the symmetry-adapted

dipole coefficients using the

and (3.47)

expand

A more complex example is the factor $\hat{r}_\beta \hat{r}_z R_\beta$. This can be expanded in spherical harmonics as

$$\hat{r}_\beta \hat{r}_z R_\beta = \sum_{\lambda,L,m} a(\lambda,L)\, Y_\lambda^m(\hat{r})\, Y_\lambda^{-m}(\hat{R})\, C(\lambda L1;m,-m) , \qquad (C.2)$$

where the $a(\lambda,L)$ must be determined. We consider first $\lambda = 2$ and $L = 1$ ($\lambda > 2$ or $L > 1$ need not be considered). We integrate Eq. (C.2) with $[Y_2^0(\hat{r})\, Y_1^0(\hat{R})]^*$, where

$$Y_2^0(\hat{r}) = (\frac{5}{16\pi})^{1/2} (3 \cos^2\theta_r - 1)$$

and

$$Y_1^0(\hat{R}) = (\frac{3}{4\pi})^{1/2} \cos^2\theta_R .$$

The right hand side of Eq. (C.2) is just $a(2,1)\, C(211;00)$, while the left hand side becomes

$$\begin{aligned} &\int d\Omega_r \int d\Omega_R\, \hat{r}_\beta\, \hat{r}_z\, R_\beta\, [Y_2^0(\hat{r})\, Y_1^0(\hat{R})]^* \\ &= \frac{(15)^{1/2}}{8\pi} \int d\Omega_r \int d\Omega_R\, \hat{r}_\beta\, \hat{r}_z\, R_\beta\, (3 \cos^2\theta_r - 1) \cos\theta_R \\ &= \frac{(15)^{1/2}}{8\pi} \int d\Omega_r\, \hat{r}_\beta\, \hat{r}_z\, (3\, \hat{r}_z\, \hat{r}_z - 1) \int d\Omega_R\, \hat{R}_\beta\, \hat{R}_z\, R . \qquad (C.3) \end{aligned}$$

The first integral in the above, $\int d\Omega_r\, \hat{r}_\beta \hat{r}_z \hat{r}_z \hat{r}_z$, is the βzzz component of an isotropic fourth rank tensor, with all indices interchangeable:

$$\int d\Omega_r\ \hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma \hat{r}_\delta = A\ (\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\ .$$

We compute A from

$$\int d\Omega_r\ \hat{r}_z \hat{r}_z \hat{r}_z \hat{r}_z = 3\ A = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\Theta \cos^4\Theta\ d\Theta$$
$$= 2\pi \cdot \frac{2}{5} = \frac{4\pi}{5}\ .$$

So

$$\int d\Omega_r\ \hat{r}_\beta \hat{r}_z \hat{r}_z \hat{r}_z = 3\ A\ \delta_{\beta z} = \frac{4\pi}{5}\ \delta_{\beta z}\ . \tag{C.4}$$

The next integral is

$$\int d\Omega_r\ \hat{r}_\beta \hat{r}_z = A'\ \delta_{\beta z}$$

with

$$A' = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\Theta \cos^2\Theta\ d\Theta = 2\pi \cdot \frac{2}{3} = \frac{4\pi}{3}\ .$$

Thus

$$\int d\Omega_r\ \hat{r}_\beta \hat{r}_z = \frac{4\pi}{3}\ \delta_{\beta z} = \int d\Omega_R\ \hat{R}_\beta\ \hat{R}_z\ . \tag{C.5}$$

Using Eqs. (C.4) and (C.5) in Eq. (C.3) results in

$$\int d\Omega_r \int d\Omega_R\ \hat{r}_\beta\ \hat{r}_z\ R_\beta\ [Y_2^0\ (\hat{r})\ Y_1^0\ (\hat{R})]^*$$
$$= \frac{(15)^{1/2}}{8\pi}\ [3 \cdot \frac{4\pi}{5}\ \delta_{\beta z} - \frac{4\pi}{3}\ \delta_{\beta z}]\ \frac{4\pi}{3}\ \delta_{\beta z}\ R$$

$$= \frac{(15)^{1/2}}{2} \cdot \frac{16\pi}{15} \cdot \frac{1}{3} R$$

$$= \frac{8\pi}{3(15)^{1/2}} R = a(2,1)\ C(211;00)$$

$$\Rightarrow a(2,1) = \frac{1}{C(211;00)} \cdot \frac{8\pi}{3(15)^{1/2}} R\ . \qquad (C.6)$$

Is there a contribution from $\lambda = 2$, $L = 0$ in Eq. (C.2)? No, since $C(201;m,-m) = 0$. There may be a contribution from $\lambda = 1$, $L = 1$. Integrating with $[Y_1^0(\hat{r})\ Y_1^0(\hat{R})]^*$, the left hand side of Eq. (C.2) becomes

$$\int d\Omega_r \int d\Omega_R\ \hat{r}_\beta\ \hat{r}_z\ R_\beta\ [Y_1^0(\hat{r})\ Y_1^0(\hat{R})]^*$$

$$= \frac{3}{4\pi} \int d\Omega_r \int d\Omega_R\ \hat{r}_\beta\ \hat{r}_z\ R_\beta\ \cos\theta_r\ \cos\theta_R$$

$$= \frac{3}{4\pi} \int d\Omega_r\ \hat{r}_\beta\ \hat{r}_z\ \hat{r}_z \int d\Omega_R\ \hat{R}_\beta\ \hat{R}_z\ R\ .$$

But the first integral vanishes no matter how β is chosen. Thus there is no contribution from $\lambda = 1$, $L = 1$. Similarly, the $\lambda = 1$, $L = 0$ instance makes no contribution. What about $\lambda = 0$, $L = 1$? Integrating with $[Y_0^0(\hat{r})\ Y_1^0(\hat{R})]^*$ gives

$$\int d\Omega_r \int d\Omega_R\ \hat{r}_\beta\ \hat{r}_z\ R_\beta\ [Y_0^0(\hat{r})\ Y_1^0(\hat{R})]^*$$

$$= \frac{(3)^{1/2}}{4\pi} \int d\Omega_r \int d\Omega_R\ \hat{r}_\beta\ \hat{r}_z\ R_\beta\ \cos\theta_R$$

$$= \frac{(3)^{1/2}}{4\pi} \int d\Omega_r\ \hat{r}_\beta\ \hat{r}_z \int d\Omega_R\ \hat{R}_\beta\ \hat{R}_z\ R$$

$$= \frac{(3)^{1/2}}{4\pi} \cdot \frac{4\pi}{3} \delta_{\beta z} \cdot \frac{4\pi}{3} \delta_{\beta z}\ R$$

$$= \frac{4\pi}{3(3)^{1/2}} R = a(0,1)\ C(011;00)$$

$$\Rightarrow a(0,1) = \frac{1}{C(011;00)} \cdot \frac{4\pi}{3(3)^{1/2}} R\ . \qquad (C.7)$$

Finally, there is no contribution from $\lambda = 0$, $L = 0$ since $C(001;m,-m) = 0$. Using Eqs. (C.6) and (C.7) in Eq. (C.2) gives

$$\begin{aligned}
\hat{r}_\beta \hat{r}_z R_\beta &= \sum_{m=-1}^{1} a(2,1)\, Y_2^m(\hat{r})\, Y_1^{-m}(\hat{R})\, C(211;m,-m) \\
&\quad + a(0,1)\, Y_0^0(\hat{r})\, Y_1^0(\hat{R})\, C(011;00) \\
&= \sum_{m=-1}^{1} \frac{1}{C(211;00)} \cdot \frac{8\pi}{3(15)^{1/2}} R\, Y_2^m(\hat{r})\, Y_1^{-m}(\hat{R})\, C(211;m,-m) \\
&\quad + \frac{1}{C(011;00)} \cdot \frac{4\pi}{3(3)^{1/2}} R\, Y_0^0(\hat{r})\, Y_1^0(\hat{R})\, C(011;00)\ .
\end{aligned} \tag{C.8}$$

Using this method, expansions of all the Cartesian terms were carried out. These were then inserted into the expressions for VDW_z and IND_z, which were used in Eqs. (3.22), (3.36), (3.49), and (3.72) to yield the symmetry-adapted dipole coefficients $D_{\lambda L}$ and $D_{\lambda_1\lambda_2\lambda L}$.

Appendix D. Clebsch-Gordan Coefficients

Clebsch-Gordan coefficients are used in combining states of different angular momentum. Suppose that we want to add two commuting angular momenta $\underline{J}_1$ and $\underline{J}_2$. The product ket

$$|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle , \tag{D.1}$$

where $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ are eigenvectors of $\underline{J}_1^2$ and $\underline{J}_2^2$ respectively, constitutes a basis in the product space. From this basis, we can construct a new basis which comprises the eigenvectors of J_z and $\underline{J}^2$, where $\underline{J}$ is the total angular momentum of the combined system. The transformation equation is

$$|j_1 j_2 JM\rangle = \Sigma \; |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | JM\rangle , \tag{D.2}$$

where the summation is carried out over m_1 and m_2, for fixed values of j_1 and j_2. The ket $|j_1 j_2 JM\rangle$ is the new basis, and the transformation coefficients $\langle j_1 j_2 m_1 m_2 | JM\rangle$ are the Clebsch-Gordan coefficients. Several different notations are used for these coefficients; the one used in the dissertation is $C(j_1 j_2 J; m_1 m_2)$. A general formula for calculating Clebsch-Gordan coefficients is [101]

$$\begin{aligned} C(j_1 j_2 J; m_1 m_2) \\ &= \left[(J+j_1-j_2)!(J-j_1+j_2)!(j_1+j_2-J)!(J+m_1+m_2)!(J-m_1-m_2)!\right]^{1/2} \\ &\quad \times \left[(J+j_1+j_2+1)!(j_1-m_1)!(j_1+m_1)!(j_2-m_2)!(j_2+m_2)!\right]^{-1/2} \end{aligned}$$

$$\times \Sigma_k (-1)^{k+j_2+m_2} (2J+1)^{1/2} (J+j_2+m_1-k)!(j_1-m_1+k)!$$
$$\times \left[(J-j_1+j_2-k)!(J+m_1-m_2-k)!k!(k+j_1-j_2-m_1-m_2)!\right]^{-1}, \quad (D.3)$$

where the summation is over all k for which the factorials in the denominator are nonnegative. This equation may be simplified for the case $m_1 = m_2 = 0$. Let $2g = j_1 + j_2 + J$. Then [101]

$$C(j_1 j_2 J;00) = 0$$

if 2g is odd, and

$$C(j_1 j_2 J;00) = (-1)^{g+J} (2J+1)^{1/2} \Delta(j_1 j_2 J) g! \left[(g-j_1)!(g-j_2)!(g-J)!\right]^{-1} \quad (D.4)$$

if 2g is even, where

$$\Delta(j_1 j_2 J) = \left[(j_1+j_2-J)!(j_1+J-j_2)!(j_2+J-j_1)!/(j_1+j_2+J+1)!\right]^{1/2} . \quad (D.5)$$

Table D.1 lists values for several Clebsch-Gordan coefficients.

Table D.1

Values of Clebsch-Gordan coefficients

j_1	j_2	J	m_1	m_2	$C(j_1 j_2 J; m_1 m_2)$
0	1	1	0	0	1
2	1	1	0	0	$-(\frac{2}{5})^{1/2}$
2	3	1	0	0	$(\frac{9}{35})^{1/2}$
4	3	1	0	0	$-(\frac{4}{21})^{1/2}$
4	5	1	0	0	$(\frac{5}{33})^{1/2}$
6	5	1	0	0	$-(\frac{18}{143})^{1/2}$
2	0	2	0	0	1
2	2	0	0	0	$(\frac{1}{5})^{1/2}$
2	2	2	0	0	$-(\frac{2}{7})^{1/2}$
2	2	4	0	0	$(\frac{18}{35})^{1/2}$
4	0	4	0	0	1
4	2	2	0	0	$(\frac{2}{7})^{1/2}$
4	2	4	0	0	$-(\frac{20}{77})^{1/2}$
4	2	6	0	0	$(\frac{5}{11})^{1/2}$
4	4	0	0	0	$\frac{1}{3}$

Table D.1 (continued)

j_1	j_2	J	m_1	m_2	$C(j_1 j_2 J; m_1 m_2)$
2	2	0	1	0	0
2	2	1	1	0	$-(\frac{3}{10})^{1/2}$
2	2	2	1	0	$-(\frac{1}{14})^{1/2}$
2	2	3	1	0	$(\frac{1}{5})^{1/2}$
2	2	4	1	0	$(\frac{3}{7})^{1/2}$
4	2	2	1	0	$(\frac{5}{21})^{1/2}$
4	2	3	1	0	$-(\frac{1}{12})^{1/2}$
4	2	4	1	0	$-(\frac{289}{1540})^{1/2}$
4	2	5	1	0	$(\frac{1}{15})^{1/2}$
4	2	6	1	0	$(\frac{14}{33})^{1/2}$

Table D.1 (continued)

j_1	j_2	J	m_1	m_2	$C(j_1 j_2 J; m_1 m_2)$
0	1	1	1	-1	0
1	1	1	1	-1	$(\frac{1}{2})^{1/2}$
2	1	1	1	-1	$(\frac{3}{10})^{1/2}$
2	3	1	1	-1	$-(\frac{8}{35})^{1/2}$
3	3	1	1	-1	$(\frac{1}{28})^{1/2}$
4	3	1	1	-1	$(\frac{5}{28})^{1/2}$
4	5	1	1	-1	$-(\frac{8}{55})^{1/2}$
5	5	1	1	-1	$(\frac{1}{110})^{1/2}$
6	5	1	1	-1	$(\frac{35}{286})^{1/2}$
2	2	0	1	-1	$-(\frac{1}{5})^{1/2}$
2	2	2	1	-1	$(\frac{1}{14})^{1/2}$
2	2	4	1	-1	$(\frac{8}{35})^{1/2}$
4	2	2	1	-1	$-(\frac{5}{21})^{1/2}$
4	2	4	1	-1	$(\frac{3}{154})^{1/2}$
4	2	6	1	-1	$(\frac{8}{33})^{1/2}$

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