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NONLOCAL DIELECTRIC MODEL FOR INTERMOLECULAR INTERACTIONS AT SECOND AND HIGHER ORDERS

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NONLOCAL DIELECTRIC MODEL FOR INTERMOLECULAR INTERACTIONS AT SECOND AND HIGHER ORDERS

By

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ABSTRACT

NONLOCAL DIELECTRIC MODEL FOR INTERMOLECULAR INTERACTIONS AT SECOND AND HIGHER-ORDERS

By

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The nonlocal dielectric function of a molecule determines the effective potential at a certain point due to an applied external potential at a different point, within the molecule. The effective potential at point $\mathbf{r}$ is determined by the nonlocal dielectric function $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ within linear response and by the nonlocal dielectric function $\varepsilon_Q(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,\omega')$ within nonlinear response to the lowest order. The nonlocal dielectric functions $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ and $\varepsilon_Q(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,\omega')$ depend on the charge-density susceptibilities $\chi(\mathbf{r},\mathbf{r}';\omega)$ and $\chi_Q(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,\omega')$ of the molecule, respectively. This work shows that for a group of interacting molecules with weak or negligible charge overlap, the nonlocal dielectric model gives the interaction energies and forces at second and higher-orders, in agreement with the results from quantum mechanical perturbation theory. The dielectric model accounts for screening due to electronic charge redistribution in the interacting molecules; it accounts for polarization and fluctuations in the charge densities that act as sources of the external potentials. The model applies within the Born-Oppenheimer approximation.

At second order, both two-body pairwise additive and three-body non-additive induction energies appear. We prove that the two-body induction energy is determined from changes in the static Coulomb interactions within each molecule, caused by a neighboring molecule that acts as the dielectric medium, whereas the three-body

induction energy is determined by the changes in the static Coulomb interactions between two molecules, due to the presence of a third molecules which acts as the dielectric medium. Dispersion energy is pairwise additive at second order and results from changes in the intramolecular exchange-correlation energy caused by the dielectric screening due to a neighboring molecule. The interaction energies at second order include linear screening only, while the induction and dispersion forces on nuclei result from both linear and nonlinear screenings. We show that induction forces result from nonlinear screening of the potential due to permanent charge distribution of the neighboring molecule and linear screening of the potential due to induced polarization of the neighbor, while dispersion forces result from nonlinear screening of the fluctuating charge distribution of the neighboring molecule and linear screening of the dynamic reaction field from the neighbor. The linear screening present in the dispersion force is described by transition susceptibility of the molecule. Moreover, the dispersion force includes effects which don't have a dielectric interpretation.

At third and fourth order of molecular interactions, the induction and the induction-dispersion energies show both linear and nonlinear screening, while the dispersion energy includes linear screening only. Depending on the nature of interaction, the induction energy can be classified into different categories, each category showing a different screening effect. Screening in the dispersion energy can be described either by the dielectric function of a single molecule, or by the dielectric functions of two or three molecules.

To my parents

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Chapter 1: Introduction

A nonlocal dielectric function,[1] $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ characterizes the screening of an applied scalar potential $\varphi_{ex}(\mathbf{r}';\omega)$, due to electronic charge redistribution within a molecule. Within linear response, the effective potential $\varphi_{eff}(\mathbf{r};\omega)$ at a point $\mathbf{r}$ within a molecule is related to an applied potential $\varphi_{ex}(\mathbf{r}';\omega)$ of frequency ω by

$$\varphi_{eff} = \varepsilon_0 \int d\mathbf{r}' \varepsilon_V^{-1}(\mathbf{r},\mathbf{r}';\omega)\varphi_{ex}(\mathbf{r}';\omega), \tag{1.1}$$

where ε_0 is the permittivity of vacuum. Thus, $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ is defined as the function which acts as the integral kernel to determine the effective potential at point $\mathbf{r}$, within linear response, when an external potential $\varphi_{ex}(\mathbf{r}';\omega)$ acts at point $\mathbf{r}'$. The dielectric function $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ depends both on the response point $\mathbf{r}$ and on the point $\mathbf{r}'$ at which the external potential acts. In this work we show that a generalized dielectric model of potential screening holds for two-body interactions (treated here through second order) and for three- and four-body interactions (treated here through fourth order) of quantum perturbation theory. For two or more interacting molecules, the source of the external potential can be either the permanent charge distributions or the charge-density fluctuations within the molecules. We prove that the interaction energies and the interaction-induced forces on the nuclei of the molecules are accurately described within the nonlocal dielectric model, where the interacting molecules behave as the dielectric medium. In treating intermolecular interactions, we assume that the overlap between the electronic charge clouds of the interacting molecules is weak or negligible. Once the interaction energies are known, the interaction-induced forces on a particular nucleus are

obtained as the negative gradient of the interaction energy with respect to the coordinate of the nucleus. Throughout the derivations, we work within the Born-Oppenheimer approximation.

The nonlocal dielectric function $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ is related to the nonlocal charge-density susceptibility[2] $\chi(\mathbf{r},\mathbf{r}';\omega)$ of the molecule. Using quantum perturbation theory, Jenkins and Hunt[1] have proved that the nonlocal dielectric function and the nonlocal charge-density susceptibility are related by

$$\varepsilon_0\,\varepsilon_V^{-1}(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}')+(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}''|\mathbf{r}-\mathbf{r}''|^{-1}\chi(\mathbf{r}'',\mathbf{r}';\omega)\,, \tag{1.2}$$

within the Born-Oppenheimer approximation. The nonlocal charge-density susceptibility in Eq. (1.2) is given by[2]

$$\chi(\mathbf{r},\mathbf{r}';\omega) = -[\langle 0|\,\hat{\rho}(\mathbf{r})G(\omega)\hat{\rho}(\mathbf{r}')\,|0\rangle + \langle 0|\,\hat{\rho}(\mathbf{r}')G(-\omega)\hat{\rho}(\mathbf{r})\,|0\rangle\,]. \tag{1.3}$$

In Eq. (1.3), $|0\rangle$ denotes the ground state of the isolated molecule, $\hat{\rho}(\mathbf{r})$ is the charge-density operator, $G(\omega)$ is the resolvent operator,

$$G(\omega) = (1 - \wp_0)(H_0 - E_0 - \hbar\omega)^{-1}(1-\wp_0), \tag{1.4}$$

$\wp_0$ denotes the ground-state projection operator $|0\rangle\langle 0|$, H_0 is the unperturbed Hamiltonian of the molecule, and E_0 is the unperturbed ground-state energy. For a molecule with fixed nuclear positions, $\chi(\mathbf{r},\mathbf{r}';\omega)$ determines the change in the electronic charge density $\Delta\rho(\mathbf{r},\omega)$ within linear response to a frequency-dependent external potential $\varphi_{ex}(\mathbf{r},\omega)$, via

$$\Delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}'\,\chi(\mathbf{r},\mathbf{r}';\omega)\varphi_{ex}(\mathbf{r}',\omega)\,. \tag{1.5}$$

The effective potential $\varphi_{\mathrm{eff}}(\mathbf{r};\omega)$ within the molecule is given by

$$\varphi_{\mathrm{eff}}(\mathbf{r},\omega) = \varphi_{\mathrm{ex}}(\mathbf{r},\omega) + (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}' |\mathbf{r}-\mathbf{r}'|^{-1} \Delta\rho(\mathbf{r}',\omega), \tag{1.6}$$

without restriction to linear response in calculating $\Delta\rho(\mathbf{r},\omega)$. Thus, $\varphi_{\mathrm{eff}}(\mathbf{r},\omega)$ has a source term containing the sum of the external charge density $\rho_{\mathrm{ex}}(\mathbf{r}',\omega)$ that generates $\varphi_{\mathrm{ex}}(\mathbf{r}',\omega)$ and the *change* in the molecular charge density $\Delta\rho(\mathbf{r},\omega)$ induced by $\varphi_{\mathrm{ex}}(\mathbf{r}',\omega)$. Hence $\varphi_{\mathrm{eff}}(\mathbf{r},\omega)$ satisfies the Poisson equation by

$$\nabla^2 \varphi_{\mathrm{eff}}(\mathbf{r},\omega) = -[\rho_{\mathrm{ex}}(\mathbf{r},\omega) + \Delta\rho(\mathbf{r},\omega)] / \varepsilon_0 . \tag{1.7}$$

The linear response theory suffices to describe the intermolecular interactions at first order. At second and higher orders, we must include nonlinear response of the molecule to the applied potentials. Including the lowest-order nonlinear response to $\varphi_{\mathrm{ex}}(\mathbf{r}',\omega)$, we obtain

$$\Delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}';\omega)\varphi_{\mathrm{ex}}(\mathbf{r}',\omega) + (1/2)\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}' d\mathbf{r}'' \zeta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega-\omega',\omega') \times \varphi_{\mathrm{ex}}(\mathbf{r}',\omega-\omega')\varphi_{\mathrm{ex}}(\mathbf{r}'',\omega'), \tag{1.8}$$

where the quadratic charge-density susceptibility $\zeta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega-\omega',\omega')$ satisfies the relation

$$\begin{aligned}\zeta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,\omega') = S(\mathbf{r}',\mathbf{r}'';\omega,\omega')[&\left\langle 0 \left| \hat{\boldsymbol{\rho}}(\mathbf{r}) \mathrm{G}(\omega_\sigma) \hat{\boldsymbol{\rho}}^0(\mathbf{r}'') \mathrm{G}(\omega) \hat{\boldsymbol{\rho}}(\mathbf{r}') \right| 0 \right\rangle \\ &+ \left\langle 0 \left| \hat{\boldsymbol{\rho}}(\mathbf{r}'') \mathrm{G}^*(-\omega') \hat{\boldsymbol{\rho}}^0(\mathbf{r}') \mathrm{G}^*(-\omega_\sigma) \hat{\boldsymbol{\rho}}(\mathbf{r}) \right| 0 \right\rangle \\ &+ \left\langle 0 \left| \hat{\boldsymbol{\rho}}(\mathbf{r}'') \mathrm{G}^*(-\omega') \hat{\boldsymbol{\rho}}^0(\mathbf{r}) \mathrm{G}(\omega) \hat{\boldsymbol{\rho}}(\mathbf{r}') \right| 0 \right\rangle].\end{aligned} \tag{1.9}$$

The operator $S(\mathbf{r}',\mathbf{r}'';\omega,\omega')$ denotes the sum of the terms obtained by permuting the charge-density operators $\hat{\boldsymbol{\rho}}(\mathbf{r}')$ and $\hat{\boldsymbol{\rho}}(\mathbf{r}'')$ together with their associated frequencies ω and ω' in the expression that follows S. In Eq. (1.9) and below, $\omega_\sigma = \omega + \omega'$, and the operator $\hat{\boldsymbol{\rho}}^0(\mathbf{r})$ is defined by $\hat{\boldsymbol{\rho}}^0(\mathbf{r}) = \hat{\boldsymbol{\rho}}^0(\mathbf{r}) - \langle 0|\hat{\boldsymbol{\rho}}(\mathbf{r})|0\rangle$. We do not assume that damping is negligible in general (particularly near resonance), but in cases where damping is negligible, $\zeta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,\omega'')$ is symmetric under permutation of all of the variable pairs: $(\mathbf{r},-\omega_\sigma)$, $(\mathbf{r}',\omega)$, and $(\mathbf{r}'',\omega'')$. The method used by Orr and Ward[3] to derive multipole polarizabilities yields Eq. (1.9), when applied to charge-density operators: cf. Eq. (43b) of ref. 3. Eq. (1.9) is also consistent with the results for multipole hyperpolarizabilities derived by Bishop, in Eq. (41) of ref. (4). From Eq. (1.8), a quadratic dielectric function can be defined by

$$\varepsilon_0\,\varepsilon_q^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,\omega') = (4\pi\varepsilon_0)^{-1}\int d\mathbf{r}'''\,|\mathbf{r}-\mathbf{r}'''|^{-1}\,\zeta(\mathbf{r}''',\mathbf{r}',\mathbf{r}'',\omega,\omega'). \tag{1.10}$$

Thus, within nonlinear response to the lowest order, the effective potential within a molecule is obtained as

$$\begin{aligned}\varphi_{\mathrm{eff}}(\mathbf{r},\omega) = \varepsilon_0 \int d\mathbf{r}'\,\varepsilon_v^{-1}(\mathbf{r},\mathbf{r}';\omega)\,\varphi_{\mathrm{ex}}(\mathbf{r}',\omega)\\ +(1/2)\varepsilon_0\int_{-\infty}^{\infty} d\omega' \int d\mathbf{r}'\,d\mathbf{r}''\,\varepsilon_q^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega-\omega',\omega')\\ \times\varphi_{\mathrm{ex}}(\mathbf{r}',\omega-\omega')\,\varphi_{\mathrm{ex}}(\mathbf{r}'',\omega').\end{aligned} \tag{1.11}$$

Within a nonlocal dielectric framework, Eq. (1.11) gives a complete description of the interaction energies and the interaction-induced forces at first and second orders, and the interaction energies at third and fourth orders, for three- and four-body systems.

Nonlocal response theory has been applied earlier to study the properties of polar fluids,[5] to find expressions for the equilibrium dielectric constants of fluids consisting of molecules possessing arbitrary polarizability densities,[6] to perform calculations for solvation of an ion in a cavity,[7] to determine the inverse dielectric function of quantum wells in terms of the random phase approximation,[8] and to study the properties of small conducting particles and thin films in an oscillating longitudinal electric field.[9] For systems with full translational invariance[10-13] the dielectric function depends only on the distance between the response point and the point where the perturbation acts $(\mathbf{r}-\mathbf{r}')$, while for molecules, the intramolecular dielectric functions depend both on $\mathbf{r}$ and $\mathbf{r}'$ due to inhomogeneity within the molecules. Previously, systems with full translational invariance[10-13] or spatial periodicity[14,15] have been described in terms of dielectric theories, where the dielectric function depends on a single spatial variable.

Dielectric functions depending on a single spatial variable can be described either by $\varepsilon(\mathbf{r}-\mathbf{r}')$ or by its spatial Fourier transform $\varepsilon(\mathbf{k})$. Dielectric models using the function $\varepsilon(\mathbf{k},\omega)$ have been used to describe quantum many-body problems,[16] to characterize the behavior of quantum dots or quantum wires in microcavities,[17] metal clusters and colloidal aggregates,[18] quantum dot crystals,[19] localization of hydrated electrons,[20,21] hydration forces,[22] dipole-dipole interactions near surfaces,[23] and normal mode coupling in semiconductor microcavities.[24] Zaremba and Sturm[25] have calculated $\varepsilon(\mathbf{k},\omega)$ of alkali metals at the level of the random phase approximation, using the soft x-ray absorption spectra. A cluster expansion method has been used by Felderhof and

Cohen[26] to obtain the wave-vector-dependent effective dielectric tensor of a suspension of spherical inclusions. They showed that in the cluster expansion, the terms corresponding to the "overlapping" regions of the spherical inclusions lead to the Clausius-Mossotti formula. Dielectric functions of the form $\varepsilon(\mathbf{k},\omega)$ have also been used in linear response within the density functional theory.[27] In liquids, the dielectric friction[28,29] and solvation dynamics[30-37] depend on the dielectric function $\varepsilon(\mathbf{k},\omega)$, and that affects the fluorescence spectra and rates of charge-transfer reactions[38-40] in liquids. Dielectric functions of the form $\varepsilon(\mathbf{k},\omega)$ have been used to study electron transfer,[41-45] charge-density fluctuations in translationally invariant systems,[46-48] and polarization fluctuations in liquids.[49]

Extension of the dielectric model to the intramolecular domain was suggested in several early works. Theimer and Paul[50] introduced the polarizability density of atoms in the context of light scattering by monatomic gases. Quantum mechanical calculations of that function were done for the hydrogen atom. Polarizability density was introduced by Frisch and McKenna[51] as a correction to the local polarization in the study of light scattering by fluids. Oxtoby and Gelbart[52] calculated the pair polarizability anisotropy of interacting noble gas atoms using the polarizability density instead of point dipoles. Application of a nonlocal dielectric model instead of a classical continuum dielectric model to atomic interiors was suggested by Orttung and co-workers.[53] Dielectric effects were used by Levine and Soven[54] to calculate the optical polarizabilities and the photoemission cross sections of nitrogen and acetylene using a time-dependent local-

density theory. In a few later works,[55-58] single-point response functions have been used where one of the two spatial variables **r** and **r′** is being integrated. Response functions that depend both on **r** and **r′** have been used in the study of light scattering by fluids.[6, 36, 59-62] The Nonlocal dielectric model has been applied for theoretical calculations of surface enhanced Raman scattering (SERS) from metallic nanoshells.[63] It has been found that the nonlocal optical effects can be significant for molecules very close to the shells and for shells of very small dimensions.

Dielectric models have a wide range of applications in the study of conformational energetics and noncovalent bonding in proteins and biomolecules.[64-76] For proteins, no universal dielectric constant (or constants) exists because of the inhomogeneities within the protein interiors. Typically, the dielectric function is approximated as a constant or as a simple function of distance between a perturbing charge and a response point. Early calculations on proteins[77-79] in solutions used an effective dielectric constant that represents the overall effect of the medium, i.e. water + protein. However, it was shown[80] that this model leads to erroneous results for the interaction of an ion pair inside the protein.[69] The dielectric constant of a protein depends on the particular property used in its definition.[69] For a powder sample of protein, ε can be found by applying a weak electric field and using the Clausius-Mossotti equation. This method has been applied in many physical measurements and the ε has been found to be quite low (about 2).[81,82] At a microscopic level, ε of a protein can be determined from Coulomb's law[69,83,84] or from The Born formula of self energy.[85] Simonson and co-workers[86] have investigated the microscopic mechanism of charge screening in proteins.

By introducing a fixed, perturbing point charge, they have calculated the Fröhlich-Kirkwood dielectric constants and the generalized susceptibilities of deca-alanine and cytochrome c. Values of ε depend on the particular kind of interaction inside the protein and can range from $\varepsilon = 2$,[69] through $4 \leq \varepsilon \leq 8$ for dipole-charge interactions,[70] up to $\varepsilon \geq 20$ for charge-charge interactions.[71-75] Attempts have been made[87,88] to calculate ε at the different sites of protein. However, the solvent reaction field effect was not considered in any of those attempts. As a result, they all underestimate the value of ε. The need for site-dependent values of ε has also been noted in other works.[86,89-93] More recently, Song has used the effective polarizabilities of the individual amino acid residues to develop an approximate site-dependent dielectric function for proteins.[94] Spatial variation of the dielectric function may influence electron or proton transfer, ligand binding,[95] molecular recognition,[96] ion transport through channels,[97] and conformational dynamics of biomolecules.

The present work derives a dielectric screening model to treat the two- and three-body intermolecular interaction energies at second order, three- and four-body interaction energies at third and fourth orders, and the interaction-induced forces on nuclei at second order. The screening is nonlocal, since it depends both on $\mathbf{r}$ and $\mathbf{r}'$.

For a pair of interacting molecules, the interaction energy at different orders of perturbation theory can be obtained by solving the electronic Schrödinger equation $[\hat{H}_0^A + \hat{H}_0^B + \hat{V}^{AB}]|\psi_{AB}\rangle = E_{AB}|\psi_{AB}\rangle$, where $\hat{H}_0^A$ is the unperturbed Hamiltonian of molecule A, $\hat{V}^{AB}$ is the interaction Hamiltonian, E_{AB} is the energy of the A-B pair and $|\psi_{AB}\rangle$ is the wavefunction of the interacting system. This particular separation of the

Hamiltonian is known as the polarization approximation.[98-100] At first order, the interaction energy for a pair of molecules is purely electrostatic[100,101] and depends on the permanent charge densities (and hence on the permanent moments) of the molecules. A perturbation analysis for the first-order interaction energy $\Delta E^{(1)}$ of a pair of molecules A and B with fixed nuclei and negligible charge overlap yields

$$\Delta E^{(1)} = (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, \rho_0^A(\mathbf{r})\rho_0^B(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}, \tag{1.12}$$

where $\rho_0^A(\mathbf{r})$ and $\rho_0^B(\mathbf{r}')$ are the permanent charge distributions in molecule A and B respectively. Following Longuet-Higgins,[102,103] the charge-density operator $\hat{\rho}^A(\mathbf{r})$ for molecule A can be defined as

$$\hat{\rho}^A(\mathbf{r}) = \sum_j e\,\delta(\mathbf{r}-\mathbf{r}_j) + \sum_I Z^I\,\delta(\mathbf{r}-\mathbf{R}^I), \tag{1.13}$$

where the sum over j is for all the electrons assigned to molecule A, with position operators $\mathbf{r}_j$, and the sum over I is for all the nuclei in A with charges Z^I and positions $\mathbf{R}^I$. For a pair of molecules with fixed nuclear configurations and negligible charge overlap, the first-order interaction energy can be expressed using a multipole expansion[104] in terms of the charge q, permanent dipole μ_0, permanent quadrupole Θ_0, and higher moments of each molecule

$$\begin{aligned}\Delta E^{(1)} &= q^A \varphi_0^B - \mu_{0\alpha}^A \Im_{0\alpha}^B - (1.3)\Theta_{0\alpha\beta}^A \Im'^B_{0\alpha\beta} + \ldots \\ &\equiv q^B \varphi_0^A - \mu_{0\alpha}^B \Im_{0\alpha}^A - (1.3)\Theta_{0\alpha\beta}^B \Im'^A_{0\alpha\beta} + \ldots\end{aligned} \tag{1.14}$$

φ_0^B is the potential at the origin $\mathbf{R}^A$ of molecule A due to the permanent, unperturbed charge distribution in molecule B. $\Im_{0\alpha}^B$ and $\Im'^B_{0\alpha\beta}$ are the field and the field gradients at $\mathbf{R}^A$ respectively, due to the unperturbed charge distribution in B. The Einstein summation convention over repeated Greek indices has been used in Eq. (1.14). Since the interaction at first order depends on the unperturbed charge distributions (and hence on the permanent moments) of the molecules, no screening effect is apparent in the first-order interaction energy. The first-order force on a particular nucleus I in molecule A can be obtained from Eq. (1.12) using an energy-based approach, employing the relation

$$\mathbf{F}^{I(1)} = -\nabla^I \Delta E^{(1)}, \tag{1.15}$$

where ∇^I denotes differentiation with respect to the coordinate of nucleus I, $\mathbf{R}^I$. Electrostatic forces on nuclei can also be derived using the Hellmann-Feynman theorem[105,106] and Sternheimer-type shielding tensors.[107] The forces on a nucleus in an atom in presence of an external field have been related to the dipole shielding factors by Epstein[108] and Sambe,[109] where the dipole shielding factor γ has been defined as $\gamma = 1 - \sigma$, with σ the fraction of the external field actually felt by the nucleus. For diatomic or polyatomic molecules, the dipole shielding factor is a second-rank tensor represented by $\gamma_{\alpha\beta}$, and relates the effective field at the nucleus to the external field by[110] $\Im_\alpha^I = (\delta_{\alpha\beta} - \gamma_{\alpha\beta})\Im_\beta$. Calculations on the dipole shielding factors have been done by several groups.[111-123] $\gamma_{\alpha\beta}$ was related to a molecular property in the works of Lazzeretti

and Zanasi,[124,125] Sambe,[109] and Epstein.[108] It was shown that $\gamma_{\alpha\beta}$ is related to the derivative of the molecular dipole moment with respect to the nuclear coordinate by

$$Z^I(\delta_{\alpha\beta} - \gamma^I_{\alpha\beta}) = \partial\mu^0_\beta / \partial R^I_\alpha . \tag{1.16}$$

Fowler and Buckingham[126] extended the shielding factor to include non-uniform applied fields and non-linear terms. In terms of their formulation, the net electric field on nucleus I in molecule A in presence of an external field is

$$\begin{aligned}\Im^I_\alpha = \Im^{(0)I}_\alpha &+ (\delta_{\alpha\beta} - \gamma^I_{\alpha\beta})\Im^e_\beta + (1/2)\varphi^I_{\alpha\beta\gamma}\Im^e_\beta\Im^e_\gamma + \ldots \\ &+ (1/3)[(3/2)(R^I_\beta - R^A_\beta)\delta_{\alpha\gamma} + (3/2)(R^I_\gamma - R^A_\gamma)\delta_{\alpha\beta} - (R^I_\alpha - R^A_\alpha)\delta_{\beta\gamma} \\ &+ \nu^I_{\alpha\beta\gamma}]\Im'^e_{\beta\gamma} + (1/3)\xi^I_{\alpha\beta\gamma\delta}\Im^e_\beta\Im'^e_{\gamma\delta} + \ldots,\end{aligned} \tag{1.17}$$

where we have kept only the terms which depend linearly and quadratically on the fields and the field gradients. $\Im^e$ is the external field with gradient $\Im'^e$, applied at $\mathbf{R}^A$. $\gamma^I_{\alpha\beta}$ is the Sternheimer shielding tensor, $\nu^I_{\alpha\beta\gamma}$ is the field-gradient shielding tensor, and $\varphi^I_{\alpha\beta\gamma}$, $\xi^I_{\alpha\beta\gamma\delta}$ are the nonlinear shielding tensors. $\Im^{(0)I}_\alpha$ is the field that acts on nucleus I in absence of any external perturbation. Using an analogy with the expansion of the induced dipole moment in powers the external fields and field gradients and the Hellmann-Feynman theorem, they connected the higher-order nuclear shielding tensors to the derivatives of molecular multipole moments and polarizabilities with respect to the nuclear coordinates:

$$Z^I\varphi^I_{\alpha\beta\gamma} = \partial\alpha_{\beta\gamma} / \partial R^I_\alpha , \tag{1.18a}$$

$$Z^I[(3/2)R^I_\beta \delta_{\alpha\gamma} + (3/2)R^I_\gamma \delta_{\alpha\beta} - R^I_\alpha \delta_{\beta\gamma} + \nu^I_{\alpha\beta\gamma}] = \partial\Theta^0_{\beta\gamma}/\partial R^I_\alpha, \tag{1.18b}$$

$$Z^I \xi^I_{\alpha\beta\gamma\delta} = \partial A_{\beta\gamma\delta}/\partial R^I_\alpha, \tag{1.18c}$$

α is the dipole polarizability and A is the dipole-quadrupole polarizability. However, neither in their work nor in the work by Lazzeretti and Zanasi were the derivatives of the molecular moments and the polarizabilities expressed in terms of molecular response tensors. Derivatives of the molecular dipole moment and polarizability density with respect to the nuclear coordinate were evaluated by Hunt,[127] and later generalized by Hunt, Liang, Nimalakirthi, and Harris.[128] It was proved[127] that the Sternheimer shielding tensor is related to the nonlocal polarizability density $\alpha(\mathbf{r},\mathbf{r}')$ [127,128,60-62,6,129,130] by

$$\gamma^I_{\alpha\beta} = -\int d\mathbf{r}\, d\mathbf{r}'\, T_{\alpha\gamma}(\mathbf{R}^I,\mathbf{r})\alpha_{\gamma\beta}(\mathbf{r},\mathbf{r}'). \tag{1.19}$$

Within the framework of the nonlocal polarizability density $\alpha(\mathbf{r},\mathbf{r}';0)$, the first-order forces on nuclei were derived by Hunt and Liang.[131] Specifically they showed that although the first-order interaction energy depends only on the permanent charge distributions in the molecules, the first-order force on nucleus I in molecule A depends on the electronic polarization induced in A by B:

$$\Delta F^{I(1)}_\alpha = Z^I \int d\mathbf{r}'\, \rho^B_0(\mathbf{r}')(R^I_\alpha - r'_\alpha)\left|\mathbf{R}^I - \mathbf{r}'\right|^{-1}$$

$$+ Z^I \int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r})\Delta P^{A(1)}_\beta(\mathbf{r}). \tag{1.20}$$

$\Delta P^{A(1)}_\beta(\mathbf{r})$ is the first-order polarization in A induced by the field from B and $T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r})$ is the dipole propagator. $\Delta P^{A(1)}_\beta(\mathbf{r})$ depends on the nonlocal polarizability

density of A. The results in their work were obtained using an equation derived by Hunt which shows that the infinitesimal motion of a nucleus within a molecule changes the Coulomb field, and the response of the electronic charge density to that change in the field is determined by the same nonlocal polarizability density that determines the induced polarization of a molecule in presence of a static external field. In a later work, Liang and Hunt[132] showed that both the energy-based theory using Eq. (1.15) and the electrostatic-force theory based on Hellmann-Feynman theorem and the shielding tensors yield identical result for the first-order forces on the nuclei. In that work, they explicitly connected the shielding tensors and the nonlocal polarizability densities. The first order forces on nucleus I due to interaction with B were showed to be

$$F_\alpha^{I(1)} = Z^I(\delta_{\alpha\beta} - \gamma^I_{\alpha\beta})\Im^B_{0\beta} + (1/3)[(3/2)(R^I_\beta - R^A_\beta)\delta_{\alpha\gamma} + (3/2)(R^I_\gamma - R^A_\gamma)\delta_{\alpha\beta} - (R^I_\alpha - R^A_\alpha)\delta_{\beta\gamma} + \nu^I_{\alpha\beta\gamma}]\Im'^B_{0\beta\gamma} + \ldots, \quad (1.21)$$

where $\Im^B_{0\beta}$ is the static external field at $\mathbf{R}^A$ due to the permanent charge distribution in B, and

$$\nu^I_{\alpha\beta\gamma} = \int d\mathbf{r}\, d\mathbf{r}'\, T_{\alpha\delta}(\mathbf{R}^I, \mathbf{r})\alpha_{\delta\varepsilon}(\mathbf{r}, \mathbf{r}')[(3/2)(r'_\beta - R^A_\beta)\delta_{\gamma\varepsilon} + (3/2)(r'_\gamma - R^A_\gamma)\delta_{\beta\varepsilon} - (r'_\varepsilon - R^A_\varepsilon)\delta_{\beta\gamma}]. \quad (1.22)$$

Thus the force obtained using the shielding-tensor approach was related to the force derived using the nonlocal polarizability density. However, the polarizability-based approach was not connected to a dielectric framework.

The intramolecular nonlocal dielectric model was first applied to intermolecular interactions by Jenkins and Hunt.[1] In their work, it was shown that the force on nucleus I

in molecule A depends not on the "bare" Coulomb potential due to the unperturbed charge distribution in B, but on an effective potential. The effective potential on nucleus I is determined by the nonlocal dielectric function $\varepsilon_V(\mathbf{r},\mathbf{r}';0)$ of molecule A due to redistribution of the electronic charge cloud within A. Using a susceptibility-based approach, they proved that the first order force $\mathbf{F}^{I(1)}$ on nucleus I is

$$\mathbf{F}^{I(1)} = -Z^I \varepsilon_0 \partial / \partial \mathbf{r}[\int d\mathbf{r}' \varepsilon^{-1}_{V,A}(\mathbf{r},\mathbf{r}';0)\varphi^B_{ex}(\mathbf{r}';0)]\Big|_{\mathbf{r}=\mathbf{R}^I}, \tag{1.23}$$

where the notation $[\partial / \partial \mathbf{r}\, f(\mathbf{r})]\big|_{\mathbf{r}=\mathbf{R}^I}$ means that the derivative is first evaluated with respect to the coordinate $\mathbf{r}$ and then $\mathbf{r}$ is set equal to $\mathbf{R}^I$ .Thus, the first-order force on the nucleus was connected to the nonlocal dielectric model.

At second order, the interaction energy consists of a sum of induction and dispersion terms. The induction term $\Delta E^{(2)}_{ind}$ is classical and appears from static, linear response of one molecule to the potential from the unperturbed charge distribution of the neighboring molecule. The dispersion term $\Delta E^{(2)}_{disp}$ is purely quantum mechanical and depends on correlations between the spontaneous charge-density fluctuations within the interacting molecules.[133] Both induction and dispersion energy are obtained from time-independent perturbation theory with the second-order correction to the energy given by

$$\Delta E^{(2)} = -\sum_m \sum_n \left\langle 0^A 0^B \middle| \hat{V}^{AB} \middle| m^A n^B \right\rangle \left\langle m^A n^B \middle| \hat{V}^{AB} \middle| 0^A 0^B \right\rangle / (E_m + E_n - E_0). \tag{1.24}$$

m^A and n^B are the excited states in molecules A and B respectively, $\hat{V}^{AB}$ is the interaction Hamiltonian, and E_m, E_n, and E_0 are the unperturbed energies of excited state

and ground state respectively. The sum of the terms from Eq. (1.24) with excited states confined to either molecule A or B yields the induction energy, while the sum of the terms with excited states on both molecules gives the dispersion energy.

The induction energy depends on the permanent charge distributions and the molecular polarizabilities of the interacting molecules. In terms of the permanent moments of the molecules,[104]

$$\Delta E_{ind}^{(2)} = -(1/2)\alpha^{A}_{\alpha\beta}\,\Im^{B}_{0\alpha}\,\Im^{B}_{0\beta} - (1/3)A^{A}_{\alpha\beta\gamma}\,\Im^{B}_{0\alpha}\,\Im'^{B}_{0\beta\gamma} - (1/6)C^{A}_{\alpha\beta\gamma\delta}\,\Im'^{B}_{0\alpha\beta}\,\Im'^{B}_{0\gamma\delta}$$
$$-(1/15)E^{A}_{\alpha\beta\gamma\delta}\,\Im^{B}_{0\alpha}\,\Im''^{B}_{0\beta\gamma\delta} - (1/2)\alpha^{B}_{\alpha\beta}\,\Im^{A}_{0\alpha}\,\Im^{A}_{0\beta} - (1/3)A^{B}_{\alpha\beta\gamma}\,\Im^{A}_{0\alpha}\,\Im'^{A}_{0\beta\gamma}$$
$$-(1/6)C^{B}_{\alpha\beta\gamma\delta}\,\Im'^{A}_{0\alpha\beta}\,\Im'^{A}_{0\gamma\delta} - (1/15)E^{B}_{\alpha\beta\gamma\delta}\,\Im^{A}_{0\alpha}\,\Im''^{A}_{0\beta\gamma\delta} + \ldots, \qquad (1.25)$$

where $\Im''$ is the gradient of the field-gradient, C is the quadrupole polarizability, and E is the dipole-octopole polarizability.[104] Within a nonlocal response model, the induction energy is described by the nonlocal polarizability density and the static polarizations of the molecules.[131] The induction energy can also be expressed in terms of nonlocal charge-density susceptibilities and the static external potentials from the unperturbed charge distributions of the interacting molecules. We give a detailed description of that in chapter 2. Since the induction energy depends not only on the permanent moments of the interacting molecules, but also on the induced polarization in one molecule due to permanent moments in the other, it is apparent that induction energy can be described in terms of intramolecular screening. However, the induction energy has not been connected to a dielectric screening model previously.

The induction force at second order can be calculated using Eq. (1.15), where the induction energy is given by Eq. (1.25) or in terms of the static polarizations and the nonlocal polarizability densities of the interacting molecules. Within the nonlocal polarizability density model, the second-order induction force on nucleus I in molecule A depends on the derivatives of the static nonlocal polarizability density $\alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}';0)$ and the field $\Im^{A}_{0\alpha}(\mathbf{r})$ at B due to permanent moments of A. Unlike the first-order force which depends on the permanent charge distribution in B and the first-order induced polarization of A, induction force at second order depends on the first-order induced polarization in B and the second-order induced polarization in A[131]:

$$F^{I(2)}_{ind,\alpha} = \int d\mathbf{r}\, Z^{I}\, T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})[\Delta P^{A(2)}_{\beta}(\mathbf{r}) + \Delta P^{B(1)}_{\beta}(\mathbf{r})], \tag{1.26}$$

where the second-order induced polarization is determined by the nonlocal hyperpolarizability density,[130,134] $\beta^{A}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$. Induction force on nucleus I can also be determined using Sternheimer-type shielding tensors by[132]

$$\begin{aligned}\Delta F^{I(2)}_{ind,\alpha} = {} & Z^{I}(\delta_{\alpha\beta} - \gamma^{I}_{\alpha\beta})\Im^{B}_{R\beta} + (1/3)Z^{I}\nu^{I}_{\alpha\beta\gamma}\Im'^{B}_{R\beta\gamma} \\ & + (1/3)Z^{I}[(3/2)(R^{I}_{\beta} - R^{A}_{\beta})\delta_{\alpha\gamma} + (3/2)(R^{I}_{\gamma} - R^{A}_{\gamma})\delta_{\alpha\beta} \\ & - (R^{I}_{\alpha} - R^{A}_{\alpha})\delta_{\beta\gamma}]\Im'^{B}_{R\beta\gamma} + (1/2)Z^{I}\phi^{I}_{\alpha\beta\gamma}\Im^{B}_{0\beta}\Im^{B}_{0\gamma}, \\ & + (1/3)Z^{I}\xi^{I}_{\alpha\beta\gamma\delta}\Im^{B}_{0\beta}\Im'^{B}_{0\gamma\delta} + \ldots\end{aligned} \tag{1.27}$$

where $\Im^{B}_{R\beta}$ and $\Im'^{B}_{R\beta\gamma}$ are the reaction field and its gradient from the first-order polarization of B, induced by the unperturbed charge-distribution in A. Thus, the second-order induction force on nucleus I depends on linear screening of the reaction field and its gradients due to the first-order induced polarization of B and nonlinear screening of the field and its gradients due to the unperturbed charge distribution in B. The two different approaches used to calculate the induction force are connected to each other by Eqs. (1.19), (1.22), and the relations[132] between the nonlinear shielding tensors $\phi^{I}_{\alpha\beta\gamma}$, $\xi^{I}_{\alpha\beta\gamma\delta}$ and the nonlocal hyperpolarizability density,

$$\phi^{I}_{\alpha\beta\gamma} = \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, T_{\alpha\delta}(\mathbf{R}^{I},\mathbf{r})\beta_{\delta\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,. \tag{1.28a}$$

$$\begin{aligned}\xi^{I}_{\alpha\beta\gamma} = \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, T_{\alpha\varepsilon}(\mathbf{R}^{I},\mathbf{r})\beta_{\varepsilon\beta\varphi}(\mathbf{r},\mathbf{r}',\mathbf{r}'') \\ \times[(3/2)(r''_{\gamma}-R^{A}_{\gamma})\delta_{\delta\varphi}+(3/2)(r''_{\delta}-R^{A}_{\delta})\delta_{\gamma\varphi} \\ -(r''_{\varphi}-R^{A}_{\varphi})\delta_{\gamma\delta}]\,.\end{aligned} \tag{1.28b}$$

Electrostatic force theory based on the Hellmann-Feynman theorem was also applied by Nakatsuji and Koga[135] to calculate the forces on nuclei of interacting molecules. In their work, the force on nucleus A in atom A was expressed in terms of the density matrices of the atomic orbitals and the forces were categorized into three different classes: 1) the atomic dipole (AD) force, which originates due to the attraction between nucleus A and the polarized electron distribution within molecule A, 2) the exchange (EC) force, due to the attraction between nucleus A and the electron distribution in the region between atoms A and B, 3) the extended gross charge (EGC) force, caused by the interaction

between nucleus A and the gross charge on atom B. At long range, only the atomic dipole and the extended gross charge forces are significant. At first order the atomic dipole force and the extended gross charge force correspond to the first-order forces on the nuclei derived within the nonlocal polarizability density approach, where the AD force depends on $\Delta P^{A(1)}(\mathbf{r})$ and the EGC force depends on $\rho_0^B(\mathbf{r})$. At second order, the AD force and the EGC force are related to $\Delta P^{A(2)}(\mathbf{r})$ and $\Delta P^{B(1)}(\mathbf{r})$, respectively.

The dispersion energy at second order arises due to the correlation between the charge-density fluctuations in the interacting molecules.[133,2,129,136] The spontaneous quantum mechanical fluctuations in the charge density in one molecule create a field that acts on the second molecule and induces a shift in the charge density. The induced shift in the charge density in the second molecule causes a dynamic reaction field that acts back on the first molecule and results in a net energy-shift. The induced shift in the charge density is determined by the dynamic polarizability density $\alpha(\mathbf{r},\mathbf{r}';\tau)$ [or $\alpha(\mathbf{r},\mathbf{r}';\omega)$ in the frequency-dependent form] or by the dynamic charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\tau)$ and the charge-density fluctuations are correlated according to the fluctuation-dissipation theorem.[137] Although the charge-density fluctuations and the reaction field are time-dependent, the dispersion energy is time-independent.[138] The overall dispersion energy for a pair of interacting molecules A and B depends on the nonlocal polarizability densities (or the charge-density susceptibilities) of the molecules at imaginary frequencies.[129]

$$\Delta E_d^{AB(2)} = -(\hbar/2\pi)\int_0^\infty d\omega \int d\mathbf{r}...d\mathbf{r}''' \, \alpha^A_{\alpha\beta}(\mathbf{r},\mathbf{r}';i\omega)\, T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')$$

$$\times \alpha^{B}_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''';i\omega)\, T_{\delta\alpha}(\mathbf{r}''',\mathbf{r}). \qquad (1.29)$$

The dispersion energy can also be calculated from second-order perturbation theory (cf. Eq. (1.24)). For example, Longuet-Higgins and Salem[103] calculated the dispersion energy for a pair of interacting molecules at long range, after applying the Unsöld approximation. They expressed the dispersion energy in terms of correlation functions of the charge-density fluctuations. However, the dynamic natures of the correlation functions were not considered explicitly. The dispersion energy in terms of the frequency-dependent susceptibilities was first derived by McLachlan.[139] In his work the interaction between two quantum-mechanical systems A and B was considered and the interaction Hamiltonian was expressed in terms of fluctuations in the physical quantities x_i and y_i, belonging to A and B respectively. The second-order dispersion energy was given by

$$W = -(\hbar/2\pi)\int_0^\infty d\xi\, \alpha_{ik}(i\xi)\beta_{ki}(i\xi), \qquad (1.30)$$

where $\alpha_{ik}(i\xi)$ and $\beta_{ki}(i\xi)$ are the susceptibilities of A and B respectively and ξ denotes the frequency. The susceptibilities given in McLachlan's work depend on the transition matrix elements of the current and charge-density four vectors, and thus include magnetic contributions to the van der Waals interaction energy. McLachlan's work was followed by the work of Longuet-Higgins,[140] where the fluctuations were specifically given in terms of transition matrix elements of the charge-density operator and the second-order dispersion energy was showed to be explicitly dependent on the susceptibilities of the interacting molecules:

$$W = -(\hbar/4\pi^2)\int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_1' \int d\mathbf{r}_2' \int_0^\infty d\xi \frac{\alpha(\mathbf{r}_1,\mathbf{r}_2,i\xi)\,\alpha(\mathbf{r}_1',\mathbf{r}_2',i\xi)}{|\mathbf{r}_1-\mathbf{r}_1'||\mathbf{r}_2-\mathbf{r}_2'|}. \quad (1.31)$$

$\alpha(\mathbf{r}_1,\mathbf{r}_2,i\xi)$ and $\alpha(\mathbf{r}_1',\mathbf{r}_2',i\xi)$ are the susceptibilities of the first and the second molecule respectively, at imaginary frequencies. $\alpha(\mathbf{r}_1,\mathbf{r}_2,i\xi)$ was described as "the mutual susceptibility at imaginary frequency $i\xi$ of two points $\mathbf{r}_1$ and $\mathbf{r}_2$ of the first molecule," that measures the response of the electron density at $\mathbf{r}_1$ due to an applied exponentially-increasing potential at $\mathbf{r}_2$, with time dependence $\exp(\xi t)$. Thus, $\alpha(\mathbf{r}_1,\mathbf{r}_2,i\xi)$ corresponds to the charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';i\omega)$ used in later works. The second-order dispersion energy has been calculated by Langhoff,[141] who has employed the contour-integration technique of Casimir and Polder[142] to separate the dispersion energy as integrals over response functions of the interacting systems. Langhoff Fourier-transformed the Coulomb potential to give the dispersion energy. Jacobi and Csanak[143] followed the same method used by Langhoff to evaluate the dipole-dipole interaction term in the dispersion energy of two closed-shell atoms. Specifically in their work, the dispersion energy was expressed in terms of the Born amplitude $\chi_n(\mathbf{q})$, which is the Fourier transform of the transition density $\chi_n(\mathbf{r}\,\mathbf{r})$. The Born amplitude was then separated into radial and angular parts and the dipole-dipole interaction term was evaluated in terms of the frequency-dependent polarizabilities. The dispersion energy can also be calculated by expanding the Coulomb operator into the interactions between multipole moments.[144] However, this method has a disadvantage that the expansion diverges asymptotically. Koide[145] has formulated a convergent expansion of the Coulomb operator into interactions between spherical waves. The charge operators were

transformed from configuration space to the wave vector space and the energy denominators were separated using the contour-integration technique of Casimir and Polder. The final form of the dispersion energy was obtained in terms of the frequency-dependent polarizabilities of the interacting atoms in the wave vector space, the spherical Bessel functions, and the Clebsch-Gordan coefficients. It was shown that in the limit $\mathbf{r} \rightarrow 0$, the dispersion energy goes to zero, while in the limit $\mathbf{r} \rightarrow \infty$, it yields the well known multipole expansion series. Derivations and calculations of the dispersion energy in terms of approximate charge density susceptibilities have been given in Ref. 146 - 152.

Within the density functional theory (DFT),[153,154] dispersion energy is contained within the exchange-correlation energy. Density functional theory has been employed to calculate van der Waals interaction energies by Langreth and Perdew,[155] Harris and Griffin,[156] Gunnarsson and Lundqvist.[157] Anderson *et al.* [158] evaluated the frequency-dependent polarizabilities for different atoms and ions and the van der Waals C_6 constants for several atomic and molecular interactions by using a modified effective density n_{eff}, originally used by Rapcewicz and Ashcroft.[159] Several research groups[160-163] have used the method of a coupling constant λ, that turns on the electron-electron interactions. Kohn, Meir, and Makarov[164] (see also chapter 4) have employed DFT to calculate van der Waals interaction energy between small and large intersystem distances. They have approximated the density distribution $n(\mathbf{r})$ by the local density approximation (LDA)[154] or by the generalized gradient approximations (GGA).[165] The Coulomb interaction energy was separated into short and long-range parts, and the long-range contributions to the interaction energy were expressed using the adiabatic connection

formula. Finally, the expression was transformed to the time domain and was applied to the calculations of the asymptotic van der Waals interaction between H-He and He-He. In their work, the van der Waals energy was obtained as

$$E_{vdW} = -C_6 / R^6, \tag{1.32}$$

where

$$C_6 = (3/\pi) \int_0^\infty dt_1 \int_0^\infty dt_2 \frac{\chi_A^{zz}(t_1)\chi_B^{zz}(t_2)}{t_1 + t_2}. \tag{1.33}$$

χ^{zz} is the z component of the density response to a perturbation in the z direction. A seamless van der Waals density functional has been formulated and applied to the interaction between two self-consistent jellium metal slabs by Dobson and co-workers.[166] In their work, the correlation energy (E_C) has been determined by the adiabatic connection fluctuation-dissipation formula (ACFD), which relates E_C to the Kubo density-density response function $\chi_{\lambda S}$, the electron-electron interaction V_{Coul}, and the Kohn-Sham density-density response function χ_{KS}. χ_{KS} depends on the average ground-state electron density. $\chi_{\lambda S}$ is determined from χ_{KS}, the exchange-correlation kernel $f_{xc,\lambda S}$, and a modified electron-electron interaction λV_{Coul}, by the Dyson-like screening equation. A related derivation and calculation have been done in later work by Dobson and Wang.[167] For a detailed review of van der Waals studies using conventional density functionals, we refer the reader to ref. 186. In more recent work, Hunt[168] has derived the electronic energy as a functional of the average electronic charge density and the average of the gradient of the charge-density fluctuations with respect to an external

potential. The functional is nonlocal. However, it is distinct from the other nonlocal functionals being used.[163,164,170-181]

Jenkins and Hunt[182] have derived a model where the correlation between the polarization fluctuations has been connected to a nonlocal dielectric function $\varepsilon_d(\mathbf{r},\mathbf{r}';i\omega)$. The nonlocal dielectric function $\varepsilon_d(\mathbf{r},\mathbf{r}';\omega)$ determines the dielectric displacement $\mathbf{D}(\mathbf{r},\omega)$ within a molecule, due to an applied external field $\mathbf{E}(\mathbf{r}',\omega)$ at $\mathbf{r}'$. For a translationally invariant system, $\varepsilon_d(\mathbf{r},\mathbf{r}';\omega)$ depends solely on $\mathbf{r}-\mathbf{r}'$, and hence can be represented as the spatial Fourier transform $\varepsilon_d(\mathbf{k};\omega)$. For these systems, $\varepsilon_d(\mathbf{k};\omega)$ is connected to the potential screening function $\varepsilon_V(\mathbf{k};\omega)$. On the intramolecular scale, the two dielectric functions are quite different due to the inhomogeneity of the intramolecular environment.

The dispersion force on nucleus I in molecule A can be calculated by taking the negative gradient of the dispersion energy with respect to $\mathbf{R}^I$, the coordinate of nucleus I. Within the nonlocal polarizability density model, the dispersion force on I depends on the derivative of the dynamic nonlocal polarizability density of A and the derivative of the correlation of the polarization fluctuations within A, with respect to $\mathbf{R}^I$. The derivative of the frequency-dependent nonlocal polarizability density with respect to $\mathbf{R}^I$ is related to the frequency-dependent hyperpolarizability.[128] Thus, this component of the dispersion force results from the interaction between the nucleus and the nonlinear polarization of A induced by the polarization fluctuations in B. If we denote this component by $\Delta\mathbf{F}_{d,1}^{I(2)}$, then[132]

$$\Delta F^{I(2)}_{d,1\alpha} = Z^I \int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r})\, \Delta P^{A(2)}_{\beta}(\mathbf{r},\omega)\,. \tag{1.34}$$

Thus, the first component of the dispersion force resembles the first component of the induction force from Eq. (1.26), with the difference that in the case of the induction force the polarization in A is induced by the fields from the static polarizations in B, while for dispersion force the polarization is induced by the fields from polarization fluctuations in B. This part of the dispersion force also corresponds to the atomic dipole force in the work by Nakatsuji and Koga,[135] although the dispersion forces and dispersion induced dipole were not considered explicitly in their work.

The second component of the dispersion force depends on the derivative of the correlation between the polarization fluctuations within A with respect to $\mathbf{R}^I$. The correlation between the polarization fluctuations at $\mathbf{r}$ and $\mathbf{r}'$ depends on the imaginary part of the nonlocal polarizability density by the fluctuation-dissipation theorem[137]

$$(1/2)\left\langle \delta P^A_\alpha(\mathbf{r},\omega)\delta P^A_\beta(\mathbf{r}',\omega') + \delta P^A_\beta(\mathbf{r}',\omega')\delta P^A_\alpha(\mathbf{r},\omega)\right\rangle$$

$$= (\hbar/2\pi)\alpha''^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega)\,\delta(\omega+\omega')\coth(\hbar\omega/2kT)\,. \tag{1.35}$$

The infinitesimal shift of nucleus I within molecule A changes the static Coulomb field that modifies the above correlation. This is similar to the field-induced fluctuation correlations[183,184] studied earlier. Due to the change of the nuclear Coulomb field, the correlation depends on the imaginary part of the frequency-dependent hyperpolarizability density, $\beta''^{A}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$. Thus the magnitude of the correlation is changed. As pointed out by Liang and Hunt,[132] the change in the static external field may also introduce new

types of correlations in molecule A. In chapter 3 of this work, we show that the Coulomb field from nucleus actually brings in new correlation within the molecule. One thing to note here is that at second order, both the induction and the dispersion force depends on interaction of nucleus I with the polarization induced in molecule A. Within the context of dispersion force for interacting atoms, this is known as the Feynman's "conjecture".[105] Quoting from Feynman's work on the electrostatic description of forces between interacting atoms[105],

"It is not the interaction of these dipoles that leads to van der Waals' force, but rather the attraction of each nucleus for the distorted charge distribution of its *own* electrons that gives the attractive $1 / R^7$ force."

Feynman's conjecture was first proved by Hirschfelder and Eliason[186] for the special case of two hydrogen atoms, both in the 1s state. It was also addressed by Nakatsuji and Koga[135] in their work on electrostatic force theory. Hellmann-Feynman forces on the nuclei of two interacting He atoms have been calculated in later work by Allen and Tozer.[187] The first general proof of Feynman's conjecture was given by Hunt.[188] In that work it was shown that the dispersion force on nucleus I in molecule A results from the interaction of I with the dispersion-induced change in the polarization of A:

$$\Delta F_{d\varepsilon}^{I(2)} = Z^I \int d\mathbf{r}\, \Delta P_{\varphi}^{A}(\mathbf{r})\, T_{\varphi\varepsilon}(\mathbf{R}^I, \mathbf{r}), \tag{1.36}$$

where $\Delta P_{\varphi}^{A}(\mathbf{r})$ depends on the nonlocal hyperpolarizability density of A and the nonlocal polarizability density of B, at imaginary frequencies. In the later work by Liang and

Hunt[132] it was mentioned that the dispersion force on nucleus I depends entirely on the hyperpolarizability of molecule A; and that it does contain a component that stems directly from the polarization of B. In chapter 3, we prove that a part of the second component of the dispersion force actually depends on the linear response of A to the field from the induced polarization of B, as determined by the transition-polarizability[189,190] of A. Thus, this part of the dispersion force is similar to the second component of the induction force in Eq. (1.26).

For three or more interacting molecules, nonadditivity appears at second and higher orders. At second order, nonadditivity appears only in the induction energy. At third and higher orders, the intermolecular interactions consist of induction energy, dispersion energy and induction-dispersion energy[253,258,261-264]. All of the three types of interactions show nonadditivities. The first calculation of the three-body interaction energy was done by Axilrod and Teller[191] and by Muto,[192] who calculated the long-range triple-dipole energy of three interacting atoms with spherical charge distributions using third-order perturbation theory. The interaction energy was found to be

$$\Delta E_{DDD} = C_9 \frac{1+3\cos(\theta_1)\cos(\theta_2)\cos(\theta_3)}{r_{12}^3 r_{23}^3 r_{31}^3}. \qquad (1.37)$$

r_{12}, r_{23}, r_{31} are the sides and $\theta_1, \theta_2, \theta_3$ are the angles of the triangle formed by the atoms, $C_9 \approx (9/16)V\alpha^3$, where V is the atomic ionization potential and α is the polarizability. The triple-dipole interaction was first applied by Axilrod[193] to study the preferred lattice structures of the rare gases. Long-range many-body interactions are more dominant in condensed phases than in molecular clusters.[194] The importance of many

body effects has been investigated in studies of the thermodynamic properties of fluids,[195,196] calculations of third virial coefficients[197-200] , and studies of molecular crystal structures.[193,201-205] Formisano *et al.*[206] have related the small-k behavior of the static structure factor S(k) in a noble gas fluid to the two (London)- and three (Axilrod-Teller triple-dipole)-body potentials. More recently, Jakse and co-workers[207] have used a potential energy function based on the two-body potential of Aziz and Slaman[208,209] and the triple-dipole Axilrod-Teller potential to study the structural and thermodynamic properties of liquid krypton. Evidence for many-body effects has been found in the preferred structures[193,201,202,204,205] and binding energies[210] of rare gas crystals. In recent work, Donchev[211] has studied the role of dispersion forces for cubic lattices using a coupled fluctuated dipole model (CFDM), where the particles have been treated as three-dimensional harmonic oscillators, coupled by the dipole-dipole potential.

Deviations from pairwise properties have also been noted in studies of structure, dynamics, light scattering, IR and far-IR absorption spectra[212-220] of van der Waals clusters,[216-225] liquids,[226-235] and solids.[193,201-205] Computations and experiments on the spectroscopic properties of van der Waals trimers have specially inspired research in the field of many-body effects. Studies in this field include rotational spectra of Ar_2HF,[236] Ar_2DF,[236] Ar_2HCl,[237] Ar_2DCl,[238] $(HCN)_3$,[239] Ar_2HCN,[240] Ar_2CO_2,[241] Ar_2OCS,[242] Ne_2Kr,[243] and Ne_2Xe_2.[243] Far-IR intermolecular vibrations have been observed in Ar_2HCl,[216] Ar_2DCl,[217] and in $(H_2O)_3$.[218] Vibrations in the mid-IR in Ar_nHF,[244] DF_3,[245] $(HCN)_3$,[246] and $(H_2O)_3$[247] also show nonadditive effects. The role of nonadditive effects

in the properties of water trimer and liquid water has been analyzed by Gregory and Clary,[248] and by Li *et al.*[249] Collision-induced absorption spectra of compressed gases and liquids show evidence of nonadditive three-body dipoles,[250] since the pairwise-additive dipole is not sufficient to explain the observed intensities of the transitions. Reddy, Xiang, and Varghese[251] detected an absorption between 12 300 and 12 700 cm^{-1} for compressed H_2. This absorption corresponds to the $v = 0 \rightarrow 1$ transition on all three of the molecules in an $H_2 \cdots H_2 \cdots H_2$ complex. This particular transition is known as a triple transition[252] and it is forbidden with pairwise additive dipoles.

Early theoretical studies of nonadditive interactions were done using the point-multipole form. The Axilrod-Teller-Muto triple-dipole formulation was extended by Stogryn[253] to evaluate the three-body dispersion energy of molecules with arbitrary symmetry. The energy denominator from third-order perturbation theory was separated using Buckingham's method of evaluating the second-order dispersion energy and the dispersion energy was obtained in terms of the polarizability tensors, the mean polarizabilities of the molecules, and the dipole propagators. The method was applied to calculate the cohesive energies of molecular crystals. A similar method was used to calculate the third virial coefficients of CO_2 and N_2, where the spherically symmetric component of the two-body potential was described by Lennard-Jones (12-6) or (18-6) potentials. Martin[254] derived the three-body dipole moment of three spherical atoms from the fourth-order perturbed energy with the perturbing Hamiltonian expanded in terms of the spherical multipole moments of the interacting atoms. For H_3, coefficients of the leading terms were calculated by diagonalizing the unperturbed H-atom matrix with s, p,

and d basis sets. The numerical values of these coefficients were then estimated for He_3 . A similar method was followed by Gray and Lo[255] to evaluate the long range part of the three-body dipole moment of three interacting atoms and to estimate the density required to observe the collision induced infrared absorption in rare gases experimentally. The multipole-moment expansion method has been used by Bruch and co-workers[256,257] to study the three-body dipoles of interacting spherical atoms. In later work, Stogryn[258] did a systematic analysis of the third-order perturbation energy for a system of N asymmetric molecules where the perturbing Hamiltonian was defined in terms of the multipole moment tensors, as used earlier by Kielich.[259] The overall third-order energy was separated into induction, dispersion and induction-dispersion energies. The induction energy was further separated into two components: one component (W_B) is linear in the hyperpolarizability and the other one (W_A) is bilinear in the polarizabilities. The dispersion energy was separated into three parts: One involves the polarizabilities of the interacting molecules at imaginary frequencies (W_D), one (W_{BA}) contains the polarizability of one molecule and the hyperpolarizability of the other, and the last part (W_{CD}) extends to asymmetric molecules of the result found by Chan and Dalgarno.[260]

Nonadditivity of the induction energy at second order was derived explicitly by Piecuch.[261] In his work, the Rayleigh-Schrödinger perturbation theory was used to express the second-order correction to the energy in a system of N interacting molecules. The pairwise nonadditive induction energy was obtained as

$$\Delta = -\sum_{\substack{i,j,k=1 \\ (k\neq i,j)}}^{N} \sum_{p_j \neq g_j} \frac{\langle\, |V_{ij}|p_j\rangle\langle p_j|V_{jk}|\,\rangle}{\in(p_j)}, \tag{1.38}$$

where Stogryn's notation[258] has been used. i, j, k are the interacting molecules, $|\,\rangle$ and $|p\rangle$ are respectively the unperturbed ground and excited states, and $\in(p_j) = E_{p_a} - E_{g_a}$. The interaction Hamiltonian V_{ij} was then expressed in terms of the multipole expansion using a spherical tensor technique, to obtain

$$\Delta = -4\pi \sum_{\substack{i,j,k=1 \\ (k\neq i,j)}}^{N} \sum_{\substack{l_i\, l'_j\, l''_j\, l_k \\ l_j\, L_{ik}\, L_{ikj}}} (-1)^{l_i+l''_j} R_{ij}^{-l_i-l'_j-1} R_{jk}^{-l''_j-l_k-1}$$

$$\times \begin{pmatrix} 2l_i + 2l'_j \\ 2l_i \end{pmatrix}^{1/2} \begin{pmatrix} 2l''_j + 2l_k \\ 2l_k \end{pmatrix}^{1/2} [l_j, L_{ik}, L_{ikj}] \begin{Bmatrix} l_i & l_k & L_{ik} \\ l'_j & l''_j & l_j \\ l_i + l'_j & l''_j + l_k & L_{ikj} \end{Bmatrix}$$

$$\times [[[\mathbf{Q}_{l_i} \cdot \mathbf{D}^{l_i}(\omega_i^{-1}) \otimes \mathbf{Q}_{l_k} \cdot \mathbf{D}^{l_k}(\omega_k^{-1})]_{L_{ik}} \otimes \boldsymbol{\alpha}_{l_j}\{l'_j l''_j\} \cdot \mathbf{D}^{l_j}(\omega_j^{-1})]_{L_{ikj}}$$

$$\otimes [\mathbf{Y}_{l_i+l'_j}(\hat{R}_{ij}) \otimes \mathbf{Y}_{l''_j+l_k}(\hat{R}_{jk})]_{L_{ikj}}]_0^0. \tag{1.39}$$

$\mathbf{R}_{ij}$ is the vector pointing from i to j and $(R_{ij}, \hat{R}_{ij})$ are the spherical components of $\mathbf{R}_{ij}$ in the global coordinate system fixed in space. $\mathbf{Q}_{l_i}$ is the spherical multipole moment of i, $\omega_i, \omega_j, \omega_k$ are the Euler angles describing orientations of local coordinate systems fixed in molecules i, j, k with respect to the local coordinate system fixed in space. $\mathbf{D}^j(\omega)$ is the matrix that represents a rotation ω in the (2j + 1)-dimensional irreducible representation of the SO(3) group. $\boldsymbol{\alpha}_j$ denotes the irreducible spherical polarizability of

atom j and L_{ik}, L_{ikj} are tensors which couple the molecular moments and the polarizabilities. Eq.(1.39) gives the three-body induction energy at second order, where the dependence on orientation is simplified as far as possible and the overall energy is completely separated into the spherical multipole moments and irreducible spherical polarizabilities of the isolated atoms.

In three successive later works, the same method was used by Piecuch to derive the induction energies,[262] dispersion energies,[263] and the isotropic interaction energies[264] at the first three orders of perturbation theory. In those works, the interaction energies at first, second and third orders were explicitly derived in terms of the spherical tensor formalism and the physical significance of the third-order interaction energies from Stogryn's work[258] were explained very clearly. The overall third-order interaction energy was given by

$$E^{(3)} = E^{(3)\mathrm{ind}}_{Q,\beta QQ} + E^{(3)\mathrm{ind}}_{Q,\alpha\alpha Q} + E^{(3)\mathrm{disp}}_{\alpha,\alpha,\alpha} + E^{(3)\mathrm{disp}}_{\alpha,\beta Q} + E^{(3)\mathrm{disp}}_{\beta,\beta}, \qquad (1.40)$$

where α is the polarizability tensor and β is the hyperpolarizability tensor. In Eq. (1.40) a right Q denotes the field from the permanent multipole moment of one molecule and a left Q denotes the permanent multipole moment of another molecule. The induction energies were farther separated into two-body, three-body and four-body interactions. The induction and dispersion energies from Eq. (1.40) correspond to the interaction energies in Stogryn's work by, $W_B \equiv E^{(3)\mathrm{ind}}_{Q,\beta QQ}$, $W_A \equiv E^{(3)\mathrm{ind}}_{Q,\alpha\alpha Q}$, $W_D \equiv E^{(3)\mathrm{disp}}_{\alpha,\alpha,\alpha}$, $W_{BA} \equiv E^{(3)\mathrm{disp}}_{\alpha,\beta Q}$, and $W_{CD} \equiv E^{(3)\mathrm{disp}}_{\beta,\beta}$.

A complete description of the three-body interactions must include short range interactions. These interactions can be included either by *ab initio* calculations[222-225] or by using exchange-perturbation methods such as symmetry-adapted perturbation theory (SAPT)[265-271] or intermolecular perturbation theory/Moller-Plesset perturbation theory (IMPT/MPPT).[272-275] A symmetry-adapted Rayleigh-Schrödinger perturbation method was used by Moszynski *et al.*[271] to calculate the nonadditive three-body interaction energies of van der Waals trimers. The three-body terms from the polarization and exchange effects were separated and the polarization terms were evaluated using the linear and the quadratic polarization propagators.[276] The three-body polarization terms were obtained as induction: $E_{ind}^{(210)}(B \leftarrow A,C), E_{ind}^{(210)}(A \leftarrow B;B \leftarrow C), E_{ind}^{(1,1,1)}(A \leftarrow B;C \leftarrow B)$; dispersion: $E_{disp}^{(3,3)}(3,3)$; and induction-dispersion: $E_{ind\text{-}disp}^{(210)}$. Nonadditive effects have been calculated by a IMPT/MPPT method developed by Chałasiński *et al.*[272-275]

Nonadditive dispersion interactions have been described within a reaction-field approach by Linder and Hoernschemyer,[2,277] and by Langbein.[201] In their works, a nonlocal response theory has been used to obtain the nonadditive dispersion energies in terms of frequency-dependent polarizabilities or susceptibilities. Li and Hunt[278] have used a nonlocal polarizability density model to evaluate the three-body polarizations and three-body forces on nuclei of interacting molecules. The three-body polarizations and forces were determined from the three-body interaction energies at the third order. The overall third-order interaction energy was derived as a sum of three-body dispersion

energy, three-body induction energy, and three-body induction-dispersion energy. The induction energy was farther separated into hyperpolarization, static reaction field and third-body reaction field. It was also shown that the energies obtained using the nonlocal polarizability density method correspond the third-order interaction energies obtained by Stogryn,[258] Piecuch,[261-264] and Moszynski *et al.*[271] In the present work, we have used the nonlocal response model used by Li and Hunt to treat the three-body and four-body interaction energies. However we have worked within a charge-density susceptibility based model to connect the interaction energies explicitly to a nonlocal dielectric model. In a later work, Li and Hunt[279] evaluated the nonadditive three-body dipoles of inert gas trimers and $H_2 \cdots H_2 \cdots H_2$ using the model based on nonlocal polarizability and hyperpolarizability.

In chapter 2 of this work, we derive the two-body induction and dispersion energies at second order within the nonlocal dielectric model. These interaction energies have not been described previously in terms of intramolecular screening. Chapter 3 shows the dielectric screening present in the second-order induction and dispersion forces. We also derive a new fluctuation-correlation and the physical origin of the terms present in the second-order dispersion forces. In chapter 4 we extend the nonlocal dielectric model to derive the three-body induction energy at second order. We prove that at second order, the nonadditive three-body induction energy results from dielectric screening, where a particular molecule acts as the nonlocal dielectric medium to screen the electrostatic interaction between the other two molecules. Finally in chapter 5, we use the nonlocal dielectric model to derive the nonadditive three-body and four-body interactions and third and fourth orders. We specifically describe the induction energy at

third order and the dispersion and induction-dispersion energies at third and fourth orders. Chapter 6 includes a brief summary and conclusions.

Chapter 2: Nonlocal dielectric functions on the nanoscale: Screening of two-body induction and dispersion energies at second order

2.1 Dielectric screening and the induction energy

Within quantum perturbation theory for intermolecular interactions, the energy changes due to static reaction fields determine the induction energy. The permanent charge distribution of each molecule sets up a field that polarizes the neighboring molecule; in turn, this produces a reaction field that acts back on the first molecule, shifting its energy. Thus the induction energy depends on the static, nonlocal polarizability densities $\alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}';0)$ and $\alpha^{B}_{\alpha\beta}(\mathbf{r},\mathbf{r}';0)$ of interacting molecules, as shown in earlier work;[131]

$$\Delta E_{ind} = -(1/2)\int d\mathbf{r}\, d\mathbf{r}'\, \alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}';0)\,\mathfrak{I}^{B}_{0\alpha}(\mathbf{r})\,\mathfrak{I}^{B}_{0\beta}(\mathbf{r}')$$

$$-(1/2)\int d\mathbf{r}\, d\mathbf{r}'\, \alpha^{B}_{\alpha\beta}(\mathbf{r},\mathbf{r}';0)\,\mathfrak{I}^{A}_{0\alpha}(\mathbf{r})\,\mathfrak{I}^{A}_{0\beta}(\mathbf{r}'), \qquad (2.1.1)$$

to second order in the intermolecular interaction. In Eq. (2.1.1), $\mathfrak{I}^{B}_{0\alpha}(\mathbf{r})$ denotes the α component of the field acting on A due to the unperturbed, static charge distribution $\rho^{B}_{0}(\mathbf{r})$ of molecule B, and similarly for $\mathfrak{I}^{A}_{0\alpha}(\mathbf{r})$. The Einstein convention of summation over repeated Greek subscripts is followed in Eq. (2.1.1) and below. The result for ΔE_{ind} includes higher-multipole polarization, as well as the dipole-induced dipole interactions, because $\alpha(\mathbf{r},\mathbf{r}';\omega)$ is defined to allow for the distribution of polarization within the molecule,

$$\alpha(\mathbf{r},\mathbf{r}';\omega) = \langle 0|\hat{\mathbf{P}}(\mathbf{r})G(\omega)\hat{\mathbf{P}}(\mathbf{r}')|0\rangle + \langle 0|\hat{\mathbf{P}}(\mathbf{r}')G(-\omega)\hat{\mathbf{P}}(\mathbf{r})|0\rangle . \tag{2.1.2}$$

In Eq. (2.1.2), $\hat{\mathbf{P}}(\mathbf{r})$ is the polarization operator and $G(\omega)$ is the resolvent operator defined in Eq. (1.4). The polarization operator $\hat{\mathbf{P}}(\mathbf{r})$ is related to the charge-density operator $\hat{\rho}(\mathbf{r})$ by

$$\nabla\cdot\hat{\mathbf{P}}(\mathbf{r}) = -\hat{\rho}(\mathbf{r}), \tag{2.1.3}$$

and hence, from Eqs. (1.3), (2.1.2), and (2.1.3),

$$\nabla\nabla' : \alpha(\mathbf{r},\mathbf{r}';\omega) = -\chi(\mathbf{r},\mathbf{r}';\omega). \tag{2.1.4}$$

From Eqs. (1.5) and (2.1.2) – (2.1.4), $\alpha(\mathbf{r},\mathbf{r}';\omega)$ functions as an integral kernel, to give the polarization $\mathbf{P}(\mathbf{r},\omega)$ at point $\mathbf{r}$ in a molecule by an applied field $\mathfrak{I}(\mathbf{r}';\omega)$ acting at $\mathbf{r}'$.

The field $\mathfrak{I}_0^A(\mathbf{r})$ due to the unperturbed charge distribution $\rho_0^A(\mathbf{r})$ of molecule A is related to the electrostatic potential $\varphi_0^A(\mathbf{r},\omega=0)$ by $\mathfrak{I}_0^A(\mathbf{r}) = -\nabla\varphi_0^A(\mathbf{r},\omega=0)$. Below, we use the notation $\varphi_0^A(\mathbf{r})$ for the potential $\varphi_0^A(\mathbf{r},\omega=0)$. Integration by parts in Eq. (2.1.1) gives the induction energy in terms of the charge-density susceptibilities of A and B, and the potentials $\varphi_0^A(\mathbf{r})$ and $\varphi_0^B(\mathbf{r})$,

$$\Delta E_{ind} = 1/2\int d\mathbf{r}\,d\mathbf{r}'\,\chi^A(\mathbf{r},\mathbf{r}';0)\varphi_0^B(\mathbf{r})\varphi_0^B(\mathbf{r}') + 1/2\int d\mathbf{r}\,d\mathbf{r}'\,\chi^B(\mathbf{r},\mathbf{r}';0)\varphi_0^A(\mathbf{r})\varphi_0^A(\mathbf{r}'). \tag{2.1.5}$$

With the potentials expressed in terms of the permanent charge densities of the two molecules,

$$\Delta E_{ind} = 1/2(1+\wp_{AB})\int d\mathbf{r}\,d\mathbf{r}'\,\chi^A(\mathbf{r},\mathbf{r}';0)[(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}''|\mathbf{r}-\mathbf{r}''|^{-1}\rho_0^B(\mathbf{r}'')]$$

$$\times[(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}'''|\mathbf{r}'-\mathbf{r}'''|^{-1}\rho_0^B(\mathbf{r}''')], \qquad (2.1.6)$$

where $\wp_{AB}$ interchanges the molecule labels A and B. From Eqs. (1.2) and (2.1.6), with a change of the labels on the integration variables, it follows that the induction energy is accurately expressed in the dielectric model, by

$$\Delta E_{ind} = 1/2(4\pi\varepsilon_0)^{-1}(1+\wp_{AB})\{\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\rho_0^B(\mathbf{r})[\varepsilon_0\,\varepsilon_{v,A}^{-1}(\mathbf{r},\mathbf{r}'';0)]|\mathbf{r}''-\mathbf{r}'|^{-1}\rho_0^B(\mathbf{r}')$$

$$-\int d\mathbf{r}\,d\mathbf{r}'\rho_0^B(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1}\rho_0^B(\mathbf{r}')\}, \qquad (2.1.7)$$

where $\varepsilon_{v,A}(\mathbf{r},\mathbf{r}'';0)$ is the static, nonlocal dielectric function of molecule A. The first term in Eq. (2.1.7) gives the static Coulomb energy of the unperturbed charge distribution $\rho_0^B(\mathbf{r})$ of molecule B in presence of molecule A, which acts as a dielectric medium to screen the interactions within molecule B. The screening is nonlocal, since $\varepsilon_{v,A}^{-1}(\mathbf{r},\mathbf{r}'';0)$ depends on both $\mathbf{r}$ and $\mathbf{r}''$. The second term in Eq. (2.1.7) is the single-molecule, static Coulomb energy of the permanent charge distribution of molecule B in absence of A. The operator $\wp_{AB}$ generates the corresponding terms that depend on the static Coulomb energy of A. Thus the induction energy depends on the *difference* between the dielectrically screened and unscreened interactions of the permanent charge distributions within each molecule.

2.2 Dielectric screening and the dispersion energy

The dispersion energy ΔE_d results from spontaneous, quantum-mechanical fluctuations of the charge density in each of the interacting molecules; these give rise to fluctuating fields acting on the neighboring molecules, polarizing it, and thus producing a dynamic reaction field, which acts on the original field source, shifting its energy. To derive the dispersion energy within the dielectric framework, we start from a standard expression for ΔE_d, which is obtained both from time-independent perturbation theory and from reaction-field theory,[2,201]

$$\Delta E_d = -(\hbar/2\pi)^{-2}(4\pi\varepsilon_0)^{-2}\int_0^\infty d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \chi^A(\mathbf{r},\mathbf{r}';i\omega)|\mathbf{r}'-\mathbf{r}''|^{-1}$$

$$\times \chi^B(\mathbf{r}'',\mathbf{r}''';i\omega)|\mathbf{r}'''-\mathbf{r}|^{-1}. \qquad (2.2.1)$$

From Eq. (2.1.4) and integration by parts, Eq. (2.2.1) is equivalent to an expression for ΔE_d in terms of the nonlocal polarizability densities of A and B,[129]

$$\Delta E_d = -(\hbar/2\pi)\int_0^\infty d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \alpha^A_{\alpha\beta}(\mathbf{r},\mathbf{r}';i\omega)\, T_{\beta\gamma}(\mathbf{r}',\mathbf{r}'')$$

$$\times \alpha^B_{\gamma\delta}(\mathbf{r}'',\mathbf{r}''';i\omega)\, T_{\delta\alpha}(\mathbf{r}''',\mathbf{r}), \qquad (2.2.2)$$

where the tensor $\mathbf{T}(\mathbf{r},\mathbf{r}')$ is the dipole propagator,

$$T_{\alpha\beta}(\mathbf{r},\mathbf{r}') = (4\pi\varepsilon_0)^{-1}\nabla_\alpha \nabla_\beta |\mathbf{r}-\mathbf{r}'|^{-1}. \qquad (2.2.3)$$

For molecules A and B interacting at long range, Eq. (2.2.2) reduces to the well-known form,[188]

$$\Delta E_d = -(\hbar/2\pi)T_{\beta\gamma}(\mathbf{R})T_{\delta\alpha}(\mathbf{R})\int_0^\infty d\omega\, \alpha^A_{\alpha\beta}(i\omega)\alpha^B_{\gamma\delta}(i\omega), \qquad (2.2.4)$$

to leading order in R^{-1}, where **R** is the vector from A to B and $R = |\mathbf{R}|$. However, Eqs. (2.2.1) and (2.2.2) also include the effects of higher-multipole fluctuation correlations (beyond the dipole); so these equations give accurate results for the dispersion energies of nonoverlapping molecules, when the molecules can not be adequately approximated as point-polarizable multipoles – e.g. for large molecules in configurations such that typical intramolecular distances may exceed the shortest intermolecular distances.

In order to show the connection to charge-density fluctuations at real frequencies explicitly, we reverse the steps of the derivation by Linder and Rabenold (Ref. 2), Eqs. (61) – (\67). We assume that the temperature is sufficiently low that the susceptibility densities $\chi^A(\mathbf{r},\mathbf{r}';i\omega)$ and $\chi^B(\mathbf{r}'',\mathbf{r}''';i\omega)$ change little over an interval of $\Delta\omega = 2\pi ikT/\hbar$ on the imaginary axis; then the integral in Eq. (2.2.1) can be approximated by the discrete sum,

$$\Delta E_d = -kT(4\pi\varepsilon_0)^{-2} \sum_{n=0}^{\infty'} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \chi^A(\mathbf{r},\mathbf{r}';2\pi inkT/\hbar)|\mathbf{r}'-\mathbf{r}''|^{-1}$$

$$\times \chi^B(\mathbf{r}'',\mathbf{r}''';2\pi inkT/\hbar)|\mathbf{r}'''-\mathbf{r}|^{-1}, \qquad (2.2.5)$$

where the prime on the summation indicates that the n = 0 term is multiplied by 1/2. Equivalently,

$$\Delta E_d = (i\hbar/4\pi)(4\pi\varepsilon_0)^{-2} \int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \chi^A(\mathbf{r},\mathbf{r}';\omega)|\mathbf{r}'-\mathbf{r}''|^{-1}$$

$$\times \chi^B(\mathbf{r}'',\mathbf{r}''';\omega)|\mathbf{r}'''-\mathbf{r}|^{-1} \coth(\hbar\omega/2kT), \qquad (2.2.6)$$

as shown by evaluating the frequency integral in Eq. (2.2.6) in the upper ω half-plane, around a closed contour C that runs along the real ω axis from $\omega = -W$ to $\omega = -\varepsilon$ ($\varepsilon > 0$), clockwise around the small semicircle $\omega = \varepsilon \exp(i\theta)$ from $\theta = \pi$ to $\theta = 0$, along the real

axis from $\omega = \varepsilon$ to $\omega = W$, and then counterclockwise around the large semicircle $\omega = W \exp(i\theta)$ from $\theta = 0$ to $\theta = \pi$. In the limit as $W \to \infty$, the integral around the large semicircle vanishes, since both $\chi^A(\mathbf{r},\mathbf{r}';\omega)$ and $\chi^B(\mathbf{r}'',\mathbf{r}''';\omega)$ fall off as ω^{-2} for large ω. The poles of the susceptibilities are located in the lower complex half-plane, by causality. Therefore, the only poles within the contour C are those of the hyperbolic cotangent function, and Eq. (2.2.6) is equivalent to Eq. (2.2.5) by the residue theorem.

The susceptibilities have both real and imaginary parts, denoted by χ' and χ'',

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \chi'(\mathbf{r},\mathbf{r}';\omega) + i\chi''(\mathbf{r},\mathbf{r}';\omega). \tag{2.2.7}$$

The real part $\chi'(\mathbf{r},\mathbf{r}';\omega)$ is an even function of frequency, while the imaginary part $\chi''(\mathbf{r},\mathbf{r}';\omega)$ is odd in ω. Since $\coth(\hbar\omega/2kT)$ is odd in ω, Eq. (2.2.6) is also equivalent to

$$\Delta E_d = -(\hbar/4\pi)(4\pi\varepsilon_0)^{-2}(1+\wp_{AB})\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \chi^{A''}(\mathbf{r},\mathbf{r}';\omega)|\mathbf{r}'-\mathbf{r}''|^{-1}$$

$$\times \chi^B(\mathbf{r}'',\mathbf{r}''';\omega)|\mathbf{r}'''-\mathbf{r}|^{-1}\coth(\hbar\omega/2kT). \tag{2.2.8}$$

As above, $\wp_{AB}$ permutes the labels A and B.

By the fluctuation-dissipation theorem,[137,138,2] the imaginary part of the charge-density susceptibility is related to the spectrum of charge-density fluctuations by

$$-(\hbar/4\pi)\chi^{A''}(\mathbf{r},\mathbf{r}';\omega)\coth(\hbar\omega/2kT)$$

$$= (1/2\pi)\int_{-\infty}^{\infty} d(t-t')\exp[-i\omega(t-t')]\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+, \tag{2.2.9}$$

where

$$\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+ \equiv \left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t') + \delta\rho^A(\mathbf{r}',t')\delta\rho^A(\mathbf{r},t)\right\rangle. \tag{2.2.10}$$

Therefore,

$$\Delta E_d = (1/8\pi)(4\pi\varepsilon_0)^{-2}(1+\wp_{AB})\int_{-\infty}^{\infty} d\omega \int \mathbf{dr}\,\mathbf{dr}'\,\mathbf{dr}''\,\mathbf{dr}''' \int_{-\infty}^{\infty} d(t-t')\exp[-i\omega(t-t')]$$

$$\times\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+ |\mathbf{r}'-\mathbf{r}''|^{-1}\chi^B(\mathbf{r}'',\mathbf{r}''';\omega)|\mathbf{r}'''-\mathbf{r}|^{-1}$$

$$= (1/4)(4\pi\varepsilon_0)^{-2}(1+\wp_{AB})\int \mathbf{dr}\,\mathbf{dr}'\,\mathbf{dr}''\,\mathbf{dr}''' \int_{-\infty}^{\infty} d(t-t')\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+$$

$$\times |\mathbf{r}'-\mathbf{r}''|^{-1}\chi^B(\mathbf{r}'',\mathbf{r}''';t\text{-}t')|\mathbf{r}''-\mathbf{r}|^{-1}. \qquad (2.2.11)$$

Next, we use the relation between $\chi(\mathbf{r},\mathbf{r}';t-t')$ and $\varepsilon_V^{-1}(\mathbf{r},\mathbf{r}';t-t')$ in the time domain,

$$\varepsilon_0\,\varepsilon_V^{-1}(\mathbf{r},\mathbf{r}';t-t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')+(4\pi\varepsilon_0)^{-1}\int \mathbf{dr}''|\mathbf{r}-\mathbf{r}''|^{-1}\chi(\mathbf{r}'',\mathbf{r}';t\text{-}t'), \qquad (2.2.12)$$

along with the Born symmetry $[\chi^B(\mathbf{r},\mathbf{r}';t-t') = \chi^B(\mathbf{r}',\mathbf{r};t-t')]$, to obtain

$$\Delta E_d = (1/4)(4\pi\varepsilon_0)^{-1}(1+\wp_{AB})\int \mathbf{dr}\,\mathbf{dr}'\,\mathbf{dr}'' \int_{-\infty}^{\infty} d(t-t')\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+$$

$$\times|\mathbf{r}'-\mathbf{r}''|^{-1}\varepsilon_0\,\varepsilon_{V,B}^{-1}(\mathbf{r},\mathbf{r}'';t-t')$$

$$-(1/4)(4\pi\varepsilon_0)^{-1}(1+\wp_{AB})\int \mathbf{dr}\,\mathbf{dr}'\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+ |\mathbf{r}-\mathbf{r}'|^{-1}. \qquad (2.2.13)$$

The first term shown explicitly in Eq. (2.2.13) gives the Coulomb energy associated with interactions of the fluctuating charge densities $\delta\rho^A(\mathbf{r},t)$ and $\delta\rho^A(\mathbf{r}',t')$, in the presence of molecule B, which acts as a dielectric medium with the nonlocal screening function $\varepsilon_{V,B}^{-1}(\mathbf{r},\mathbf{r}'',t-t')$, introduced by Jenkins and Hunt.[1] A charge-density fluctuation at $\mathbf{r}',t'$ sets up a potential at $\mathbf{r}'',t'$ (in the Coulomb gauge, with retardation neglected). Molecule B gives a screened potential at $\mathbf{r},t$, via $\varepsilon_{V,B}^{-1}(\mathbf{r},\mathbf{r}'',t-t')$, and the screened potential affects the energy of a charge-density fluctuation at $\mathbf{r},t$. The response is integrated over

all "time lags" $t-t'$, but $\varepsilon^{-1}_{v,B}(\mathbf{r},\mathbf{r}'',t-t')=0$ if $t-t'<0$, so the response is causal. The second term in Eq. (2.2.13) gives the Coulomb energy of associated with the charge-density fluctuations in molecule A, in the absence of molecule B. The operator $\wp_{AB}$ generates the corresponding term, in which molecule A acts as a dielectric medium for fluctuating charge interactions in B.

The Coulomb energy of interaction between the charge-density fluctuations in the same molecule equals the intramolecular exchange-correlation energy in density functional theory (after the self-energy has been removed). With Eq. (2.2.13), this implies that – for molecules with weak or negligible charge overlap – the dispersion energy is equal to the *screening-induced change* in the intramolecular exchange-correlation energy, summed for the two molecules.

A different dielectric function $\varepsilon_d(\mathbf{r},\mathbf{r}';i\omega)$ at imaginary frequencies[183] is directly related to the correlation of the polarization fluctuations at $\mathbf{r}$ and $\mathbf{r}'$. On intramolecular scale, $\varepsilon_d(\mathbf{r},\mathbf{r}';\omega)$ is distinct from $\varepsilon_v(\mathbf{r},\mathbf{r}';\omega)$. Thus, $\varepsilon_v(\mathbf{r},\mathbf{r}';i\omega)$ does not relate directly to the charge density fluctuations. However, Eq. (2.2.13) proves that $\varepsilon_v(\mathbf{r},\mathbf{r}';t-t')$ and hence $\varepsilon_v(\mathbf{r},\mathbf{r}';\omega)$ is directly related to the screening of the correlations of the intramolecular charge density fluctuations.

Since the correlations between the permanent charge density and the fluctuating charge density vanish for each molecule, there is no net Coulomb energy associated with the interactions between $\rho_0(\mathbf{r})$ and $\delta\rho(\mathbf{r}',t)$. Hence, in the region of negligible overlap, Eqs. (2.1.7) and (2.2.13) give the energy to second order, in a dielectric framework; and the results are consistent with quantum perturbation theory.

Chapter 3: Dielectric screening of second-order induction and dispersion forces on nuclei of interacting molecules

In this chapter, we express the second-order induction and dispersion forces on the nuclei of interacting molecules within the dielectric framework. The force on nucleus K in molecule A is determined by the negative gradient of the interaction energy of the molecule with respect to the coordinate $\mathbf{R}^K$ of nucleus K.

$$\mathbf{F}^K = -\nabla^K \Delta E, \tag{3.1}$$

where ∇^K denotes differentiation with respect to $\mathbf{R}^K$. In the following sections we use Eq. (3.1) to derive the induction and dispersion forces on the nuclei. Throughout the derivations, we use the Born-Oppenheimer approximation: The forces on the nuclei are determined as functions of the nuclear coordinates, fixed within individual calculations but not restricted to the equilibrium configuration.

3.1 Dielectric screening and the second-order induction forces on nuclei

The induction force $\mathbf{F}^K_{ind}$ on nucleus K in molecule A is given by the derivative of the induction energy with respect to coordinate $\mathbf{R}^K$ of nucleus K, $\mathbf{F}^K_{ind} = -\nabla^K \Delta E_{ind}$. From Eq. (2.1.1) and the Born symmetry[280] of the polarizability density $\alpha^A_{\alpha\beta}(\mathbf{r},\mathbf{r}';0) = \alpha^A_{\alpha\beta}(\mathbf{r}',\mathbf{r};0)$, we obtain

$$\mathbf{F}^K_{ind} = 1/2 \int d\mathbf{r}\, d\mathbf{r}'\, \partial \alpha^A_{\alpha\beta}(\mathbf{r},\mathbf{r}';0)/\partial \mathbf{R}^K\, \Im^B_{0\alpha}(\mathbf{r})\, \Im^B_{0\beta}(\mathbf{r}')$$

$$+\int d\mathbf{r}\,d\mathbf{r}'\,\alpha^{B}_{\alpha\beta}(\mathbf{r},\mathbf{r}';0)\,\partial\,\Im^{A}_{0\alpha}(\mathbf{r})/\partial\mathbf{R}^{K}\,\Im^{A}_{0\beta}(\mathbf{r}'). \tag{3.1.1}$$

The derivative of the polarizability density of molecule A with respect to the nuclear coordinate depends on the nonlocal hyperpolarizability density $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ of A,[127,128]

$$\partial\,\alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega)/\partial R^{K}_{\gamma} = Z^{K}\int d\mathbf{r}''\,\beta^{A}_{\alpha\beta\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)\,T_{\delta\gamma}(\mathbf{r}'',\mathbf{R}^{K}), \tag{3.1.2}$$

where $\mathbf{T}(\mathbf{r}'',\mathbf{R}^{K})$ is the dipole propagator defined in Eq. (2.2.3) and the hyperpolarizability density is given by[130,134]

$$\begin{aligned}\beta_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega',\omega'') = S_{\beta\gamma}(\mathbf{r}',\mathbf{r}'',\omega',\omega'')[&\left\langle 0\left|\hat{\mathbf{P}}_{\alpha}(\mathbf{r})\mathbf{G}(\omega_{\sigma})\hat{\mathbf{P}}^{0}_{\gamma}(\mathbf{r}'')\mathbf{G}(\omega')\hat{\mathbf{P}}_{\beta}(\mathbf{r}')\right|0\right\rangle\\ &+\left\langle 0\left|\hat{\mathbf{P}}_{\gamma}(\mathbf{r}'')\mathbf{G}^{*}(-\omega'')\hat{\mathbf{P}}^{0}_{\beta}(\mathbf{r}'')\mathbf{G}(-\omega_{\sigma})\hat{\mathbf{P}}_{\alpha}(\mathbf{r}')\right|0\right\rangle\\ &+\left\langle 0\left|\hat{\mathbf{P}}_{\gamma}(\mathbf{r}'')\mathbf{G}^{*}(-\omega'')\hat{\mathbf{P}}^{0}_{\alpha}(\mathbf{r})\mathbf{G}(\omega')\hat{\mathbf{P}}_{\beta}(\mathbf{r}')\right|0\right\rangle.\end{aligned} \tag{3.1.3}$$

The polarization operator $\hat{\mathbf{P}}(\mathbf{r})$ satisfies Eq. (2.1.3). In Eq. (3.1.3), the operator $S_{\beta\gamma}(\mathbf{r}',\mathbf{r}'',\omega',\omega'')$ denotes the sum of terms obtained by permuting $\hat{\mathbf{P}}_{\beta}(\mathbf{r}')$ and $\hat{\mathbf{P}}_{\gamma}(\mathbf{r}'')$, together with there associated frequencies ω' and ω'' in the expression that follows the operator, $\omega_{\sigma}=\omega'+\omega''$, and $\hat{\mathbf{P}}^{0}_{\alpha}(\mathbf{r})=\hat{\mathbf{P}}_{\alpha}(\mathbf{r})-\left\langle 0\left|\hat{\mathbf{P}}_{\alpha}(\mathbf{r})\right|0\right\rangle$.

The derivative of the field due to molecule A, taken with respect to a nuclear coordinate in molecule A, is given by

$$\partial\,\Im^{A}_{0\alpha}(\mathbf{r})/\partial R^{K}_{\beta} = (4\pi\varepsilon_{0})^{-1}\int d\mathbf{r}'(r_{\alpha}-r'_{\alpha})|\mathbf{r}-\mathbf{r}'|^{-3}\,\partial\,\rho^{eA}_{0}(\mathbf{r}')/\partial R^{K}_{\beta}$$

$$+Z^K(4\pi\varepsilon_0)^{-1}\nabla_\beta^K(r_\alpha - R_\alpha^K)\left|\mathbf{r}-\mathbf{R}^K\right|^{-3}, \tag{3.1.4}$$

and the derivative of the electronic charge density with respect to the position of nucleus K depends on the charge-density susceptibility of molecule A,

$$\partial\rho_0^{eA}(\mathbf{r})/\partial\mathbf{R}^K = Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}'\chi^A(\mathbf{r},\mathbf{r}')\nabla^K\left|\mathbf{r}'-\mathbf{R}^K\right|^{-1}. \tag{3.1.5}$$

Eq. (3.1.5) is equivalent (after integration by parts) to the relation derived by Hunt[131] between the nonlocal polarizability density $\alpha(\mathbf{r},\mathbf{r}';0)$ and the change in the electronic polarization when a nucleus shifts infinitesimally within a molecule.

Thus, from Eqs. (3.1.1), (3.1.2), (3.1.4), and (3.1.5), we obtain

$$\begin{aligned}
F_{ind,\alpha}^K = {} & (1/2)Z^K\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\beta_{\beta\gamma\delta}^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\Im_{0\beta}^B(\mathbf{r})\Im_{0\gamma}^B(\mathbf{r}')T_{\delta\alpha}(\mathbf{r}'',\mathbf{R}^K) \\
& + Z^K(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\alpha_{\beta\gamma}^B(\mathbf{r},\mathbf{r}';0)(r_\beta - r_\beta'')\left|\mathbf{r}-\mathbf{r}''\right|^{-3} \\
& \times\chi^A(\mathbf{r}'',\mathbf{r}''';0)\nabla_\alpha^K\left|\mathbf{r}'''-\mathbf{R}^K\right|^{-1}\Im_{0\gamma}^A(\mathbf{r}') \\
& + Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\alpha_{\beta\gamma}^B(\mathbf{r},\mathbf{r}';0)\Im_{0\gamma}^A(\mathbf{r}')\nabla_\alpha^K(r_\beta - R_\beta^K)\left|\mathbf{r}-\mathbf{R}^K\right|^{-3}.
\end{aligned} \tag{3.1.6}$$

Next, we show that $F_{ind,\alpha}^K$ in Eq. (3.1.6) is equivalent to the force on nucleus K calculated with a dielectric screening model and the static – but perturbed – charge distribution of molecule B.

First we write $F^K_{ind,\alpha}$ from Eq. (3.1.6) in terms of $\Delta P^B_{1,\alpha}(\mathbf{r},0)$, the induced change in the static polarization of molecule B at first order, due to the field from the permanent charge distribution of A. $\Delta P^B_{1,\alpha}(\mathbf{r},0)$ is given by

$$\Delta P^B_{1,\alpha}(\mathbf{r},0) = \int d\mathbf{r}' \alpha^B_{\alpha\beta}(\mathbf{r},\mathbf{r}';0) \Im^A_{0\beta}(\mathbf{r}'). \tag{3.1.7}$$

Then from Eqs. (2.2.3), (3.1.6), (3.1.7) and

$$\nabla''_\alpha \nabla''_\delta \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1} = -\nabla^K_\alpha \nabla''_\delta \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1}, \tag{3.1.8}$$

we obtain

$$\begin{aligned} F^K_{ind,\alpha} = -(1/2) Z^K (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'' \beta^A_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0) \Im^B_{0\beta}(\mathbf{r}) \Im^B_{0\gamma}(\mathbf{r}') \\ \times \nabla^K_\alpha \nabla''_\delta \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1} \\ - Z^K (4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'' \Delta P^B_{1,\alpha}(\mathbf{r},0) \nabla_\beta \left|\mathbf{r} - \mathbf{r}''\right|^{-1} \\ \times \chi^A(\mathbf{r}'',\mathbf{r}''';0) \nabla^K_\alpha \left|\mathbf{r}''' - \mathbf{R}^K\right|^{-1} \\ - Z^K (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, \Delta P^B_{1,\beta}(\mathbf{r},0) \nabla^K_\alpha \nabla_\beta \left|\mathbf{r} - \mathbf{R}^K\right|^{-1}. \end{aligned} \tag{3.1.9}$$

The potential acting on molecule A is the sum of the potential $\varphi^B_0(\mathbf{r})$ due to the unperturbed charge distribution of B and the potential $\Delta\varphi^B_1(\mathbf{r})$ due to the change in the charge density of B, caused by its interaction with A. From Eq. (3.1.9), the force $F^K_{ind,\alpha}$

depends quadratically on $\varphi_0^B(\mathbf{r})$, since $\mathfrak{I}_0^B(\mathbf{r}) = -\nabla\varphi_0^B(\mathbf{r})$. The potential $\Delta\varphi_1^B(\mathbf{r},0)$ due to the first-order change in the polarization of B is given by

$$\Delta\varphi_1^B(\mathbf{r},0) = (4\pi\varepsilon_0)^{-1}\int d\mathbf{r}'\,\nabla'_\alpha\,|\mathbf{r}-\mathbf{r}'|^{-1}\,\Delta P_{1,\alpha}^B(\mathbf{r}',0), \tag{3.1.10}$$

since $\Delta\rho_1^B(\mathbf{r}',0)$ is related to $\Delta P_1^B(\mathbf{r}',0)$ by the same relation that connects the corresponding operators [Eq. (2.1.3)]. Then from Eqs. (3.1.9), (3.1.10), and repeated use of the divergence theorem, we obtain

$$\begin{aligned} F_{\mathrm{ind},\alpha}^K = (1/2)Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,[\nabla_\beta\nabla'_\gamma\nabla''_\delta\beta^A_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)] \\ \times\varphi_0^B(\mathbf{r})\varphi_0^B(\mathbf{r}')\nabla_\alpha^K\left|\mathbf{r}''-\mathbf{R}^K\right|^{-1} \\ -Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\,\chi^A(\mathbf{r},\mathbf{r}';0)\nabla_\alpha^K\left|\mathbf{r}-\mathbf{R}^K\right|^{-1}\Delta\varphi_1^B(\mathbf{r}',0) \\ -Z^K\nabla_\alpha^K[\Delta\varphi_1^B(\mathbf{R}^K,0)]. \end{aligned} \tag{3.1.11}$$

The Born symmetry of $\chi^A(\mathbf{r},\mathbf{r}';0)$ with respect to an interchange of its arguments has been used in deriving Eq. (3.1.11).

From Eqs. (1.9) and (3.1.3), the β-hyperpolarizability density is related to the quadratic charge-density susceptibility $\zeta(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$ by

$$\nabla_\beta\nabla'_\gamma\nabla''_\delta\beta_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'') = -\zeta(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0). \tag{3.1.12}$$

With this result and a relabeling of the variables of integration, Eq. (3.1.11) becomes

$$\begin{aligned} F_{\mathrm{ind},\alpha}^K = -(1/2)Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}''\,d\mathbf{r}'''\,\zeta^A(\mathbf{r}',\mathbf{r}'',\mathbf{r}''';0,0) \\ \times\varphi_0^B(\mathbf{r}')\varphi_0^B(\mathbf{r}'')\partial/\partial r_\alpha\,|\mathbf{r}'''-\mathbf{r}|^{-1}\Big|_{\mathbf{r}=\mathbf{R}^K} \end{aligned}$$

$$-Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}'\,d\mathbf{r}''\,\chi^A(\mathbf{r}'',\mathbf{r}';0)\,\partial/\partial r_\alpha\,|\mathbf{r}''-\mathbf{r}|^{-1}\,\Delta\varphi_1^B(\mathbf{r}',0)\Big|_{\mathbf{r}=\mathbf{R}^K}$$

$$-Z^K\,\nabla_\alpha^K[\Delta\varphi_1^B(\mathbf{R}^K,0)]. \qquad (3.1.13)$$

From Eqs. (1.2), (1.10), and (3.1.13), the induction force on nucleus K in molecule A is given by

$$F_{ind,\alpha}^K = -Z^K\varepsilon_0\,\partial/\partial r_\alpha\,[\int d\mathbf{r}'\,\varepsilon_{v,A}^{-1}(\mathbf{r},\mathbf{r}';0)\,\Delta\varphi_1^B(\mathbf{r}',0)]\Big|_{\mathbf{r}=\mathbf{R}^K}$$

$$-(1/2)Z^K\varepsilon_0\,\partial/\partial r_\alpha\,[\int d\mathbf{r}'\,d\mathbf{r}''\,\varepsilon_{q,A}^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'',0,0)$$

$$\times\,\varphi_0^B(\mathbf{r}';0)\,\varphi_0^B(\mathbf{r}'';0)]\Big|_{\mathbf{r}=\mathbf{R}^K}. \qquad (3.1.14)$$

Eq. (3.1.14) shows that the induction force on a nucleus in molecule A results from dielectric screening of the potential from molecules B; the first-order change in the potential $\Delta\varphi_1^B(\mathbf{r}',0)$ is screened linearly within A, while the unperturbed potential is screened quadratically to give $F_{ind,\alpha}^K$. As shown earlier by Jenkins and Hunt,[1] linear screening within A of the unperturbed potential $\varphi_0^B(\mathbf{r}';0)$ from B gives the force derived from the electrostatic potential energy.

The effective potential $\varphi_{eff}^A(\mathbf{r},0)$ within A due to B is sum of terms of first and second order in the A–B interaction, given by

$$\varphi_{1,eff}^A(\mathbf{r},0) = \varepsilon_0\int d\mathbf{r}'\,\varepsilon_{v,A}^{-1}(\mathbf{r},\mathbf{r}';0)\,\varphi_0^B(\mathbf{r}',0), \qquad (3.1.15)$$

and

$$\varphi^{A}_{2,\mathrm{eff}}(\mathbf{r},0) = \varepsilon_0 \int d\mathbf{r}'\, \varepsilon^{-1}_{v,A}(\mathbf{r},\mathbf{r}';0)\,\Delta\varphi^{B}_{1}(\mathbf{r}',0)$$

$$+(1/2)\varepsilon_0 \int d\mathbf{r}'\, d\mathbf{r}''\, \varepsilon^{-1}_{q,A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\,\varphi^{B}_{0}(\mathbf{r}',0)\,\varphi^{B}_{0}(\mathbf{r}'',0), \qquad (3.1.16)$$

respectively. From Eqs. (3.1.14) and (3.1.16),

$$F^{K}_{\mathrm{ind},\alpha} = -Z^{K}\,\partial/\partial r_\alpha\,[\varphi^{A}_{2,\mathrm{eff}}(\mathbf{r},0)]\Big|_{\mathbf{r}=\mathbf{R}^{K}}. \qquad (3.1.17)$$

Hence we conclude that the dielectric screening model gives the second-order induction forces on each of the nuclei in a pair of interacting molecules, consistent with the results from perturbation theory.

3.2 Dielectric screening and the second order dispersion forces on nuclei

In this section, we derive the dispersion forces on the nuclei of interacting molecules within the dielectric model. We explicitly show the new field-induced fluctuation correlations which appear in the dispersion force and we explain the physical origin of the terms present in the dispersion force using perturbation theory.

The dispersion force $\mathbf{F}_d^K$ on nucleus K (with charge Z^K) in molecule A is derived from the dispersion energy ΔE_d: $\mathbf{F}_d^K = -\nabla^K \Delta E_d$. From Eq. (2.2.8) for ΔE_d,

$$\mathbf{F}_d^K = (\hbar/4\pi)(4\pi\varepsilon_0)^{-2}\nabla^K \int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}''' \chi^{A'}(\mathbf{r},\mathbf{r}';\omega)|\mathbf{r}'-\mathbf{r}''|^{-1}$$

$$\times \chi^{B''}(\mathbf{r}'',\mathbf{r}''';\omega)|\mathbf{r}'''-\mathbf{r}|^{-1}\coth(\hbar\omega/2kT)$$

$$+ (\hbar/4\pi)(4\pi\varepsilon_0)^{-2}\nabla^K \int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}''' \chi^{A''}(\mathbf{r},\mathbf{r}';\omega)|\mathbf{r}'-\mathbf{r}''|^{-1}$$

$$\times \chi^{B'}(\mathbf{r}'',\mathbf{r}''';\omega)|\mathbf{r}'''-\mathbf{r}|^{-1}\coth(\hbar\omega/2kT). \qquad (3.2.1)$$

Below, the first and the second terms in Eq. (3.2.1) are designated by $\mathbf{F}_{d(1)}^K$ and $\mathbf{F}_{d(2)}^K$, respectively, for convenience in the analysis. From fluctuation-dissipation theorem,[2,137]

$$\mathbf{F}_{d(1)}^K = -(1/8\pi)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}''' \nabla^K \chi^{A'}(\mathbf{r},\mathbf{r}';\omega)|\mathbf{r}-\mathbf{r}'''|^{-1}$$

$$\times \int_{-\infty}^{\infty} d(t-t')\exp[-i\omega(t-t')]\left\langle \delta\rho^B(\mathbf{r}'',t)\delta\rho^B(\mathbf{r}''',t')\right\rangle_+ |\mathbf{r}'-\mathbf{r}''|^{-1}. \qquad (3.2.2)$$

The derivative of the real part of $\chi^A(\mathbf{r},\mathbf{r}';\omega)$ with respect to $\mathbf{R}^K$ is connected to the real part of quadratic charge-density susceptibility via the relation

$$\partial\chi^{A'}(\mathbf{r},\mathbf{r}';\omega)/\partial\mathbf{R}^K = -Z^K(4\pi\varepsilon_0)^{-1}$$

$$\times \int d\mathbf{r}^{\mathbf{iv}}\, Re\,\zeta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}^{\mathbf{iv}};\omega,0)(\mathbf{R}^{K}-\mathbf{r}^{\mathbf{iv}})\left|\mathbf{r}^{\mathbf{iv}}-\mathbf{R}^{K}\right|^{-3}. \quad (3.2.3)$$

Eq. (3.2.3) follows from the contraction of Eq. (3.1.2) with $\nabla_\alpha \nabla_\beta'$ and integration by parts. From Eqs. (3.2.2) and (3.2.3), with $\delta\varphi(\mathbf{r},t)$ used to denote the potential acting on A, due to the fluctuations $\delta\rho^{B}(\mathbf{r},t)$ in the charge density of molecule B (and neglecting retardation effects),

$$\mathbf{F}^{K}_{d(1)} = (1/8\pi)Z^{K}(4\pi\varepsilon_0)^{-1}\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, Re\,\zeta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$$

$$\times(\mathbf{R}^{K}-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-3}$$

$$\times\int_{-\infty}^{\infty} d(t-t')\exp[-i\omega(t-t')]\left\langle \delta\varphi^{B}(\mathbf{r}',t)\delta\varphi^{B}(\mathbf{r},t')\right\rangle_{+}. \quad (3.2.4)$$

The quantum mechanical average of $\delta\varphi^{B}(\mathbf{r}',t)$ vanishes; however, the average of the product $\delta\varphi^{B}(\mathbf{r}',t)\delta\varphi^{B}(\mathbf{r},t')$ is nonvanishing, because the charge-density fluctuations that give rise to the potentials are correlated.

The Fourier transform of the correlation function $\left\langle \delta\varphi^{B}(\mathbf{r}',t)\delta\varphi^{B}(\mathbf{r},t')\right\rangle_{+}$ in Eq. (3.2.4) is

$$\left\langle \delta\varphi^{B}(\mathbf{r}',\omega')\delta\varphi^{B}(\mathbf{r},\omega'')\right\rangle_{+} = \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \left\langle \delta\varphi^{B}(\mathbf{r}',t)\delta\varphi^{B}(\mathbf{r},t')\right\rangle_{+} \exp(i\omega' t + i\omega'' t'). \quad (3.2.5)$$

Since $\left\langle \delta\varphi^{B}(\mathbf{r}',t)\delta\varphi^{B}(\mathbf{r},t')\right\rangle_{+}$ is a function only of the time interval $t-t'$, after changing the variables of integration in Eq. (3.2.5) to $t-t'$ and t', we obtain

$$\left\langle \delta\varphi^{B}(\mathbf{r}',\omega')\delta\varphi^{B}(\mathbf{r},\omega'')\right\rangle_{+} = \int_{-\infty}^{\infty} d(t-t') \int_{-\infty}^{\infty} dt' \left\langle \delta\varphi^{B}(\mathbf{r}',t-t')\delta\varphi^{B}(\mathbf{r},t'=0)\right\rangle_{+}$$

$$\times \exp[i\omega'(t-t')+i(\omega'+\omega'')t']$$

$$= 2\pi \left\langle \delta\varphi^{B}(\mathbf{r}',\omega')\delta\varphi^{B}(\mathbf{r},t'=0)\right\rangle_{+} \delta(\omega'+\omega''). \qquad (3.2.6)$$

In Eq. (3.2.4), we express $\left\langle \delta\varphi^{B}(\mathbf{r}',t)\delta\varphi^{B}(\mathbf{r},t')\right\rangle_{+}$ as the inverse Fourier transform of its Fourier transform, to obtain

$$\mathbf{F}^{K}_{d(1)} = (1/8\pi)(1/2\pi)^2 Z^{K} (4\pi\varepsilon_0)^{-1} \int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, Re\,\zeta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$$

$$\times (\mathbf{R}^{K}-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-3}$$

$$\times \int_{-\infty}^{\infty} d(t-t')\, \exp[-i\omega(t-t')]$$

$$\times \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \left\langle \delta\varphi^{B}(\mathbf{r}',\omega')\delta\varphi^{B}(\mathbf{r},\omega''\right\rangle_{+} \exp(-i\omega' t - i\omega'' t'), \qquad (3.2.7)$$

which is identical to

$$\mathbf{F}^{K}_{d(1)} = (1/8\pi)(1/2\pi)^2 Z^{K} (4\pi\varepsilon_0)^{-1}$$

$$\times \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, Re\,\zeta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$$

$$\times (\mathbf{R}^{K}-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-3}$$

$$\times \int_{-\infty}^{\infty} d(t-t') \exp[-i(\omega+\omega')(t-t')]\exp[-i(\omega'+\omega'')t']$$

$$\times \left\langle \delta\varphi^{B}(\mathbf{r}',\omega')\delta\varphi^{B}(\mathbf{r},\omega'')\right\rangle_{+} \qquad (3.2.8)$$

Next, we evaluate the $t-t'$ integral:

$$\mathbf{F}^{\mathrm{K}}_{\mathrm{d(1)}} = (1/8\pi)(1/2\pi)Z^{\mathrm{K}}(4\pi\varepsilon_0)^{-1}$$

$$\times\int_{-\infty}^{\infty}\mathrm{d}\omega\int_{-\infty}^{\infty}\mathrm{d}\omega'\int_{-\infty}^{\infty}\mathrm{d}\omega''\int\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}''\,Re\,\zeta^{\mathrm{A}}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$$

$$\times(\mathbf{R}^{\mathrm{K}}-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^{\mathrm{K}}\right|^{-3}$$

$$\times\delta(\omega+\omega')\exp\left[-\mathrm{i}(\omega'+\omega'')t'\right]\left\langle\delta\varphi^{\mathrm{B}}(\mathbf{r}',\omega')\delta\varphi^{\mathrm{B}}(\mathbf{r},\omega'')\right\rangle_{+}. \qquad (3.2.9)$$

After evaluating the ω' integral, use Eq. (3.2.6) for $\left\langle\delta\varphi^{\mathrm{B}}(\mathbf{r}',-\omega)\delta\varphi^{\mathrm{B}}(\mathbf{r},\omega'')\right\rangle_{+}$, to obtain

$$\mathbf{F}^{\mathrm{K}}_{\mathrm{d(1)}} = (1/8\pi)Z^{\mathrm{K}}(4\pi\varepsilon_0)^{-1}$$

$$\times\int_{-\infty}^{\infty}\mathrm{d}\omega\int_{-\infty}^{\infty}\mathrm{d}\omega''\int\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}''\,Re\,\zeta^{\mathrm{A}}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$$

$$\times(\mathbf{R}^{\mathrm{K}}-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^{\mathrm{K}}\right|^{-3}$$

$$\times\exp[-\mathrm{i}(\omega''-\omega)t']\left\langle\delta\varphi^{\mathrm{B}}(\mathbf{r}',-\omega)\delta\varphi^{\mathrm{B}}(\mathbf{r},t'=0)\right\rangle_{+}\delta(\omega''-\omega). \qquad (3.2.10)$$

Then we evaluate the ω'' integral, which gives

$$\mathbf{F}^{\mathrm{K}}_{\mathrm{d(1)}} = (1/8\pi)Z^{\mathrm{K}}(4\pi\varepsilon_0)^{-1}$$

$$\times\int_{-\infty}^{\infty}\mathrm{d}\omega\int\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}''\,Re\,\zeta^{\mathrm{A}}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$$

$$\times(\mathbf{R}^{\mathrm{K}}-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^{\mathrm{K}}\right|^{-3}\left\langle\delta\varphi^{\mathrm{B}}(\mathbf{r}',-\omega)\delta\varphi^{\mathrm{B}}(\mathbf{r},t'=0)\right\rangle_{+}. \qquad (3.2.11)$$

The real part of the quadratic charge-density susceptibility, $Re\,\zeta^{\mathrm{A}}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$, has the permutation symmetry,

$$Re\zeta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0) = Re\zeta^{A}(\mathbf{r}'',\mathbf{r},\mathbf{r}';-\omega,\omega)\,, \tag{3.2.12}$$

and it is even in ω; so

$$Re\zeta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0) = Re\zeta^{A}(\mathbf{r}'',\mathbf{r},\mathbf{r}';\omega,-\omega)\,. \tag{3.2.13}$$

Therefore

$$\mathbf{F}^{K}_{d(1)} = (1/8\pi)Z^{K}(4\pi\varepsilon_0)^{-1}$$

$$\times\int_{-\infty}^{\infty}d\omega\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,Re\zeta^{A}(\mathbf{r}'',\mathbf{r},\mathbf{r}';\omega,-\omega)$$

$$\times(\mathbf{R}^{K}-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-3}\left\langle\delta\varphi^{B}(\mathbf{r}',-\omega)\delta\varphi^{B}(\mathbf{r},t'=0)\right\rangle_{+}. \tag{3.2.14}$$

We insert an integration over ω', using a delta function,

$$\mathbf{F}^{K}_{d(1)} = (1/8\pi)Z^{K}(4\pi\varepsilon_0)^{-1}$$

$$\times\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,Re\zeta^{A}(\mathbf{r}'',\mathbf{r},\mathbf{r}';\omega',-\omega)\delta(\omega'-\omega)$$

$$\times(\mathbf{R}^{K}-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-3}\left\langle\delta\varphi^{B}(\mathbf{r}',-\omega)\delta\varphi^{B}(\mathbf{r},t'=0)\right\rangle_{+}. \tag{3.2.15}$$

From Eq. (3.2.6),

$$2\pi\left\langle\delta\varphi^{B}(\mathbf{r}',-\omega)\delta\varphi^{B}(\mathbf{r},t'=0)\right\rangle_{+}\delta(\omega'-\omega) = \left\langle\delta\varphi^{B}(\mathbf{r}',-\omega)\delta\varphi^{B}(\mathbf{r},\omega')\right\rangle_{+}, \tag{3.2.16}$$

from which we obtain

$$\mathbf{F}^{K}_{d(1)} = (1/16\pi^{2})Z^{K}(4\pi\varepsilon_0)^{-1}$$

$$\times\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,Re\zeta^{A}(\mathbf{r}'',\mathbf{r},\mathbf{r}';\omega',-\omega)$$

$$\times(\mathbf{R}^K-\mathbf{r}'')\left|\mathbf{r}''-\mathbf{R}^K\right|^{-3}\left\langle\delta\varphi^B(\mathbf{r},\omega')\delta\varphi^B(\mathbf{r}',-\omega)\right\rangle_+, \tag{3.2.17}$$

or equivalently,

$$\mathbf{F}^K_{d(1)} = (1/16\pi^2)Z^K(4\pi\varepsilon_0)^{-1}$$

$$\times\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,Re\,\zeta^A(\mathbf{r}'',\mathbf{r},\mathbf{r}';\omega',\omega)$$

$$\times(\nabla^K\left|\mathbf{r}''-\mathbf{R}^K\right|^{-3})\left\langle\delta\varphi^B(\mathbf{r},\omega')\delta\varphi^B(\mathbf{r}',\omega)\right\rangle_+. \tag{3.2.18}$$

In a form that makes the dielectric screening interpretation clear,

$$\mathbf{F}^K_{d(1)} = -(1/16\pi^2)Z^K\varepsilon_0\nabla''\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,\varepsilon^{-1}_{q,A}(\mathbf{r}'',\mathbf{r},\mathbf{r}';\omega,\omega')$$

$$\times\left\langle\delta\varphi^B(\mathbf{r},\omega)\delta\varphi^B(\mathbf{r}',\omega')\right\rangle_+\Big|_{\mathbf{r}''=\mathbf{R}^K}. \tag{3.2.19}$$

Eq. (3.2.19) shows that the first term in the dispersion force on nucleus K in molecule A results from the nonlinear dielectric screening of the correlated fluctuations in potential due to molecule B. This component of the force is analogous to the component of induction force that results from quadratic screening of the static potential due to molecule B.

The remaining component of the dispersion force on a nucleus in molecule A is given by the second term in Eq. (3.2.1), denoted by $\mathbf{F}^K_{d(2)}$, with

$$\mathbf{F}^K_{d(2)} = (\hbar/4\pi)(4\pi\varepsilon_0)^{-2}\nabla^K\int_{-\infty}^{\infty}d\omega\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,\chi^{A''}(\mathbf{r},\mathbf{r}';\omega)\left|\mathbf{r}'-\mathbf{r}''\right|^{-1}$$

$$\times\chi^{B'}(\mathbf{r}'',\mathbf{r}''';\omega)\left|\mathbf{r}'''-\mathbf{r}\right|^{-1}\coth(\hbar\omega/2kT). \tag{3.2.20}$$

In appendix A, we derive a relation that connects $\nabla^K \chi^{A''}(\mathbf{r},\mathbf{r}';\omega)$ to the imaginary part of the quadratic charge-density susceptibility, $\zeta^{A''}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$,

$$\nabla^K \chi^{A''}(\mathbf{r},\mathbf{r}';\omega) = (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}''\, Z^K \nabla^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1} \zeta^{A''}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\omega,0), \qquad (3.2.21)$$

To show the dielectric screening present in $\mathbf{F}^K_{d(2)}$, we take Eq. (3.2.21) and separate the terms with n = j and n ≠ j. We obtain

$$\begin{aligned}
\mathbf{F}^K_{d(2)} = {} & (\pi/\hbar^2)(\hbar/4\pi)(4\pi\varepsilon_0)^{-3} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, Z^K \nabla^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1} \\
& \times \{ \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{j0}^{-1} \delta(\omega_{n0} - \omega) \\
& + \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \\
& \qquad \times Re\,[(\omega_{j0}^{-1} - i\Gamma_j/2 - \omega)^{-1}]\delta(\omega_{n0} - \omega) \\
& + \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} \delta(\omega_{n0} - \omega) \\
& + \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')|0\rangle \\
& \qquad \times Re[(\omega_{j0}^{-1} - i\Gamma_j/2 - \omega)^{-1}]\delta(\omega_{n0} - \omega) \\
& - \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} \delta(\omega_{n0} + \omega) \\
& - \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|0\rangle
\end{aligned}$$

$$\times Re[(\omega_{j0}^{-1} + i\Gamma_j / 2 + \omega)^{-1}]\delta(\omega_{n0} + \omega)$$

$$- \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \omega_{j0}^{-1}\, \delta(\omega_{n0} + \omega)$$

$$- \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle$$

$$\times Re[(\omega_{j0}^{-1} + i\Gamma_j / 2 + \omega)^{-1}]\delta(\omega_{n0} + \omega)$$

$$+ \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}) - \rho_{00}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{no}^{-1}\, \delta(\omega_{n0} - \omega)$$

$$+ \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}') - \rho_{00}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{no}^{-1}\, \delta(\omega_{n0} - \omega)$$

$$- \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}') - \rho_{00}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \omega_{no}^{-1}\, \delta(\omega_{n0} + \omega)$$

$$- \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}) - \rho_{00}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{no}^{-1}\, \delta(\omega_{n0} + \omega)$$

$$+ \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$\times Re[(\omega_{n0} - \omega)^{-1}]\, \delta(\omega_{n0} - \omega)$$

$$+ \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle$$

$$\times Re[(\omega_{n0} - \omega)^{-1}]\, \delta(\omega_{n0} - \omega)$$

$$- \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$\times Re[(\omega_{n0} + \omega)^{-1}]\, \delta(\omega_{n0} + \omega)$$

$$-\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')\text{-}\rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle$$

$$\times Re[(\omega_{n0}+\omega)^{-1}]\,\delta(\omega_{n0}+\omega)\}$$

$$\times|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv},\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}\coth(\hbar\omega/2kT). \qquad (3.2.22)$$

The first eight terms in Eq. (3.2.22) can be described as correlation between the charge-density fluctuations and the susceptibility fluctuations in molecule A. To show this correlation explicitly, we define a transition susceptibility of molecule A, $\chi^{A}_{n0}(\mathbf{r},\omega_1;\mathbf{r}',\omega_2)$ following first-order transition hyperpolarizability defined by Hanna, Yuratich, and Cotter in Eq. (2.19) of Ref. (281). In particular, we need only the real part of the transition susceptibility; assuming for simplicity that the states of A are real, we have

$$Re\,\chi_{n0}(\mathbf{r},\omega_1;\mathbf{r}',\omega_2)=(1/\hbar)\sum_{j\neq 0}[\langle n|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}')|0\rangle Re(\omega_{j0}-i\Gamma_j/2-\omega_2)^{-1}$$

$$+\langle n|\hat{\rho}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|0\rangle Re(\omega_{j0}-i\Gamma_j/2-\omega_1)^{-1}]. \qquad (3.2.23)$$

From the definition of the transition hyperpolarizability in Eq. (3.2.23), we introduce the transition susceptibility of molecule A as

$$\chi^{A}_{0n}(\mathbf{r},\omega;\mathbf{r}'',0)=\sum_{j\neq 0,j\neq n}[\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\omega_{j0}^{-1}$$

$$+\langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle Re(\omega_{j0}-i\Gamma_j/2-\omega)^{-1}]. \qquad (3.2.24)$$

Thus, the first eight terms in Eq. (3.2.22) give the correlation between a charge-density fluctuation at $\mathbf{r}$ and a susceptibility fluctuation at $\mathbf{r}'$ (and vice versa), within molecule A. To illustrate the quantum mechanical nature of this fluctuation, we consider the

correlation between a susceptibility fluctuation at $\mathbf{r}$ with frequency $-\omega$ and a charge-density fluctuation at $\mathbf{r}'$ with frequency ω. In the limit $T\rightarrow 0$, the fluctuation-correlation is given by

$$(1/2)\left\langle \delta\chi(\mathbf{r}'',0;\mathbf{r},-\omega)\delta\rho(\mathbf{r}',\omega)\right\rangle_{+}$$

$$=(1/2)\left\langle \delta\chi(\mathbf{r}'',0;\mathbf{r},-\omega)\delta\rho(\mathbf{r}',\omega)+\delta\rho^{\dagger}(\mathbf{r}',\omega)\delta\chi^{\dagger}(\mathbf{r},-\omega;\mathbf{r}'',0)\right\rangle. \tag{3.2.25}$$

Using the facts that

$$\delta\chi^{\dagger}(\mathbf{r},\omega;\mathbf{r}'',0)=\delta\chi(\mathbf{r},-\omega;\mathbf{r}'',0), \tag{3.2.26}$$

and

$$\delta\rho^{\dagger}(\mathbf{r},\omega)=\delta\rho(\mathbf{r},-\omega), \tag{3.2.27}$$

we obtain

$$\begin{aligned}
&(1/2)\left\langle \delta\chi(\mathbf{r}'',0;\mathbf{r},-\omega)\,\delta\rho(\mathbf{r}',\omega)\right\rangle_{+}\\
&=(1/2)[\chi_{0n}(\mathbf{r}'',0;\mathbf{r},-\omega)\rho_{n0}(\mathbf{r}')\delta(\omega_{n0}+\omega)+\rho_{0n}(\mathbf{r}')\chi_{n0}(\mathbf{r},\omega;\mathbf{r}'',0)\delta(\omega_{0n}+\omega)]\\
&=(1/2)[\chi_{0n}(\mathbf{r}'',0;\mathbf{r},-\omega)\rho_{n0}(\mathbf{r}')\delta(\omega_{n0}+\omega)+\rho_{0n}(\mathbf{r}')\chi_{n0}(\mathbf{r},\omega;\mathbf{r}'',0)\delta(\omega-\omega_{n0})]\\
&=(1/2)[\chi_{0n}(\mathbf{r}'',0;\mathbf{r},-\omega)\rho_{n0}(\mathbf{r}')\delta(\omega_{n0}+\omega)+\rho_{0n}(\mathbf{r}')\chi_{n0}(\mathbf{r},\omega;\mathbf{r}'',0)\delta(\omega_{n0}-\omega)].
\end{aligned} \tag{3.2.28}$$

From Eq. (3.2.28), we can describe the first eight terms in $\mathbf{F}^{K}_{d(2)}$ (which we denote as $\mathbf{F}^{K}_{d(2),1}$ below, for convenience) as

$$\mathbf{F}^{K}_{d(2),1}=(1/4)(4\pi\varepsilon_0)^{-3}\int_{-\infty}^{\infty}d\omega\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,d\mathbf{r}d\mathbf{r}^{iv}\,Z^{K}\nabla^{K}\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-1}$$

$$\times[\left\langle \delta\chi(\mathbf{r}'',0;\mathbf{r},-\omega)\delta\rho(\mathbf{r}',\omega)\right\rangle^{A}_{+}+\left\langle \delta\chi(\mathbf{r}'',0;\mathbf{r}',-\omega)\delta\rho(\mathbf{r},\omega)\right\rangle^{A}_{+}]$$

$$\times\left|\mathbf{r}-\mathbf{r}'''\right|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}. \qquad (3.2.29)$$

Eq. (3.2.29) can also be represented as

$$\mathbf{F}^{K}_{d(2),1} = (1/4)(4\pi\varepsilon_0)^{-3}\int_{-\infty}^{\infty}d\omega'\int_{-\infty}^{\infty}d\omega\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,d\mathbf{r}d\mathbf{r}^{iv}$$

$$\times Z^{K}\nabla^{K}\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-1}\delta(\omega+\omega')$$

$$\times[\langle\,\delta\chi(\mathbf{r}'',0;\mathbf{r},\omega')\delta\rho(\mathbf{r}',\omega)\,\rangle^{A}_{+}+\langle\,\delta\chi(\mathbf{r}'',0;\mathbf{r}',\omega')\delta\rho(\mathbf{r},\omega)\,\rangle^{A}_{+}]$$

$$\times\left|\mathbf{r}-\mathbf{r}'''\right|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}. \qquad (3.2.30)$$

Eq. (3.2.30) proves the fact that when a nucleus shifts in the molecule, the change in the nuclear Coulomb field due to the position shift brings in new correlations within the molecule. When nucleus K in molecule A shifts infinitesimally, it changes the static Coulomb field, given by

$$\mathfrak{I}^{e}_{\alpha}(\mathbf{r}'') = (4\pi\varepsilon_0)^{-1}Z^{K}T_{\alpha\beta}(\mathbf{r}'',\mathbf{R}^{K})\delta R^{K}_{\beta}. \qquad (3.2.31)$$

Previously, Liang and Hunt[132] noted that the change in the nuclear Coulomb field may introduce new types of fluctuation correlations in the molecules, as well as altering the magnitude of the correlations. Eq. (3.2.29) establishes the fact that the shift in the position of nucleus K does bring new fluctuation correlations within the molecule, namely the correlation between charge-density fluctuation and susceptibility fluctuation. In absence of any external field, the charge-density fluctuations are correlated by the imaginary part of the charge-density susceptibility, $\chi''(\mathbf{r},\mathbf{r}',\omega)$. The nuclear Coulomb field alters that fluctuation, brings in new fluctuations, and also introduces a new

correlation function, $\zeta''(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$. From Eqs. (3.2.21), (3.2.22), and (3.2.30), we can relate the correlation between the charge-density fluctuation and the susceptibility fluctuation as

$$(1/2)[\langle \delta\chi(\mathbf{r}'',0;\mathbf{r},\omega')\delta\rho(\mathbf{r}',\omega)\rangle_{+}^{A} + \langle \delta\chi(\mathbf{r}'',0;\mathbf{r},\omega')\delta\rho(\mathbf{r},\omega)\rangle_{+}^{A}]$$

$$= (\hbar/2\pi)\zeta_{j\neq n,0}^{A''}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)\delta(\omega+\omega')\coth(\hbar\omega/2kT), \tag{3.2.32}$$

where $\zeta_{j\neq n,0}^{A''}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ means that only the terms with $j \neq n,0$ of $\zeta^{A''}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ determine the correlation.

Next, we show the dielectric screening present in $\mathbf{F}_{d(2),1}^{K}$. The spontaneous charge-density fluctuation in molecule A gives rise to a perturbing potential that acts on molecule B, shifting the charge density in B and therefore producing a fluctuating reaction potential $\delta\varphi^{B}(\mathbf{r},\omega)$ that acts on A:

$$\delta\varphi^{B}(\mathbf{r},\omega) = (4\pi\varepsilon_0)^{-2}\int d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''|\mathbf{r}-\mathbf{r}'|^{-1}\chi^{B}(\mathbf{r}',\mathbf{r}'';\omega)|\mathbf{r}''-\mathbf{r}'''|^{-1}\delta\rho^{A}(\mathbf{r}''',\omega). \tag{3.2.33}$$

Using Eq. (3.2.32), we can simplify Eq. (3.2.29) to

$$\mathbf{F}_{d(2),1}^{K} = (1/4)(4\pi\varepsilon_0)^{-1}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}''\,Z^{K}\nabla^{K}\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-1}$$

$$\times\delta(\omega+\omega')\left\langle \delta\chi^{A}(\mathbf{r}'',0;\mathbf{r},\omega')\delta\varphi^{B}(\mathbf{r},\omega)\right\rangle_{+}$$

$$+(1/4)(4\pi\varepsilon_0)^{-1}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}'\,d\mathbf{r}''\,Z^{K}\nabla^{K}\left|\mathbf{r}''-\mathbf{R}^{K}\right|^{-1}$$

$$\times\delta(\omega+\omega')\left\langle \delta\chi^{A}(\mathbf{r}'',0;\mathbf{r}',\omega')\delta\varphi^{B}(\mathbf{r}',\omega)\right\rangle_{+}. \tag{3.2.34}$$

The fluctuations in the susceptibility $\delta\chi^{A}(\mathbf{r}'',0;\mathbf{r},\omega)$ correspond to fluctuations in the dielectric function $\delta\varepsilon^{-1}_{v,A}(\mathbf{r}'',0;\mathbf{r},\omega)$, with the same relation as in Eq. (1.2); thus we obtain

$$\mathbf{F}^{K}_{d(2),1} = (1/4)\partial/\partial\mathbf{r}' \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \int d\mathbf{r}'' Z^{K} \left|\mathbf{r}' - \mathbf{r}''\right|^{-1} \delta(\omega+\omega')$$

$$\times \varepsilon_0 \left\langle \delta\varepsilon^{-1}_{v,A}(\mathbf{r}'',0;\mathbf{r},\omega')\delta\varphi^{B}(\mathbf{r},\omega) \right\rangle_{+}\Big|_{\mathbf{r}' = \mathbf{R}^{K}}$$

$$-(1/4)\partial/\partial\mathbf{r}' \int_{-\infty}^{\infty} d\omega\, Z^{K} \left\langle \delta\varphi^{B}(\mathbf{r}',\omega) \right\rangle_{+}\Big|_{\mathbf{r}' = \mathbf{R}^{K}} . \qquad (3.2.35)$$

Thus, $\mathbf{F}^{K}_{d(2),1}$ in the second component of the dispersion force on a nucleus in molecule A comes from the dielectrically screened dispersion potential, due to the change in the charge density of B induced by the spontaneous fluctuations in A. In this case, the average of the dispersion potential from molecule B vanishes; however, the fluctuations in the dielectric screening function are correlated with the fluctuations that give rise to the dispersion potential. Hence, the screened field vanishes, but the screening effect does not.

The remaining terms in the second component of the dispersion force can not be described in the dielectric framework, because they do not stem from the field induced fluctuation correlations described above. These remaining terms are not related to a nonlocal response function of molecule A. In the next part we explain the physical origin of all the terms present in $\mathbf{F}^{K}_{d(2)}$ using time-dependent perturbation theory. We use the fact that a charge-density fluctuation in A at $\mathbf{r}',t'$ creates a potential in B at $\mathbf{r}^{iv},t'$, which induces a shift in the charge density in B at $\mathbf{r}''',t$. The induced shift in the charge

density in B creates a reaction potential on A at **r**, t. This reaction potential acts as an external time-dependent perturbation and perturbs the ground and the excited states of molecule A. That results in field induced transitions and perturbed transition charge density in molecule A. Below we show a systematic analysis of these effects and relate them to the second component of the dispersion force.

The interaction between the charge-density of A, and the reaction potential from B is given by the Hamiltonian

$$\hat{H}^{(1)}(t) = \int d\mathbf{r}\, \hat{\rho}(\mathbf{r}) \cdot \delta\varphi^{B}(r,t), \tag{3.2.36}$$

where $\hat{\rho}(\mathbf{r})$ denotes the charge-density operator for molecule A. Using standard time-dependent perturbation theory, the ground and excited state wave functions of A to first order in the applied potential are given by

$$|\psi_i(t)\rangle = |n\rangle \exp[-i\omega_n t] + (1/i\hbar)\int_{-\infty}^{t} dt' \int d\mathbf{r}\{\sum_j \langle j|\hat{\rho}(\mathbf{r})|n\rangle \delta\varphi^{B}(\mathbf{r};t') \exp[i\omega_{jn} t']\}\, |j\rangle \exp[-i\omega_j t], \tag{3.2.37}$$

and

$$|\psi_f(t)\rangle = |0\rangle \exp[-i\omega_0 t] + (1/i\hbar)\int_{-\infty}^{t} dt' \int d\mathbf{r}\{\sum_j \langle j|\hat{\rho}(\mathbf{r})|0\rangle \delta\varphi^{B}(\mathbf{r};t') \exp[i\omega_{j0} t']\}\, |j\rangle \exp[-i\omega_j t], \tag{3.2.38}$$

respectively. The average value of the charge density at $\mathbf{r}'',t$ between the perturbed ground and excited states in molecule A is $\delta\rho(\mathbf{r}'',t) = \langle \psi_f(t)|\hat{\rho}(\mathbf{r}'')|\psi_i(t)\rangle + cc$, where cc means the complex conjugate of the expression. From Eqs. (3.2.37) and (3.2.38),

$$\delta\rho(\mathbf{r}'',t) = \langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle \exp[i\omega_{0n}t]$$

$$+ (1/i\hbar)\int_{-\infty}^{t} dt' \int d\mathbf{r}\{\sum_j \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle$$

$$\times \delta\varphi^B(\mathbf{r};t')\exp[i\omega_{jn}t']\}\exp[i\omega_{0j}t]$$

$$- (1/i\hbar)\int_{-\infty}^{t} dt' \int d\mathbf{r}\{\sum_j \langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle$$

$$\times \delta\varphi^B(\mathbf{r};t')\exp[i\omega_{0j}t']\}\exp[i\omega_{jn}t]. \qquad (3.2.39)$$

In Eq. (3.2.39), the first term represents the unperturbed charge-density fluctuations between the ground and the excited states at $\mathbf{r}'',t$. The average of this unperturbed fluctuation vanishes. The second and the third term are the transition charge densities between the ground and the excited state, perturbed by the reaction potential. We call these terms the "first-order transition charge density", $\delta\rho_{0n}^{(1)}(\mathbf{r}'',t)$ between the ground state $|0\rangle$ and the excited state $|n\rangle$. Using Eq. (3.2.29) along with a Fourier transform of the potential to the frequency domain, we obtain

$$\delta\rho_{0n}^{(1)}(\mathbf{r}'';t) = (1/2i\hbar)\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{t} dt' \int d\mathbf{r} \sum_j \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle$$

$$\times\{\delta\varphi^B(\mathbf{r};\omega)\exp[i(\omega_{jn}+\omega)t'] + \delta\varphi^{B*}(\mathbf{r};\omega)\exp\{i(\omega_{jn}-\omega)t'\}\}\exp[i\omega_{0j}t]$$

$$
\begin{aligned}
&-(1/2i\hbar)\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{t}dt'\int d\mathbf{r}\sum_{j}\langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle \\
&\times\{\delta\varphi^{B}(\mathbf{r};\omega)\exp[i(\omega_{0j}+\omega)t']+\delta\varphi^{B*}(\mathbf{r};\omega)\exp\{i(\omega_{0j}-\omega)t']\}\exp[i\omega_{jn}t] \\
&=-(1/2\hbar)\int_{-\infty}^{\infty}d\omega\int d\mathbf{r}\sum_{j}\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle \\
&\qquad\times\{(\omega_{jn}+\omega)^{-1}\exp[i\omega t]\delta\varphi^{B}(\mathbf{r};\omega) \\
&\qquad+(\omega_{jn}-\omega)^{-1}\exp[-i\omega t]\delta\varphi^{B*}(\mathbf{r};\omega)\}\exp[i\omega_{0n}t] \\
&+(1/2\hbar)\int_{-\infty}^{\infty}d\omega\int d\mathbf{r}\sum_{j}\langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle \\
&\qquad\times\{(\omega_{0j}+\omega)^{-1}\exp[i\omega t]\delta\varphi^{B}(\mathbf{r};\omega) \\
&\qquad+(\omega_{0j}-\omega)^{-1}\exp[-i\omega t]\delta\varphi^{B*}(\mathbf{r};\omega)\}\exp[i\omega_{0n}t] \\
&=(-1/2\hbar)\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\sum_{j}\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle \\
&\qquad\times\{(\omega_{jn}+\omega)^{-1}\exp[i\omega t]\delta\varphi^{B}(\mathbf{r};\omega) \\
&\qquad+(\omega_{jn}-\omega)^{-1}\exp[-i\omega t]\delta\varphi^{B*}(\mathbf{r};\omega)\}\exp[i\omega' t]\delta(\omega_{0n}-\omega') \\
&+(1/2\hbar)\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\sum_{j}\langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\,\hat{\rho}(\mathbf{r}'')\,|n\rangle \\
&\qquad\times\{(\omega_{0j}+\omega)^{-1}\exp[i\omega t]\delta\varphi^{B}(\mathbf{r};\omega) \\
&\qquad+(\omega_{0j}-\omega)^{-1}\exp[-i\omega t]\delta\varphi^{B*}(\mathbf{r};\omega)\}\exp[i\omega' t]\delta(\omega_{0n}-\omega').
\end{aligned}
\tag{3.2.40}
$$

The reaction potential $\delta\varphi^{B}(\mathbf{r};\omega)$ acting at $\mathbf{r}$ in A is due to the shift in the charge density in B induced by the charge-density fluctuations at $\mathbf{r}'$ in A. So

$$\delta\varphi^{B}(\mathbf{r};\omega)=(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}'\,d\mathbf{r}'''\,d\mathbf{r}^{iv}\,|\mathbf{r}-\mathbf{r}'''|^{-1}\,\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}$$

$$\times\langle n|\hat{\rho}(\mathbf{r}')|0\rangle\delta(\omega-\omega_{no}). \qquad (3.2.41)$$

From Eqs. (3.2.40) and (3.2.41), the first order transition charge-density at $\mathbf{r}'',t$ in molecule A is given by

$$\delta\rho_{0n}^{(1)}(\mathbf{r}'';t) = -(1/2\hbar)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}'''\,d\mathbf{r}^{iv}$$

$$\times\sum_j\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\{(\omega_{jn}+\omega)^{-1}\exp[i(\omega+\omega')t]\delta(\omega_{n0}-\omega)\delta(\omega_{0n}-\omega')$$

$$+(\omega_{jn}-\omega)^{-1}\exp[i(\omega-\omega')t]\delta(\omega_{n0}+\omega)\delta(\omega_{0n}-\omega')\}$$

$$\times|\mathbf{r}-\mathbf{r}'''|^{-1}\,\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}\langle n|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$+(1/2\hbar)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}'''\,d\mathbf{r}^{iv}$$

$$\times\sum_j\langle 0|\hat{\rho}(\mathbf{r})\,|j\rangle\langle j|\,\hat{\rho}(\mathbf{r}'')\,|n\rangle\{(\omega_{0j}+\omega)^{-1}\exp[i(\omega+\omega')t]\delta(\omega_{n0}-\omega)\delta(\omega_{0n}-\omega')$$

$$+(\omega_{0j}-\omega)^{-1}\exp[i(\omega-\omega')t]\delta(\omega_{n0}+\omega)\delta(\omega_{0n}-\omega')\}$$

$$\times|\mathbf{r}-\mathbf{r}'''|^{-1}\,\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}\langle n|\hat{\rho}(\mathbf{r}')|0\rangle. \qquad (3.2.42)$$

Eq. (3.2.42) is obtained using the fact that the charge-density operator is not self-adjoint in the frequency domain. Equivalently

$$\delta\rho_{0n}^{(1)}(\mathbf{r}'';t) = -(1/2\hbar)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}'''\,d\mathbf{r}^{iv}$$

$$\times\sum_j\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\{(\omega_{jn}+\omega)^{-1}\exp[i(\omega+\omega')t]\delta(\omega_{n0}-\omega)\delta(\omega+\omega')$$

$$+(\omega_{jn}-\omega)^{-1}\exp[i(\omega-\omega')t]\delta(\omega_{n0}+\omega)\delta(\omega-\omega')\}$$

$$\times|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^B(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}\langle n|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$+(1/2\hbar)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}'''\,d\mathbf{r}^{iv}$$

$$\times\sum_j\langle 0|\hat{\rho}(\mathbf{r})\,|j\rangle\langle j|\,\hat{\rho}(\mathbf{r}'')\,|n\rangle\{(\omega_{0j}+\omega)^{-1}\exp[i(\omega+\omega')t]\delta(\omega_{n0}-\omega)\delta(\omega+\omega')$$

$$+(\omega_{0j}-\omega)^{-1}\mathrm{Exp}[i(\omega-\omega')t]\delta(\omega_{n0}+\omega)\delta(\omega-\omega')\}$$

$$\times|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^B(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}\langle n|\hat{\rho}(\mathbf{r}')|0\rangle. \qquad (3.2.43)$$

Eq. (3.2.43) shows that although the reaction potential acting on A is time-dependent, the perturbed first-order charge density in A is time-independent.

From Eq. (3.2.43), we collect the terms with $j \neq n, 0$. Then integrating over ω' and rearranging the terms, we obtain

$$\delta\rho_{0n}^{(1)}(\mathbf{r}'';t) = -[(1/2\hbar)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty}d\omega\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}'''\,d\mathbf{r}^{iv}$$

$$\times\sum_{j\neq 0,n}[\{\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\omega_{j0}^{-1}+\langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle$$

$$\times(\omega_{j0}-\omega)^{-1}\}\delta(\omega_{n0}-\omega)$$

$$+\{\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\omega_{j0}^{-1}+\langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle$$

$$+\langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle(\omega_{j0}+\omega)^{-1}\}\delta(\omega_{n0}+\omega)]$$

$$\times|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}\langle n|\hat{\rho}(\mathbf{r}')|0\rangle]. \quad (3.2.44)$$

Interchanging $\mathbf{r}$ and $\mathbf{r}'$ in the terms and adding them to the terms in Eq. (3.244) yield the terms present in $\mathbf{F}^{K}_{d(2),1}$. Thus, the first eight terms present in the second component of the dispersion force arise due to the interaction of the first-order transition charge density in A with nucleus K. The first order transition charge density at $\mathbf{r}''$ is induced by the reaction potential $\delta\varphi^{B}(\mathbf{r},t)$ and is determined by the transition susceptibility of A. From Eq. (3.2.44), we can write $\mathbf{F}^{K}_{d(2),1}$ as

$$\mathbf{F}^{K}_{d(2),1} = -(1/2)(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}''Z^{K}\nabla^{K}\left|\mathbf{R}^{K}-\mathbf{r}''\right|^{-1}\sum_{n\neq 0}\delta\rho^{(1)}_{n0}(\mathbf{r}'',t). \quad (3.2.45)$$

One thing to note here (and also in the next sections) is that in Eq. (3.2.44), both terms appear with the same sign, whereas in Eq. (3.2.22) they appear with opposite signs. This apparent disagreement of sign is due to the fact that in the time-dependent perturbation formulation, we are considering the charge density fluctuations in the limit of zero temperature. At a finite temperature, we will have to consider the canonical distribution of the eigenstates. We will solve discuss this later in this chapter.

Next, we explain the second set of four terms [we denote them by $\mathbf{F}^{K}_{d(2),2}$] in Eq. (3.22.2). We use the same formulation as in the previous section, but here we only consider the terms with j = n in the initial state and j = 0 in the final state (which are

considered as secular terms in time-dependent perturbation theory). Integrating over ω', we obtain

$$\delta\rho_{0n}^{(1)}(\mathbf{r}'';t) = -(1/2\hbar)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'''\, d\mathbf{r}^{iv} [\langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|n\rangle\omega_{n0}^{-1}$$

$$\times\{\delta(\omega_{n0}-\omega)+\delta(\omega_{n0}+\omega)\}-\langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle 0|\hat{\rho}(\mathbf{r})|0\rangle\omega_{n0}^{-1}$$

$$\times\{\delta(\omega_{n0}-\omega)+\delta(\omega_{n0}+\omega)\}]|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}\langle n|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$= -(1/2\hbar)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'''\, d\mathbf{r}^{iv} [\langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})\text{-}\rho_{00}(\mathbf{r})|n\rangle$$

$$\times\{\delta(\omega_{n0}-\omega)+\delta(\omega_{n0}+\omega)\}|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)$$

$$\times\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}\langle n|\hat{\rho}(\mathbf{r}')|0\rangle. \qquad (3.2.46)$$

Thus, Eq. (3.2.46) shows that the second set of four terms in $\mathbf{F}_{d(2)}^{K}$ are due to the interaction between the first order transition charge-density and the nucleus, where the first order transition charge-density is induced by the interaction between the reaction potential and the difference in the permanent charge densities between excited state $|n\rangle$ and ground state. These four terms can not be explained within the dielectric framework, because they do arise from the response of molecule A to the reaction potential from B.

In the next part of this section, we explain the last four terms in the second component of dispersion force. The spontaneous charge-density fluctuation in molecule A brings it from the ground state to the excited state $|n\rangle$. During the time interval $t-t'$, molecule A remains in the excited electronic state $|n\rangle$ and that creates a change in the potential at the nucleus due to the change in the average electronic charge density. When

the reaction potential $\delta\rho^{B}(\mathbf{r},t)$ acts back on molecule A, it brings A from exited state $|n\rangle$ to the ground state. The first-order amplitude for this induced transition $|n\rangle \rightarrow |0\rangle$ together with the change in the potential at the nucleus determine the last four terms in $\mathbf{F}^{K}_{d(2)}$. The change in the potential at the nucleus during the time interval $t-t'$ is given by

$$\Delta\varphi^{e}(\mathbf{R}^{K};t-t') = -(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}''\, Z^{K}\left|\mathbf{R}^{K}-\mathbf{r}''\right|^{-1}\left[\langle n|\hat{\rho}(\mathbf{r}'')|n\rangle - \langle 0|\hat{\rho}(\mathbf{r}'')|0\rangle\right]. \tag{3.2.47}$$

From time-dependent perturbation theory, the first order amplitude for the transition $|n\rangle \rightarrow |0\rangle$ due to interaction with an external time-dependent Coulomb potential is given by

$$\begin{aligned} C^{(1)}_{|n\rangle\rightarrow|0\rangle}(t) = -(1/2\hbar)\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'''\, d\mathbf{r}^{iv} \{ &\langle 0|\hat{\rho}(\mathbf{r})|n\rangle(\omega_{0n}+\omega)^{-1} \\ &\times \exp[i(\omega_{0n}+\omega)t]\varphi_{ex}(\mathbf{r},\omega) + \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle(\omega_{0n}-\omega)^{-1} \\ &\times \exp[i(\omega_{0n}-\omega)t]\varphi^{*}_{ex}(\mathbf{r},\omega)\}. \end{aligned} \tag{3.2.48}$$

Using the reaction potential $\delta\varphi^{B}(\mathbf{r},\omega)$ in Eq. (3.2.48), we obtain

$$\begin{aligned} C^{(1)}_{|n\rangle\rightarrow|0\rangle}(t) = -(1/2\hbar)(4\pi\varepsilon_0)^{-2}\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'''\, d\mathbf{r}^{iv} \{ &\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \\ &\times(\omega_{0n}+\omega)^{-1}\exp[i(\omega_{0n}+\omega)t]\delta(\omega_{no}-\omega) \\ &+\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle(\omega_{0n}-\omega)^{-1}\delta(\omega_{no}+\omega)\} \\ &\times|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}. \end{aligned}$$

$$= (1/2\hbar)(4\pi\varepsilon_0)^{-2} \int_{-\infty}^{\infty} d\omega \int \mathbf{dr}\, \mathbf{dr}'\, \mathbf{dr}'''\, \mathbf{dr}^{iv} \{\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle(\omega_{n0}-\omega)^{-1}$$

$$\times\delta(\omega_{n0}-\omega)+\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle(\omega_{n0}+\omega)^{-1}\delta(\omega_{n0}+\omega)\}$$

$$\times|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}. \qquad (3.2.49)$$

Thus, from Eqs. (3.2.47) and (3.2.49), the last four terms in $\mathbf{F}^{K}_{d(2)}$ are given by

$$\mathbf{F}^{K}_{d(2),3} = -(1/2)\Delta\varphi^{e}(\mathbf{R}^{K};t-t')\sum_{n\neq 0} C^{(1)}_{|n\rangle\rightarrow|0\rangle}(t). \qquad (3.2.50)$$

These four terms are not connected to the dielectric model, since they do not originate from the response of A to the perturbing potential.

Eqs. (3.2.45), (3.2.46), and (3.2.50) show the physical significance of the second component of dispersion force. We have proved the origin of the terms using perturbation theory. Although the external perturbation is time-dependent, the dispersion force does not show time-dependent behavior, which is the exact same result obtained using reaction field theory.[2,129]

Finally in this chapter we discuss the apparent disagreement between the signs of the terms from perturbation theory and the terms we obtain from the derivative of the imaginary part of the charge-density susceptibility. The hyperbolic cotangent function in the dispersion energy appears from the fact that when we consider the charge-density fluctuations at a finite temperature T, we need to use the canonical distribution of the molecular eigenstates.[138,282] The ratio of the spectrum of the charge-density fluctuations and the imaginary part of the charge-density susceptibility yields the hyperbolic cotangent function in the dispersion energy. In the formulation described above, we have

used zero-temperature fluctuations. In the limit $T \rightarrow 0$, $\coth(\hbar\omega/2kT) \rightarrow [\theta(\omega) - \theta(-\omega)]$, where $\theta(\omega)$ is the Heaviside step function.[278] Thus in the limit $T \rightarrow 0$, Eq. (3.2.22) simplifies to

$$\mathbf{F}^{K}_{d(2)} = (\pi/\hbar^2)(\hbar/4\pi)(4\pi\varepsilon_0)^{-3} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, Z^K \nabla^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1}$$

$$\times \{ \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{j0}^{-1} \delta(\omega_{n0} - \omega)$$

$$+ \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$\times Re\,[(\omega_{j0}^{-1} - i\Gamma_j/2 - \omega)^{-1}]\delta(\omega_{n0} - \omega)$$

$$+ \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} \delta(\omega_{n0} - \omega)$$

$$+ \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$\times Re[(\omega_{j0}^{-1} - i\Gamma_j/2 - \omega)^{-1}]\delta(\omega_{n0} - \omega)$$

$$- \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} \delta(\omega_{n0} + \omega)$$

$$- \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|0\rangle$$

$$\times Re[(\omega_{j0}^{-1} + i\Gamma_j/2 + \omega)^{-1}]\delta(\omega_{n0} + \omega)$$

$$- \sum_{n\neq 0} \sum_{j\neq 0, j\neq n} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \omega_{j0}^{-1} \delta(\omega_{n0} + \omega)$$

$$-\sum_{n\neq 0}\sum_{j\neq 0, j\neq n}\langle 0|\hat{\rho}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle$$

$$\times Re[(\omega_{j0}^{-1}+i\Gamma_j/2+\omega)^{-1}]\delta(\omega_{n0}+\omega)$$

$$+\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})\text{-}\rho_{00}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle\omega_{no}^{-1}\,\delta(\omega_{n0}-\omega)$$

$$+\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')\text{-}\rho_{00}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|0\rangle\omega_{no}^{-1}\,\delta(\omega_{n0}-\omega)$$

$$-\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')\text{-}\rho_{00}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle\omega_{no}^{-1}\,\delta(\omega_{n0}+\omega)$$

$$-\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})\text{-}\rho_{00}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|0\rangle\omega_{no}^{-1}\,\delta(\omega_{n0}+\omega)$$

$$+\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')\text{-}\rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$\times Re[(\omega_{n0}-\omega)^{-1}]\,\delta(\omega_{n0}-\omega)$$

$$+\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')\text{-}\rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle$$

$$\times Re[(\omega_{n0}-\omega)^{-1}]\,\delta(\omega_{n0}-\omega)$$

$$-\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')\text{-}\rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle$$

$$\times Re[(\omega_{n0}+\omega)^{-1}]\,\delta(\omega_{n0}+\omega)$$

$$-\sum_{n\neq 0}\langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')\text{-}\rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle$$

$$\times Re[(\omega_{n0}+\omega)^{-1}]\,\delta(\omega_{n0}+\omega)$$

$$\times|\mathbf{r}-\mathbf{r}'''|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv},\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1}[\theta(\omega)-\theta(-\omega)]. \qquad (3.2.51)$$

Since $\theta(\omega)$ vanishes for $\omega < 0$, Eq. (3.2.51) yields exactly what we have obtained using perturbation theory.

Thus, we can write the total dispersion force on nucleus K in molecule A as a sum of four terms,

$$\mathbf{F}_{d}^{K} = \mathbf{F}_{d(1)}^{K} + \mathbf{F}_{d(2),1}^{K} + \mathbf{F}_{d(2),2}^{K} + \mathbf{F}_{d(2),3}^{K}. \qquad (3.2.52)$$

Both $\mathbf{F}_{d(1)}^{K}$ and $\mathbf{F}_{d(2),1}^{K}$ are described within the dielectric framework. $\mathbf{F}_{d(1)}^{K}$ results from the nonlinear screening of the fluctuating potentials from B within A, while $\mathbf{F}_{d(2),1}^{K}$ appear due to linear screening of the fluctuating potential from B, due to the susceptibility fluctuations in A. $\mathbf{F}_{d(2),2}^{K}$ and $\mathbf{F}_{d(2),3}^{K}$ do not have dielectric interpretations, since they are not related to response functions of A and they do not show any dielectric screening. All of the terms in dispersion force result from the interaction of the nucleus with an induced shift in the electronic charge density (or change in the average electronic charge density) of the same molecule. This is known as the Feynman's conjecture about the origin of dispersion forces.[105] The first general proof of Feynman's conjecture was given by Hunt,[188] where the dispersion force was given as a function of imaginary frequencies. In this work, we have showed the general proof of Feynman's conjecture in the real frequency domain.

Chapter 4: Dielectric screening and the three-body nonadditive interactions at second order

4.1 Dielectric screening of the three-body induction energy at second order

In this section we show that the nonlocal dielectric model can accurately describe the three-body induction energy at second order of molecular interaction. In section 2.1, we have showed that for a pair of interacting molecules, the two-body induction energy results from changes in the static Coulomb interactions within each molecule, due to the presence of the second molecule, which acts as the dielectric medium. In the present chapter, we consider a group of three interacting molecules A···B···C with weak or negligible charge overlap. We prove that At second order, the three-body induction energy results from the change in the two-body induction energy of a pair of molecules, due to the presence of a third molecule, which acts as a dielectric medium.

The interaction energy of two test charges is affected by the presence of a dielectric medium. The shift in the interaction energy of two test charges in presence of a linear dielectric medium characterized by the potential screening function $\varepsilon_V(\mathbf{r},\mathbf{r}';0)$ is given by

$$\Delta E = \int d\mathbf{r}d\mathbf{r}'d\mathbf{r}'' \frac{\rho(\mathbf{r})\rho(\mathbf{r}'')}{4\pi\varepsilon_V(\mathbf{r},\mathbf{r}';0)|\mathbf{r}''-\mathbf{r}'|} - \int d\mathbf{r}\, d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}, \tag{4.1.1}$$

where the first term gives the screened interaction energy due to the presence of the dielectric medium and the second term gives the direct, unscreened interaction energy of the two test charges. We prove that Eq. (4.1.1) describes the second-order three-body induction energy for a group of three interacting molecules, where the permanent charge

distributions of two molecules act as the test charges and the third molecule acts as the dielectric medium with the same nonlocal dielectric function given above.

For a group of interacting molecules A···B···C, the nonadditive three-body induction energy results as follows: the permanent charge distribution of one molecule sets up a potential that shifts the charge distribution of the second molecule; in turn, this produces a potential that acts on the third molecule, creating a non-additive shift in the energy. Thus the three-body induction energy depends on the static, nonlocal charge-density susceptibilities $\chi^{A}(\mathbf{r},\mathbf{r}';0)$, $\chi^{B}(\mathbf{r},\mathbf{r}';0)$, and $\chi^{C}(\mathbf{r},\mathbf{r}';0)$ of the interacting molecules:

$$\Delta E_{ind}^{(2,3)} = \int d\mathbf{r}\, d\mathbf{r}'\, \chi^{A}(\mathbf{r},\mathbf{r}';0)\varphi_0^{B}(\mathbf{r})\varphi_0^{C}(\mathbf{r}') + \int d\mathbf{r}\, d\mathbf{r}'\, \chi^{B}(\mathbf{r},\mathbf{r}';0)\varphi_0^{C}(\mathbf{r})\varphi_0^{A}(\mathbf{r}') + \int d\mathbf{r}\, d\mathbf{r}'\, \chi^{C}(\mathbf{r},\mathbf{r}';0)\varphi_0^{A}(\mathbf{r})\varphi_0^{B}(\mathbf{r}') . \quad (4.1.2)$$

Here and below, $\Delta E_X^{(m,n)}$ denotes an energy shift in molecule X, of order m in the interactions among n distinct molecules. In Eq. (4.1.2), $\varphi_0^{B}(\mathbf{r})$ denotes the static external potential acting on A due to the permanent charge distributions in B (and similarly for B and C). The first term in Eq. (4.1.2) can be interpreted as follows: the static external potential from C acts at $\mathbf{r}'$ in A, creating an induced shift in the charge density at $\mathbf{r}$ within A. The induced shift in the charge density at $\mathbf{r}$ then interacts with the static external potential from B at $\mathbf{r}$, thus producing a net energy shift. Eq. (4.1.2) can be written for more compactness as

$$\Delta E_{ind}^{(2,3)} = (1+C_{ABC}) \int d\mathbf{r}\, d\mathbf{r}'\, \chi^{A}(\mathbf{r},\mathbf{r}';0)\varphi_0^{B}(\mathbf{r})\varphi_0^{C}(\mathbf{r}') , \quad (4.1.3)$$

where the operator C_{ABC} denotes cyclic permutation of the indices A, B, and C in the expression that follows.

Expanding the potentials in terms of the permanent charge densities in Eq. (4.1.3), we obtain

$$\Delta E_{ind}^{(2,3)} = (1+C_{ABC})(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \rho_0^B(\mathbf{r}'')|\mathbf{r}''-\mathbf{r}|^{-1}$$

$$\times \chi^A(\mathbf{r},\mathbf{r}';0)|\mathbf{r}'-\mathbf{r}'''|^{-1}\rho_0^C(\mathbf{r}'''), \qquad (4.1.4)$$

where as usual, $\rho_X^0(\mathbf{r})$ is the permanent charge density at $\mathbf{r}$ in molecule X. From Eqs. (1.1) and (4.1.4), with a change in the labels of the integration variables, it follows that the second-order three-body induction energy is accurately expressed within the dielectric model by

$$\Delta E_{ind}^{(2,3)} = (1+C_{ABC})(4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \rho_0^B(\mathbf{r})[\varepsilon_0\, \varepsilon_{v,A}^{-1}(\mathbf{r},\mathbf{r}'';0)]|\mathbf{r}''-\mathbf{r}'|^{-1}\rho_0^C(\mathbf{r}')$$

$$-(4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, \rho_0^B(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1}\rho_0^C(\mathbf{r}')$$

$$-(4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, \rho_0^C(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1}\rho_0^A(\mathbf{r}')$$

$$-(4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, \rho_0^A(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1}\rho_0^B(\mathbf{r}'), \qquad (4.1.5)$$

where $\varepsilon_{v,A}(\mathbf{r},\mathbf{r}';0)$ is the static nonlocal dielectric function of A defined in Eq. (1.1). The first term in Eq. (4.1.5) gives the screened interaction energy due to the Coulomb interaction between the permanent charge distributions of two molecules, in presence of a third molecule, which acts as the dielectric medium. For example, the first term in Eq. (4.1.5) gives the static Coulomb energy of the interaction of $\rho_0^B(\mathbf{r})$ and $\rho_0^C(\mathbf{r}')$ in presence of molecule A, which acts as the dielectric medium to screen the interaction

between the unperturbed charge distributions of B and C. The screening is nonlocal, since $\varepsilon^{-1}_{v,A}(\mathbf{r},\mathbf{r}'';0)$ depends both on $\mathbf{r}$ and $\mathbf{r}''$. The sum of the last three terms in Eq. (4.1.5) gives the static Coulomb energy of the unscreened interactions between the unperturbed charge distributions of the molecular pairs. Thus, the three-body induction energy at second order depends on the difference between the dielectrically screened and unscreened interactions between the unperturbed charge distributions in two molecules. The results are in accordance with Eq. (4.1.1) for the interaction between test charges in presence of a dielectric medium. A fundamental difference between the two-body induction energy and the three-body induction energy at second order is that the two-body induction energy results from screening of *intramolecular* interactions, while the three-body induction energy results from screening of *intermolecular* interactions.

4.2 Dielectric screening of second-order three-body induction forces on nuclei of interacting molecules

In this section, we prove that the dielectric screening model can also describe the three-body induction forces at second order on nuclei of interacting molecules. Following Eq. (3.1), the second-order three-body force on nucleus K in molecule A is given by

$$\mathbf{F}_{\text{ind}}^{\text{K}(2,3)} = -\nabla^{\text{K}}\, \Delta E_{\text{ind}}^{(2,3)}, \tag{4.2.1}$$

where as usual, ∇^{K} means derivative with respect to the coordinates of nucleus K. Following an expression derived earlier by Li and Hunt, we can write the three-body induction energy at second order as

$$\Delta E_{\text{ind}}^{(2,3)} = -(1+C_{\text{ABC}}) \int d\mathbf{r}\, d\mathbf{r}' \alpha_{\alpha\beta}^{\text{A}}(\mathbf{r},\mathbf{r}';0)\, \mathfrak{I}_{0\alpha}^{\text{B}}(\mathbf{r})\, \mathfrak{I}_{0\beta}^{\text{C}}(\mathbf{r}'), \tag{4.2.2}$$

where $\mathfrak{I}_{0\alpha}^{\text{B}}(\mathbf{r})$ denotes the α component of the field acting on A due to the unperturbed, static charge distribution $\rho_0^{\text{B}}(\mathbf{r})$ of molecule B, and similarly for $\mathfrak{I}_{0\beta}^{\text{C}}(\mathbf{r}')$. In Eq. (4.2.2) $\alpha_{\alpha\beta}^{\text{A}}(\mathbf{r},\mathbf{r}';0)$ is the static nonlocal polarizability density of A, defined in Eq. (2.1.2). Expanding Eq. (4.2.2) and using Eq. (4.2.1), we obtain

$$\begin{aligned}\mathbf{F}_{\text{ind}}^{\text{K}(2,3)} = {} & \int d\mathbf{r}\, d\mathbf{r}' \partial\alpha_{\alpha\beta}^{\text{A}}(\mathbf{r},\mathbf{r}';0)/\partial\mathbf{R}^{\text{K}}\, \mathfrak{I}_{0\alpha}^{\text{B}}(\mathbf{r})\, \mathfrak{I}_{0\beta}^{\text{C}}(\mathbf{r}') \\ & + (1+\wp_{\text{BC}}) \int d\mathbf{r}\, d\mathbf{r}' \alpha_{\alpha\beta}^{\text{B}}(\mathbf{r},\mathbf{r}';0)\, \partial\mathfrak{I}_{0\alpha}^{\text{A}}(\mathbf{r})/\partial\mathbf{R}^{\text{K}}\, \mathfrak{I}_{0\beta}^{\text{C}}(\mathbf{r}'),\end{aligned} \tag{4.2.3}$$

where the operator $\wp_{\text{BC}}$ permutes the labels B and C in the expression that follows. Using the relation between the derivative of the nonlocal polarizability density with respect to $\mathbf{R}^{\text{K}}$ and the nonlocal hyperpolarizability density from Eq. (3.1.2), the derivative

of the field $\mathfrak{I}^{A}_{0\alpha}(\mathbf{r})$ with respect to $\mathbf{R}^{K}$ from Eq. (3.1.4), and the relation between the derivative of the permanent electronic charge density $\rho_0^{eA}(\mathbf{r})$ with respect to $\mathbf{R}^{K}$ and the nonlocal charge-density susceptibility $\chi^{A}(\mathbf{r},\mathbf{r}';0)$ from Eq. (3.1.5), we obtain

$$
\begin{aligned}
F^{K(2,3)}_{\mathrm{ind},\alpha} = Z^{K} \int & d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \beta^{A}_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\, \mathfrak{I}^{B}_{0\beta}(\mathbf{r})\, \mathfrak{I}^{C}_{0\gamma}(\mathbf{r}')\, T_{\delta\alpha}(\mathbf{r}'',\mathbf{R}^{K}) \\
& + (1+\wp_{BC})\, Z^{K} (4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \alpha^{B}_{\beta\gamma}(\mathbf{r},\mathbf{r}';0)(\mathfrak{r}_\beta - \mathfrak{r}''_\beta)\left|\mathbf{r}-\mathbf{r}''\right|^{-3} \\
& \qquad \times \chi^{A}(\mathbf{r}'',\mathbf{r}''';0)\, \nabla^{K}_{\alpha} \left|\mathbf{r}''' - \mathbf{R}^{K}\right|^{-1} \mathfrak{I}^{C}_{0\gamma}(\mathbf{r}') \\
& + (1+\wp_{BC})\, Z^{K} (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, \alpha^{B}_{\beta\gamma}(\mathbf{r},\mathbf{r}';0)\, \mathfrak{I}^{C}_{0\gamma}(\mathbf{r}') \\
& \qquad \times \nabla^{K}_{\alpha} (\mathfrak{r}_\beta - R^{K}_{\beta}) \left|\mathbf{r}-\mathbf{R}^{K}\right|^{-3}. \qquad (4.2.4)
\end{aligned}
$$

The first two terms in Eq. (4.2.4) yield the force on nucleus K due to its interaction with the second-order three-body polarization of A. To show it explicitly, we note that the β component of the field at **r** in A due to the permanent charge density in B is related to the potential at **r** by $\mathfrak{I}^{B}_{0\beta}(\mathbf{r}) = -\nabla_\beta \varphi^{B}_0(\mathbf{r}) = -\nabla_\beta (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}''' \left|\mathbf{r}-\mathbf{r}'''\right|^{-1} \rho^{B}_0(\mathbf{r}''')$ and the charge density at $\mathbf{r}'''$ in B is related to the polarization by Eq. (2.1.3). Thus, the first term in Eq. (4.2.4) gives

$$
\begin{aligned}
& Z^{K} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \beta^{A}_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\, \mathfrak{I}^{B}_{0\beta}(\mathbf{r})\, \mathfrak{I}^{C}_{0\gamma}(\mathbf{r}')\, T_{\delta\alpha}(\mathbf{r}'',\mathbf{R}^{K}) \\
& = Z^{K} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{\mathbf{iv}}\, \beta^{A}_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0) [T_{\beta\varepsilon}(\mathbf{r},\mathbf{r}''')\, P^{B}_{0\varepsilon}(\mathbf{r}''')] \\
& \qquad \times [T_{\gamma\eta}(\mathbf{r}',\mathbf{r}^{\mathbf{iv}})\, P^{C}_{0\eta}(\mathbf{r}^{\mathbf{iv}})]\, T_{\delta\alpha}(\mathbf{r}'',\mathbf{R}^{K}). \qquad (4.2.5)
\end{aligned}
$$

Using the relation between the charge-density susceptibility and the nonlocal polarizability density from Eq. (2.1.4), the second term in Eq. (4.2.4) can be written as

$$(1+\wp_{BC})Z^K(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,\alpha^B_{\beta\gamma}(\mathbf{r},\mathbf{r}';0)(r_\beta-r''_\beta)|\mathbf{r}-\mathbf{r}''|^{-3}$$

$$\times\chi^A(\mathbf{r}'',\mathbf{r}''';0)\nabla^K_\alpha\left|\mathbf{r}'''-\mathbf{R}^K\right|^{-1}\Im^C_{0\gamma}(\mathbf{r}')$$

$$=(1+\wp_{BC})Z^K\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,d\mathbf{r}^{iv}\,[\alpha^A_{\eta\delta}(\mathbf{r}''',\mathbf{r}'';0)T_{\delta\beta}(\mathbf{r}'',\mathbf{r})\alpha^B_{\beta\gamma}(\mathbf{r},\mathbf{r}';0)$$

$$\times T_{\gamma\varepsilon}(\mathbf{r}',\mathbf{r}^{iv})P^C_{0\varepsilon}(\mathbf{r}^{iv})]T_{\alpha\eta}(\mathbf{r}''',\mathbf{R}^K). \qquad (4.2.6)$$

Thus from Eq. (4.2.4), (4.2.5), and (4.2.6), the sum of the first two terms [denoted by $F^K_{ind,\alpha(1)}$] are given by

$$F^{K(2,3)}_{ind,\alpha(1)}=Z^K\int d\mathbf{r}\,T_{\alpha\beta}(\mathbf{R}^K,\mathbf{r})P^{A(2,3)}_{ind,\beta}, \qquad (4.2.7)$$

in accordance with Eq. (58) in ref. (278) derived by Li and Hunt. The last term in Eq. (4.2.4) [denoted by $F^K_{ind,\alpha(2)}$] yields

$$F^{K(2,3)}_{ind,\alpha(2)}=(1+\wp_{BC})Z^K\int d\mathbf{r}\,T_{\alpha\beta}(\mathbf{R}^K,\mathbf{r})P^{B(1)}_{ind}(\mathbf{r}). \qquad (4.2.8)$$

In the next part of this section, we connect the three-body induction force on nucleus K to the dielectric model. First, we write the induction force from Eq. (4.2.4) in terms of $\Delta P^B_{1,\alpha}(\mathbf{r},0)$, the induced change in the static polarization of molecule B (at first order), due to the permanent charge distribution of C (and similarly for C), given by

$$\Delta P^B_{1,\alpha}(\mathbf{r})=\int d\mathbf{r}'\,\alpha^B_{\alpha\beta}(\mathbf{r},\mathbf{r}';0)\Im^C_{0\beta}(\mathbf{r}'). \qquad (4.2.9)$$

Using Eqs. (2.2.3), (4.2.4), (4.2.9) and (3.1.8), we obtain

$$F_{ind,\alpha}^{K(2,3)} = -Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\beta^A_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\Im^B_{0\beta}(\mathbf{r})\Im^C_{0\gamma}(\mathbf{r}')$$

$$\times\nabla^K_\alpha\nabla''_\delta\left|\mathbf{r}''-\mathbf{R}^K\right|^{-1}$$

$$-[1+C(B\rightarrow C)][\,Z^K(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}''\,d\mathbf{r}'''\,\Delta P^B_{1,\beta}(\mathbf{r})\,\nabla_\beta\left|\mathbf{r}-\mathbf{r}''\right|^{-1}$$

$$\times\chi^A(\mathbf{r}'',\mathbf{r}''';0)\nabla^K_\alpha\left|\mathbf{r}'''-\mathbf{R}^K\right|^{-1}$$

$$+Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,\Delta P^B_{1,\beta}(\mathbf{r})\nabla^K_\alpha\,\nabla_\beta\left|\mathbf{r}-\mathbf{R}^K\right|^{-1}\,].\quad(4.2.10)$$

The operator C (B → C) in Eq. (4.2.10) means replacing the molecular label B by C in the expression that follows. The potential acting on molecule A is the sum of the potential due to the unperturbed charge distributions of B and C, and the potential due to the shift in the charge density of B, induced by the potential due to the unperturbed charge distribution in C (and similarly the potential due to the shift in the charge density of C, caused by the potential from B). Thus from Eq. (4.2.10), the three-body induction force on nucleus K depends quadratically on the potentials from the permanent charge distributions in B and C and linearly on the potential, $\Delta\varphi^B_1(\mathbf{r})$, due to the first-order shift in the charge distribution in B, $\Delta\rho^B_1(\mathbf{r}')$ (and similarly for C). Using $\Delta\varphi^B_1(\mathbf{r})$ from Eq. (3.1.10) in Eq. (4.2.10) and by repeated use of divergence theorem, we obtain

$$F_{ind,\alpha}^{K(2,3)} = Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''[\,\nabla_\beta\,\nabla'_\gamma\,\nabla''_\delta\,\beta^A_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]$$

$$\times\varphi^B_0(\mathbf{r})\varphi^C_0(\mathbf{r}')\nabla^K_\alpha\left|\mathbf{r}''-\mathbf{R}^K\right|^{-1}$$

$$-[1+C(B\to C)][Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\,\chi^A(\mathbf{r},\mathbf{r}';0)\nabla_\alpha^K\left|\mathbf{r}-\mathbf{R}^K\right|^{-1}$$

$$\times\Delta\varphi_1^B(\mathbf{r}',0)$$

$$+Z^K\nabla_\alpha^K[\Delta\varphi_1^B(\mathbf{R}^K,0)]], \qquad (4.2.11)$$

where we have used the Born symmetry of the charge-density susceptibility $\chi^A(\mathbf{r},\mathbf{r}';0)$ with respect to an interchange of its arguments.

Next, we use the relation between the nonlocal hyperpolarizability density $\beta^A_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$ and the quadratic charge-density susceptibility $\zeta(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$ from Eq. (3.1.12) and a relabeling of the integration variables, to obtain

$$F^{K(2,3)}_{ind,\alpha} = -Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,\zeta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$$

$$\times\varphi_0^B(\mathbf{r})\varphi_0^C(\mathbf{r}')\partial/\partial r_\alpha\left|\mathbf{r}'''-\mathbf{r}\right|^{-1}\Big|_{\mathbf{r}=\mathbf{R}^K}$$

$$-[1+C(B\to C)][Z^K(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}'\,d\mathbf{r}''\,\chi^A(\mathbf{r}'',\mathbf{r};0)$$

$$\times\partial/r_\alpha\left|\mathbf{r}-\mathbf{R}^K\right|^{-1}\Delta\varphi_1^B(\mathbf{r}',0)\Big|_{\mathbf{r}=\mathbf{R}^K}$$

$$-Z^K\nabla_\alpha^K[\Delta\varphi_1^B(\mathbf{R}^K,0)]] \qquad (4.2.12)$$

Using Eqs. (1.1), (1.10), and (4.2.12), the second-order three-body induction force on nucleus K in molecule A is given by

$$F^{K(2,3)}_{ind,\alpha} = -[1+C(B\to C)]Z^K\varepsilon_0\,\partial/\partial r_\alpha[\int d\mathbf{r}'\,\varepsilon^{-1}_{v,A}(\mathbf{r},\mathbf{r}';0)\Delta\varphi_1^B(\mathbf{r}',0)]\Big|_{\mathbf{r}=\mathbf{R}^K}$$

$$-Z^K \varepsilon_0 \partial / \partial r_\alpha [\int d\mathbf{r}' d\mathbf{r}'' \varepsilon^{-1}_{q,A}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]$$

$$\times \varphi_0^B(\mathbf{r}',0)\varphi_0^C(\mathbf{r}'',0)]\Big|_{\mathbf{r}=\mathbf{R}^K}. \tag{4.2.13}$$

Equation (30) shows that the second-order three-body induction force on a nucleus in molecule A results from screening of the potentials from neighboring molecules B and C; the first-order potential due to the induced shift in the charge density in B (or in C) is screened linearly within A , while the unperturbed potentials from B and C are screened quadratically.

At second order, the effective three-body potential within molecule A is given by

$$\varphi_{\text{eff}}^{A(2,3)}(\mathbf{r},0) = [1+C(B\to C)]\varepsilon_0 \int d\mathbf{r}' \varepsilon^{-1}_{v,A}(\mathbf{r},\mathbf{r}';0)\Delta\varphi_1^B(\mathbf{r}',0)$$

$$+\varepsilon_0 \int d\mathbf{r}' d\mathbf{r}'' \varepsilon_q^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\varphi_0^B(\mathbf{r}',0)\varphi_0^C(\mathbf{r}'',0). \tag{4.2.14}$$

Thus, using Eqs. (4.2.13) and (4.2.14), the second-order three-body induction force on nucleus K is

$$\mathbf{F}_{\text{ind}}^{K(2,3)} = -Z^K \partial / \partial \mathbf{r}[\varphi_{\text{eff}}^{A(2,3)}(\mathbf{r},0)]\Big|_{\mathbf{r}=\mathbf{R}^K}. \tag{4.2.15}$$

Eqs. (4.2.13) and (4.2.15) prove the fact that the three-body induction force on nucleus K in molecule A at second order can be exactly described by the dielectric screening model.

Chapter 5: Dielectric screening of three-body and four-body interactions at third and fourth orders

In this chapter, we derive the three-body and four-body intermolecular interaction energies at third and fourth order within the dielectric model. We show that the results are in agreement with the results from quantum perturbation theory. In chapter 4, we have showed that at second order, the three-body induction energy results from dielectric screening of the Coulomb interactions between the permanent charge densities of two molecules and the screening arises due to the presence of a third molecule which acts as the dielectric medium. In the present chapter, we prove that at third order the induction energy results from either intermolecular or intramolecular screening, depending on the type of interaction. Moreover, nonlinearity appears in the induction energy at third order, resulting quadratic response and nonlinear screening. At second order, the interaction energies show linear screening only.

Nonadditivity in dispersion energy first appears at third order. In chapter 2, we have proved that the second-order dispersion energy results due to the dielectric screening of the intramolecular exchange-correlation energy. We show that at third and fourth orders, the dispersion energy still appears due to screening-induced change in the intramolecular exchange-correlation energy. However, at third and fourth order, the dielectric medium consists of two and three molecules respectively and that brings many-body effects in the screening function. We derive the many-body dielectric functions from the many-body susceptibilities of the interacting molecules and we describe the screening of the dispersion energy at third and fourth orders in terms of these dielectric

functions. We also prove that the dispersion energy at third and fourth orders results from screening of the dispersion energy at second and third orders respectively, and that screening appears due to the presence of a third or a fourth molecule which acts as the dielectric medium.

The third category of interaction that appears at third and fourth orders is the induction-dispersion. It results form the perturbation of the dispersion energy by a static external field. The external field perturbs the response function of the molecules and brings in new type of fluctuation correlations. Dispersion energy shows linear screening only, but the perturbation by an external field produces nonlinear response, and hence nonlinear screening in the induction-dispersion energy. At third order, induction-dispersion energy includes nonlinear screening only. At fourth order, both linear and nonlinear screenings appear.

We prove that the screenings present in the interaction energies at third and fourth order are described by the nonlocal dielectric functions introduced in chapters 2 and 3.

5.1 Dielectric screening of the induction energy at third order

In this section, we show that at third order, the three- and four-body nonadditive induction energies are described within the nonlocal dielectric model. We work within the third order of perturbation theory and express the nonadditive induction energies in terms of the static nonlocal charge-density susceptibilities of the interacting molecules. Then we relate them to the nonlocal dielectric functions $\varepsilon_V(\mathbf{r},\mathbf{r}';0)$ and $\varepsilon_q(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$ introduced earlier, in order to show the dielectric screening.

Depending upon the type of interaction (and hence the molecular excitation pattern), both linear and nonlinear responses contribute to the induction energy at third order. In presence of a dielectric medium, the interaction energy of two test charges is screened. The shift in the interaction energy caused by a nonlocal dielectric medium with linear screening is described by Eq. (4.1.1) in the last chapter, and we have proved that Eq. (4.1.1) accurately describes the dielectric screening in the induction energy at second order. In the present section, we prove that the same equation still applies for the third-order induction energy. However, at second order the interacting test charges correspond only to the unperturbed, permanent charge distributions of the molecules. At third order, $\rho(\mathbf{r})$ in Eq. (4.1.1) can be either the permanent charge distribution of a molecule, or the induced shift in the charge density of one molecule cause by the permanent charge density of another molecule. Depending on whether the two interacting charge distributions are permanent or induced shifts caused by an applied potential, the interaction can be categorized as a particular many-body type (i.e. three-body, four-body etc.).

Nonlinear screening appears at the third-order induction energy. In presence of a nonlinear dielectric medium characterized by the quadratic dielectric function $\varepsilon_q(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$, the interaction energy of three charge distributions is given by

$$\Delta E = (4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv} \rho(\mathbf{r})[4\pi\varepsilon_q(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]^{-1}$$

$$\times |\mathbf{r}' - \mathbf{r}'''|^{-1} \rho(\mathbf{r}''') |\mathbf{r}'' - \mathbf{r}^{iv}|^{-1} \rho(\mathbf{r}^{iv}). \qquad (5.1.1)$$

At third order, the charge distributions in Eq. (5.1.1) correspond to the permanent charge densities of the interacting molecules. Unlike the screening caused by the linear response of the dielectric medium, nonlinear screening does not stem from the screening of a lower-order interaction. This is because, at different orders of perturbation theory the interactions arising purely due to the nonlinear response are characterized by response functions of different orders and they can not be interrelated to each other.

From intermolecular perturbation theory, the third-order energy for a cluster of molecules A···B···C···D of arbitrary symmetry, interacting at long range is given by

$$\Delta E^{(3)} = \sum_{m\neq 0} \sum_{n\neq 0} \frac{\langle 0|\hat{V}|m\rangle\langle m|\hat{V}^0|n\rangle\langle n|\hat{V}|0\rangle}{(E_m - E_0)(E_n - E_0)}, \qquad (5.1.2)$$

where $|m\rangle$ and $|n\rangle$ are the excited states of the molecules. $\hat{V}$ is the interaction Hamiltonian and for a pair of molecule A and B,

$$\hat{V}^{AB} = (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, \hat{\rho}^A(\mathbf{r})\, \hat{\rho}^B(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1}. \qquad (5.13)$$

In Eq. (5.1.2), the operator $\hat{V}^0 = \hat{V} - \langle 0|\hat{V}|0\rangle$. Following Li and Hunt, we separate the third-order induction energy $\Delta E^{(3)}_{ind}$ into the hyperpolarization energy $\Delta E^{(3)}_{hyp}$, the static reaction potential energy $\Delta E^{(3)}_{srp}$, and the third-body reaction potential energy $\Delta E^{(3)}_{tbp}$.

Hyperpolarization energy results from Eq. (5.1.2), with the excited states $|m\rangle$, $|n\rangle$ confined to one molecule and m, n $\neq$ 0. For molecule A, the three-body and four-body hyperpolarization energies at third order are given by

$$\Delta E^{A(3,3)}_{hyp} = (1/2)\,(1+\wp_{BC}) \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \zeta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\, \varphi^B_0(\mathbf{r})\, \varphi^C_0(\mathbf{r}')\, \varphi^C_0(\mathbf{r}'')$$

$$+(1/2)\,(1+\wp_{BD}) \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \zeta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\, \varphi^B_0(\mathbf{r})\, \varphi^D_0(\mathbf{r}')\, \varphi^D_0(\mathbf{r}'')$$

$$+(1/2)\,(1+\wp_{CD}) \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \zeta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\, \varphi^C_0(\mathbf{r})\, \varphi^D_0(\mathbf{r}')\, \varphi^D_0(\mathbf{r}''), \tag{5.1.4}$$

and

$$\Delta E^{A(3,4)}_{hyp} = \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \zeta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)\, \varphi^B_0(\mathbf{r})\, \varphi^C_0(\mathbf{r}')\, \varphi^D_0(\mathbf{r}''), \tag{5.1.5}$$

respectively. In Eqs. (5.1.4) and (5.1.5), $\zeta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$ is the quadratic charge-density susceptibility of molecule A. The operator $\wp_{BC}$ permutes the labels B and C in the expression that follows. The hyperpolarization energy of A in Eqs. (5.1.4) and (5.1.5) can be interpreted as due to reaction field effects, where the potentials from the permanent charge distributions of two neighboring molecules create a nonlinear shift in the charge density at **r** in A. The induced shift in the charge density interacts with the potential due to the permanent charge distribution of the third molecule, thus resulting an overall

energy shift of A. To connect the hyperpolarization energy to the dielectric model, we expand the potentials in Eqs. (5.1.4) and (5.1.5), and then use Eq. (1.10), to obtain

$$\Delta E_{hyp}^{A(3,3)} = (1/2)\,(1+\wp_{BC})(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,d\mathbf{r}^{iv}\rho_0^B(\mathbf{r})$$

$$\times[\varepsilon_0\,\varepsilon_{q,A}^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]|\mathbf{r}'-\mathbf{r}'''|^{-1}\rho_0^C(\mathbf{r}''')|\mathbf{r}''-\mathbf{r}^{iv}|^{-1}\rho_0^C(\mathbf{r}^{iv})$$

$$+(1/2)\,(1+\wp_{BD})(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,d\mathbf{r}^{iv}\rho_0^B(\mathbf{r})[\varepsilon_0\,\varepsilon_{q,A}^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]$$

$$\times|\mathbf{r}'-\mathbf{r}'''|^{-1}\rho_0^D(\mathbf{r}''')|\mathbf{r}''-\mathbf{r}^{iv}|^{-1}\rho_0^D(\mathbf{r}^{iv})$$

$$+(1/2)\,(1+\wp_{CD})(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,d\mathbf{r}^{iv}\rho_0^C(\mathbf{r})[\varepsilon_0\,\varepsilon_{q,A}^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]$$

$$\times|\mathbf{r}'-\mathbf{r}'''|^{-1}\rho_0^D(\mathbf{r}''')|\mathbf{r}''-\mathbf{r}^{iv}|^{-1}\rho_0^D(\mathbf{r}^{iv}),\qquad(5.1.6)$$

and

$$\Delta E_{hyp}^{A(3,4)} = (4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,d\mathbf{r}^{iv}\rho_0^B(\mathbf{r})[\varepsilon_0\,\varepsilon_{q,A}^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]$$

$$\times|\mathbf{r}'-\mathbf{r}'''|^{-1}\rho_0^C(\mathbf{r}''')|\mathbf{r}''-\mathbf{r}^{iv}|^{-1}\rho_0^D(\mathbf{r}^{iv}).\qquad(5.1.7)$$

If we define the two-body and the three-body effective potentials at $\mathbf{r}$ due to nonlinear screening by $\varphi_{eff}^{(2)}(\mathbf{r})$ and $\varphi_{eff}^{(3)}(\mathbf{r})$ respectively, then

$$\Delta E_{hyp}^{A(3,3)} = (1/2)[C(B\rightarrow C)]\int d\mathbf{r}\,\rho_0^B(\mathbf{r})\varphi_{eff}^{(2,AC)}(\mathbf{r})$$

$$+(1/2)[C(B\rightarrow D)]\int d\mathbf{r}\,\rho_0^B(\mathbf{r})\varphi_{eff}^{(2,AD)}(\mathbf{r})$$

$$+(1/2)[C(C\rightarrow D)]\int d\mathbf{r}\,\rho_0^B(\mathbf{r})\varphi_{eff}^{(2,AD)}(\mathbf{r}), \tag{5.1.8}$$

and

$$\Delta E_{hyp}^{A(3,4)} = \int d\mathbf{r}\,\rho_0^B(\mathbf{r})\varphi_{eff}^{(3,ACD)}(\mathbf{r}). \tag{5.1.9}$$

The effective potentials in Eqs. (5.18) and (5.1.9) are given by

$$\varphi_{eff}^{(2,AC)}(\mathbf{r}) = \int d\mathbf{r}'\,d\mathbf{r}''[\varepsilon_0\,\varepsilon_{q,A}^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]\varphi_0^C(\mathbf{r}')\varphi_0^C(\mathbf{r}''), \tag{5.1.10}$$

and

$$\varphi_{eff}^{(2,ACD)}(\mathbf{r}) = \int d\mathbf{r}'\,d\mathbf{r}''[\varepsilon_0\,\varepsilon_{q,A}^{-1}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)]\varphi_0^C(\mathbf{r}')\varphi_0^D(\mathbf{r}''). \tag{5.1.11}$$

The operator C (B $\rightarrow$ C) in Eq. (5.1.8) replaces the labels B by C in the expression that follows it.

Eqs. (5.1.6) – (5.1.9) prove that the hyperpolarization energy at third order is accurately described within the dielectric framework, where one molecule acts as the nonlinear dielectric medium to screen the interaction between the permanent charge distributions of other two or three molecules. The results are consistent with Eq. (5.1.1). The net three-body and four-body hyperpolarization energy at third is obtained by summing the $\Delta E_{hyp}^{(3,3)}$ and $\Delta E_{hyp}^{(3,4)}$ for A, B, C, and D.

Static reaction-potential effects correspond to the dynamic effects in dispersion interaction, with the difference that the reaction-potential is produced in response to the permanent charge-density in this case, rather than the charge-density fluctuation. Static reaction potential energy results from linear screening and is obtained from Eq. (5.1.2) with $m \neq 0$ in one molecule and $n \neq 0$ in the other molecule. For molecule A,

$$\Delta E^{(3,3)}_{srp,A} = \Delta E^{A(3,BC)}_{srp} + \Delta E^{A(3,BD)}_{srp} + \Delta E^{A(3,CD)}_{srp}$$

$$= (1/2)(4\pi\varepsilon_0)^{-3}\,[\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, d\mathbf{r}^{v}\, \rho_0^A(\mathbf{r})\,|\mathbf{r}-\mathbf{r}'|^{-1}\,\chi^B(\mathbf{r}',\mathbf{r}'';0)$$

$$\times|\mathbf{r}''-\mathbf{r}'''|^{-1}\,\chi^C(\mathbf{r}''',\mathbf{r}^{iv};0)\,|\mathbf{r}^{iv}-\mathbf{r}^{v}|^{-1}\,\rho_0^A(\mathbf{r}^{v})$$

$$+\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, d\mathbf{r}^{v}\, \rho_0^A(\mathbf{r})\,|\mathbf{r}-\mathbf{r}'|^{-1}\,\chi^B(\mathbf{r}',\mathbf{r}'';0)$$

$$\times|\mathbf{r}''-\mathbf{r}'''|^{-1}\,\chi^D(\mathbf{r}''',\mathbf{r}^{iv};0)\,|\mathbf{r}^{iv}-\mathbf{r}^{v}|^{-1}\,\rho_0^A(\mathbf{r}^{v})$$

$$+\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, d\mathbf{r}^{v}\, \rho_0^A(\mathbf{r})\,|\mathbf{r}-\mathbf{r}'|^{-1}\,\chi^C(\mathbf{r}',\mathbf{r}'';0)$$

$$\times|\mathbf{r}''-\mathbf{r}'''|^{-1}\,\chi^D(\mathbf{r}''',\mathbf{r}^{iv};0)\,|\mathbf{r}^{iv}-\mathbf{r}^{v}|^{-1}\,\rho_0^A(\mathbf{r}^{v}), \qquad (5.1.12)$$

where each term accounts for two different polarization routes. For example, $\Delta E^{(3,BC)}_{srp,A}$ accounts for the polarization routes A→B→C→A and A→C→B→A. Summing $\Delta E^{(3,3)}_{srp,A}$ from Eq. (5.1.12) with $\Delta E^{B(3,3)}_{srp}$, $\Delta E^{C(3,3)}_{srp}$ and $\Delta E^{D(3,3)}_{srp}$ gives the total static reaction-potential energy $\Delta E^{(3,3)}_{srp}$ at third order. $\Delta E^{A(3,BC)}_{srp}$ can be viewed as the induction energy of molecule B, in the presence of the unscreened external potential from molecule A and the *screening* potential from the shift in the charge density induced in C by A. Alternatively, it can be interpreted as the unscreened interaction between the first order shifts in the charge densities of B and C, caused by the permanent charge distribution in A. To show the dielectric screening present in the static reaction potential energy, we take $\Delta E^{B(3,BC)}_{srp}$ from Eq. (5.1.12), the second-order two-body induction

energy of B from Eq. (2.1.5), and the relation between the nonlocal dielectric function and the charge-density susceptibility from Eq. (1.2), to obtain

$$\Delta E_{srp}^{A(3,BC)} = (1/2)(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, \rho_0^A(\mathbf{r}) |\mathbf{r}-\mathbf{r}'|^{-1} \chi^B(\mathbf{r}',\mathbf{r}'';0)$$

$$\times [\varepsilon_0\, \varepsilon_{v,C}^{-1}(\mathbf{r}'',\mathbf{r}^{iv})] \left|\mathbf{r}^{iv}-\mathbf{r}'''\right|^{-1} \rho_0^A(\mathbf{r}''')$$

$$-(1/2) \int d\mathbf{r}\, d\mathbf{r}'\, \chi^B(\mathbf{r},\mathbf{r}';0) \varphi_0^A(\mathbf{r}) \varphi_0^A(\mathbf{r}')$$

$$= (1/2)(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, \rho_0^A(\mathbf{r}) |\mathbf{r}-\mathbf{r}'|^{-1} \chi^B(\mathbf{r}',\mathbf{r}'';0)$$

$$\times [\varepsilon_0\, \varepsilon_{v,C}^{-1}(\mathbf{r}'',\mathbf{r}^{iv})] \left|\mathbf{r}^{iv}-\mathbf{r}'''\right|^{-1} \rho_0^A(\mathbf{r}''')$$

$$-(1/2)(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \chi^B(\mathbf{r},\mathbf{r}';0)$$

$$\times |\mathbf{r}-\mathbf{r}''|^{-1}\, \rho_0^A(\mathbf{r}'') |\mathbf{r}'-\mathbf{r}'''|^{-1} \rho_0^A(\mathbf{r}'). \qquad (5.1.13)$$

The first term in Eq. (5.1.13) gives the screened induction energy of B due to its interaction with A, in presence of C which acts as the dielectric medium. The second term is the unscreened second-order induction energy of B. Eq. (5.1.13) proves that the static reaction potential energy at third order results due to the difference between dielectrically screened and unscreened second-order induction energy of a molecule. Note that $\Delta E_{srp}^{(3,4)} = 0$. Four-body terms in the static reaction potential first appear at the fourth order of perturbation theory.

Third-body potential energy has terms with polarization routes that begin and end at different molecules. At third-order, the third body potential energy shows both three-body and four-body effects and is obtained from Eq. (5.1.2) with the same excitation

pattern as in the case of static reaction potential energy. Thus, it includes linear screening only. First we consider the third-body potential energy corresponding to the polarization routes A→B→C→B and B→C→B→A.

$$\Delta E^{(3,3)}_{tbp,ABC} = (1/2)(4\pi\varepsilon_0)^{-3} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, d\mathbf{r}^{v}\, \rho_0^B(\mathbf{r}) |\mathbf{r}-\mathbf{r}'|^{-1}$$

$$\times \chi^C(\mathbf{r}',\mathbf{r}'';0) |\mathbf{r}''-\mathbf{r}'''|^{-1} \chi^B(\mathbf{r}''',\mathbf{r}^{iv};0) \left|\mathbf{r}^{iv}-\mathbf{r}^{v}\right|^{-1} \rho_0^A(\mathbf{r}^{v}). \tag{5.1.14}$$

$\Delta E^{(3,3)}_{tbp,ABC}$ can be described as the interaction between the permanent charge density of B and the first-order shift in the charge density in B induced by A, in presence of C which acts as the dielectric medium. The first-order shift in the charge density of B induced by the potential due to the permanent charge distribution in A is given by

$$\Delta\rho_1^B(\mathbf{r}) = (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}'\, \chi^B(\mathbf{r},\mathbf{r}';0) |\mathbf{r}-\mathbf{r}'|^{-1} \rho_0^A(\mathbf{r}'). \tag{5.1.15}$$

From Eqs. (5.1.14) and (5.1.15),

$$\Delta E^{(3,3)}_{tbp,ABC} = (1/2)(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \rho_0^B(\mathbf{r}) |\mathbf{r}-\mathbf{r}'|^{-1}$$

$$\times \chi^C(\mathbf{r}',\mathbf{r}'';0) |\mathbf{r}''-\mathbf{r}'''|^{-1} \Delta\rho_1^B(\mathbf{r}'''). \tag{5.1.16}$$

Energy shift of B due to direct intramolecular interaction between its permanent charge density and the first-order induced shift in the charge density is

$$\Delta E^B = (1/2)(4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, \rho_0^B(\mathbf{r}) |\mathbf{r}-\mathbf{r}'|^{-1} \Delta\rho_1^B(\mathbf{r}'). \tag{5.1.17}$$

From Eqs. (5.1.16), (5.1.17), and (1.2), along with a change of the integration variables, we obtain

$$\Delta E^{(3,3)}_{tbp,ABC} = (1/2)\,(4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \rho_0^B(\mathbf{r})[\varepsilon_0 \varepsilon^{-1}_{v,C}(\mathbf{r},\mathbf{r}'';0)]|\mathbf{r}''-\mathbf{r}'|^{-1}\, \Delta\rho_1^B(\mathbf{r}')$$

$$-(1/2)(4\pi\varepsilon_0)^{-1} \int d\mathbf{r}\, d\mathbf{r}'\, \rho_0^B(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1}\, \Delta\rho_1^B(\mathbf{r}'). \qquad (5.1.18)$$

The first term in Eq. (5.1.18) is the intramolecular interaction between the permanent charge density of B at $\mathbf{r}$ and the first-order induced shift in the charge density at $\mathbf{r}'$, in presence of molecule C which acts as a dielectric medium to screen the interaction. Thus, within the dielectric model the three-body terms present in the third-body potential energy depend on the difference between the dielectrically screened and the unscreened Coulomb interactions between the permanent charge density and the first-order shift in the charge density within a molecule. This result can be compared to the second-order two-body induction energy described in chapter 2, where we showed that the two-body induction energy at second-order depends on the difference between the screened and the unscreened Coulomb interactions between the permanent charge densities within a molecule. Thus, the three-body terms in the third-body potential energy show the similar screening effect, but at the next order.

Finally in this section, we derive the four-body effects in the third-body potential energy within the dielectric framework. Interactions present in the four-body terms in the third-body potential energy at third order are purely intermolecular. For example, the interaction energy associated with the polarization route B→D→C→A is given by

$$\Delta E^{(3,4)}_{tbp,BDC} = (1/4)(4\pi\varepsilon_0)^{-3} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, d\mathbf{r}^{v}\, \rho_0^A(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1}\, \chi^C(\mathbf{r}',\mathbf{r}'';0)$$

$$\times|\mathbf{r}''-\mathbf{r}'''|^{-1}\, \chi^D(\mathbf{r}''',\mathbf{r}^{iv};0)\left|\mathbf{r}^{iv}-\mathbf{r}^{v}\right|^{-1} \rho_0^B(\mathbf{r}^{v}). \qquad (5.1.19)$$

Eq. (5.1.19) can be viewed as the induction energy of C, in the direct potential from the permanent charge density in A and the screening potential from the induced shift in the charge density in D, caused by the potential from B. Alternatively, it can be described as the energy due to the intermolecular interaction between the first-order shift in the charge density of C induced by A, and the first-order shift in the charge density in D induced by B. Note that this energy corresponds to the term $E^{(3),ind}_{Q,\alpha\alpha Q}$ introduced by Piecuch,[262] with $i \neq j \neq k$. To connect $\Delta E^{(3,4)}_{tbp,BDC}$ to the dielectric model, we take Eq. (5.1.19) along with all the polarization routes with C and D in the excited states, the second-order three-body induction energy of C from Eq. (4.1.2), and the relation between the nonlocal dielectric function and the charge-density susceptibility from Eq. (1.2), to obtain

$$\Delta E^{(3,4)}_{tbp,BDC} = (4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, \rho_0^A(\mathbf{r}) |\mathbf{r}-\mathbf{r}''|^{-1} \chi^C(\mathbf{r}'',\mathbf{r}''';0)$$
$$\times [\varepsilon_0\, \varepsilon^{-1}_{v,D}(\mathbf{r}''',\mathbf{r}^{iv};0)] \left|\mathbf{r}^{iv}-\mathbf{r}'\right|^{-1} \rho_0^B(\mathbf{r}')$$
$$-(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \rho_0^A(\mathbf{r}) |\mathbf{r}-\mathbf{r}''|^{-1} \chi^C(\mathbf{r}'',\mathbf{r}''';0)$$
$$\times |\mathbf{r}'''-\mathbf{r}'|^{-1} \rho_0^B(\mathbf{r}'). \qquad (5.1.20)$$

In Eq. (5.1.20), the first term is the induction energy of C due its interaction with A and B, in presence of D which acts as the dielectric medium to screen the interaction. The second term is the unscreened three-body induction energy of C at second order. Thus, the four-body effects in the third-body potential energy are obtained as the difference between the screened and the unscreened second-order three-body induction energy. The second-order three body induction energy itself results from screening of the Classical

electrostatic interactions between two molecules. Hence, the four-body terms in the third-body potential energy are described as the screening effects present in the same type of interaction, but at the next higher order.

5.2 Dielectric screening and the nonadditive dispersion energy

In this section, we derive the nonadditive dispersion energy within the dielectric model. We focus on the dispersion energy of a particular molecule and relate the change in the correlation between the *intramolecular* charge density fluctuations of that molecule with the nonlocal dielectric functions of other molecules. In section 5.2 A, we show the screening present in the three-body dispersion energy. In section 5.2 B, we derive the nonadditive four-body dispersion energy and show the screening present in the four-body dispersion energy of a particular molecule. The direct effects of overlap damping are included in the expression of the dispersion energy, but not modifications due to exchange or orbital distortion.

5.2A Dielectric screening of nonadditive three-body dispersion energy at third order

Previously, Li and Hunt[278] have developed a theory for the nonadditive three-body dispersion energy, based on the correlations in the fluctuating polarization of interacting molecules A, B, and C. The three-body dispersion energy derived in their work is given by

$$\Delta E_d^{(3,3)} = -\frac{\hbar}{\pi}\int_0^\infty d\omega \int \mathbf{dr}\,\mathbf{dr}'\,\mathbf{dr}''\,\mathbf{dr}'''\,\mathbf{dr}^{\mathbf{iv}}\,\mathbf{dr}^{\mathbf{v}}\,\mathbf{Tr}[\,T(\mathbf{r}^{\mathbf{v}},\mathbf{r}^{\mathbf{iv}})\alpha^C(\mathbf{r}^{\mathbf{iv}},\mathbf{r}''';i\omega)$$

$$\times T(\mathbf{r}''',\mathbf{r}'')\alpha^B(\mathbf{r}'',\mathbf{r}';i\omega)\,T(\mathbf{r}',\mathbf{r})\alpha^A(\mathbf{r},\mathbf{r}^{\mathbf{v}};i\omega)\,]. \qquad (5.2A.1)$$

In Eq. (5.2A.1), $\alpha(\mathbf{r},\mathbf{r}';i\omega)$ denotes the nonlocal polarizability density generalized to imaginary frequencies, and $T(\mathbf{r},\mathbf{r}')$ is the dipole propagator defined in Eq. (2.2.3). **Tr** means the trace of the expression that follows. The result in Eq. (5.2A.1) is derived after

summing the three-body dispersion energies of A, B, and C, and using the Kramers-Kronig relation between the real and the imaginary parts of the nonlocal polarizability density.

In the present section we use a susceptibility based approach that we used in section 2.2 to show the screening present in the intramolecular charge density fluctuations due to the two-body dispersion interaction. Following the same approach that we used in section 2.2, we show that the average energy shift of molecule A at third order due to the correlation between the charge density fluctuations at points $\mathbf{r}$ and $\mathbf{r}'$, in presence of molecules B and C is given by

$$\Delta E_d^{A(3,3)} = -(\hbar/4\pi)(4\pi\varepsilon_0)^{-3}(1+\wp_{BC})\int_{-\infty}^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, d\mathbf{r}^{v} \chi^{A''}(\mathbf{r},\mathbf{r}';\omega)$$

$$\times |\mathbf{r}'-\mathbf{r}''|^{-1} \chi^{B}(\mathbf{r}'',\mathbf{r}''';\omega) \left|\mathbf{r}'''-\mathbf{r}^{iv}\right|^{-1} \chi^{C}(\mathbf{r}^{iv},\mathbf{r}^{v};\omega) \left|\mathbf{r}^{v}-\mathbf{r}\right|^{-1}$$

$$\times \coth(\hbar\omega/2kT), \qquad (5.2A.2)$$

where $\chi^{A''}(\mathbf{r},\mathbf{r}';\omega)$ is the imaginary part of the charge-density susceptibility of A, defined in chapter 2. Charge-density fluctuations in A at time t' induces a shift in the charge density in B at time t'' which eventually induces a shift in the charge density in C at time t, thus creating a reaction potential on A at time t. Using the fluctuation-dissipation theorem from Eq. (2.2.9), we obtain

$$\Delta E_d^{A(3,3)} = (1/4)(4\pi\varepsilon_0)^{-3}(1+\wp_{BC}) \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, d\mathbf{r}^{v} \int_{-\infty}^{\infty} d(t-t')$$

$$\times \int_{-\infty}^{\infty} d(t''-t') \left\langle \delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t') \right\rangle_{+} \left|\mathbf{r}-\mathbf{r}^{v}\right|^{-1}$$

$$\times\chi^{C}(\mathbf{r}^{v},\mathbf{r}^{iv};t-t'')\left|\mathbf{r}^{iv}-\mathbf{r}'''\right|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}'';t''-t')\left|\mathbf{r}''-\mathbf{r}'\right|^{-1}. \quad (5.2A.3)$$

From Eq. (5.2A.3), the two-body dispersion energy of A from Eq. (2.2.11), and the relation between the nonlocal dielectric function and the charge-density susceptibility in the time domain from Eq. (2.2.12),

$$\Delta E_{d}^{A(3,3)} = (1/4)(4\pi\varepsilon_0)^{-2}(1+\wp_{BC})\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,d\mathbf{r}^{iv}\int_{-\infty}^{\infty}d(t-t')\int_{-\infty}^{\infty}d(t''-t')$$

$$\times\left\langle\delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}\left|\mathbf{r}-\mathbf{r}^{iv}\right|^{-1}\varepsilon_0\,\varepsilon_{v,C}^{-1}(\mathbf{r}^{iv},\mathbf{r}''';t-t'')$$

$$\times\chi^{B}(\mathbf{r}''',\mathbf{r}'';t''-t')\left|\mathbf{r}''-\mathbf{r}'\right|^{-1}$$

$$-(1/4)(4\pi\varepsilon_0)^{-2}[1+C(B\rightarrow C)]\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\int_{-\infty}^{\infty}d(t-t')$$

$$\times\left\langle\delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}\left|\mathbf{r}'-\mathbf{r}''\right|^{-1}\chi^{B}(\mathbf{r}'',\mathbf{r}''';t-t')\left|\mathbf{r}'''-\mathbf{r}\right|^{-1},$$

(5.2A.4)

where the operator C (B → C) replaces the label B by C in the expression that follows. The first term in Eq. (5.2A.4) gives the screened two-body dispersion energy of A due to interaction with B (or C), in presence of C (or B), which acts as the dielectric medium with the nonlocal dielectric screening function $\varepsilon_{v,C}^{-1}(\mathbf{r}^{iv},\mathbf{r}''';t-t'')$. A charge density fluctuation in A at $\mathbf{r}',t'$ sets up a potential in B at $\mathbf{r}'',t'$ (in the Coulomb gauge, with retardation neglected) which induces a shift in the charge density in B at $\mathbf{r}''',t''$. The reaction potential in A at $\mathbf{r},t$ due to the shift in the charge density in B is screened by the presence of C via its nonlocal dielectric function $\varepsilon_{v,C}^{-1}(\mathbf{r}^{iv},\mathbf{r}''';t-t'')$, and the screened

potential affects the two-body dispersion energy of A. The second term gives the second-order two-body dispersion energy of A in presence of molecules B and C. Thus, the three-body dispersion energy at third-order depends on the difference between the dielectrically screened and the unscreened two-body dispersion energy at second order.

In an alternate way, we can describe the three-body dispersion energy of A in terms of an effective, two-body susceptibility of B and C. Following Kohn, Meir, and Makarov,[164] if the long-range interaction between B and C acts as a small perturbation, this two-body susceptibility is given by

$$\chi^{BC}(\mathbf{r},\mathbf{r}';\omega) = \lambda \int d\mathbf{r}_1\, d\mathbf{r}_2\, \chi^{B}(\mathbf{r},\mathbf{r}_1;\omega)\, \frac{1}{4\pi\varepsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}\, \chi^{C}(\mathbf{r}_2,\mathbf{r}';\omega), \tag{5.2A.5}$$

where λ is a coupling constant that "turns on" the long-range interaction between B and C. If B and C are non-interacting, the overall susceptibility is given by

$$\chi^{BC} = \chi^{B}(\mathbf{r},\mathbf{r}_1;\omega) + \chi^{C}(\mathbf{r}_2,\mathbf{r}';\omega). \tag{5.2A.6}$$

Previously, Li and Hunt[283] have showed that for a pair of interacting centrosymmetric linear molecules A and B, the overall polarizability in presence of an external field $\mathfrak{I}^e$ is given by

$$\lim \mathfrak{I}^e \to 0\, \frac{\partial(\mu_\alpha^A + \mu_\alpha^B)}{\partial \mathfrak{I}_\beta^e} = \alpha_{\alpha\beta}^A + \alpha_{\alpha\beta}^B + \Delta\alpha_{\alpha\beta}^{ind}, \tag{5.2A.7}$$

where $\alpha_{\alpha\beta}^A$ and $\alpha_{\alpha\beta}^B$ are the polarizabilities of the isolated molecules and $\Delta\alpha_{\alpha\beta}^{ind}$ is the collision-induced electronic polarizability of the pair. Using a self-consistent solution of a set of equations that relate the induced dipole moment to the local field, they showed that, at first order

$$\Delta\alpha_{\alpha\beta}^{\text{ind}} = (1+\wp_{AB})\alpha_{\alpha\gamma}^{A} T_{\gamma\delta}(\mathbf{R})\alpha_{\delta\beta}^{B}. \tag{5.2A.8}$$

In Eq. (5.2A.8), $\alpha_{\alpha\beta}^{A}$ is the dipole polarizability of molecule A, **R** is the vector from an origin at the center of symmetry of molecule A to the origin at the center of molecule B, $T_{\alpha\beta}(\mathbf{R})$ is the dipole propagator given by, $T_{\alpha\beta}(\mathbf{R}) = \nabla_\alpha\nabla_\beta(R^{-1})$, and $\wp_{AB}$ permutes the labels A and B in the expression that follows. The collision-induced electronic polarizability defined in Eq. (5.2A.8) determines the first-order dipole-induced-dipole. Here we use the same method to derive the two-body susceptibility for a pair of interacting molecules A and B, in presence of a fluctuating external potential $\varphi_{\text{ext}}(\mathbf{r};\omega)$. Within linear response, the shifts in charge densities of A and B are related to the applied potential by the equations

$$\Delta\rho^{A}(\mathbf{r};\omega) = \int d\mathbf{r}'\chi^{A}(\mathbf{r},\mathbf{r}';\omega)\varphi_{\text{app}}^{A}(\mathbf{r}';\omega). \tag{5.2A.9}$$

$$\Delta\rho^{B}(\mathbf{r};\omega) = \int d\mathbf{r}'\chi^{B}(\mathbf{r},\mathbf{r}';\omega)\varphi_{\text{app}}^{B}(\mathbf{r}';\omega). \tag{5.2A.10}$$

The applied potential at A is related to the external potential $\varphi_{\text{ext}}(\mathbf{r};\omega)$ and to the potential due to the shift in the charge density of B, $\Delta\rho^{B}(\mathbf{r};\omega)$ by

$$\varphi_{\text{app}}^{A}(\mathbf{r};\omega) = \varphi_{\text{ext}}(\mathbf{r};\omega) + \int d\mathbf{r}' \frac{\Delta\rho^{B}(\mathbf{r}';\omega)}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}$$

$$= \varphi_{\text{ext}}(\mathbf{r};\omega) + \int d\mathbf{r}'\,d\mathbf{r}'' \frac{1}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}\chi^{B}(\mathbf{r}',\mathbf{r}'';\omega)\varphi_{\text{ext}}(\mathbf{r}'';\omega). \tag{5.2A.11}$$

The self-consistent solution of Eqs. (5.2A.9) – (5.2A.11) yields

$$\Delta\rho^{A}(\mathbf{r};\omega) + \Delta\rho^{B}(\mathbf{r};\omega)$$

$$= \int d\mathbf{r}'\,[\chi^{A}(\mathbf{r},\mathbf{r}';\omega)+\chi^{B}(\mathbf{r},\mathbf{r}';\omega)]\,\varphi_{ext}(\mathbf{r}';\omega)$$

$$+(1+\wp_{AB})\int d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,\chi^{A}(\mathbf{r},\mathbf{r}'';\omega)\,\frac{1}{4\pi\varepsilon_0|\mathbf{r}''-\mathbf{r}'''|}\,\chi^{B}(\mathbf{r}''',\mathbf{r}';\omega)\,\varphi_{ext}(\mathbf{r}';\omega).$$

(5.2A.12)

From Eq. (5.2A.12), the two-body part of the susceptibility of molecules A and B, within linear response is given by

$$\Delta\chi^{AB}(\mathbf{r},\mathbf{r}';\omega) = (1+\wp_{AB})\int d\mathbf{r}''\,d\mathbf{r}'''\,\chi^{A}(\mathbf{r},\mathbf{r}'';\omega)\,\frac{1}{4\pi\varepsilon_0|\mathbf{r}''-\mathbf{r}'''|}\,\chi^{B}(\mathbf{r}''',\mathbf{r}';\omega).$$

(5.2A.13)

From Eqs. (5.2A.3) and (5.2A.13) the two-body susceptibility in the time domain is

$$\Delta\chi^{BC}(\mathbf{r},\mathbf{r}';t-t') = (1+\wp_{AB})\int d\mathbf{r}''\,d\mathbf{r}'''\int_{-\infty}^{\infty} d(t''-t')\,\chi^{B}(\mathbf{r},\mathbf{r}'';t''-t')$$

$$\times\frac{1}{4\pi\varepsilon_0|\mathbf{r}''-\mathbf{r}'''|}\,\chi^{C}(\mathbf{r}''',\mathbf{r}';t-t''). \qquad (5.2A.14)$$

Using the two-body susceptibility from Eq. (5.2A.14) and a change in the integration variables, the three-body dispersion energy of A from Eq. (5.2A.3) is written as

$$\Delta E_d^{A(3,3)} = (1/4)(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\int_{-\infty}^{\infty} d(t-t')\left\langle \delta\rho^{A}(\mathbf{r},t)\,\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}$$

$$\times|\mathbf{r}-\mathbf{r}''|^{-1}\,\chi^{BC}(\mathbf{r}'',\mathbf{r}''';t-t')\,|\mathbf{r}'''-\mathbf{r}|^{-1}. \qquad (5.2A.15)$$

Finally, using Eqs. (5.2A.15), (2.2.11), and (2.2.12), we obtain

$$\Delta E_d^{A(3,3)} = (1/4)(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\int_{-\infty}^{\infty} d(t-t')\left\langle \delta\rho^{A}(\mathbf{r},t)\,\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}$$

$$\times|\mathbf{r}'-\mathbf{r}''|^{-1}\,\varepsilon_0\,\varepsilon_{v,BC}^{-1}(\mathbf{r}'',\mathbf{r};t-t')$$

$$-(1/4)(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\left\langle \delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}|\mathbf{r}-\mathbf{r}'|^{-1}. \quad (5.2A.16)$$

The first term in Eq. (5.2A.16) gives the Coulomb energy associated with interactions between the fluctuating charge densities $\delta\rho^{A}(\mathbf{r},t)$ and $\delta\rho^{A}(\mathbf{r}',t')$ in presence of the pair of molecules B and C, which together act as the dielectric medium with the nonlocal screening function $\varepsilon^{-1}_{v,BC}(\mathbf{r}'',\mathbf{r};t-t')$. The second term is the Coulomb energy of direct intramolecular interactions of the charge-density fluctuations in molecule A, in absence of B and C. Thus, Eq. (5.2A.16) proves that the three-body dispersion energy of A results from the difference between dielectrically screened and unscreened interactions between its *intramolecular* charge-density fluctuations, where the dielectric screening is characterized by a two-body screening function, defined in Eq. (5.2A.14).

5.2B Dielectric screening of nonadditive four-body dispersion energy at fourth order

In this section, we describe the nonadditive four-body dispersion energy at fourth order within the nonlocal dielectric model. We consider the dispersion energy of molecule A in a cluster of interacting molecules A···B···C···D, and derive the dispersion energy using the same susceptibility base approach that we used in chapter 2 and in the previous section. In appendix B, we derive a new equation which gives the four-body dispersion energy of the A···B···C···D cluster at fourth order. We show that

$$\Delta E_d^{A(4,4)} = -\frac{3\hbar}{\pi}(4\pi\varepsilon_0)^{-4}\int_0^\infty d\omega \int d\mathbf{r}...d\mathbf{r}^{\mathbf{vii}}\,\chi^A(\mathbf{r},\mathbf{r}';i\omega)|\mathbf{r}'-\mathbf{r}''|^{-1}\chi^B(\mathbf{r}'',\mathbf{r}''';i\omega)$$
$$\times|\mathbf{r}'''-\mathbf{r}^{\mathbf{iv}}|^{-1}\chi^C(\mathbf{r}^{\mathbf{iv}},\mathbf{r}^{\mathbf{v}};i\omega)|\mathbf{r}^{\mathbf{v}}-\mathbf{r}^{\mathbf{vi}}|^{-1}$$
$$\times\chi^D(\mathbf{r}^{\mathbf{vi}},\mathbf{r}^{\mathbf{vii}};i\omega)|\mathbf{r}^{\mathbf{vii}}-\mathbf{r}|^{-1}. \qquad (5.2B.1)$$

In terms of real frequencies, the four-body dispersion energy of A is given by

$$\Delta E_d^{A(4,4)} = -(\hbar/4\pi)(4\pi\varepsilon_0)^{-4}(1+\wp_{BCD})\int d\mathbf{r}...d\mathbf{r}^{\mathbf{vii}}\int_{-\infty}^{\infty}d\omega\,\chi^{A''}(\mathbf{r},\mathbf{r}';\omega)$$
$$\times|\mathbf{r}'-\mathbf{r}''|^{-1}\chi^B(\mathbf{r}'',\mathbf{r}''';\omega)|\mathbf{r}'''-\mathbf{r}^{\mathbf{iv}}|^{-1}\chi^C(\mathbf{r}^{\mathbf{iv}},\mathbf{r}^{\mathbf{v}};\omega)$$
$$\times|\mathbf{r}^{\mathbf{v}}-\mathbf{r}^{\mathbf{vi}}|^{-1}\chi^D(\mathbf{r}^{\mathbf{vi}},\mathbf{r}^{\mathbf{vii}};\omega)|\mathbf{r}^{\mathbf{vii}}-\mathbf{r}|^{-1}\coth(\hbar\omega/2kT). \qquad (5.2B.2)$$

In Eq. (5.2B.2), the operator $\wp_{BCD}$ permutes the labels B, C, and D. Using the fluctuation-dissipation theorem from Eq. (2.2.9),

$$\Delta E_d^{A(4,4)} = (1/4)(4\pi\varepsilon_0)^{-4}(1+\wp_{BCD})\int d\mathbf{r}...d\mathbf{r}^{vii}\int_{-\infty}^{\infty} d(t-t')\int_{-\infty}^{\infty} d(t'''-t'')$$

$$\times\int_{-\infty}^{\infty} d(t''-t')\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+ \left|\mathbf{r}-\mathbf{r}^{vii}\right|^{-1}$$

$$\times\chi^D(\mathbf{r}^{vii},\mathbf{r}^{vi};t-t''')\left|\mathbf{r}^{vi}-\mathbf{r}^{v}\right|^{-1}\chi^C(\mathbf{r}^{v},\mathbf{r}^{iv};t'''-t'')$$

$$\times\left|\mathbf{r}^{iv}-\mathbf{r}'''\right|^{-1}\chi^B(\mathbf{r}''',\mathbf{r}'';t''-t')\left|\mathbf{r}''-\mathbf{r}'\right|^{-1}. \qquad (5.2B.3)$$

From Eqs. (5.2B.3), (2.2.12), and the three-body dispersion energy of A from Eq. (5.2A.3), we show that

$$\Delta E_d^{A(4,4)} = (1/4)(4\pi\varepsilon_0)^{-3}(1+\wp_{BCD})\int d\mathbf{r}...d\mathbf{r}^{vi}\int_{-\infty}^{\infty} d(t-t')\int_{-\infty}^{\infty} d(t'''-t'')$$

$$\times\int_{-\infty}^{\infty} d(t''-t')\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+ \left|\mathbf{r}-\mathbf{r}^{vi}\right|^{-1}$$

$$\times\varepsilon_0\,\varepsilon_{v,D}^{-1}(\mathbf{r}^{vi},\mathbf{r}^{v};t-t''')\,\chi^C(\mathbf{r}^{v},\mathbf{r}^{iv};t'''-t'')$$

$$\times\left|\mathbf{r}^{iv}-\mathbf{r}'''\right|^{-1}\chi^B(\mathbf{r}''',\mathbf{r}'';t''-t')\left|\mathbf{r}''-\mathbf{r}'\right|^{-1}$$

$$-\Delta E_{BCD}^{A(3,3)}. \qquad (5.2B.4)$$

In Eq. (5.2B.4), the first term gives the screened three-body dispersion energy of A in presence of molecule D (or B or C) which acts as the dielectric medium with the nonlocal screening function $\varepsilon_{v,D}(\mathbf{r}^{vi},\mathbf{r}^{v};t-t''')$. The second term gives the unscreened three-body dispersion energy of A at third order in the molecular cluster A···B···C···D. Thus, from Eq. (5.2B.4), the four-body dispersion energy of A depends on the difference

between its dielectrically screened and unscreened three-body dispersion energies at third order.

Finally in this section we show that the four-body dispersion interaction can also be described as screening to the direct intramolecular interactions between fluctuating charge densities, where the other three molecules provide the dielectric screening. To show this screening effect, we derive a three-body susceptibility in terms of the nonlocal charge density susceptibilities of three interacting molecules. Previously, Champagne, Li, and Hunt[284] have showed that for a cluster of non-overlapping, isotropic species A, B, and C, interacting at long range, the nonadditive three-body polarizability at second order is

$$\Delta\alpha_{\alpha\beta}^{(2,3)} = \alpha^{A}\,\alpha^{B}\,\alpha^{C}\,S_{ABC}\,T_{\alpha\delta}(\mathbf{R}^{A},\mathbf{R}^{B})\,T_{\beta\delta}(\mathbf{R}^{A},\mathbf{R}^{C}) + (1/3)S_{ABC}C^{A}\,\alpha^{B}\alpha^{C}\,T_{\alpha\gamma\delta}(\mathbf{R}^{A},\mathbf{R}^{B}), \qquad (5.2B.5)$$

where the species centers are located at $\mathbf{R}^{A}$, $\mathbf{R}^{B}$, and $\mathbf{R}^{C}$ respectively; S_{ABC} denotes the sum over all permutations of the labels A, B, and C in the expression that follows it; and the propagators $T_{\alpha\beta\ldots\omega}(\mathbf{r},\mathbf{r}')$ of arbitrary rank are given by $T_{\alpha\beta\ldots\omega}(\mathbf{r},\mathbf{r}') = \nabla_{\alpha}\nabla_{\beta}\cdots\nabla_{\omega}\left|\mathbf{r}-\mathbf{r}'\right|^{-1}$. In Eq. (5.2B.5), α^{A} is the dipole polarizability of the isotropic species A, and the C tensor determines the quadrupole induced by a uniform field gradient, within linear response. Here we derive the three-body susceptibility of three molecules A, B, and C, interacting at long range, in presence of a fluctuating external potential. Following Eq. (5.2A.9) – (5.2A.10), the shifts in the charge densities of A, B, and C, within linear response is given by

$$\Delta\rho^{A}(\mathbf{r};\omega)+\Delta\rho^{B}(\mathbf{r};\omega)+\Delta\rho^{C}(\mathbf{r};\omega)$$

$$= \int d\mathbf{r}'\,\chi^{A}(\mathbf{r},\mathbf{r}';\omega)\varphi^{A}_{app}(\mathbf{r}';\omega)+\int d\mathbf{r}'\,\chi^{B}(\mathbf{r},\mathbf{r}';\omega)\varphi^{B}_{app}(\mathbf{r}';\omega)$$

$$+\int d\mathbf{r}'\,\chi^{C}(\mathbf{r},\mathbf{r}';\omega)\varphi^{C}_{app}(\mathbf{r}';\omega). \qquad (5.2B.6)$$

The applied potential at A depends on the external potential and on the potentials due to the shifts in the charge densities of B and C. Thus,

$$\varphi^{A}_{app}(\mathbf{r};\omega) = \varphi_{ext}(\mathbf{r};\omega)+\int d\mathbf{r}'\,\frac{\Delta\rho^{B}(\mathbf{r}';\omega)}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}+\int d\mathbf{r}'\,\frac{\Delta\rho^{C}(\mathbf{r}';\omega)}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}. \qquad (5.2B.7)$$

The charge density shift of B, in turn, depends on the charge density shift of C (and vice versa), which finally yields

$$\varphi^{A}_{app}(\mathbf{r};\omega) = \varphi_{ext}(\mathbf{r};\omega)+\int d\mathbf{r}'\,d\mathbf{r}''\,\frac{1}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}\chi^{B}(\mathbf{r}',\mathbf{r}'';\omega)\varphi_{ext}(\mathbf{r}'';\omega)$$

$$+\int d\mathbf{r}'\,d\mathbf{r}''\,\frac{1}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}\chi^{C}(\mathbf{r}',\mathbf{r}'';\omega)\varphi_{ext}(\mathbf{r}'';\omega)$$

$$+(1+\wp_{BC})\int d\mathbf{r}'...d\mathbf{r}^{iv}\,\frac{1}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}\chi^{B}(\mathbf{r}',\mathbf{r}'';\omega)\frac{1}{4\pi\varepsilon_0|\mathbf{r}''-\mathbf{r}'''|}$$

$$\times\chi^{C}(\mathbf{r}''',\mathbf{r}^{iv};\omega)\varphi_{ext}(\mathbf{r}^{iv};\omega)+... \qquad (5.2B.8)$$

Solution of Eqs. (5.2B.6) and (5.2B.8) gives

$$\Delta\rho^{A}(\mathbf{r};\omega)+\Delta\rho^{B}(\mathbf{r};\omega)+\Delta\rho^{C}(\mathbf{r};\omega)$$

$$= \int d\mathbf{r}'\,\chi^{A}(\mathbf{r},\mathbf{r}';\omega)\varphi_{ext}(\mathbf{r}';\omega)+\int d\mathbf{r}'\,\chi^{B}(\mathbf{r},\mathbf{r}';\omega)\varphi_{ext}(\mathbf{r}';\omega)+\int d\mathbf{r}'\,\chi^{C}(\mathbf{r},\mathbf{r}';\omega)\varphi_{ext}(\mathbf{r}';\omega)$$

$$+\int d\mathbf{r}'\,\Delta\chi^{AB}(\mathbf{r},\mathbf{r}';\omega)\varphi_{ext}(\mathbf{r}';\omega)+\int d\mathbf{r}'\,\Delta\chi^{BC}(\mathbf{r},\mathbf{r}';\omega)\varphi_{ext}(\mathbf{r}';\omega)$$

$$+\int d\mathbf{r}'\,\Delta\chi^{CA}(\mathbf{r},\mathbf{r}';\omega)\varphi_{ext}(\mathbf{r}';\omega)$$

$$+\int d\mathbf{r}'\,\Delta\chi^{ABC}(\mathbf{r},\mathbf{r}';\omega)\varphi_{ext}(\mathbf{r}';\omega)+... \qquad (5.2B.9)$$

In Eq. (5.2B.9), $\Delta\chi^{AB}(\mathbf{r},\mathbf{r}';\omega)$ denotes the two-body part of the susceptibility defined in Eq. (5.2A.13), and $\Delta\chi^{ABC}(\mathbf{r},\mathbf{r}';\omega)$ is the three-body part of the susceptibility, given by

$$\Delta\chi^{ABC}(\mathbf{r},\mathbf{r}';\omega) = S_{ABC}\int d\mathbf{r}''...d\mathbf{r}^{v}\,\chi^{A}(\mathbf{r},\mathbf{r}'';\omega)\frac{1}{4\pi\varepsilon_0|\mathbf{r}''-\mathbf{r}'''|}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};\omega)$$

$$\times\frac{1}{4\pi\varepsilon_0|\mathbf{r}^{iv}-\mathbf{r}^{v}|}\chi^{C}(\mathbf{r}^{v},\mathbf{r}';\omega), \qquad (5.2B.10)$$

In time domain, the three-body susceptibility is

$$\Delta\chi^{ABC}(\mathbf{r},\mathbf{r}';t-t') = S_{ABC}\int d\mathbf{r}''...d\mathbf{r}^{v}\int_{-\infty}^{\infty}d(t'''-t'')\int_{-\infty}^{\infty}d(t''-t')\chi^{A}(\mathbf{r},\mathbf{r}'';t-t''')$$

$$\times\frac{1}{4\pi\varepsilon_0|\mathbf{r}''-\mathbf{r}'''|}\chi^{B}(\mathbf{r}''',\mathbf{r}^{iv};t'''-t'')\frac{1}{4\pi\varepsilon_0|\mathbf{r}^{iv}-\mathbf{r}^{v}|}\chi^{C}(\mathbf{r}^{iv},\mathbf{r}^{v};t'''-t').$$

(5.2B.11)

Using the definition of the three-body susceptibility in the time domain from Eq. (5.2B.11) and a change in the integration variables, the four-body dispersion energy of A in Eq. (5.2B.3) can be written as

$$\Delta E_d^{A(4,4)} = (1/4)(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\int_{-\infty}^{\infty}d(t-t')\left\langle\delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}$$

$$\times|\mathbf{r}'-\mathbf{r}''|^{-1}\chi^{BCD}(\mathbf{r}'',\mathbf{r}''';t-t')|\mathbf{r}'''-\mathbf{r}|^{-1}. \qquad (5.2B.12)$$

Thus, from Eqs. (5.2B.12), (2.2.11), and (2.2.12), we obtain

$$\Delta E_d^{A(4,4)} = (1/4)(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\int_{-\infty}^{\infty}d(t-t')\left\langle\delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}$$

$$\times|\mathbf{r}'-\mathbf{r}''|^{-1}\varepsilon_0\,\varepsilon^{-1}_{v,BCD}(\mathbf{r}'',\mathbf{r};t-t')$$

$$-(1/4)(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}\,d\mathbf{r}'\left\langle \delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}|\mathbf{r}-\mathbf{r}'|^{-1} \quad (5.2B.13)$$

Eq. (5.2B.13) proves that the four-body dispersion energy at fourth order results from the screening of the intramolecular exchange-correlation energy, where the dielectric screening depends on molecules B, C, and D which together act as the dielectric medium. Thus, the many-body effects are contained within the nonlocal dielectric function.

5.3 Dielectric screening and induction-dispersion energy at third and fourth orders

In this section, we prove that the dielectric screening model also describes the simultaneous induction-dispersion energy of a cluster of molecules. Simultaneous induction-dispersion effects appear, because the permanent charge-density of one molecule acts as the source of a static external potential φ_0 that perturbs the two-body or three-body dispersion interaction of two or three other molecules respectively: Each of the two or three molecules in the cluster is hyperpolarized by the simultaneous action of the static external potential and the fluctuating potentials from its partners. The static external potential also alters the correlations of the spontaneous, quantum mechanical fluctuations in the charge densities of the other interacting molecules. Within the dielectric model, the induction-dispersion interaction can be interpreted as the perturbation of the dielectric medium by the external potential. This perturbation brings in nonlinear screenings into the dielectric medium, which are of secondary importance in the case of pure dispersion interaction. Previously, Hunt and Bohr[183,184] developed a theory for the dispersion dipole of an A···B pair, based on the change in dispersion energy due to a uniform, static external field $\mathfrak{F}^e$. Li and Hunt[278] applied the same analysis to the dispersion energy of the A···B pair in presence of the static external field $\mathfrak{F}_0^C$ due to the permanent charge distribution of molecule C, after allowing for the nonuniformity of the field. In the present work, we relate the three-body and four-body induction-dispersion interactions to the dielectric model. We focus on the energy shift of a particular molecule due to the correlation between its intramolecular charge density fluctuations in presence

of the static external potential. We use the charge density susceptibility based reaction potential approach that we used in the previous section, to describe the induction-dispersion energy of the interacting molecules, where the overlap between the charge distributions of the molecules is assumed to be weak or negligible.

In presence of the static external potential φ_0^C due to the permanent charge distribution in molecule C, the two-body dispersion energy of molecule A is given by

$$\Delta E_d^{A(2,2)} = (1/4)(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'' \int_{-\infty}^{\infty} d(t-t') \left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t') \right\rangle_+$$

$$\times |\mathbf{r}'-\mathbf{r}''|^{-1} \chi^B(\mathbf{r}'',\mathbf{r}''';\varphi_0^C,t-t') |\mathbf{r}'''-\mathbf{r}|^{-1}. \qquad (5.3.1)$$

In Eq. (5.3.1), $\chi^B(\mathbf{r}'',\mathbf{r}''';\varphi_0^C,t-t')$ denotes the nonlocal charge density susceptibility of molecule B in time domain in presence of the static external potential φ_0^C. If the external potential is significantly small, $\chi(\varphi,t-t')$ can be expanded in Taylor series,

$$\chi(\varphi_0^C,\omega) = \chi(t-t') + \zeta(t-t',0)\varphi_0^C + \ldots, \qquad (5.3.2)$$

where $\chi(t-t')$ and $\zeta(t-t',0)$ denote the linear and the quadratic charge-density susceptibilities respectively, in the absence of the perturbing potential. Substituting Eq. (5.3.2) in Eq. (5.3.1), we obtain

$$\Delta E_d^{A(2,2)} = (1/4)(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'' \int_{-\infty}^{\infty} d(t-t') \left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t') \right\rangle_+$$

$$\times |\mathbf{r}'-\mathbf{r}''|^{-1} \chi^B(\mathbf{r}'',\mathbf{r}''';t-t') |\mathbf{r}'''-\mathbf{r}|^{-1}$$

$$+ (1/4)(4\pi\varepsilon_0)^{-2} \int d\mathbf{r}\ldots d\mathbf{r}^{\mathbf{iv}} \int_{-\infty}^{\infty} d(t-t') \left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t') \right\rangle_+$$

$$\times|\mathbf{r}'-\mathbf{r}''|^{-1}\zeta(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{iv};t-t',0)|\mathbf{r}'''-\mathbf{r}|^{-1}\varphi_0^C(\mathbf{r}^{iv}). \qquad (5.3.3)$$

The first term in Eq. (5.3.3) is the unperturbed two-body dispersion energy of A. The second term gives the three-body induction-dispersion energy of A at third order. Expanding the potential $\varphi_0^C(\mathbf{r}^{iv})$ in Eq. (5.3.3),

$$\Delta E_{i+d}^{A(3,3)} = (1/4)(4\pi\varepsilon_0)^{-3}\int d\mathbf{r}...d\mathbf{r}^{v}\int_{-\infty}^{\infty} d(t-t')\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+$$

$$\times|\mathbf{r}'-\mathbf{r}''|^{-1}\zeta^B(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{iv};t-t',0)|\mathbf{r}'''-\mathbf{r}|^{-1}\left|\mathbf{r}^{iv}-\mathbf{r}^{v}\right|^{-1}\rho_0^C(\mathbf{r}^{v}).$$

(5.3.4)

The energy in Eq. (5.3.4) can be interpreted as the hyperpolarization energy of B caused by the fluctuating potentials from A and the static potential from C. The nonlinear shift in the charge density of B caused by the potentials due to the charge density fluctuations in A interacts with the static external potential from C, thus giving an overall energy shift. Using Eq. (5.3.4) and the nonlinear dielectric function in the time domain, the three-body induction-dispersion energy of A is given by

$$\Delta E_{i+d}^{A(3,3)} = (1/4)(4\pi\varepsilon_0)^{-2}\int d\mathbf{r}...d\mathbf{r}^{iv}\int_{-\infty}^{\infty} d(t-t')\left\langle \delta\rho^A(\mathbf{r},t)\delta\rho^A(\mathbf{r}',t')\right\rangle_+$$

$$\times|\mathbf{r}'-\mathbf{r}''|^{-1}[\varepsilon_0\,\varepsilon_{q,B}^{-1}(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{iv};t-t',0)]|\mathbf{r}'''-\mathbf{r}|^{-1}\rho_0^C(\mathbf{r}^{iv}).$$

(5.3.5)

Thus from Eq. (5.3.5), the induction-dispersion energy of A is described within the dielectric model as the energy shift due to the nonlinear interaction between the charge-density fluctuations in A and the permanent charge distribution in C, in presence of B which acts as the nonlinear dielectric medium. This interaction is analogous to the

hyperpolarization energy described in section 5.1, with the difference that the hyperpolarization energy appears due to the nonlinear interaction between permanent charge distributions, while the induction-dispersion energy is due to the nonlinear interaction between permanent charge distribution and charge-density fluctuations.

Following the same line of argument, we can relate the four-body induction-dispersion energy of molecule A with the dielectric model. Here we consider the three-body dispersion energy of A in presence of B and C, perturbed by the external potential due to the permanent charge distribution of D. Expanding the charge density susceptibilities of B and C in Taylor series with respect to the external potential and keeping only the lowest order terms, the four-body induction-dispersion energy of A is given by

$$\Delta E_{i+d}^{A(4,4)} = (1/4)(4\pi\varepsilon_0)^{-3}(1+\wp_{BC})\int d\mathbf{r}...d\mathbf{r}^{vi}\int_{-\infty}^{\infty} d(t-t')\int_{-\infty}^{\infty} d(t''-t')$$

$$\times\left\langle \delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+} |\mathbf{r}'-\mathbf{r}''|^{-1}\chi^{B}(\mathbf{r}'',\mathbf{r}''';t''-t')\left|\mathbf{r}'''-\mathbf{r}^{iv}\right|^{-1}$$

$$\times\zeta^{C}(\mathbf{r}^{iv},\mathbf{r}^{v},\mathbf{r}^{vi};t-t'',0)\left|\mathbf{r}^{v}-\mathbf{r}\right|^{-1}\varphi_0^{D}(\mathbf{r}^{vi}). \qquad (5.3.6)$$

Eq. (5.3.6) can be interpreted as the hyperpolarization energy of C (or B) caused by the fluctuating potential from A, potential due to the shift in the charge density of B (or C) caused by the fluctuating potential from A, and the static external potential due to the unperturbed charge density in D. Using Eq. (5.36) and the relation between the quadratic charge-density susceptibility and the nonlinear dielectric function, we obtain

$$\Delta E_{i+d}^{A(4,4)} = (1/4)(4\pi\varepsilon_0)^{-3}(1+\wp_{BC})\int d\mathbf{r}...d\mathbf{r}^{vi}\int_{-\infty}^{\infty} d(t-t')\int_{-\infty}^{\infty} d(t''-t')$$

$$\times\left\langle \delta\rho^{A}(\mathbf{r},t)\,\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}|\mathbf{r}'-\mathbf{r}''|^{-1}\chi^{B}(\mathbf{r}'',\mathbf{r}''';t''-t')\left|\mathbf{r}'''-\mathbf{r}^{\mathbf{iv}}\right|^{-1}$$

$$\times[\varepsilon_0\,\varepsilon^{-1}_{q,C}(\mathbf{r}^{\mathbf{iv}},\mathbf{r}^{\mathbf{v}},\mathbf{r}^{\mathbf{vi}};t-t'',0)]\left|\mathbf{r}^{\mathbf{v}}-\mathbf{r}\right|^{-1}\rho^{D}_{0}(\mathbf{r}^{\mathbf{vi}}). \qquad (5.3.7)$$

Eq. (5.3.7) proves that the four-body induction-dispersion energy of A arises due to the interaction between the charge density fluctuations at $\mathbf{r}$ and the reaction potential caused by the shift in the charge density of B (or C), induced by the potential from the charge density fluctuations in A at $\mathbf{r}'$, in presence of C (or B) which acts as a nonlinear dielectric medium, perturbed by the potential from the permanent charge density in D.

This interaction energy can also be explained as screening to the three-body induction-dispersion energy of A defined in Eq. (5.3.5). To show this screening effect, we consider the cluster of molecules A, B, and C, in presence of the external potential from the permanent charge density of D, where the dispersion energy arises due to the charge density fluctuations in A. The overall induction-dispersion energy of A in this case is given by the sum of the three-body terms $\Delta E^{(3,3)}_{(A\to B\to A)\leftarrow D}$ and $\Delta E^{(3,3)}_{(A\to C\to A)\leftarrow D}$, and the four body terms from Eq. (5.3.7). Using the relation between the nonlocal dielectric function and the charge-density susceptibility from Eq. (2.2.11), we can show that

$$\Delta E^{A(4,4)}_{i+d} = (1/4)(4\pi\varepsilon_0)^{-2}(1+\wp_{BC})\int d\mathbf{r}...d\mathbf{r}^{\mathbf{v}}\int_{-\infty}^{\infty}d(t-t')\int_{-\infty}^{\infty}d(t''-t')$$

$$\times\left\langle \delta\rho^{A}(\mathbf{r},t)\,\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}|\mathbf{r}'-\mathbf{r}''|^{-1}[\varepsilon_0\,\varepsilon^{-1}_{B}(\mathbf{r}'',\mathbf{r}''';t''-t')]$$

$$\times[\varepsilon_0\,\varepsilon^{-1}_{q,C}(\mathbf{r}''',\mathbf{r}^{\mathbf{iv}},\mathbf{r}^{\mathbf{v}};t-t'',0)]\left|\mathbf{r}^{\mathbf{iv}}-\mathbf{r}\right|^{-1}\rho^{D}_{0}(\mathbf{r}^{\mathbf{v}})$$

$$- (1/4)(4\pi\varepsilon_0)^{-2}[1+C(B\to C)\int d\mathbf{r}...d\mathbf{r}^{iv}\int_{-\infty}^{\infty} d(t-t')$$

$$\times\left\langle \delta\rho^{A}(\mathbf{r},t)\delta\rho^{A}(\mathbf{r}',t')\right\rangle_{+}|\mathbf{r}'-\mathbf{r}''|^{-1}[\varepsilon_0\,\varepsilon^{-1}_{q,B}(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{iv};t-t',0)]$$

$$\times|\mathbf{r}'''-\mathbf{r}|^{-1}\rho_0^{D}(\mathbf{r}^{iv}). \qquad (5.3.8)$$

In Eq. (5.3.8), the first term gives the screened three-body induction-dispersion energy of A. Here molecule B (or C) acts as the dielectric medium to screen the induction-dispersion interaction, and the screening is linear. The second term gives the unscreened three-body induction-dispersion energy of A. Thus, the induction-dispersion energy at fourth order depends on the difference between the screened and the unscreened three-body induction-dispersion energy.

Chapter 6: Summary and conclusions

The present work proves that the intermolecular interactions at second, third and fourth orders are accurately derived in terms of the nonlocal dielectric model, where the overlap between the interacting molecules is weak or negligible. Within linear response, the nonlocal dielectric function $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ determines the effective potential at $\mathbf{r}$, when an external frequency-dependent potential $\varphi(\mathbf{r}',\omega)$ acts at $\mathbf{r}'$. A separate dielectric function $\varepsilon_d(\mathbf{r},\mathbf{r}';\omega)$ relates the dielectric displacement $\mathbf{D}(\mathbf{r},\omega)$ to the external field $\mathbf{E}(\mathbf{r}',\omega)$. For translationally invariant systems, the isotropic average of $\varepsilon_d(\mathbf{r},\mathbf{r}';\omega)$ reduces to $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$. Within the intramolecular environment, $\varepsilon_d(\mathbf{r},\mathbf{r}';\omega)$ and $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ are different. The nonlocal dielectric function $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ is related to the nonlocal charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';\omega)$ by Eq. (1.2). $\chi(\mathbf{r},\mathbf{r}';\omega)$ determines the induced shift in the charge density $\delta\rho(\mathbf{r},\omega)$ at point $\mathbf{r}$ in the molecule due to an applied potential $\varphi(\mathbf{r}',\omega)$ at $\mathbf{r}'$. Molecular properties which are related to the charge-density susceptibility are nonlocal polarizability density,[129,188] infrared intensities,[127] the Sternheimer electric field shielding tensor, [127] charge reorganization terms in vibrational force constants,[286] and the softness kernel of density functional theory.[287,288]

Dielectric response of translationally invariant systems or systems with spatial periodicity can be described by a dielectric function which depends only on the distance between the response point $\mathbf{r}$ and the point $\mathbf{r}'$ where the external perturbation acts. For these systems a convenient choice is to use the dielectric function $\varepsilon(\mathbf{k},\omega)$, which is the spatial Fourier transform of $\varepsilon(\mathbf{r}-\mathbf{r}',\omega)$. Dielectric functions of the form $\varepsilon(\mathbf{k},\omega)$ have

been used in order to study quantum many-body problems, properties of quantum dots, solvation dynamics and polarization fluctuations in liquids, and electron transfer.

Dielectric models have been applied to study interactions within proteins and biomolecules. Models have been developed to probe the dielectric environment inside protein molecules and these models have been used to interpret different experimental observations such as determination of pK_a shifts of inserted amino acid residues,[289] dynamic shifts of the fluorescence, for the markers placed at various sites of protein,[290] measurements of Stark effect on absorption bands of different chromophores,[291] and determination of the apparent basicities of the different charge states of protein.[292] Inhomogeneities inside the protein molecules make it impossible to define a universal dielectric constant (or constants) for proteins. The choice of the value of protein's dielectric constant depends on the particular property or interaction to be studied and the model used to study those properties. To give a complete description of the dielectric nature within the protein environment, it is necessary to develop a model in terms of the site-dependent dielectric constants.

Extension of the dielectric model to describe interactions within the intramolecular framework was suggested in several works. Early works on light scattering by fluids and collisional polarizability anisotropy of interacting noble gas atoms used a polarizability density instead of the point dipole approach. In later works on light scattering by fluids, response functions were used that depend both on $\mathbf{r}$ and $\mathbf{r}'$. Importance of nonlocal response has been noted in recent works on surface enhanced Raman scattering by metal nanoshells.

Intermolecular interactions at first order are purely electrostatic in nature. Within quantum perturbation theory, first-order intermolecular interactions are obtained as Coulomb interactions between the unperturbed charge distributions or polarizations of the molecules. When the molecules are far apart, the electrostatic interaction energy is obtained as a sum of the interaction energy of permanent multipole moments of the molecules, given by Eq. (1.14). For a pair of interacting molecules, the first-order force on nucleus I in molecule A is calculated by taking the negative gradient of the first-order interaction energy with respect to the coordinate $\mathbf{R}^I$ of nucleus I. Thus, it depends on the derivative of the permanent charge distribution of A with respect to $\mathbf{R}^I$. When using a multipole expansion, the first-order force is given in terms of the derivatives of the permanent multipole moments of A. First-order forces on nuclei can also be calculated using the electrostatic Hellmann-Feynman theorem and the Sternheimer-type shielding tensors, where the force on nucleus I is obtained as sum of the interactions between the charge on nucleus I and effective fields and field gradients at I due to molecule B, given by Eq. (1.21). The effective field at I due to molecule B depends on the field from B due to its permanent moments and the nuclear shielding tensors of I. At first order, the effective field and the field gradient originate due to linear screening of the external field and the field gradient and are determined by the linear shielding tensors of nucleus I. These linear shielding tensors are related to the derivatives of permanent multipole moments of molecule A with respect to $\mathbf{R}^I$ [Eqs. (1.16), (1.18b)]. Physically, the shielding appears due to the electronic screening of the external field. Within the nonlocal polarizability density model the electronic screening is shown by the nonlocal polarizability density $\alpha(\mathbf{r},\mathbf{r}';0)$, where the first-order force depends on the fields at I from

the unperturbed charge distribution in B and the first-order induced shift in the polarization of A [Eq. (1.20)] which is determined by $\alpha(\mathbf{r},\mathbf{r}';0)$ of A and the field due to unperturbed charge distribution in B. The Sternheimer-type shielding tensor $\gamma^{I}_{\alpha\beta}$ is connected to the nonlocal polarizability density $\alpha_{\gamma\beta}(\mathbf{r},\mathbf{r}')$ by Eq. (1.19). The first-order force on nucleus I in molecule A was first derived within the nonlocal dielectric model by Jenkins and Hunt. A susceptibility-based approach was used to express the first-order force on I in terms of the static nonlocal charge-density susceptibility of A and the potential from the unperturbed charge-distribution in B. Using the relation between the charge-density susceptibility and the nonlocal dielectric function from Eq. (1.2), the first-order force was expressed [Eq. (1.23)] as interaction between nucleus I and the external potential from B in presence of the intramolecular dielectric medium A which is characterized by the nonlocal dielectric function $\varepsilon_{v,A}(\mathbf{r},\mathbf{r}';0)$.

In chapter 2 of this work, we have proved that the induction and dispersion energies at second order are derived within the nonlocal dielectric model. Using quantum perturbation theory, the second-order induction energy is obtained from Eq. (1.24) with the excited states confined to either molecule A or molecule B. At second order, the induction energy depends on the static fields due to the permanent charge distributions of the interacting molecules and the responses of the molecules to those static fields. Induction energy is given within the nonlocal polarizability model by Eq. (2.1.1). When the molecules are far apart, the induction energy can be written in terms of the permanent moments and the multipole polarizabilities of the interacting molecules [Eq. (1.25)].

In section 2.1 of chapter 2, we derived the second-order induction energy in terms of the static charge-density susceptibilities and the potentials due to the permanent charge distributions of the interacting molecules [Eq. (2.15)]. In order to derive Eq. (2.15), we expressed the fields in terms of the potentials and used the relationship between the charge-density susceptibility and the nonlocal polarizability density from Eq. (2.14). Then using the relation between the charge-density susceptibility and the nonlocal dielectric function $\varepsilon_V(\mathbf{r},\mathbf{r}';0)$ in Eq. (1.1) we have proved that the induction energy at second order results from the difference between the dielectrically screened and the unscreened Coulomb energies due to the permanent charge distributions within a molecule, where the second molecule acts as the nonlocal dielectric medium. The result is given in Eq. (2.1.7), where the first and the second term give the screened and the unscreened Coulomb interactions respectively, within a molecule. Thus, we conclude that the two-body induction energy at second order is derived within the nonlocal dielectric model as the difference between the dielectrically screened and the unscreened *intramolecular* interactions between the unperturbed charge densities of the molecules.

In section 2.2, we have derived the second-order dispersion energy within the dielectric framework. Dispersion energy results from the correlation between the charge-density fluctuations or polarization fluctuations within a molecule. Using a reaction field method, the dispersion energy is derived as an integral over frequency, where the integrand is factored into the nonlocal polarizability densities of the molecules at imaginary frequencies. This result is given in Eq. (1.29). Dispersion energy is also obtained from the second-order perturbation theory using Eq. (1.24) with excitations confined to both molecules. Second-order perturbation theory has been applied to

calculate the dispersion energy in several works. Within the density functional theory, dispersion energy is obtained as the exchange-correlation energy.

In the present work in section 2.2, we have expressed the dispersion energy in Eq. (2.2.1) as an integral over frequencies with the integrand factored into the charge-density susceptibilities of molecule A and B at imaginary frequencies. Then we have used a contour-integration technique and the symmetries of the real and the imaginary parts of the susceptibility to write the dispersion energy in terms of the charge-density susceptibilities of the molecules at real frequencies [Eq. (2.2.8)]. Using the fluctuation-dissipation theorem from Eq. (2.2.9), we have expressed the dispersion energy in the time domain. Finally, from Eq. (2.2.9) and the relation between the charge-density susceptibility and the nonlocal dielectric function in the time domain from Eq. (2.2.12), we have derived the dispersion energy as the difference between the screened and the unscreened Coulomb interactions between the charge-density fluctuations within the molecules. The final result is given in Eq. (2.2.13). The first term in Eq. (2.2.13) is the screened interaction between the charge-density fluctuations in A in presence of B, which acts as the dielectric medium (and similarly for B). The second term gives the unscreened interactions between the charge-density fluctuations within the molecules. Thus, we have proved that the second-order dispersion energy results from the screening of the *intramolecular* charge-density fluctuations.

Induction and dispersion forces on nuclei at second order are calculated by taking the negative gradients of the second-order induction and dispersion energies with respect to the nuclear coordinates. At second order, the induction force on nucleus I in molecule A depends on the first-order and the second-order induced polarizations in A, as given in

Eq. (1.26). The second-order polarization in A results from the nonlinear response of A to the static fields from B and is determined by the nonlocal hyperpolarizability density $\beta^{A}_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$ of A. The first-order polarization of A in Eq. (1.26) is induced by the first-order polarization of B caused by the unperturbed polarization in A. Thus, the second order induction force on I is related both to the linear and the nonlinear response of A. It is important to note here that the induction force on nucleus I does not stem from the interaction of I with the polarization of B, but from the interaction of I with the polarizations induced in A. The induction force can also be described in terms of the nuclear shielding tensors by Eq. (1.27). The terms which depend linearly on the reaction field from B and its gradients, correspond to the first term of Eq. (1.26) [i.e. the first-order induced polarization in A]. Terms depending quadratically on the reaction field and its gradients are related to the second term of Eq. (1.26) [nonlinear polarization of A]. The nonlinear shielding tensors depend on the derivatives of the molecular polarizability densities with respect to the nuclear coordinates [Eqs. (1.18a), (1.18c)] and hence, on the nonlocal hyperpolarizability densities [Eq. (1.28a) – (1.28b)]. Eqs. (1.19), (1.22), (1.28a) and (1.28b) connect the electrostatic and the second-order induction forces calculated within the nonlocal polarizability density model to the forces calculated applying the electrostatic Hellmann-Feynman theorem.

In section 3.1 of chapter 3, we have derived the second-order induction force on nucleus K in molecule A in terms of the nonlocal dielectric model. We began the derivation with the induction energy expressed in terms of the static polarizabilities of the molecules and the fields from the unperturbed charge distributions in the molecules. Within this approach, the second-order induction force on nucleus K depends on the

derivatives of the nonlocal polarizability density $\alpha^{A}(\mathbf{r},\mathbf{r}';0)$ of A and the field $\mathfrak{I}_0^{A}(\mathbf{r})$ at B, with respect to $\mathbf{R}^{K}$. The derivative of $\alpha^{A}(\mathbf{r},\mathbf{r}';0)$ with respect to $\mathbf{R}^{K}$ depends on $\beta^{A}(\mathbf{r},\mathbf{r}';0)$, the nonlocal hyperpolarizability density susceptibility of A [Eq. (3.1.2)]. The field $\mathfrak{I}_0^{A}(\mathbf{r})$ in molecule B depends both on the electronic and the nuclear charge densities of A and the derivative of the electronic charge density with respect to $\mathbf{R}^{K}$ is related to the nonlocal charge-density susceptibility $\chi^{A}(\mathbf{r},\mathbf{r}';0)$ of A., given by Eq. (3.1.5). Thus, we have expressed the induction force on nucleus K in terms of the nonlocal charge-density susceptibility and the nonlocal hyperpolarizability density of A. Next, we have written the fields in terms of the potentials, used the potential from the first-order shift in the polarization of B from Eq. (3.1.10), and used the relation between the nonlocal hyperpolarizability density and the quadratic charge-density susceptibility $\zeta(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$ from Eq. (3.1.12), to obtain the second-order induction force on K within the susceptibility based approach in Eq. (3.1.13). Eq. (3.1.13) shows that the induction force on K depends on the nonlinear screening of the potentials due to the unperturbed charge distribution in B and linear screening of the potential from the first-order shift in the charge distribution of B. This result is consistent with the induction force obtained previously using the nonlocal polarizability density model and the nuclear shielding tensors. In order to show the nonlinear screening in the induction force, we have used the nonlinear dielectric function given in Eq. (1.10). Finally using the effective potentials in A due to linear and nonlinear screenings we have expressed the induction force on K by Eq. (3.1.17). Eq. (3.1.17) proves that the second-order induction force on nucleus K

depends on the intramolecular screening of the external potential acting on A. This result is similar to the first-order force derived by Jenkins and Hunt. The difference is that the first-order force includes linear screening only, while the second-order induction force results both from linear and nonlinear screenings within molecule A.

The dispersion force on nucleus K can be calculated the same way, by evaluating the negative gradient of the second-order dispersion energy with respect to $\mathbf{R}^K$. Within the real frequency domain, the dispersion force on K in molecule A contains two different terms: one includes the derivative of the frequency-dependent polarizability $\alpha(\mathbf{r},\mathbf{r}';\omega)$ of A with respect to $\mathbf{R}^K$, and the second one contains the derivative of the correlation between the polarization fluctuations within A with respect to $\mathbf{R}^K$. The derivative of $\alpha^A(\mathbf{r},\mathbf{r}';\omega)$ with respect to $\mathbf{R}^K$ depends on the nonlocal hyperpolarizability density $\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ of A. From the fluctuation-dissipation theorem, the correlation between the polarization fluctuations is related to the imaginary part of the nonlocal polarizability density, $\alpha^{A''}(\mathbf{r},\mathbf{r}';\omega)$. Thus the derivative of the correlation is given by the derivative of $\alpha^{A''}(\mathbf{r},\mathbf{r}';\omega)$ with respect to $\mathbf{R}^K$, which is related to the imaginary part of the nonlocal hyperpolarizability density $\beta^{A''}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$. The first component of the dispersion force resembles the first component of the induction force, with the difference that in the case of later, the external fields are time dependent and the nonlocal hyperpolarizability density depends on frequency. The second is quite different, since it depends on the imaginary part of $\beta^A(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ and shows no linear screening like in the case of the induction force. In earlier work, it was concluded that this part of

dispersion force might depend on the polarization of B. Moreover, since the correlation between the polarization fluctuations is affected by the change in the nuclear Coulomb field, it was noted that this field might bring new correlations and could even change the magnitude of the correlation function (field induced fluctuation correlations). However, those new type of correlations were not derived explicitly.

In section 3.2, we have derived the second-order dispersion force within the nonlocal dielectric model. The dispersion energy was written within the frequency domain, where it depends on the real part of the charge-density susceptibility of one molecule and the imaginary part of the charge-density susceptibility of the other [Eq. (3.2.1)]. Using Eq. (3.2.1), the first part of the dispersion force ($\mathbf{F}^{K}_{d(1)}$) on nucleus K has been derived in terms of the real part of the quadratic charge-density susceptibility of A and the correlation of the charge-density fluctuations in B. This part of the dispersion force appears due to the nonlinear screening of the fluctuating potentials from molecule B. Thus it is similar to the first part of the induction force. We have showed the nonlinear screening present in the dispersion force using the frequency-dependent nonlinear dielectric function of A [Eq. (3.2.19).

The second component of the dispersion force ($\mathbf{F}^{K}_{d(2)}$) depends on the derivative of $\chi^{A''}(\mathbf{r},\mathbf{r}';\omega)$ with respect to $\mathbf{R}^{K}$, and hence on $\zeta^{A''}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$. We have expressed $\mathbf{F}^{K}_{d(2)}$ explicitly by expanding $\zeta^{A''}(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ in terms of the charge-density matrix elements of the unperturbed eigenstates and the unperturbed Bohr frequencies. From that, we have separated the terms with $j = n$ and $j \neq n$. The terms with $j \neq n$ have been written in terms of the transition susceptibility of A. Then we have showed that this part of the

second order dispersion force [designated by $\mathbf{F}^{K}_{d(2),1}$] actually results from the correlation between the charge-density fluctuations and the susceptibility fluctuations within molecule A. This result has been given in Eq. (3.2.30), which proves the fact that when nucleus K shifts infinitesimally within molecule A, the change in the Coulomb from K modifies the correlation of the charge-density fluctuations in A and actually introduces new type of correlation, namely, the correlation between charge-density fluctuations and susceptibility fluctuations. Finally, the dielectric screening present in $\mathbf{F}^{K}_{d(2),1}$ has been given by Eq. (3.2.35), which shows that $\mathbf{F}^{K}_{d(2),1}$ results from screening of the fluctuating potential from B within A and the screening depends on the fluctuation of the nonlocal dielectric function $\varepsilon_{v,A}(\mathbf{r}'',0;\mathbf{r},\omega)$. Terms with j = n in $\mathbf{F}^{K}_{d(2)}$ were separated into two sets. One set of terms where $\mathbf{r}''$ is directly connected to $\mathbf{R}^{K}$ (denoted by $\mathbf{F}^{K}_{d(2),2}$) and the other set where either $\mathbf{r}$ or $\mathbf{r}'$ is directly connected to $\mathbf{R}^{K}$ (denoted by $\mathbf{F}^{K}_{d(2),3}$). We have used time-dependent perturbation theory to explain the physical significance of all the terms present in $\mathbf{F}^{K}_{d(2),1}$, $\mathbf{F}^{K}_{d(2),2}$, and $\mathbf{F}^{K}_{d(2),3}$. The external potential in the perturbation Hamiltonian is the reaction potential from molecule B. Using the first-order perturbed wave functions for the initial and final states of molecule A, we have showed that $\mathbf{F}^{K}_{d(2),1}$ and $\mathbf{F}^{K}_{d(2),2}$ result from the interaction between the transition charge density of A with nucleus K [Eqs. (3.2.45) and (3.2.46)]. The difference between $\mathbf{F}^{K}_{d(2),1}$ and $\mathbf{F}^{K}_{d(2),2}$ is that $\mathbf{F}^{K}_{d(2),1}$ is determined by the transition-susceptibility of A,

while $\mathbf{F}^{K}_{d(2),2}$ appears due to the transition charge density induced by the interaction of the reaction potential from B with the difference between the permanent charge densities of A in excited state n and in the ground state. Thus, $\mathbf{F}^{K}_{d(2),2}$ does not have a dielectric interpretation. $\mathbf{F}^{K}_{d(2),3}$ results from the fact that when molecule A remains in excited state n during the time interval $t-t'$, the potential at nucleus K due to the average electronic charge density changes. The transition of molecule A from state n back to the ground state is induced by the reaction potential from B. The first-order amplitude for this transition, along with the change in the potential at nucleus K, yield $\mathbf{F}^{K}_{d(2),3}$. This result is given by Eq. (3.2.50). Like $\mathbf{F}^{K}_{d(2),2}$, $\mathbf{F}^{K}_{d(2),3}$ can not be connected to the dielectric model.

Nonadditivities appear in the intermolecular interactions at second and higher orders. At second order, only the induction energy is nonadditive. At third and higher orders, all kinds of interactions show nonadditivity. For three or more interacting molecules, if one of the molecules has a permanent charge density, that brings a new type of interaction, known as the induction-dispersion. This interaction first appears at third order. Importance of nonadditivity has been noted in several experimental and theoretical works on thermodynamic properties of fluids, structures, dynamics, and spectroscopic properties of van der Waals complexes and collision induced transitions in compressed gases. Several theoretical works on nonadditivity have employed the multipole expansion technique to evaluate the many-body interaction energies, dipoles and higher multipoles at second and third orders. Short range effects are incorporated in the many-body

interactions by using methods that include exchange (examples are SAPT, IMPT/MPPT). Nonadditive interactions are also described within the reaction field method.

In chapter 4 of the present work, we have proved that the nonlocal dielectric model describes the nonadditive three-body induction at second order. In section 4.1, we have showed that the three-body induction energy at second order results from the dielectric screening of the first-order Coulomb interaction between two molecules. The result is given in Eq. (4.1.5). The screening appears due to the presence of a third molecule, which acts as the dielectric medium. Thus, the second-order three-body induction energy depends on the *intermolecular* screening of the Coulomb interaction between the permanent charge distributions of two interacting molecules. This result is different from the second-order two-body induction energy, which depends on the *intramolecular* screening of the Coulomb interactions within two molecules. In section 4.2, we have derived the second-order three-body induction force on nucleus K. We have followed the same method that we used to derive the second-order induction force in section 3.1. The second-order three-body dispersion force on nucleus K has been derived in terms of the effective three-body potential in molecule A, which depends on nonlinear screening of the potentials from B and C due to their unperturbed charge distributions and linear screening of the potential from the first-order shift in the charge distribution of B induced by C (and vice versa). The results are given in Eqs. (4.2.14) and (4.2.15).

In chapter 5, we have derived the nonadditive three-body and four-body interaction energies at third and fourth order. We have considered a cluster of four molecules A···B···C···D and specifically focused on the three and four-body induction energies at third order and three and four body dispersion and induction-dispersion

energies at third and fourth orders respectively. The induction energy has been described in section 5.1. The induction energy at third order has been separated into three categories: hyperpolarization, static reaction potential, and third-body potential. Hyperpolarization energy results from nonlinear response of one molecule to the potentials from the permanent charge distributions in the other molecules. At third order, nonadditive part of hyperpolarization energy contains both three-body and four-body terms, given by Eqs. (5.1.4) and (5.1.5) respectively, where we have considered the hyperpolarization of molecule A. Within the dielectric model, hyperpolarization energy is described by the nonlinear screening of the interactions between the charge distributions and the screening is determined by the dielectric function $\varepsilon_q(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$ [Eqs. (5.1.6) – (5.1.7)].

Both the static reaction potential and the third-body potential effects result from linear screening and the screening present in them are characterized by the dielectric function $\varepsilon_V(\mathbf{r},\mathbf{r}',\mathbf{r}'';0,0)$. In static reaction potential terms, the polarization starts and ends at the same molecule. Thus they are purely three-body effects at third order. In Eq. (5.1.13), we have showed that the static reaction potential results from the dielectric screening of the two-body induction energy at second order and is given by the difference between the screened and the unscreened two-body induction energies. Third-body potential effect includes terms that start and end at different molecules. Thus at third order, third-body potential contains both three-body and four-body terms. In Eq. (5.1.18) we have proved that the three-body terms in the third-body potential energy results from screening of the intramolecular interactions between the permanent charge distributions and the first-order shift in the charge distributions within a molecule. Eq. (5.1.20) shows

that the four-body terms in the third-body potential energy depend on the difference between the screened and the unscreened second-order three-body induction energies, where the fourth molecule acts as the dielectric medium. Hence we conclude that the three-body terms in the third-body potential energy result from intramolecular screening, while the four-body terms result from intermolecular screening.

We have derived the three-body and four-body dispersion energies in section 5.2 within the nonlocal dielectric model. We have used the susceptibility based reaction field approach that we used in section 2.2 and in section 3.2. In section 5.2A we specifically considered the three-body dispersion energy of A in presence of B and C. The three-body dispersion energy at second order has been obtained as the difference between the screened and the unscreened two-body dispersion energy of A at second order, where the third molecule (either B or C) acts as the nonlocal dielectric medium. We have expressed the screening in Eq. (5.2A.4) where the nonlocal dielectric function and the charge-density fluctuations are given in the time domain. We have also showed that the three-body dispersion energy of A results from the screening of the interaction between the intramolecular charge density fluctuations in A, where both B and C act as a combined dielectric medium. To derive this result, we have used the two-body susceptibility used by Kohn, Meir and Makarov (Eq. 5.2A.5) and the two-body collision-induced electronic polarizability (Eq. 5.2A.8) introduced by Li and Hunt. Finally, we have derived the screening in the three-body dispersion energy in Eq. (5.2A.16) in terms of the two-body nonlocal dielectric function in the time domain. Eq. (5.2A.16) proves that the three-body dispersion energy of A depends on the screening of the intramolecular interactions of the charge-density fluctuations in A, due to the presence of B and C which together act as a

single dielectric medium. Following the same approach in section 5.2B, we have showed that the four-body dispersion energy of A at fourth order results from screening of its three-body dispersion energy, due to the presence of a fourth molecule (B or C or D). This result has been given in Eq. (5.2B.4). We have also proved that the four-body dispersion energy can be obtained as the difference between the screened and the unscreened interactions of the charge-density fluctuations within A, due to the presence of B, C, and D which together act as a three-body dielectric medium. In order to derive that result, we have used the three-body collision-induced polarizability introduced by Champagne, Li, and Hunt [Eq. (5.2B.5)]. The final result is given in Eq. (5.2B.13), where the screening has been described in terms of a three-body nonlocal dielectric function.

Finally in section 5.3, the induction-dispersion energies at third and fourth orders have been derived in terms of the dielectric model. The induction-dispersion energy results from the perturbation of one molecule in the dispersion cluster due to static external potential from another molecule. The molecules are hyperpolarized by the simultaneous action of the fluctuating potential of one molecule and the static external potential from the other molecule. Thus, the induction-dispersion energy results from nonlinear response, and hence from nonlinear screening. We have derived the dielectric screening in terms of the nonlinear dielectric function in the time domain. Eq. (5.3.5) proves that the induction-dispersion energy at third order results from nonlinear interaction of the charge-density fluctuations in A and the permanent charge density in C, due to the presence of B which acts as the nonlinear dielectric medium. Next, we have derived the four-body induction-dispersion energy within the dielectric model in Eq. (5.3.7), where we have proved that the four-body induction-dispersion energy of A

results from nonlinear interaction of the intramolecular charge-density fluctuations in A, first-order induced shift in the charge distribution in B and the permanent charge distribution in D, in presence of C that acts as the nonlinear dielectric medium. We have also showed that the four-body induction-dispersion energy depends on the difference between the screened and unscreened three-body induction energy, where the screening is linear [Eq. (5.3.8)].

Our work derives a generalized dielectric model to treat the intermolecular interactions at second, third and fourth orders. The nonlocal dielectric functions $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ and $\varepsilon_q(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,\omega')$ provide complete description of the intermolecular screenings and the effective potentials are accurately described by Eq. (1.11) within the Born-Oppenheimer approximation. As a first step of our future work, we would like to compute the numerical values of the nonlocal dielectric functions for diatomic molecules. Numerical value of the frequency-dependent charge-density susceptibility of H_2 has been computed at the CISD level in ref. 285. To calculate $\varepsilon_V(\mathbf{r},\mathbf{r}';\omega)$ we will have to use Eq. (1.2), where we will have to evaluate the nucleus-electron attraction type integrals over the atomic orbitals. We would also like to compute the nonlocal dielectric functions for larger molecules. Practical application of the dielectric model to larger molecules can be done by coarse graining the model, i.e. averaging over regions around each nuclear center, or over functional groups. Another possible future work will be to include short-range interactions within the model to account for the overlapping molecules.

APPENDICES

Appendix A. Derivation of the relation between $\zeta''(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ and the derivative of $\chi''(\mathbf{r},\mathbf{r}';\omega)$ with respect to $\mathbf{R}^K$

To derive $\nabla^K \chi''(\mathbf{r},\mathbf{r}';\omega)$, we first differentiate with respect to a real quantity (the nuclear coordinate) and then take the imaginary part of the result. We use the inverse radiative lifetime Γ_n for state $|n\rangle$ to approximate the effects of damping near resonance. This approach neglects branched or successive decays of the excited states.

$$\nabla^K \chi(\mathbf{r},\mathbf{r}';\omega) = -(1/\hbar)\nabla^K \sum_{n\neq 0} [\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle(\omega_{n0} - i\Gamma_n/2 - \omega)^{-1}$$

$$+\langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle(\omega_{n0} + i\Gamma_n/2 + \omega)^{-1}]. \quad \text{(A.1)}$$

The derivatives of the states are given by

$$\nabla_\alpha^K |0\rangle = -(1/\hbar)\sum_{j\neq 0} |j\rangle\langle j|\nabla_\alpha^K H|0\rangle\omega_{j0}^{-1}$$

$$= -(4\pi\varepsilon_0\hbar)^{-1}\int d\mathbf{r}'' Z^K \nabla_\alpha^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1} \sum_{j\neq 0} |j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle\omega_{j0}^{-1} \quad \text{(A.2)}$$

and similarly

$$\nabla_\alpha^K |n\rangle = -(4\pi\varepsilon_0\hbar)^{-1}\int d\mathbf{r}'' Z^K \nabla_\alpha^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1} \sum_{m\neq n} |m\rangle\langle m|\hat{\rho}(\mathbf{r}'')|n\rangle\omega_{mn}^{-1}, \quad \text{(A.3)}$$

where damping is neglected for static perturbations. Also

$$\nabla_\alpha^K (\omega_{n0} + i\Gamma_n/2 \pm \omega)^{-1} = -(1/\hbar)(\omega_{n0} + i\Gamma_n/2 \pm \omega)^{-2}[\langle n|\nabla_\alpha^K H|n\rangle - \langle 0|\nabla_\alpha^K H|0\rangle]$$

$$= -(\omega_{n0} + i\Gamma_n/2 \pm \omega)^{-2}(4\pi\varepsilon_0\hbar)^{-1}\int d\mathbf{r}'' Z^K \nabla_\alpha^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1}$$

$$\times\langle n|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|n\rangle, \quad \text{(A.4)}$$

where we have used the Hellmann-Feynman theorem. In Eq. (A.4) we have neglected the dependence of the inverse radiative lifetime on the nuclear coordinates, treating Γ_n as a property of the entire adiabatic electronic state. The off-diagonal elements of the derivatives of the charge-density operators themselves vanish, because the only explicit dependence of $\rho(\mathbf{r})$ on the nuclear coordinates comes from the nuclear contribution to the charge density, and states $|j\rangle$ are orthogonal Born-Oppenheimer electronic states. From Eqs. (A.2) – (A.4), the derivative in Eq. (A.1) becomes

$$\nabla^K \chi(\mathbf{r},\mathbf{r}';\omega) = (1/\hbar)^2 (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}'' Z^K \nabla^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{j0}^{-1} (\omega_{n0} - i\Gamma_n/2 - \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{k\neq n} \langle 0|\hat{\rho}(\mathbf{r})|k\rangle\langle k|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{kn}^{-1} (\omega_{n0} - i\Gamma_n/2 - \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{k\neq n} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|k\rangle\langle k|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{kn}^{-1} (\omega_{n0} - i\Gamma_n/2 - \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} (\omega_{n0} - i\Gamma_n/2 - \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \omega_{j0}^{-1} (\omega_{n0} + i\Gamma_n/2 + \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{k\neq n} \langle 0|\hat{\rho}(\mathbf{r}')|k\rangle\langle k|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \omega_{kn}^{-1} (\omega_{n0} + i\Gamma_n/2 + \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{k\neq n} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|k\rangle\langle k|\hat{\rho}(\mathbf{r})|0\rangle \omega_{j0}^{-1} (\omega_{n0} + i\Gamma_n/2 + \omega)^{-1}$$

$$\times [\sum_{n\neq 0}\sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} (\omega_{n0}+i\Gamma_n/2+\omega)^{-1}$$

$$\times \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle\langle n|\hat{\rho}(\mathbf{r}'')-\rho_{00}(\mathbf{r}'')|n\rangle (\omega_{n0}-i\Gamma_n/2-\omega)^{-2}$$

$$\times \sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle\langle n|\hat{\rho}(\mathbf{r}'')-\rho_{00}(\mathbf{r}'')|n\rangle (\omega_{n0}+i\Gamma_n/2+\omega)^{-2}].$$

(A.5)

Next, we separate the terms with k = 0, in the summation over $k \neq n$; this gives

$$\nabla^K \chi(\mathbf{r},\mathbf{r}';\omega) = (1/\hbar)^2 (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}'' Z^K \nabla^K \left|\mathbf{r}''-\mathbf{R}^K\right|^{-1}$$

$$\times [\sum_{n\neq 0}\sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{j0}^{-1} (\omega_{n0}-i\Gamma_n/2-\omega)^{-1}$$

$$\times [\sum_{n\neq 0}\sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} (\omega_{n0}-i\Gamma_n/2-\omega)^{-1}$$

$$\times [\sum_{n\neq 0}\sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \omega_{j0}^{-1} (\omega_{n0}+i\Gamma_n/2-\omega)^{-1}$$

$$\times [\sum_{n\neq 0}\sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} (\omega_{n0}+i\Gamma_n/2+\omega)^{-1}$$

$$\times [\sum_{\substack{n\neq 0\\ k\neq 0\\ k\neq n}}\sum \langle 0|\hat{\rho}(\mathbf{r})|k\rangle\langle k|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{kn}^{-1} (\omega_{n0}-i\Gamma_n/2-\omega)^{-1}$$

$$\times [\sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|0\rangle\langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{0n}^{-1} (\omega_{n0}-i\Gamma_n/2-\omega)^{-1}$$

$$\times [\sum_{\substack{n\neq 0\\ k\neq 0\\ k\neq n}}\sum \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|k\rangle\langle k|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{kn}^{-1} (\omega_{n0}-i\Gamma_n/2-\omega)^{-1}$$

$$\times [\sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|0\rangle\langle 0|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{0n}^{-1} (\omega_{n0} - i\Gamma_n/2 - \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{\substack{k\neq 0 \\ k\neq n}} \langle 0|\hat{\rho}(\mathbf{r}')|k\rangle\langle k|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{kn}^{-1} (\omega_{n0} + i\Gamma_n/2 + \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|0\rangle\langle 0|\hat{\rho}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \omega_{0n}^{-1} (\omega_{n0} + i\Gamma_n/2 + \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{\substack{k\neq 0 \\ k\neq n}} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|k\rangle\langle k|\hat{\rho}(\mathbf{r})|0\rangle \omega_{kn}^{-1} (\omega_{n0} + i\Gamma_n/2 + \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'')|0\rangle\langle 0|\hat{\rho}(\mathbf{r})|0\rangle \omega_{0n}^{-1} (\omega_{n0} + i\Gamma_n/2 + \omega)^{-1}$$

$$\times [\sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle\langle n|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|0\rangle (\omega_{n0} - i\Gamma_n/2 - \omega)^{-2}$$

$$\times [\sum_{n\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle\langle n|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|0\rangle (\omega_{n0} + i\Gamma_n/2 + \omega)^{-2}]$$

(A.6)

We interchange the labels n and k in the 7th and 11th terms in Eq. (A.6) and combine the terms, to obtain

$$\nabla^K \chi(\mathbf{r},\mathbf{r}';\omega) = (1/\hbar)^2 (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}'' Z^K \nabla^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1}$$

$$\times [\sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}) - \rho_{00}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \omega_{j0}^{-1} (\omega_{n0} - i\Gamma_n/2 - \omega)^{-1}$$

$$\times \sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}') - \rho_{00}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1} (\omega_{n0} - i\Gamma_n/2 - \omega)^{-1}$$

$$\times \sum_{n\neq 0}\sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')-\rho_{00}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \omega_{j0}^{-1}(\omega_{n0}+i\Gamma_n/2+\omega)^{-1}$$

$$\times \sum_{n\neq 0}\sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})-\rho_{00}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1}(\omega_{n0}+i\Gamma_n/2+\omega)^{-1}$$

$$\times \sum_{n\neq 0}\sum_{k\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|k\rangle\langle k|\hat{\rho}(\mathbf{r}'')-\rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle(\omega_{n0}-i\Gamma_n/2-\omega)^{-1}$$

$$\times(\omega_{n0}-i\Gamma_n/2-\omega)^{-1}$$

$$\times \sum_{n\neq 0}\sum_{k\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|k\rangle\langle k|\hat{\rho}(\mathbf{r}'')-\rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle(\omega_{n0}+i\Gamma_n/2+\omega)^{-1}$$

$$\times(\omega_{n0}-i\Gamma_n/2-\omega)^{-1}]. \qquad \text{(A.7)}$$

We assume that the inverse radiative lifetimes Γ_n and Γ_k are much smaller than the transition frequencies ω_{nk}, ω_{nk}. Using the identity

$$\lim_{y\to 0}\frac{1}{x\pm iy}=P\left(\frac{1}{x}\right)\mp i\pi\delta(y), \qquad \text{(A.8)}$$

we take the imaginary part of Eq. (A.7) and the relabel the summation indices to obtain

$$\nabla^K\chi''(\mathbf{r},\mathbf{r}';\omega)=(\pi/\hbar)^2(4\pi\varepsilon_0)^{-1}\int d\mathbf{r}''\,Z^K\nabla^K\left|\mathbf{r}''-\mathbf{R}^K\right|^{-1}$$

$$\times\{\sum_{n\neq 0}\sum_{j\neq 0}\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})-\rho_{00}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle\omega_{j0}^{-1}\delta(\omega_{n0}-\omega)$$

$$+\sum_{n\neq 0}\sum_{j\neq 0}\langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}')-\rho_{00}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle\omega_{j0}^{-1}\delta(\omega_{n0}-\omega)$$

$$-\sum_{n\neq 0}\sum_{j\neq 0}\langle 0|\hat{\rho}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')-\rho_{00}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle\omega_{j0}^{-1}\delta(\omega_{n0}+\omega)$$

$$- \sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}) - \rho_{00}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'')|0\rangle \omega_{j0}^{-1}\, \delta(\omega_{n0} - \omega)$$

$$+ \sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|j\rangle\langle j|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r}')|0\rangle \delta(\omega_{n0} - \omega)$$

$$\times Re[(\omega_{j0} - i\Gamma_j/2 - \omega)^{-1}]$$

$$+ \sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r})|n\rangle\langle n|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r}')|0\rangle \delta(\omega_{n0} - \omega)$$

$$\times Re[(\omega_{j0} - i\Gamma_j/2 - \omega)^{-1}]$$

$$- \sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|j\rangle\langle j|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|n\rangle\langle n|\hat{\rho}(\mathbf{r})|0\rangle \delta(\omega_{n0} + \omega)$$

$$\times Re[(\omega_{j0} + i\Gamma_j/2 + \omega)^{-1}]$$

$$- \sum_{n\neq 0} \sum_{j\neq 0} \langle 0|\hat{\rho}(\mathbf{r}')|n\rangle\langle n|\hat{\rho}(\mathbf{r}'') - \rho_{00}(\mathbf{r}'')|j\rangle\langle j|\hat{\rho}(\mathbf{r})|0\rangle \delta(\omega_{n0} + \omega)$$

$$\times Re[(\omega_{j0} + i\Gamma_j/2 + \omega)^{-1}]\}. \qquad \text{(A.9)}$$

A comparison of Eq. (A.9) and $\zeta''(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0)$ yields

$$\nabla^K \chi''(\mathbf{r},\mathbf{r}';\omega) = (4\pi\varepsilon_0)^{-1} \int d\mathbf{r}''\, Z^K \nabla^K \left|\mathbf{r}'' - \mathbf{R}^K\right|^{-1} \zeta''(\mathbf{r},\mathbf{r}',\mathbf{r}'';\omega,0). \qquad \text{(A.10)}$$

Appendix B: Derivation of the four-body irreducible dispersion energy for the cluster of four interacting molecules

In this section we derive the four-body irreducible dispersion energy of a cluster of interacting molecules A···B···C···D using the reaction field approach. We derive the dispersion energy as an integral over frequencies, where the integrand is factored into the charge-density susceptibilities of the interacting molecules at imaginary frequencies.

The charge density fluctuation $\delta\rho^{A}(\mathbf{r}';\omega)$ in molecule A at $\mathbf{r}'$ produces a fluctuating potential that propagates through the surrounding molecules inducing transient changes in their charge densities. The potential which acts back on molecule A at $\mathbf{r}$ and time t is the reaction potential, and it's given by

$$\delta\varphi^{A}(\mathbf{r};\omega) = (4\pi\varepsilon_0)^{-4}\,\mathcal{S}_{BCD}\int d\mathbf{r}'...d\mathbf{r}^{vii}\left|\mathbf{r}-\mathbf{r}^{vii}\right|^{-1}\chi^{D}(\mathbf{r}^{vii},\mathbf{r}^{vi};\omega)$$

$$\times\left|\mathbf{r}^{vi}-\mathbf{r}^{v}\right|^{-1}\chi^{C}(\mathbf{r}^{v},\mathbf{r}^{iv};\omega)\left|\mathbf{r}^{iv}-\mathbf{r}'''\right|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}'';\omega)\left|\mathbf{r}''-\mathbf{r}'\right|^{-1}\delta\rho^{A}(\mathbf{r}';\omega). \tag{B.1}$$

The operator $\mathcal{S}_{BCD}$ denotes the sum of the terms obtained by permuting the labels B, C, and D in the expression that follows the operator. The average energy shift of molecule A due to the interaction between the fluctuating potential $\delta\varphi^{A}(\mathbf{r};t)$ and the charge density fluctuation $\delta\rho^{A}(\mathbf{r};t)$ is

$$\Delta E^{A} = (1/2)\int d\mathbf{r}\left\langle \delta\rho^{A}(\mathbf{r},t)\delta\varphi^{A}(\mathbf{r},t)\right\rangle. \tag{B.2}$$

From Eqs. (B.1) and (B.2) along with the Fourier transforms of the charge-density fluctuation and the potential, we obtain

$$\Delta E^{A} = (1/2)(4\pi\varepsilon_0)^{-4} \boldsymbol{S}_{BCD} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \int dr...dr^{vii} \left\langle \delta\rho^{A}(\mathbf{r},\omega') \left| \mathbf{r} - \mathbf{r}^{vii} \right|^{-1} \right.$$

$$\times \chi^{D}(\mathbf{r}^{vii},\mathbf{r}^{vi};\omega) \left| \mathbf{r}^{vi} - \mathbf{r}^{v} \right|^{-1} \chi^{C}(\mathbf{r}^{v},\mathbf{r}^{iv};\omega) \left| \mathbf{r}^{iv} - \mathbf{r}''' \right|^{-1} \chi^{B}(\mathbf{r}''',\mathbf{r}'';\omega)$$

$$\left. \times |\mathbf{r}'' - \mathbf{r}'|^{-1} \delta\rho^{A}(\mathbf{r}',\omega) \right\rangle_{+} \exp[-i(\omega+\omega')t. \qquad \text{(B.3)}$$

The charge density fluctuations $\delta\rho^{A}(\mathbf{r},\omega')$ and $\delta\rho^{A}(\mathbf{r}',\omega)$ are correlated by the fluctuation-dissipation theorem[137]

$$(1/2)\left\langle \delta\rho^{A}(\mathbf{r},\omega')\delta\rho^{A}(\mathbf{r}',\omega) + \delta\rho^{A}(\mathbf{r}',\omega)\delta\rho^{A}(\mathbf{r},\omega') \right\rangle$$

$$= -(\hbar/2\pi)\chi^{A''}(\mathbf{r},\mathbf{r}';\omega)\delta(\omega+\omega')\coth(\hbar\omega/2kT). \qquad \text{(B.4)}$$

Substituting (B.4) in (B.3) and integrating over ω', we obtain

$$\Delta E^{A} = -(1/2)(\hbar/2\pi)(4\pi\varepsilon_0)^{-4} \boldsymbol{S}_{BCD} \int_{-\infty}^{\infty} d\omega \int dr...dr^{vii} \left| \mathbf{r} - \mathbf{r}^{vii} \right|^{-1} \chi^{D}(\mathbf{r}^{vii},\mathbf{r}^{vi};\omega)$$

$$\times \left| \mathbf{r}^{vi} - \mathbf{r}^{v} \right|^{-1} \chi^{C}(\mathbf{r}^{v},\mathbf{r}^{iv};\omega) \left| \mathbf{r}^{iv} - \mathbf{r}''' \right|^{-1} \chi^{B}(\mathbf{r}''',\mathbf{r}'';\omega)$$

$$\times |\mathbf{r}'' - \mathbf{r}'|^{-1} \chi^{A''}(\mathbf{r}',\mathbf{r};\omega)\coth(\hbar\omega/2kT). \qquad \text{(B.5)}$$

In the limit $T \rightarrow 0$, the hyperbolic cotangent function simplifies to $[\theta(\omega) - \theta(-\omega)]$, where $\theta(\omega)$ is the Heaviside step function (cf. chapter 3). Thus, in the limit $T \rightarrow 0$,

$$\Delta E^{A} = -(1/2)(\hbar/2\pi)(4\pi\varepsilon_0)^{-4} \boldsymbol{S}_{BCD}\, Re \int_{-\infty}^{\infty} d\omega \int dr...dr^{vii} \left| \mathbf{r} - \mathbf{r}^{vii} \right|^{-1}$$

$$\times \chi^{D}(\mathbf{r}^{vii},\mathbf{r}^{vi};\omega) \left| \mathbf{r}^{vi} - \mathbf{r}^{v} \right|^{-1} \chi^{C}(\mathbf{r}^{v},\mathbf{r}^{iv};\omega) \left| \mathbf{r}^{iv} - \mathbf{r}''' \right|^{-1} \chi^{B}(\mathbf{r}''',\mathbf{r}'';\omega)$$

$$\times |\mathbf{r}'' - \mathbf{r}'|^{-1} \chi^{A''}(\mathbf{r}',\mathbf{r};\omega), \qquad \text{(B.6)}$$

where *Re* denotes the real part of the expression that follows. Using the Kramers-Kronig relation between the real and the imaginary parts of the charge-density susceptibility,

$$\chi'(\mathbf{r},\mathbf{r}';\omega) = (1/\pi)P\int_{-\infty}^{\infty} dx\,\chi''(\mathbf{r},\mathbf{r}';x)(x-\omega)^{-1} \tag{B.7}$$

(where *P* denotes the Cauchy principal value of the integral) we can write the charge-density susceptibility as

$$\begin{aligned}\chi(\mathbf{r},\mathbf{r}';\omega) &= \chi'(\mathbf{r},\mathbf{r}';\omega)+i\chi''(\mathbf{r},\mathbf{r}';\omega)\\ &= (1/\pi)P\int_{-\infty}^{\infty} dx\,\chi''(\mathbf{r},\mathbf{r}';x)(x-\omega)^{-1}+i\int_{-\infty}^{\infty} dx\,\delta(x-\omega)\chi''(\mathbf{r},\mathbf{r}';x)\\ &= \lim_{\xi\to 0}(1/\pi)\int_{-\infty}^{\infty} dx\,\chi''(\mathbf{r},\mathbf{r}';\omega)(x-\omega-i\xi)^{-1}.\end{aligned} \tag{B.8}$$

In deriving Eq. (B.8), we have used the identity given in Eq. (A.8). From Eq. (B.8) and the fact that $\chi''(\mathbf{r},\mathbf{r}';\omega)$ is an odd function of frequency, we obtain

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \lim_{\xi\to 0}(2/\pi)\int_{-\infty}^{\infty} dx\,x\chi''(\mathbf{r},\mathbf{r}';x)[x^2-(\omega+i\xi)^2]^{-1}. \tag{B.9}$$

We use Eq. (B.9) in Eq. (B.6), take the sum $\Delta E^A+\Delta E^B+\Delta E^C+\Delta E^D$ in the limit $\xi\to 0$, and then use the symmetry of the charge-density susceptibility with respect to interchange of its arguments, to obtain

$$\Delta E_d^{(4,4)} = -(3\hbar/2\pi^4)(4\pi\varepsilon_0)^{-4}\int_{-\infty}^{\infty} du\int_{-\infty}^{\infty} dx\int_{-\infty}^{\infty} dy\int_{-\infty}^{\infty} dz\int d\mathbf{r}...d\mathbf{r}^{\mathbf{vii}}$$

$$\{[uxy(u^2-z^2)^{-1}(x^2-z^2)^{-1}(y^2-z^2)^{-1}]+[xyz(x^2-u^2)^{-1}(y^2-u^2)^{-1}(z^2-u^2)^{-1}]$$

$$+[uyz(u^2-x^2)^{-1}(y^2-x^2)^{-1}(z^2-x^2)^{-1}]+[uxz(u^2-y^2)^{-1}(x^2-y^2)^{-1}(z^2-y^2)^{-1}]\}$$

$$\times\left|\mathbf{r}-\mathbf{r}^{\mathbf{vii}}\right|^{-1}\chi^{D''}(\mathbf{r}^{\mathbf{vii}},\mathbf{r}^{\mathbf{vi}};z)\left|\mathbf{r}^{\mathbf{vi}}-\mathbf{r}^{\mathbf{v}}\right|^{-1}\chi^{C''}(\mathbf{r}^{\mathbf{v}},\mathbf{r}^{\mathbf{iv}};y)\left|\mathbf{r}^{\mathbf{iv}}-\mathbf{r}'''\right|^{-1}$$

$$\times\chi^{B''}(\mathbf{r}''',\mathbf{r}'';x)\left|\mathbf{r}''-\mathbf{r}'\right|^{-1}\chi^{A''}(\mathbf{r}',\mathbf{r};u)\,. \qquad \text{(B.10)}$$

The frequency integral over u, x, y, and z can be separated into independent quadratures using the identity

$$[uxy(u^2-z^2)^{-1}(x^2-z^2)^{-1}(y^2-z^2)^{-1}]+[xyz(x^2-u^2)^{-1}(y^2-u^2)^{-1}(z^2-u^2)^{-1}]$$

$$+[uyz(u^2-x^2)^{-1}(y^2-x^2)^{-1}(z^2-x^2)^{-1}]+[uxz(u^2-y^2)^{-1}(x^2-y^2)^{-1}(z^2-y^2)^{-1}]$$

$$=(2/\pi)\int_0^\infty d\omega\, u\,x\,y\,z\,[u^2+\omega^2]^{-1}[x^2+\omega^2]^{-1}[y^2+\omega^2]^{-1}[z^2+\omega^2]^{-1}. \qquad \text{(B.11)}$$

Using Eq. (B.11) and in Eq. (B.10) and then using the relation

$$\int_0^\infty dx\,x\,(x^2+\omega^2)^{-1}\chi''(\mathbf{r},\mathbf{r}';x)=(\pi/2)\chi(\mathbf{r},\mathbf{r}';i\omega) \qquad \text{(B.12)}$$

which holds in the limit of infinitesimal damping, we obtain

$$\Delta E_d^{(4,4)}=-\frac{3\hbar}{\pi}(4\pi\varepsilon_0)^{-4}\int_0^\infty d\omega\int d\mathbf{r}...d\mathbf{r}^{\mathbf{vii}}\left|\mathbf{r}-\mathbf{r}^{\mathbf{vii}}\right|^{-1}\chi^{D}(\mathbf{r}^{\mathbf{vii}},\mathbf{r}^{\mathbf{vi}};i\omega)\left|\mathbf{r}^{\mathbf{vi}}-\mathbf{r}^{\mathbf{v}}\right|^{-1}$$

$$\times\chi^{C}(\mathbf{r}^{\mathbf{v}},\mathbf{r}^{\mathbf{iv}};i\omega)\left|\mathbf{r}^{\mathbf{iv}}-\mathbf{r}'''\right|^{-1}\chi^{B}(\mathbf{r}''',\mathbf{r}'';i\omega)$$

$$\times\left|\mathbf{r}''-\mathbf{r}'\right|^{-1}\chi^{A}(\mathbf{r}',\mathbf{r};i\omega)\,. \qquad \text{(B.13)}$$

Eq. (B.13) gives the irreducible four-body dispersion energy at fourth order for the cluster of interacting molecules A···B···C···D.

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