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NONLOCAL POLARIZABILITY DENSITIES AND MOLECULAR SOFTNESS: NEW RESULTS FOR ELECTROMAGNETIC PROPERTIES AND INTERMOLECULAR FORCES

By

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ABSTRACT

NONLOCAL POLARIZABILITY DENSITIES AND MOLECULAR SOFTNESS: NEW RESULTS FOR ELECTROMAGNETIC PROPERTIES AND INTERMOLECULAR FORCES

By

Pao-Hua Liu

By using nonlocal polarizability densities to characterize the changes in electronic charge density induced by molecular interactions, Dr. K. Hunt's group has derived new results for dispersion, induction, and hyperpolarization forces. The first part of this thesis establishes that the nonlocal polarizability density theory meets the fundamental physical requirement for force balance between two interacting molecules A and B, order by order. Force relay plays an important role in this derivation, which stems from the application of Epstein's force theorems: in a stationary state, the total force on the electrons is zero in fixed external fields. Thus when the electronic state adjusts adiabatically to a perturbation, the force of the external field on the n*th* order term in the electronic change density equals the force on the nuclei due to the $(n+1)st$ order correction to the electronic charge density.

The second part of this thesis rigorously relates electromagnetic properties and characteristics of molecular potential energy surfaces to the empirical concept of "softness," used to categorize Lewis acids and bases, and to summarize observed patterns of reactivity. New equations are derived that connect infrared absorption intensities, vibrational force constants, intermolecular forces at first order, and linear electric-field shielding tensors to softness kernels as defined in density functional theory. A generalization to nonlinear response--by introduction of the hypersoftness--leads to new equations in density-functional terms for vibrational Raman band intensities, the cubic anharmonicities in molecular potential energy surfaces, intermolecular forces at first and second order, and nonlinear electric-field shielding tensors. The analysis employs relations of the softness and hypersoftness to nonlocal polarizability and hyperpolarizability densities that represent the intramolecular distribution of response to applied electric fields.

My dear God
my parents, Hong-Ko and Chiao-Fong
My brothers, Pao-Min and Pao-Kuo
My friend Xiao deng-deng

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I wish I will have a husband to give my thanks to....

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CHAPTER I

INTRODUCTION

This thesis contains two major parts, the first is concerned with intermolecular forces and force relay, the second is concerned with electromagnetic properties such as force constants, infrared and vibrational Raman band intensities, and nonlinear electric-field shielding tensors. Both parts employ nonlocal polarizability density theory.

As two interacting molecules approach each other, the distributions of charge and polarizability within molecules begin to affect the interaction energy before the electronic charge clouds overlap; hence representation of the molecules as point-polarizable multipoles does not suffice. Distribution effects are expected to be particularly important for large planar or rodlike molecules, in configurations where the distances between nearby, but nonbonded nuclei in the two distinct molecules are smaller than the distances between many of the nonbonded pairs of nuclei in a single molecule. Hunt has developed a theory of molecular interactions that uses nonlocal polarizability densities [1-6] and nonlocal, nonlinear susceptibility densities [6] to incorporate the distribution effects. The nonlocal response tensors $\alpha(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ and $\beta(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega_\sigma, \omega_1, \omega_2)$ determine the intramolecular charge shifts induced by an applied electric field acting on a molecule with a fixed number of electrons N; their values reflect the *distribution* of polarizable matter within a molecule. Within linear response, $\alpha(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ gives the ω-frequency component of the polarization $\mathbf{P}(\mathbf{r}, \omega)$ induced at point $\mathbf{r}$ in the molecule, due to an external field $\mathfrak{I}^{ext}(\mathbf{r}', \omega)$ acting at point $\mathbf{r}'$. The lowest-order hyperpolarizability density $\beta(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega_\sigma, \omega_1, \omega_2)$ gives the ω_σ-frequency polarization induced at $\mathbf{r}$ by the concerted action of the external field $\mathfrak{I}^{ext}(\mathbf{r}', \omega_1)$ at $\mathbf{r}'$ and $\mathfrak{I}^{ext}(\mathbf{r}'', \omega_2)$ at $\mathbf{r}''$, with

$\omega_\sigma = \omega_1 + \omega_2$. Thus, when an external field $\mathfrak{F}^{\text{ext}}(\mathbf{r}, \omega)$ is applied to a molecule, the electronic polarization $\mathbf{P}^{\text{ind}}(\mathbf{r}, \omega)$ induced in the molecule satisfies

$$\begin{aligned}
\mathbf{P}(\mathbf{r}, \omega) &= \mathbf{P}_0(\mathbf{r}, \omega) + \mathbf{P}^{\text{ind}}(\mathbf{r}, \omega) \\
&= \mathbf{P}_0(\mathbf{r}, \omega) + \int d\mathbf{r}' \alpha(\mathbf{r}, \mathbf{r}'; -\omega, \omega) \cdot \mathfrak{F}^{\text{ext}}(\mathbf{r}', \omega) \\
&\quad + \frac{1}{2}\int_{-\infty}^{\infty} d\omega' \int d\mathbf{r}' d\mathbf{r}'' \beta(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega, \omega - \omega', \omega') : \mathfrak{F}^{\text{ext}}(\mathbf{r}', \omega - \omega') \mathfrak{F}^{\text{ext}}(\mathbf{r}'', \omega') \\
&\quad + \dots . \qquad (1)
\end{aligned}$$

The polarization $\mathbf{P}^{\text{ind}}(\mathbf{r}, \omega)$ is related to $\rho^{\text{ind}}(\mathbf{r}, \omega)$, the induced change in electronic charge density in the field $\mathfrak{F}^{\text{ext}}(\mathbf{r}, \omega)$, by

$$\nabla \cdot \mathbf{P}^{\text{ind}}(\mathbf{r}, \omega) = -\rho^{\text{ind}}(\mathbf{r}, \omega) . \qquad (2)$$

One purpose of the first part of this thesis, Chapters II and III, is to prove that the forces on interacting molecules A and B are equal and opposite, order by order, within the nonlocal polarizability density theory. An explicit proof is needed because of the differences in the molecular properties that determine the forces on A and B, at each order in the interaction. For example, the first-order force on nuclei in A depends on the unperturbed charge density $\rho_0^B(\mathbf{r})$ of molecule B and on the first-order change $\rho_1^{e,A}(\mathbf{r})$ in the electronic charge density of molecule A [7]; thus it depends on the polarizability density of A. In contrast, the first-order force on nuclei in B depends on $\rho_0^A(\mathbf{r})$ and $\rho_1^{e,B}(\mathbf{r})$, and hence on the polarizability density of B; but for distinct species A and B, there is no relation between $\alpha^A(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ and $\alpha^B(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$. As a second example, the dispersion force on nuclei in A depends solely on the second-order, dispersion-induced change

$\rho_{2d}^{e,A}(\mathbf{r})$ in the electronic charge density of molecule A, while the force on nuclei in B depends on $\rho_{2d}^{e,B}(\mathbf{r})$ alone [8]. The quantity $\rho_{2d}^{e,A}(\mathbf{r})$ is determined by the hyperpolarizability density of molecule A; similarly for B [8], and the nonlinear susceptibilities of distinct species are unrelated. Identical results for the forces at each order can be obtained by differentiation of the standard perturbation expression for interation energies, or by use of the Hellmann-Feynman theorem [9,10] for intermolecular forces [7, 8, 11]; therefore, the analysis given here has general applicability beyond the nonlocal response theory.

Hunt and I [12] have found that force balance is derivable from "force relay," a physical effect occurring when the electronic state of a molecule or group of molecules adjusts adiabatically to perturbations [13]. When a fixed external field $\mathfrak{I}^{ext}(\mathbf{r})$ acts on a molecule, the force that $\mathfrak{I}^{ext}(\mathbf{r})$ exerts on the *n*th order term $\rho_n^e(\mathbf{r})$ in the electronic charge density is relayed in full to the nuclei by the (*n*+1)st order change $\rho_{n+1}^e(\mathbf{r})$ [13]. If the external field itself varies as the electronic charge density changes—for example, due to molecular interactions—force relay takes a modified form. The change $\Delta\mathbf{F}_n^{ext}$ in the external force on the electrons is passed on to the nuclei by the (*n*+1)st order change in the electronic charge density; here

$$\Delta\mathbf{F}_n^{ext} = \sum_{k=0}^{n} \langle \Psi_k \,|\int d\mathbf{r}\hat{\rho}^{e}(\mathbf{r})\hat{\mathfrak{I}}^{ext}(\mathbf{r})\,|\,\Psi_{n-k}\rangle. \tag{3}$$

In Eq. (3), Ψ_k is the *k*th order term in the normalized, perturbed wave function, including the field source, and $\hat{\rho}^{e}(\mathbf{r})$ and $\hat{\mathfrak{I}}^{ext}(\mathbf{r})$ are operators. For fixed external fields, the force relay condition has been stated previously by Epstein [13]. Chapters II and III generalize the condition to cases in which the electronic charge density and the perturbing field are correlated.

In Chapter II, the results from the nonlocal polarizability density theory for the first- and second-order forces on the nuclei in interacting molecules A and B [7, 8, 11] are summarized throughout Sections 2.1 to 2.3 and the need for an explicit proof of force balance at each order is shown. The key equations related to the adiabatic approximation are derived in Section 2.5 within the nonlocal polarizability density theory.

In Chapter III, the force relay condition based on Epstein's force theorem [13] is introduced in the first section. Section 3.2 proves that the force relay condition is satisfied within the nonlocal polarizability density theory, for fixed external fields. This is a consequence of interconnections among permanent charge densities, linear response, and nonlinear response that Hunt's group has derived earlier [14, 15]. Section 3.3 generalizes force relay to variable external fields and shows that force balance is a consequence, within the nonlocal response theory.

Chapters IV and V link a set of molecular properties including infrared intensities, electric-field shielding tensors, and harmonic force constants to softness [16] as defined in density functional theory [17, 18]. Expressions for these molecular properties have been derived previously [14, 19] in terms of nonlocal polarizability densities $\alpha(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$. Here, the connection to molecular softness is established by relating $\alpha(\mathbf{r}, \mathbf{r}'; 0, 0)$ to the softness kernel $s(\mathbf{r}, \mathbf{r}')$ [16]. A similar relation between the hyperpolarizability density and a "hypersoftness" $\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ is introduced in this work, in order to express vibrational Raman band intensities, nonlinear shielding tensors, and cubic anharmonicity constants in density functional terms. New connections are also established between $s(\mathbf{r}, \mathbf{r}')$, $\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, and long-range intermolecular forces.

Within density functional theory, the softness kernel and the hypersoftness characterize the response of the electronic charge density to external perturbations. These functions quantify [16, 20-24] the concepts of chemical hardness and softness used by Pearson [25, 26] to categorize Lewis acids and bases. Empirically, numerous reactivity patterns are summarized by the statement that hard acids "prefer" to react with hard bases, both thermodynamically and kinetically [26-27]. Typically, soft acids are large and highly polarizable species, with low positive charges. Soft bases are highly polarizable, easily oxidized, and low in electronegativity. The opposite properties hold for hard acids and bases [25, ance at each order is shown. The key equations related to the adiabatic approximation are derived in Section 2.5 within the nonlocal polarizability density theory.

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The first section in Chapter IV is a general introduction of density functional theory and the concepts of chemical hardness and softness. In Section 4.2, the softness and hypersoftness kernels which also describe nonlocal response to external fields are related to the nonlocal susceptibilities $\alpha(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ [1-5] and $\beta(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega_\sigma, \omega_1, \omega_2)$ [6]; the softness kernel is further generalized to a frequency-dependent form.

The relation between harmonic force constants and the softness kernel $s(\mathbf{r}, \mathbf{r}')$ is derived in Section 5.1, which also shows that the cubic anharmonicity constants and the intensities of vibrational Raman bands depend on $s(\mathbf{r}, \mathbf{r}')$ and $\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ within the Placzek approximation [28]. In Section 5.2, the softness kernel $s(\mathbf{r}, \mathbf{r}')$ is related to the derivative of the molecular dipole with respect to a shift in nuclear coordinates; thus the softness determines both infrared absorption frequencies (within the harmonic approximation) and infrared intensities; and the Sternheimer electric-field shielding tensors [9, 29-33] are also related to the softness and hypersoftness. The Sternheimer shielding tensors give the difference between an external electric field $\mathfrak{F}^{\text{ext}}$ applied to a molecule and the *effective* field that acts at the nuclei, because these tensors account for the shielding or deshielding effects of the electronic redistribution induced by $\mathfrak{F}^{\text{ext}}$.

In Section 5.3, long-range intermolecular forces are treated in the density-functional framework. Earlier, Gázquez has expressed the second-order induction energy in terms of the softness kernel [34]; here it is proven that the force at *first order* depends on the softness kernel and the force at *second order* depends on the softness and hypersoftness. In Section 5.3, the dispersion energy is analyzed in terms of an imaginary-frequency dependent softness kernel, $s(\mathbf{r}, \mathbf{r}'; -i\omega, i\omega)$.

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CHAPTER II

INTERMOLECULAR FORCES WITHIN NONLOCAL POLARIZABILITY DENSITY THEORY

2.1 Nonlocal Polarizability Densities

Maaskant and Oosterhoff introduced nonlocal polarizability densities in a study of optical rotation in condensed media [1]. They gave the nonlocal polarizability density in a sum-over-states form, with each matrix element itself given as an infinite series. Hunt [2] derived a simple form that permits practical calculations in cases when the field acting on a molecule is derivable from a scalar potential.

When an external field $\Im^{ext}(\mathbf{r},\omega)$ is applied to a molecule, the electronic polarization $\mathbf{P}^{ind}(\mathbf{r},\omega)$ induced in the molecule satisfies

$$\begin{aligned} \mathbf{P}(\mathbf{r},\omega) &= \mathbf{P}_0(\mathbf{r},\omega) + \mathbf{P}^{ind}(\mathbf{r},\omega) \\ &= \mathbf{P}_0(\mathbf{r},\omega) + \int d\mathbf{r}'\alpha(\mathbf{r},\mathbf{r}';-\omega,\omega)\cdot\Im^{ext}(\mathbf{r}',\omega) \\ &+ \frac{1}{2}\int_{-\infty}^{\infty} d\omega'\int d\mathbf{r}'d\mathbf{r}''\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'';-\omega,\omega-\omega',\omega') : \Im^{ext}(\mathbf{r}',\omega-\omega')\,\Im^{ext}(\mathbf{r}'',\omega') \\ &+ \dots\,. \end{aligned} \tag{1}$$

The polarization $\mathbf{P}^{ind}(\mathbf{r},\omega)$ is related to $\rho^{ind}(\mathbf{r},\omega)$, the induced change in electronic charge density in the field $\Im^{ext}(\mathbf{r},\omega)$, by

$$\nabla \cdot \mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega) = -\rho^{\mathrm{ind}}(\mathbf{r}, \omega), \tag{2}$$

and the same relationship holds for the polarization and charge density operators. From Eq. (1) one can see that the nonlocal polarizability density $\alpha(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ determines the electronic polarization $\mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega)$ induced at point **r** in a molecule by an external electric field of frequency ω acting at $\mathbf{r}'$, within linear response. It is a fundamental molecular property which reflects the *distribution* of polarizable matter within the molecule. The polarizability density for a molecule in the ground state has the form

$$\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; -\omega, \omega) = \langle 0 | \mathbf{P}_\alpha(\mathbf{r})\, G(\omega)\, \mathbf{P}_\beta(\mathbf{r}') | 0 \rangle + \langle 0 | \mathbf{P}_\beta(\mathbf{r}')\, G(-\omega)\, \mathbf{P}_\alpha(\mathbf{r}) | 0 \rangle, \tag{3}$$

where $G(\omega)$ is the reduced resolvent operator

$$G(\omega) = (1 - \wp_0)\,(H - E_0 - \hbar\omega)^{-1}\,(1 - \wp_0), \tag{4}$$

and $\wp_0$ is the ground-state projection operator $| 0 \rangle \langle 0 |$.

Hunt [3] has shown that $\alpha(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ also determines the net field $\mathfrak{I}^{\mathrm{I}}$ acting on nucleus I of a molecule in a static, external field $\mathfrak{I}^{\mathrm{ext}}(\mathbf{r})$:

$$\mathfrak{I}^{\mathrm{I}} = \mathfrak{I}^{\mathrm{I}(0)} + \mathfrak{I}^{\mathrm{ext}}(\mathbf{R}^{\mathrm{I}}) + \int d\mathbf{r}\, d\mathbf{r}'\, T(\mathbf{R}^{\mathrm{I}}, \mathbf{r}) \cdot \alpha(\mathbf{r}, \mathbf{r}'; 0, 0) \cdot \mathfrak{I}^{\mathrm{ext}}(\mathbf{r}') + \ldots. \tag{5}$$

where $\mathfrak{I}^{\mathrm{I}(0)}$ is the field at nucleus I in the absence of the external perturbation, and $T_{\alpha\beta}(\mathbf{R}^{\mathrm{I}}, \mathbf{r})$ is the dipole propagator, i.e.,

$$T_{\alpha\beta}(\mathbf{R}^{\mathrm{I}}, \mathbf{r}) = \nabla_\alpha \nabla_\beta \left| \mathbf{R}^{\mathrm{I}} - \mathbf{r} \right|^{-1}$$

$$= \left[3\,(\mathbf{R}^{\mathrm{I}}-\mathbf{r})_{\alpha}(\mathbf{R}^{\mathrm{I}}-\mathbf{r})_{\beta}-\delta_{\alpha\beta}|\mathbf{R}^{\mathrm{I}}-\mathbf{r}|^{2}\right]/|\mathbf{R}^{\mathrm{I}}-\mathbf{r}|^{5}-\frac{4\pi}{3}\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{R}^{\mathrm{I}})\,. \quad (6)$$

The hyperpolarizability density $\beta(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega, \omega-\omega', \omega')$ represents the nonlinear response of lowest order; it gives the ω-frequency polarization induced at **r** by the concerted action of the external fields $\mathfrak{I}^{\mathrm{ext}}(\mathbf{r}', \omega-\omega')$ at $\mathbf{r}'$ and $\mathfrak{I}^{\mathrm{ext}}(\mathbf{r}'', \omega')$ at $\mathbf{r}''$. Perturbation analysis gives the hyperpolarizability density in the form

$$\begin{aligned}
&\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega_\sigma, \omega_1, \omega_2) \\
&\quad = \wp_{\beta\gamma}\,[\,\langle 0\,|\,\mathbf{P}_\alpha(\mathbf{r})\,G(\omega_\sigma)\,\mathbf{P}^{\emptyset}{}_\gamma(\mathbf{r}'')\,G(\omega_1)\,\mathbf{P}_\beta(\mathbf{r}')\,|\,0\,\rangle \\
&\qquad + \langle 0\,|\,\mathbf{P}_\gamma(\mathbf{r}'')\,G(-\omega_2)\,\mathbf{P}^{\emptyset}{}_\beta(\mathbf{r}')\,G(-\omega_\sigma)\,\mathbf{P}_\alpha(\mathbf{r})\,|\,0\,\rangle \\
&\qquad + \langle 0\,|\,\mathbf{P}_\gamma(\mathbf{r}'')\,G(-\omega_2)\,\mathbf{P}^{\emptyset}{}_\alpha(\mathbf{r})\,G(\omega_1)\,\mathbf{P}_\beta(\mathbf{r}')\,|\,0\,\rangle\,], \qquad (7)
\end{aligned}$$

where the operator $\wp_{\beta\gamma}$ denotes the sum of all terms obtained by permuting $\mathbf{P}_\beta(\mathbf{r}')$ and $\mathbf{P}_\gamma(\mathbf{r}'')$ and simultaneously permuting the associated frequencies ω_1 and ω_2, in the expression following the operator; and $\omega_\sigma = \omega_1 + \omega_2$. The operator $\mathbf{P}^{\emptyset}{}_\alpha(\mathbf{r})$ is defined by $\mathbf{P}^{\emptyset}{}_\alpha(\mathbf{r}) = \mathbf{P}_\alpha(\mathbf{r}) - \langle 0\,|\,\mathbf{P}_\alpha(\mathbf{r})\,|\,0\,\rangle$.

The tensor densities $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ and $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega_\sigma, \omega_1, \omega_2)$ both represent the *distribution* of polarizable matter on the intramolecular scale. $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ has applications in theories of local fields and light scattering in condensed media [4], and in approximations for dispersion energies [2], collision-induced dipoles, and collision-induced polarizabilities [2, 5] of molecules interacting at intermediate range. $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega_\sigma, \omega_1, \omega_2)$ and the dipole propagator determine the derivatives of the polarizability density with respect to nuclear coordinates [3, 6],

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

$$\times Z^{I}\, T_{\delta\alpha}(\mathbf{r}'', \mathbf{R}^{I})\,. \tag{8}$$

where Z^I is the charge on nucleus I, and $\mathbf{R}^I$ is the nuclear position. An analogous equation also holds for any two adjacent-order polarizability densities.

The higher-order nonlocal polarizability densities can be expressed in terms of a general nth order nonlocal susceptibility density $\chi^{(n)}$ defined by [2]

$$\chi^{(n)}_{\alpha_1\alpha_2\ldots\alpha_{n+1}}(\mathbf{r},\mathbf{r}',\ldots,\mathbf{r}^{(n)\prime};-\omega;\omega-\omega'-\ldots\omega^{(n-1)\prime},\omega',\omega'',\ldots,\omega^{n-1\prime})$$

$$= \frac{1}{\hbar^{n}} S \sum_{l_1 l_2 \ldots l_n} \frac{\left[\mathbf{P}_{\alpha_1}(\mathbf{r})\right]_{0 l_1}\left[\mathbf{P}_{\alpha_2}(\mathbf{r}')\right]_{l_1 l_2}\cdots\left[\mathbf{P}_{\alpha_{n+1}}(\mathbf{r}^{(n)\prime})\right]_{l_n 0}}{(\omega_{l_1 0}-\omega)\,(\omega_{l_2 0}-\omega'-\omega''-\ldots\omega^{(n-1)\prime})\ldots(\omega_{l_n 0}-\ldots\omega^{(n-1)\prime})}, \tag{9}$$

In Eq. (9), the sum over intermediate *states* $l_1,l_2,\ldots,l_n$ runs over all electronic states including the ground state, and S represents the sum of all terms generated by permuting $\mathbf{P}_{\alpha_1}(\mathbf{r})$, $\mathbf{P}_{\alpha_2}(\mathbf{r}')\ldots$, $\mathbf{P}_{\alpha_{n+1}}(\mathbf{r}^{n\prime})$ and applying the same permutation to the frequencies $-\omega;\omega-\omega'-\ldots\omega^{(n-1)\prime},\omega',\omega'',\ldots,\omega^{n-1\prime}$ in the expression given.

2.2 The Interaction Energy

When molecules A and B interact, the net force $\mathbf{F}^I$ on nucleus I in A is the sum of the force $\mathbf{F}^{I(0)}$ on I in the absence of molecule B and an interaction force $\Delta\mathbf{F}^I$. The interaction-induced force is related to the AB interaction energy ΔE by

$$\Delta \mathbf{F}^{I}{}_{\alpha} = -\partial \Delta E / \partial \mathbf{R}^{I}{}_{\alpha}, \tag{1}$$

where $\mathbf{R}^I$ is the position of nucleus I. In this section I will show that the first-order and second-order interaction (energy separated into the induction energy and the dispersion energy) can be expressed in terms of nonlocal polarizability densities.

At long range, perturbation techniques are suited for calculating the interaction energy order by order [7]. In Rayleigh-Schrödinger theory the interaction energy ΔE can be expanded as a series in the perturbation Hamiltonian H′ [2, 8-12]. For molecules interacting without appreciable charge-cloud overlap, H′ is given by

$$H' = \int \hat{\rho}^{A}(\mathbf{r})\, \hat{\rho}^{B}(\mathbf{r}')\, |\mathbf{r} - \mathbf{r}'|^{-1} d\mathbf{r}\, d\mathbf{r}', \tag{2}$$

where $\hat{\rho}^{A}(\mathbf{r})$ and $\hat{\rho}^{B}(\mathbf{r}')$ are the charge density operators for molecules A and B, respectively;

$$\hat{\rho}^{A}(\mathbf{r}) = \sum_{j} e\,\delta(\mathbf{r} - \mathbf{r}_j) + \sum_{I} Z^{I} \delta(\mathbf{r} - \mathbf{R}^{I}); \tag{3}$$

the sum over j runs over the electrons assigned to molecule A, with position operators $\mathbf{r}_j$, and the sum over I runs over nuclei in A with charges Z^I and positions $\mathbf{R}^I$.

The first-order interaction energy $\Delta E^{(1)}$ depends upon the permanent charge densities $\rho^A{}_0(\mathbf{r})$ and $\rho^B{}_0(\mathbf{r}')$ of the unperturbed A and B molecules:

$$\Delta E^{(1)} = \langle \Psi_0 | H' | \Psi_0 \rangle$$

$$= \int \rho^A{}_0(\mathbf{r})\,\rho^B{}_0(\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1}\,d\mathbf{r}\,d\mathbf{r}', \tag{4}$$

where Ψ_0 is the product of the unperturbed molecular wave functions of A and B, and

$$\rho^A{}_0(\mathbf{r}) = \langle \Psi^A_0 | \rho^A(\mathbf{r}) | \Psi^A_0 \rangle. \tag{5}$$

The change of energy for the system at second order is

$$\begin{aligned}
\Delta E^{(2)} = &-\sum_{k\neq g} \langle \Psi^A_g \Psi^B_g | H' | \Psi^A_k \Psi^B_g \rangle \langle \Psi^A_k \Psi^B_g | H' | \Psi^A_g \Psi^B_g \rangle / (E^A_k - E^A_g) \\
&-\sum_{u\neq g} \langle \Psi^A_g \Psi^B_g | H' | \Psi^A_g \Psi^B_u \rangle \langle \Psi^A_g \Psi^B_u | H' | \Psi^A_g \Psi^B_g \rangle / (E^B_u - E^B_g) \\
&-\sum_{u,k\neq g} \langle \Psi^A_g \Psi^B_g | H' | \Psi^A_k \Psi^B_u \rangle \langle \Psi^A_k \Psi^B_u | H' | \Psi^A_g \Psi^B_g \rangle / \left[(E^A_k - E^A_g) + (E^B_u - E^B_g) \right]
\end{aligned} \tag{6}$$

The first term of the second-order perturbation energy corresponds to the permanent moments of B polarizing A. The induced moments of A then interact with the permanent moments of B. The second term corresponds to the permanent moments of A polarizing B. The third term corresponds to the second-order dispersion energy. The total interaction energy for molecules at long range is the sum of the induction energy $\Delta E^{(2)}{}_{\mathrm{ind}}$ (the first and second terms) and the dispersion energy $\Delta E^{(2)}{}_{\mathrm{disp}}$ (the third term). The induction energy is determined entirely by the first-order, linear response of each molecule to the field of its neighbor. The dispersion (van der Waals) energy results from dynamic reaction field effects, due to correlations of the spontaneous, quantum mechanical fluctuations in charge density on the interacting molecules [2, 8-12]. By using the definition of the nonlocal polarizability densities the first two terms can be rewritten as:

$$\begin{aligned}\Delta E^{(2)}_{\mathrm{ind}} &= -1/2\int d\mathbf{r}\,d\mathbf{r}'\,\alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\,\mathfrak{I}^{B}_{0\alpha}(\mathbf{r})\,\mathfrak{I}^{B}_{0\beta}(\mathbf{r}')\\ &\quad -1/2\int d\mathbf{r}\,d\mathbf{r}'\,\alpha^{B}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\,\mathfrak{I}^{A}_{0\alpha}(\mathbf{r})\,\mathfrak{I}^{A}_{0\beta}(\mathbf{r}')\,, \qquad (7)\end{aligned}$$

where $\mathfrak{I}^{A}_{0\alpha}(\mathbf{r})$ is the α component of the unperturbed field of molecule A and $\alpha_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ denotes the static susceptibility $\alpha_{\alpha\beta}(\mathbf{r},\mathbf{r}';0,0)$. The third term can be written as

$$\begin{aligned}\Delta E^{(2)}_{\mathrm{disp}} &= -(h/4\pi^{2})\int_{0}^{\infty}d\omega\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,\alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}''';-i\omega,i\omega)\\ &\quad\times\alpha^{B}_{\gamma\delta}(\mathbf{r}'',\mathbf{r}';-i\omega,i\omega)\,T_{\alpha\delta}(\mathbf{r},\mathbf{r}')\,T_{\gamma\beta}(\mathbf{r}'',\mathbf{r}''')\,. \qquad (8)\end{aligned}$$

Equation (8) is equivalent to that obtained from reaction-field theory [2, 13-15] and the fluctuation-dissipation theorem [8, 9, 16-23]

2.3 Intermolecular Forces Obtained from Nonlocal Polarizability Densities

For interacting molecules with weak or negligible electronic overlap, within the Born-Oppenheimer approximation, the forces acting on nuclei derived from the Hellmann-Feynman theorem are equivalent order by order to those obtained from standard perturbation expressions for the interaction energy [see Section 2.2] by differentiating with respect to nuclear coordinates [24-26].

At first order, the force $\Delta \mathbf{F}^{I}_{1,\alpha}$ on nucleus I in molecule A is determined by

$$\begin{aligned} \Delta \mathbf{F}^{I}_{1,\alpha} &= -\partial \Delta E^{(1)} / \partial \mathbf{R}^{I}_{\alpha} \\ &= -\int \frac{\partial \rho^{A}_{0}(\mathbf{r})}{\partial \mathbf{R}^{I}_{\alpha}} \rho^{B}_{0}(\mathbf{r}') \, |\mathbf{r} - \mathbf{r}'|^{-1} d\mathbf{r} \, d\mathbf{r}', \end{aligned} \tag{1}$$

where $\rho^{A}_{0}(\mathbf{r})$ and $\rho^{B}_{0}(\mathbf{r}')$ are the expectation values of the charge density operators $\hat{\rho}^{A}(\mathbf{r})$ and $\hat{\rho}^{B}(\mathbf{r}')$ for the unperturbed molecules A and B [see Eq. (2, 2, 3)]

$$\begin{aligned} \hat{\rho}^{A}(\mathbf{r}) &= \hat{\rho}^{e,A}(\mathbf{r}) + \sum_{I} Z^{I} \delta(\mathbf{r} - \mathbf{R}^{I}) \\ &= \sum_{j} e \delta(\mathbf{r} - \mathbf{r}_{j}) + \sum_{I} Z^{I} \delta(\mathbf{r} - \mathbf{R}^{I}), \end{aligned} \tag{2}$$

$\hat{\rho}^{e,A}(\mathbf{r})$ is the electronic charge density operator for molecule A, the second term of the right-hand side of Eq. (2) is the nuclear point charge distribution, the sum over j runs over the electrons assigned to molecule A, with position operators $\mathbf{r}_j$, and the sum over I runs over nuclei in A with charges Z^I and positions $\mathbf{R}^I$.

The differential of the electronic charge density of molecule A is related to the nonlocal polarizability $\alpha^{A}_{\beta\gamma}(\mathbf{r}, \mathbf{r}')$ [3]

$$\frac{\partial \rho^{e,A}{}_{0}(\mathbf{r})}{\partial \mathbf{R}^{I}{}_{\alpha}} = -\frac{\partial \nabla_{\beta} \mathbf{P}_{0,\beta}{}^{e,A}(\mathbf{r})}{\partial \mathbf{R}^{I}{}_{\alpha}}$$

$$= -\nabla_{\beta} Z^{I} \int d\mathbf{r}' \alpha^{A}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\, T_{\gamma\alpha}(\mathbf{r}',\mathbf{R}^{I}), \tag{3}$$

where $T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})$ is the dipole propagator: $T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r}) = \nabla_{\alpha}\nabla_{\beta}\left|\mathbf{R}^{I}-\mathbf{r}\right|^{-1}$. Greek subscripts denote Cartesian tensor components, and the Einstein convention of summation over repeated Greek subscripts is followed throughout. Substitution of Eqs. (2) and (3) into Eq. (1) shows that the first-order force is determined by the unperturbed charge density $\rho^{B}_{0}(\mathbf{r})$ of molecule B, and by the first-order interaction-induced change in the electronic polarization of molecule A, $\mathbf{P}^{e,A}_{1,\beta}(\mathbf{r})$ [24]

$$\Delta \mathbf{F}^{I}_{1,\alpha} = Z^{I} \int (\mathbf{R}^{I}-\mathbf{r})_{\alpha} \left|\mathbf{R}^{I}-\mathbf{r}\right|^{-3} \rho^{B}{}_{0}(\mathbf{r})\, d\mathbf{r}$$

$$+ Z^{I} \int T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\, \mathbf{P}^{e,A}_{1,\beta}(\mathbf{r})\, d\mathbf{r}; \tag{4}$$

where

$$\mathbf{P}^{e,A}_{1,\beta}(\mathbf{r}) = \int d\mathbf{r}' \alpha^{A}{}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\, \mathfrak{I}^{B}_{0,\gamma}(\mathbf{r}'), \tag{5}$$

in terms of the field $\mathfrak{I}^{B}_{0,\gamma}(\mathbf{r}')$ due to the unperturbed charge distribution (electronic and nuclear) of molecule B. Similarly, the first-order force on nucleus J in molecule B depends on $\alpha^{B}_{\beta\gamma}(\mathbf{r},\mathbf{r}')$

$$\Delta \mathbf{F}^{J}_{1,\alpha} = Z^{J} \int (\mathbf{R}^{J}-\mathbf{r})_{\alpha} \left|\mathbf{R}^{J}-\mathbf{r}\right|^{-3} \rho^{A}{}_{0}(\mathbf{r})\, d\mathbf{r}$$

$$+ Z^{J} \int T_{\alpha\beta}(\mathbf{R}^{J},\mathbf{r})\, \mathbf{P}^{e,B}_{1,\beta}(\mathbf{r})\, d\mathbf{r}; \tag{6}$$

and

$$\mathbf{P}^{e,B}_{1,\beta}(\mathbf{r}) = \int d\mathbf{r}'\alpha^{B}{}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\,\Im^{A}_{0,\gamma}(\mathbf{r}') . \tag{7}$$

The net force on molecule A is obtained by summing over I and the net force on B by summing over J. Since the polarizability densities of A and B are unrelated (in general), force balance is not evident from a simple comparison of Eq. (4) with Eq. (6).

At second order, the force is determined by differentiating the second-order interaction energy which is the sum of the induction energy $\Delta E^{(2)}_{ind}$ and the dispersion energy $\Delta E^{(2)}_{disp}$ [see Section 2.2],

$$\begin{aligned}\Delta\mathbf{F}^{I}{}_{2,\alpha} &= -\partial\Delta E^{(2)}/\partial\mathbf{R}^{I}{}_{\alpha}\\ &= -\partial(\Delta E^{(2)}_{ind}+\Delta E^{(2)}_{disp})/\partial\mathbf{R}^{I}{}_{\alpha}\\ &= \Delta\mathbf{F}^{I}{}_{2,\alpha,ind}+\Delta\mathbf{F}^{I}{}_{2,\alpha,disp}.\end{aligned} \tag{8}$$

The second-order induction force is

$$\begin{aligned}\Delta\mathbf{F}^{I}{}_{2,\alpha,ind} = {}& 1/2\int d\mathbf{r}\,d\mathbf{r}'\frac{\partial\alpha^{A}{}_{\beta\gamma}(\mathbf{r},\mathbf{r}')}{\partial\mathbf{R}^{I}{}_{\alpha}}\Im^{B}{}_{0\beta}(\mathbf{r})\,\Im^{B}{}_{0\gamma}(\mathbf{r}')\\ &+1/2\int d\mathbf{r}\,d\mathbf{r}'\alpha^{B}{}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\frac{\partial\left[\Im^{A}{}_{0\beta}(\mathbf{r})\,\Im^{A}{}_{0\gamma}(\mathbf{r}')\right]}{\partial\mathbf{R}^{I}{}_{\alpha}} .\end{aligned} \tag{9}$$

Hunt et al. have shown that linear and nonlinear response are related by [3, 6]

$$\frac{\partial\alpha_{\beta\gamma}(\mathbf{r},\mathbf{r}')}{\partial\mathbf{R}^{I}_{\alpha}} = Z^{I}\int d\mathbf{r}''\beta_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,T_{\delta\alpha}(\mathbf{r}'',\mathbf{R}^{I}) , \tag{10}$$

and the differential of the field of the unperturbed molecule A is

$$\frac{\partial \Im^{A}{}_{0\beta}(\mathbf{r})}{\partial \mathbf{R}^{I}{}_{\alpha}} = -\int d\mathbf{r}' \nabla_{\beta} |\mathbf{r} - \mathbf{r}'| \frac{\partial \rho^{A}{}_{0}(\mathbf{r}')}{\partial \mathbf{R}^{I}{}_{\alpha}}. \tag{11}$$

Substitution of Eqs. (2) and (3) into Eq. (11), and Eqs. (10) and (11) into Eq. (9) shows that the second-order induction force $\Delta\mathbf{F}^{I}{}_{2,\alpha,\mathrm{ind}}$ is determined by $\mathbf{P}^{e,B}_{1,\beta}(\mathbf{r})$ and $\mathbf{P}^{e,A}_{2,\beta,\mathrm{ind}}(\mathbf{r})$ assuming that nucleus I is in molecule A; therefore it depends on $\beta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'')$:

$$\Delta\mathbf{F}^{I}{}_{2,\alpha,\mathrm{ind}} = Z^{I}\int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\left[\mathbf{P}^{e,B}_{1,\beta}(\mathbf{r}) + \mathbf{P}^{e,A}_{2,\beta,\mathrm{ind}}(\mathbf{r})\right], \tag{12}$$

where

$$\begin{aligned}\mathbf{P}^{e,A}_{2,\beta,\mathrm{ind}}(\mathbf{r}) = {} & \int d\mathbf{r}'d\mathbf{r}''d\mathbf{r}'''\alpha^{A}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\,T_{\gamma\delta}(\mathbf{r}',\mathbf{r}'') \\ & \times \alpha^{B}_{\delta\beta}(\mathbf{r}'',\mathbf{r}''')\,\Im^{A}_{0,\beta}(\mathbf{r}''') \\ & + \frac{1}{2}\int d\mathbf{r}'d\mathbf{r}''\beta^{A}_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,\Im^{B}{}_{0\gamma}(\mathbf{r}')\,\Im^{B}{}_{0\delta}(\mathbf{r}'')\,.\end{aligned} \tag{13}$$

The second-order induction force on nucleus J in molecule B has a similar form to Eq. (12),

$$\Delta\mathbf{F}^{J}{}_{2,\alpha,\mathrm{ind}} = Z^{J}\int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^{J},\mathbf{r})\left[\mathbf{P}^{e,A}_{1,\beta}(\mathbf{r}) + \mathbf{P}^{e,B}_{2,\beta,\mathrm{ind}}(\mathbf{r})\right]; \tag{14}$$

Eq. (14) depends on $\beta^{B}(\mathbf{r},\mathbf{r}',\mathbf{r}'')$, but Eq. (12) depends on $\beta^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'')$, so again force balance is not evident.

The dispersion force on nuclei in A comes from the second-order, dispersion-induced change in the electronic polarization of A itself as can be proven by differentiating the second-order dispersion energy with respect to nuclear coordinates;

$$\Delta E^{(2)}{}_{\mathrm{disp}} = -(h/4\pi^2)\int_0^\infty d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, \alpha^A{}_{\alpha\beta}(\mathbf{r},\mathbf{r}''';-i\omega, i\omega)$$

$$\times\, \alpha^B{}_{\gamma\delta}(\mathbf{r}'',\mathbf{r}';-i\omega, i\omega)\, T_{\alpha\delta}(\mathbf{r},\mathbf{r}')\, T_{\gamma\beta}(\mathbf{r}'',\mathbf{r}''')\,. \qquad (15)$$

By use of Eq. (10) generalized to the imaginary-frequency dependent polarizability density, the dispersion force is obtained in the form

$$\Delta \mathbf{F}^I{}_{2,\alpha,\mathrm{disp}} = -\partial \Delta E^{(2)}_{\mathrm{disp}}/\partial \mathbf{R}^I{}_\alpha$$

$$= Z^I \int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r})\, \mathbf{P}^{e,A}_{2,\beta,\mathrm{disp}}(\mathbf{r})\,. \qquad (16)$$

The polarization $\mathbf{P}^{e,A}_{2,\beta,\mathrm{disp}}(\mathbf{r})$ is determined by the field from the fluctuating polarization of molecule B, and by the hyperpolarizability density of A, taken at imaginary frequencies [25]

$$\mathbf{P}^{e,A}_{2,\beta,\mathrm{disp}}(\mathbf{r}) = -(h/4\pi^2)\int_0^\infty d\omega \int d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}$$

$$\times\, \beta^A_{\delta\gamma\beta}(\mathbf{r}',\mathbf{r}'',\mathbf{r};-i\omega, i\omega, 0)\, T_{\gamma\varepsilon}(\mathbf{r}'',\mathbf{r}''')$$

$$\times\, \alpha^B{}_{\varepsilon\zeta}(\mathbf{r}''',\mathbf{r}^{iv};-i\omega, i\omega)\, T_{\zeta\delta}(\mathbf{r}^{iv},\mathbf{r}')\,. \qquad (17)$$

The dispersion force on nuclei J in molecule B can be derived in the same way and has a form similar to Eq. (16),

$$\Delta \mathbf{F}^J{}_{2,\alpha,\mathrm{disp}} = -\partial \Delta E^{(2)}_{\mathrm{disp}}/\partial \mathbf{R}^J{}_\alpha$$

$$= Z^J \int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^J, \mathbf{r})\, \mathbf{P}^{e,\,B}_{2,\,\beta,\,\mathrm{disp}}(\mathbf{r})\,. \tag{18}$$

The polarization $\mathbf{P}^{e,\,B}_{2,\,\beta,\,\mathrm{disp}}(\mathbf{r})$ is determined by the field from the fluctuating polarization of molecule A, and by the hyperpolarizability density of B taken at imaginary frequencies. The hyperpolarizability density of B is unrelated to the hyperpolarizability density of A, in general.

2.4 Adiabatic Approximation

In quantum mechanics an adiabatic process is a process for which the change of the Hamiltonian versus time is sufficiently slow to avoid quantum jumps from one eigenstate of the instantaneous Hamiltonian to another [27, 28]. If the external perturbing potential is small enough that perturbation theory can be used, it is possible to extend this treatment to a more general problem in which the perturbing potential undergoes a large change, but over a long period of time. Bohm [29] derived the condition that a process is adiabatic if the rate of change of the perturbation V is slow compared to the separation ΔE of the initial state from the neighboring states, in the sense that the expectation value of dV/dt must obey $dV/dt \ll (\Delta E)^2/\hbar$.

It is possible to perturb the electronic states of a molecule by slowly bringing another molecule near the first. Davydov [30] has defined an adiabatic collision as follows: if the effective collision time is appreciably larger than the period $\omega^{-1}{}_{nm}$ which characterizes the electronic energy spectrum, the collision is electronically adiabatic; in other words, in an adiabatic collision the inequality $\omega_{nm} D/\upsilon \gg 1$ is satisfied, where D is the distance of closest approach and υ is the velocity of the approaching particle (approximated as constant). In Section 2.3 the adiabatic energies of two molecules are discussed, based on the assumption that the nuclei move sufficiently slowly compared to the electrons that the force between the molecules can be calculated by differentiation of the adiabatic interaction energies [31].

Using the adiabatic approximation, one can assume that the wave function at any instant of time is nearly equal to that which would be obtained if dV/dt were zero, and V were equal to its instantaneous value. Two different approaches can be used to calculate the wavefunctions and the expectation values of forces. The first is based on time-independent perturbation theory with a fixed static external perturbation. The second is based on time-dependent perturbation theory [32], but the nonadiabatic term in the expansion for the wavefunction is subtracted out. Both methods are consistent with the force relay condition [33].

To illustrate the second method, let us suppose that the perturbation *V*(t) acts only during some finite interval of time. Let the system be in the *n*th stationary state before the perturbation begins to act (or in the limit as $t \rightarrow -\infty$). At any subsequent instant the state of the system will be determined by the function $\Psi = \sum a_{kn}\Psi_k^{(0)}$, where, in the first-order time-dependent perturbation approximation,

$$\begin{aligned} a_{kn} &= a_{kn}^{(1)} = -\frac{i}{\hbar}\int_{-\infty}^{t} V_{kn}e^{i\omega_{kn}t'}\,\mathrm{d}t' \qquad \text{for } k \neq n, \\ a_{nn} &= 1 + a_{nn}^{(1)} = 1 - \frac{i}{\hbar}\int_{-\infty}^{t} V_{nn}\,\mathrm{d}t'. \end{aligned} \tag{1}$$

For a perturbation *V*(*t*) that tends to zero as $t \rightarrow -\infty$ and to a finite non-zero limit as $t \rightarrow +\infty$, an integration by parts in Eq. (1) gives

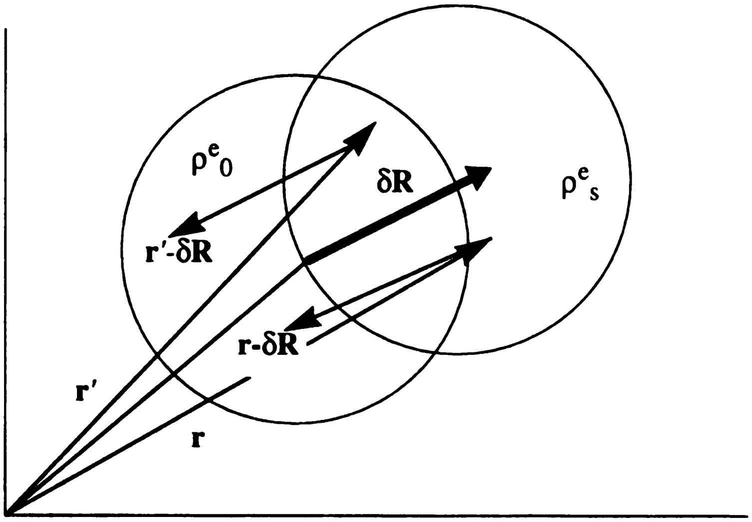
$$a_{kn} = -\frac{i}{\hbar}\int_{-\infty}^{t} V_{kn}e^{i\omega_{kn}t'}\,\mathrm{d}t' = -\left.\frac{V_{kn}e^{i\omega_{kn}t'}}{\hbar\omega_{kn}}\right|_{-\infty}^{t} + \int_{-\infty}^{t} \frac{\partial V_{kn}}{\partial t'}\frac{e^{i\omega_{kn}t'}}{\hbar\omega_{kn}}\,\mathrm{d}t'. \tag{2}$$

The first term vanishes at the lower limit, while at the upper limit it is formally identical with the expansion coefficients in time-independent perturbation theory; the presence of an additional periodic factor $exp(i\omega_{kn}t)$ is merely due to the fact that a_{kn} are the expansion coefficients of the complete wave function Ψ. At any instant of time, the first term simply gives the change in the original wave function $\Psi_n^{(0)}$ under the assumption that *V* is a constant and equal to its instantaneous value, while the second term describes transitions into other states. The magnitude of the second term depends on $\partial V_{kn}/\partial t'$, which can be neglected if it is small enough.

2.5 Rigid Translation

The forces on nuclei in a molecule can be obtained by using the Hellmann-Feynman theorem [34, 35] as well as from standard perturbation theory by differentiation of the interaction energy with respect to nuclear coordinates [24]. Because the interaction energy at different orders within the nonlocal polarizability density theory depends on electronic charge densities, nonlocal polarizability densities, hyperpolarizability densities, and higher order susceptibility densities, it is necessary to know the derivatives of nonlocal polarizability densities with respect to nuclear coordinates in order to prove force relay and force balance. It is also necessary to determine the effect on nonlocal polarizability densities of a simultaneous shift in the coordinates of all of the nuclei of the molecule in question. This section focuses on simultaneous shifts of all of the nuclei.

If the electrons adjust adiabatically to the nuclear motion, the whole molecule moves uniformly: At an arbitrary but fixed nuclear configuration, let $\rho^e(\mathbf{r})$ denotes the expectation value of electronic charge density operator $\hat{\rho}^e(\mathbf{r})$, and $\rho^e{}_s(\mathbf{r})$ denote the electronic charge density after an infinitesimal shift, and $\rho^e{}_0(\mathbf{r})$ denote the original electronic charge density, and let $\delta\mathbf{R}$ denote the displacement.



Then $\rho^e{}_s(\mathbf{r}) = \rho^e{}_0(\mathbf{r} - \delta\mathbf{R})$. Because $\delta\mathbf{R}$ is very small, a Taylor expansion can be used to connect $\rho^e{}_s(\mathbf{r})$ and $\rho^e{}_0(\mathbf{r})$:

$$\begin{aligned}\rho_s^e(\mathbf{r}) &= \rho_0^e(\mathbf{r} - \delta\mathbf{R}) \\ &= \rho_0^e(\mathbf{r}) - \delta\mathbf{R} \cdot \nabla\rho_0^e(\mathbf{r})\,; \qquad (1)\end{aligned}$$

also

$$\rho_s^e(\mathbf{r}) = \rho_0^e(\mathbf{r}) + \delta\mathbf{R} \cdot \sum_I \frac{\partial\rho_0^e(\mathbf{r})}{\partial\mathbf{R}^I}, \qquad (2)$$

where I runs over the nuclei, and ∇ denotes differentiation with respect to the spatial coordinate $\mathbf{r}$. Comparison of Eqs. (1) and (2) shows that the effect on the electronic charge density of a simultaneous shift in the coordinates of all of the nuclei of a molecule is determined by the gradient of the charge density

$$\sum_I \frac{\partial\rho_0^e(\mathbf{r})}{\partial\mathbf{R}^I} = -\nabla\rho_0^e(\mathbf{r})\,. \qquad (3)$$

The individual terms on that left-hand side of Eq. (3) are nucleus-dependent and the right-hand side is purely dependent on spatial coordinates for the electronic charge density. The rest of this section shows how to build up an analogous connection for each nonlocal polarizability density.

Equation (3) can be related to the nonlocal polarizability density $\alpha(\mathbf{r}, \mathbf{r}')$ by using the relations $\rho(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r})$ and

$$\mathbf{P}_\delta^e(\mathbf{r}) = \int d\mathbf{r}'\alpha_{\delta\beta}(\mathbf{r}, \mathbf{r}')\,\mathfrak{E}_\beta^{ext}(\mathbf{r}')\,. \qquad (4)$$

Then the left-hand side of Eq. (3) becomes

$$\sum_I \frac{\partial\rho_0^e(\mathbf{r})}{\partial\mathbf{R}_\alpha^I} = -\sum_I \frac{\partial\nabla_\delta\mathbf{P}_\delta^e(\mathbf{r})}{\partial\mathbf{R}_\alpha^I}$$

$$= -\sum_{I} \nabla_{\delta} \int d\mathbf{r}' \frac{\partial \alpha_{\delta\beta}(\mathbf{r}, \mathbf{r}')}{\partial \mathbf{R}_{\alpha}^{I}} \mathfrak{I}_{\beta}^{ext}(\mathbf{r}'), \tag{5}$$

where $\mathfrak{I}_{\beta}^{ext}(\mathbf{r}')$ is the static field which is derived from the scalar potential $\Phi^{ext}(\mathbf{r}')$, via the relation $\mathfrak{I}_{\beta}^{ext}(\mathbf{r}') = -\nabla'_{\beta}\Phi^{ext}(\mathbf{r}')$. The derivative of $\alpha(\mathbf{r}, \mathbf{r}')$ with respect to nuclear coordinates in Eq. (5) can be derived from the definition

$$\alpha_{\delta\beta}(\mathbf{r}, \mathbf{r}')$$

$$= (1 + C) \sum_{k}{}' \left[\frac{\langle \Psi_0 | \mathbf{P}_{\delta}(\mathbf{r}) | \Psi_k \rangle \langle \Psi_k | \mathbf{P}_{\beta}(\mathbf{r}') | \Psi_0 \rangle}{E_k - E_0} \right], \tag{6}$$

where C denotes complex conjugation, and **P** is polarization operator. The prime denotes the summation over all excited states k, excluding the ground state Ψ_0. By using integration by parts and the relations $\mathfrak{I}_{\alpha}^{ext}(\mathbf{r}) = -\nabla_{\alpha}\Phi^{ext}(\mathbf{r})$, $\rho(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r})$, the right-hand side of Eq. (5) can be expressed as below:

$$-\sum_{I} \nabla_{\delta} \int d\mathbf{r}' \frac{\partial \alpha_{\delta\beta}(\mathbf{r}, \mathbf{r}')}{\partial \mathbf{R}_{\alpha}^{I}} \mathfrak{I}_{\beta}^{ext}(\mathbf{r}')$$

$$= -\int d\mathbf{r}' \sum_{I} (1 + C) \sum_{k}{}' \left[\frac{\partial \rho_{0k}(\mathbf{r})}{\partial \mathbf{R}_{\alpha}^{I}} \frac{\rho_{k0}(\mathbf{r}')}{E_k - E_0} \right.$$

$$\left. + \frac{\rho_{0k}(\mathbf{r})}{E_k - E_0} \frac{\partial \rho_{k0}(\mathbf{r}')}{\partial \mathbf{R}_{\alpha}^{I}} \right] \Phi^{ext}(\mathbf{r}'). \tag{7}$$

In Eq. (7), the derivative of the energy difference $\partial(E_k - E_0)/\partial \mathbf{R}_{\alpha}^{I}$ between excited state Ψ_k and ground state Ψ_0 summed over nuclear coordinates is zero, Equation (3) also holds for the expectation value $\rho_{0k}(\mathbf{r}) = \langle \Psi_0 \big| \hat{\rho}^{e}(\mathbf{r}) \big| \Psi_k \rangle$. Substitution of the right-hand side of Eq. (3) into Eq. (7) and integration by parts give

$$-\sum_{I} \nabla_\delta \int d\mathbf{r}' \frac{\partial \alpha_{\delta\beta}(\mathbf{r},\mathbf{r}')}{\partial R^{I}_{\alpha}} \mathfrak{I}^{ext}_{\beta}(\mathbf{r}')$$

$$= -\int d\mathbf{r}' (1 + C) \sum_{k}{}' \left[\frac{\left[\nabla_\alpha \rho^{e}_{0k}(\mathbf{r})\right] \rho^{e}_{k0}(\mathbf{r}')}{E_k - E_0} \right.$$

$$\left. + \frac{\rho^{e}_{0k}(\mathbf{r}) \nabla'_\alpha \rho^{e}_{k0}(\mathbf{r}')}{E_k - E_0} \right] \Phi^{ext}(\mathbf{r}') .$$

$$= \nabla_\delta \int d\mathbf{r}' \left[\nabla_\alpha \alpha_{\delta\beta}(\mathbf{r},\mathbf{r}') + \nabla_\alpha' \alpha_{\delta\beta}(\mathbf{r},\mathbf{r}') \right] \mathfrak{I}^{ext}_{\beta}(\mathbf{r}') . \tag{8}$$

Equation (8) that shows the sum of the derivatives of the nonlocal polarizability density $\alpha(\mathbf{r}, \mathbf{r}')$ with respect to nuclear coordinates is determined by the gradients of the polarizability density:

$$\sum_{I} \frac{\partial \alpha_{\delta\beta}(\mathbf{r},\mathbf{r}')}{\partial R^{I}_{\alpha}} = -\nabla_\alpha \alpha_{\delta\beta}(\mathbf{r},\mathbf{r}') - \nabla_\alpha' \alpha_{\delta\beta}(\mathbf{r},\mathbf{r}') . \tag{9}$$

Similar steps can be used to find the effect on the hyperpolarizability density β of a simultaneous shift in the nuclear coordinates, which is given by

$$\sum_{I} \frac{\partial \beta_{\gamma\beta\delta}(\mathbf{r}',\mathbf{r}'',\mathbf{r})}{\partial R^{I}_{\alpha}} = -\nabla'_\alpha \beta_{\gamma\beta\delta}(\mathbf{r}',\mathbf{r}'',\mathbf{r})$$

$$-\nabla''_\alpha \beta_{\gamma\beta\delta}(\mathbf{r}',\mathbf{r}'',\mathbf{r})$$

$$-\nabla_\alpha \beta_{\gamma\beta\delta}(\mathbf{r}', \mathbf{r}'', \mathbf{r}) \,. \qquad (10)$$

In general, the sum of the derivatives of the *n*th order nonlocal polarizability density with respect to nuclear coordinates is

$$\sum_I \frac{\partial \chi^{(n)}{}_{\gamma\beta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})}{\partial \mathbf{R}^I_\alpha}$$

$$= -\nabla'_\alpha \chi^{(n)}{}_{\gamma\beta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})$$

$$- \nabla''_\alpha \chi^{(n)}{}_{\gamma\beta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime}) - \ldots$$

$$-\nabla_\alpha^{(n+1)\prime} \chi^{(n)}{}_{\gamma\beta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime}) \,. \qquad (11)$$

In Eq. (11), $\chi^{(1)}(\mathbf{r}, \mathbf{r}')$ denotes $\alpha(\mathbf{r}, \mathbf{r}')$, $\chi^{(2)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ denotes $\beta(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, and $\chi^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''')$ denotes $\gamma^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''')$. Eq. (11) holds not only for the static response tensors, but also for the imaginary-frequency susceptibility densities.

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CHAPTER III

FORCE RELAY AND FORCE BALANCE

3.1 Force Relay

According to Epstein's force theorem [see Appendix A] the force on any electron *i* vanishes if the electronic state adjusts adiabatically to an external perturbation. In effect, the force due to the external field passes through the electrons and acts on nuclei. This section shows how the force is relayed from the electrons to the nuclei.

Let $\mathbf{F}_e$ be the total force operator on *N* electrons,

$$\mathbf{F}_{\mathrm{e}} = \mathbf{F}_{\mathrm{eN}} + \mathbf{F}_{\mathrm{e}\Im} \tag{1}$$

where $\mathbf{F}_{\mathrm{eN}}$ is the force operator on the electrons due to the nuclei, and $\mathbf{F}_{\mathrm{e}\Im}$ is the force operator on the electrons due to a static, nonuniform external field, $\Im^{\mathrm{ext}}(\mathbf{r})$. If we use the electronic charge density operator, $\hat{\rho}^{\mathrm{e}}(\mathbf{r})$ written as a function of the continuous variable **r**, and a point charge distribution for nuclei, $\mathbf{F}_{\mathrm{eN}}$ and $\mathbf{F}_{\mathrm{e}\Im}$ can be expressed as follows: [see Eq. (2, 2, 3)]

$$\mathbf{F}_{\mathrm{eN}} = \int d\mathbf{r}\,\hat{\rho}^{\mathrm{e}}(\mathbf{r}) \sum_{\mathrm{I}} Z^{\mathrm{I}}(\mathbf{r}-\mathbf{R}^{\mathrm{I}})\left|\mathbf{r}-\mathbf{R}^{\mathrm{I}}\right|^{-3} \tag{2}$$

and

$$\mathbf{F}_{\mathrm{e}\Im} = \int d\mathbf{r}\,\hat{\rho}^{\mathrm{e}}(\mathbf{r})\,\Im^{\mathrm{ext}}(\mathbf{r}) \tag{3}$$

As the external perturbation is weak one can use time-independent perturbation theory to derive the force relay condition. The expectation value of the total force is zero in the perturbed ground state. That is,

$$\langle \mathbf{F}_{\mathrm{e}} \rangle = \langle \Psi_0 + \Psi_1 + \Psi_2 + \ldots | \mathbf{F}_{\mathrm{e}} | \Psi_0 + \Psi_1 + \Psi_2 + \ldots \rangle = 0, \tag{4}$$

and therefore

$$\langle \mathbf{F}_{\mathrm{e}\Im} \rangle = -\langle \mathbf{F}_{\mathrm{eN}} \rangle. \tag{5}$$

In Eq. (4) Ψ_0 is the ground-state wave function for the molecule in the absence of the external field, and Ψ_n is the nth correction to the ground-state wave function. The equality in Eq. (5) holds order by order in the external field. The (n+1)st order term in Eq. (5) can be rewritten as follows:

$$\int d\mathbf{r}\, \rho^{\mathrm{e}}_{n}(\mathbf{r})\, \Im^{\mathrm{ext}}(\mathbf{r}) = -\int d\mathbf{r}\, \rho^{\mathrm{e}}_{n+1}(\mathbf{r}) \sum_{\mathrm{I}} Z^{\mathrm{I}} (\mathbf{r} - \mathbf{R}^{\mathrm{I}}) \left| \mathbf{r} - \mathbf{R}^{\mathrm{I}} \right|^{-3}. \tag{6}$$

Equation (6) shows that the external force on the nth order component of the electronic charge density $\rho^{\mathrm{e}}_{n}(\mathbf{r})$ is relayed in full to the nuclei by the (n+1)st order component of the electronic charge density $\rho^{\mathrm{e}}_{n+1}(\mathbf{r})$. When the external field may be correlated with the changes in the electronic charge density of molecule A - as for induction or dispersion forces due to interactions with a second molecule - the force relay condition changes from Eq. (6) to

$$\int d\mathbf{r}\, [\rho^{\mathrm{e,A}}(\mathbf{r})\, \Im^{\mathrm{ext}}(\mathbf{r})]_n$$

$$= -\int d\mathbf{r}\, \rho^{\mathrm{e,A}}_{n+1}(\mathbf{r}) \sum_{\mathrm{I}} Z^{\mathrm{I}} (\mathbf{r} - \mathbf{R}^{\mathrm{I}}) \left| \mathbf{r} - \mathbf{R}^{\mathrm{I}} \right|^{-3}, \tag{7}$$

where $[\rho^{e,A}(\mathbf{r})\,\Im^{ext}(\mathbf{r})]_n$ denotes the change $\Delta\mathbf{F}_n^{ext}$ in the external force on the electrons,

$$\Delta\mathbf{F}_n^{ext} = \sum_{k=0}^{n} \langle \Psi_k \left| \int d\mathbf{r}\,\hat{\rho}^{e,A}(\mathbf{r})\,\hat{\Im}^{ext}(\mathbf{r}) \right| \Psi_{n-k} \rangle . \tag{8}$$

In Eq. (8), Ψ_k is the *k*th order term in the normalized, perturbed wave function, including the field source, $\hat{\rho}^{e,A}$ is the electronic charge density operator for molecule A, and $\hat{\Im}^{ext}(\mathbf{r})$ is the field operator. The sum on the right-hand side in Eq. (7) runs over nuclei I in A only. Section 3.2 shows that the condition in Eq. (7) is met at first and second order in the interaction between two molecules A and B.

3.2 Force Relay within the Nonlocal Polarizability Density Theory

This section provides a proof that the force relay condition is met within the nonlocal response theory for a molecule in a static, nonuniform external field that is independent of the molecular charge distribution. The force relay condition is [see Section 3.1, Eq. (6)]

$$\int d\mathbf{r}\,\rho_n^e(\mathbf{r})\,\Im^{ext}(\mathbf{r}) = -\int d\mathbf{r}\,\rho_{n+1}^e(\mathbf{r})\sum_I Z^I(\mathbf{r}-\mathbf{R}^I)\left|\mathbf{r}-\mathbf{R}^I\right|^{-3} \tag{1}$$

By using the relation between the electronic polarization, $\mathbf{P}^e$, and the electronic charge density, $\rho(\mathbf{r})$,

$$\nabla\cdot\mathbf{P}_n^e(\mathbf{r}) = -\rho_n^e(\mathbf{r}), \tag{2}$$

one can transform the right-hand side of Eq. (1) into

$$\begin{aligned} S_\alpha(n) &\equiv -\sum_I Z^I\int d\mathbf{r}\,\rho_{n+1}^c(\mathbf{r})\,(\mathbf{r}-\mathbf{R}^I)_\alpha\left|\mathbf{r}-\mathbf{R}^I\right|^{-3} \\ &= \sum_I Z^I\int d\mathbf{r}\,T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r})\,\mathbf{P}_{n+1,\beta}^e(\mathbf{r}), \end{aligned} \tag{3}$$

and this form is used to establish the force relay condition within the nonlocal polarizability density theory.

First, when $n = 0$,

$$S_\alpha(0) = \sum_I Z^I\int d\mathbf{r}\,T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r})\,\mathbf{P}_{1,\beta}^e(\mathbf{r}). \tag{4}$$

The first-order electronic polarization $\mathbf{P}_1^e(\mathbf{r})$ is related to the nonlocal polarizability density $\alpha_{\beta\gamma}(\mathbf{r},\mathbf{r}')$ by [see Section 2.1]

$$\mathbf{P}_{1,\beta}^e(\mathbf{r}) = \int d\mathbf{r}' \alpha_{\beta\gamma}(\mathbf{r},\mathbf{r}') \mathfrak{I}_\gamma^{ext}(\mathbf{r}') . \tag{5}$$

The nonlocal polarizability density also gives the change in the electronic charge density (or the electronic polarization) due to an infinitesimal shift in nuclear position [1].

$$\frac{\partial \mathbf{P}_{0,\gamma}^e(\mathbf{r}')}{\partial \mathbf{R}_\alpha^I} = Z^I \int d\mathbf{r}\, \alpha_{\gamma\beta}(\mathbf{r}',\mathbf{r}) T_{\beta\alpha}(\mathbf{r},\mathbf{R}^I) . \tag{6}$$

Eq. (6) expresses a general, quantum mechanical connection between linear response tensors and the permanent charge distribution. One can relate Eq. (4) to Eq. (6), using Eq. (5), the Born symmetry[2] of the nonlocal polarizability density $[\alpha_{\gamma\beta}(\mathbf{r}',\mathbf{r}) = \alpha_{\beta\gamma}(\mathbf{r},\mathbf{r}')]$, and the symmetry of the dipole propagator $[T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r}) = T_{\beta\alpha}(\mathbf{r},\mathbf{R}^I)]$.

$$\begin{aligned} S_\alpha(0) &= \sum_I Z^I \int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r}) \mathbf{P}_{1,\beta}^e(\mathbf{r}) \\ &= \sum_I Z^I \int d\mathbf{r}\, d\mathbf{r}' T_{\alpha\beta}(\mathbf{R}^I,\mathbf{r}) \alpha_{\beta\gamma}(\mathbf{r},\mathbf{r}') \mathfrak{I}_\gamma^{ext}(\mathbf{r}') \\ &= \sum_I \int d\mathbf{r}' \mathfrak{I}_\gamma^{ext}(\mathbf{r}') \frac{\partial \mathbf{P}_{0,\gamma}^e(\mathbf{r}')}{\partial \mathbf{R}_\alpha^I} \end{aligned} \tag{7}$$

The static field $\mathfrak{I}_\gamma^{ext}(\mathbf{r}')$ is derived from the scalar potential $\Phi^{ext}(\mathbf{r}')$, via the relation $\mathfrak{I}_\gamma^{ext}(\mathbf{r}') = -\nabla_\gamma' \Phi^{ext}(\mathbf{r}')$, where ∇_γ' denotes differentiation with respect to the coordinate $\mathbf{r}'_\gamma$. Hence by double integration by parts

$$S_\alpha(0) = \sum_I \int d\mathbf{r}' \left[-\nabla_\gamma' \Phi^{ext}(\mathbf{r}') \right] \frac{\partial \mathbf{P}_{0,\gamma}^e(\mathbf{r}')}{\partial \mathbf{R}_\alpha^I}$$

$$= \sum_{I} \int d\mathbf{r}' \Phi^{ext}(\mathbf{r}') \frac{\partial\left[\nabla_\gamma' \mathbf{P}^e_{0,\gamma}(\mathbf{r}')\right]}{\partial \mathbf{R}^I_\alpha}$$

$$= -\sum_{I} \int d\mathbf{r}' \Phi^{ext}(\mathbf{r}') \frac{\partial \rho^e_0(\mathbf{r}')}{\partial \mathbf{R}^I_\alpha} . \tag{8}$$

The effect on the electronic charge density of a simultaneous shift in the coordinates of all of the nuclei [see Section 2.5] is given by

$$\sum_{I} \frac{\partial \rho^e_0(\mathbf{r}')}{\partial \mathbf{R}^I_\alpha} = -\nabla_\alpha' \rho^e_0(\mathbf{r}') . \tag{9}$$

Substitution of Eq. (9) into Eq. (8) and an integration by parts yield

$$S_\alpha(0) = \int d\mathbf{r}' \rho^e_0(\mathbf{r}') \Im^{ext}_\alpha(\mathbf{r}') . \tag{10}$$

Thus, the force relay condition at lowest order ($n = 0$) has been proven within the nonlocal polarizability density theory:

$$-\sum_{I} Z^I \int d\mathbf{r}\, \rho^e_1(\mathbf{r})\, (\mathbf{r} - \mathbf{R}^I)_\alpha \left|\mathbf{r} - \mathbf{R}^I\right|^{-3} = \int d\mathbf{r}' \rho^e_0(\mathbf{r}') \Im^{ext}_\alpha(\mathbf{r}') . \tag{11}$$

Next, I will prove the force condition in Eq. (1) for $n \geq 1$. In Eq. (3) for $S_\alpha(n)$, $\mathbf{P}^e_{n+1,\beta}(\mathbf{r})$ is determined by the (n+1)st order polarizability density cast in terms of polarization operators, $\chi^{(n+1)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})$. Thus

$$S_\alpha(n) = \sum_{I} Z^I \int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^I, \mathbf{r})\, \mathbf{P}^e_{n+1,\beta}(\mathbf{r})$$

$$= 1/(n+1)!\sum_{\mathrm{I}} Z^{\mathrm{I}} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'' \ldots d\mathbf{r}^{(n+1)\prime}$$

$$\times \chi^{(n+1)}_{\beta\gamma\delta\ldots\omega}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})\, \Im^{\mathrm{ext}}_{\gamma}(\mathbf{r}')\, \Im^{\mathrm{ext}}_{\delta}(\mathbf{r}'') \cdots$$

$$\times \Im^{\mathrm{ext}}_{\omega}(\mathbf{r}^{(n+1)\prime})\, T_{\alpha\beta}(\mathbf{r}, \mathbf{R}^{\mathrm{I}}), \tag{12}$$

where $\mathbf{r}^{(n+1)\prime}$ denotes the spatial coordinate $\mathbf{r}$ with n+1 "primes." Hunt has shown that linear and nonlinear response are related by [1,3]

$$\frac{\partial \alpha_{\gamma\delta}(\mathbf{r}', \mathbf{r}'')}{\partial \mathbf{R}^{\mathrm{I}}_{\alpha}} = Z^{\mathrm{I}} \int d\mathbf{r}\, \beta_{\gamma\delta\beta}(\mathbf{r}', \mathbf{r}'', \mathbf{r})\, T_{\beta\alpha}(\mathbf{r}, \mathbf{R}^{\mathrm{I}}), \tag{13}$$

and an analogous relation holds between $\chi^{(n)}$ and $\chi^{(n+1)}$

$$\frac{\partial \chi^{(n)}_{\gamma\delta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})}{\partial \mathbf{R}^{\mathrm{I}}_{\alpha}}$$

$$= Z^{\mathrm{I}} \int d\mathbf{r}\, \chi^{(n+1)}_{\gamma\delta\ldots\omega\beta}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime}, \mathbf{r})\, T_{\beta\alpha}(\mathbf{r}, \mathbf{R}^{\mathrm{I}}). \tag{14}$$

Therefore

$$S_{\alpha}(n) = 1/(n+1)!\sum_{\mathrm{I}} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'' \ldots d\mathbf{r}^{(n+1)\prime}$$

$$\times \frac{\partial \chi^{(n)}_{\gamma\delta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})}{\partial \mathbf{R}^{\mathrm{I}}_{\alpha}} \Im^{\mathrm{ext}}_{\gamma}(\mathbf{r}')$$

$$\times \Im^{\mathrm{ext}}_{\delta}(\mathbf{r}'') \cdots \Im^{\mathrm{ext}}_{\omega}(\mathbf{r}^{(n+1)\prime}). \tag{15}$$

Now the relation between the *n*th order polarizability density and its gradient is used [see Section 2.5]

$$\sum_{\mathrm{I}} \frac{\partial \chi^{(n)}_{\gamma\delta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})}{\partial \mathbf{R}^{\mathrm{I}}_{\alpha}}$$

$$= -\nabla_{\alpha}{}' \chi^{(n)}_{\gamma\delta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})$$

$$-\nabla_{\alpha}{}'' \chi^{(n)}_{\gamma\delta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime}) \ldots$$

$$-\nabla_{\alpha}^{(n+1)\prime} \chi^{(n)}_{\gamma\delta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime}) . \tag{16}$$

By use of the permutation symmetry of $\chi^{(n)}$,

$$\mathrm{S}_{\alpha}(n) = -(1/n!) \int d\mathbf{r}' d\mathbf{r}'' \ldots d\mathbf{r}^{(n+1)\prime}$$

$$\times \nabla_{\alpha}{}' \chi^{(n)}_{\gamma\delta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime}) \Im^{\mathrm{ext}}_{\gamma}(\mathbf{r}')$$

$$\times \Im^{\mathrm{ext}}_{\delta}(\mathbf{r}'') \cdots \Im^{\mathrm{ext}}_{\omega}(\mathbf{r}^{(n+1)\prime}) , \tag{17}$$

and so

$$\mathrm{S}_{\alpha}(n) = (1/n!) \int d\mathbf{r}' d\mathbf{r}'' \ldots d\mathbf{r}^{(n+1)\prime} \; \nabla_{\gamma}{}' \nabla_{\delta}{}'' \ldots \nabla_{\omega}^{(n+1)\prime}$$

$$\times \chi^{(n)}_{\gamma\delta\ldots\omega}(\mathbf{r}', \mathbf{r}'', \ldots, \mathbf{r}^{(n+1)\prime})$$

$$\times \left[\nabla_{\alpha}{}' \Phi^{\mathrm{ext}}(\mathbf{r}')\right] \Phi^{\mathrm{ext}}(\mathbf{r}'') \ldots \Phi^{\mathrm{ext}}(\mathbf{r}^{(n+1)\prime})$$

$$= -\int d\mathbf{r}' \rho_n^{\mathrm{e}}(\mathbf{r}') \left[\nabla_\alpha' \Phi^{\mathrm{ext}}(\mathbf{r}') \right]$$

$$= \int d\mathbf{r}' \rho_n^{\mathrm{e}}(\mathbf{r}') \mathfrak{I}_\alpha^{\mathrm{ext}}(\mathbf{r}') . \qquad (18)$$

This completes the proof that the force relay condition is satisfied within the nonlocal polarizability density theory, for fixed external fields $\mathfrak{I}_\alpha^{\mathrm{ext}}(\mathbf{r})$.

3.3 Force Relay Condition and Force Balance

a. Force Balance at First Order

The sum of the first-order forces on nuclei of molecule *A* is

$$\sum_{I} \Delta F^{I}_{1,\alpha} = \sum_{I} Z^{I} \int (\mathbf{R}^{I} - \mathbf{r})_{\alpha} |\mathbf{R}^{I} - \mathbf{r}|^{-3} \rho^{B}{}_{0}(\mathbf{r})\, d\mathbf{r}$$

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

where

$$\mathbf{P}^{e,A}_{1,\beta}(\mathbf{r}) = \int d\mathbf{r}' \alpha^{A}{}_{\beta\gamma}(\mathbf{r}, \mathbf{r}')\, \Im^{B}_{0,\gamma}(\mathbf{r}'), \tag{2}$$

in terms of the field $\Im^{B}_{0,\gamma}(\mathbf{r}')$ due to the unperturbed charge distribution (electronic and nuclear) of molecule B. From the zeroth-order force relay condition, the second term of Eq. (2) can be replaced by a term containing the unperturbed electronic charge density of *A* and the unperturbed charge distribution of B,

$$\sum_{I} Z^{I} \int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^{I}, \mathbf{r})\, \mathbf{P}^{e,A}_{1,\beta}(\mathbf{r})$$

$$= -\sum_{I} Z^{I} \int d\mathbf{r}\, \rho^{e,A}_{1}(\mathbf{r})\, (\mathbf{r} - \mathbf{R}^{I})_{\alpha} |\mathbf{r} - \mathbf{R}^{I}|^{-3}$$

$$= \int d\mathbf{r}\, \rho^{e,A}{}_{0}(\mathbf{r})\, \Im^{B}_{0,\alpha}(\mathbf{r}). \tag{3}$$

After substitution of Eq. (3) into Eq. (1), Eq. (1) can be rewritten as follows

$$\sum_{I} \Delta F^{I}_{1,\alpha} = \sum_{I} Z^{I} \Im^{B}_{0,\alpha}(\mathbf{R}^{I})$$

$$+\int d\mathbf{r}\,\rho^{e,A}{}_{0}(\mathbf{r})\,\Im^{B}_{0,\alpha}(\mathbf{r})\,. \tag{4}$$

That is, the sum of the first-order forces on the nuclei of molecule *A* equals the force on the entire unperturbed charge distribution of *A* due to the entire unperturbed charged distribution of B. Equation (4) can be decomposed further into four terms, giving the total force on nuclei in molecule *A* as

$$\begin{aligned}\sum_{I}\Delta\mathbf{F}^{I}_{1,\alpha} = {} & \sum_{I} Z^{I}\int \rho_{0}^{e,B}(\mathbf{r})\,(\mathbf{R}^{I}-\mathbf{r})_{\alpha}\left|\mathbf{R}^{I}-\mathbf{r}\right|^{-3}d\mathbf{r}\\ & +\sum_{I} Z^{I}\sum_{J} Z^{J}\,(\mathbf{R}^{I}-\mathbf{R}^{J})_{\alpha}\left|\mathbf{R}^{I}-\mathbf{R}^{J}\right|^{-3}\\ & +\sum_{J} Z^{J}\int \rho_{0}^{e,A}(\mathbf{r})\,(\mathbf{r}-\mathbf{R}^{J})_{\alpha}\left|\mathbf{R}^{J}-\mathbf{r}\right|^{-3}d\mathbf{r}\\ & +\int \rho_{0}^{e,A}(\mathbf{r})\,\rho_{0}^{e,B}(\mathbf{r}')\,(\mathbf{r}-\mathbf{r}')_{\alpha}\left|\mathbf{r}'-\mathbf{r}\right|^{-3}d\mathbf{r}\,d\mathbf{r}'.\end{aligned} \tag{5}$$

Similarly, for nuclei in molecule B,

$$\begin{aligned}\sum_{J}\Delta\mathbf{F}^{J}_{1,\alpha} = {} & \sum_{J} Z^{J}\,\Im^{A}_{0,\alpha}(\mathbf{R}^{J})\\ & +\int d\mathbf{r}\,\rho^{e,B}{}_{0}(\mathbf{r})\,\Im^{A}_{0,\alpha}(\mathbf{r})\,;\end{aligned} \tag{6}$$

and so

$$\begin{aligned}\sum_{J}\Delta\mathbf{F}^{J}_{1,\alpha} = {} & \sum_{J} Z^{J}\int \rho_{0}^{e,A}(\mathbf{r})\,(\mathbf{R}^{J}-\mathbf{r})_{\alpha}\left|\mathbf{R}^{J}-\mathbf{r}\right|^{-3}d\mathbf{r}\\ & +\sum_{I} Z^{I}\sum_{J} Z^{J}\,(\mathbf{R}^{J}-\mathbf{R}^{I})_{\alpha}\left|\mathbf{R}^{J}-\mathbf{R}^{I}\right|^{-3}\\ & +\sum_{I} Z^{I}\int \rho_{0}^{e,B}(\mathbf{r})\,(\mathbf{r}-\mathbf{R}^{I})_{\alpha}\left|\mathbf{R}^{I}-\mathbf{r}\right|^{-3}d\mathbf{r}\end{aligned}$$

$$+\int \rho_0^{e,B}(\mathbf{r})\,\rho_0^{e,A}(\mathbf{r}')\,(\mathbf{r}-\mathbf{r}')_{\alpha}|\mathbf{r}'-\mathbf{r}|^{-3}d\mathbf{r}\,d\mathbf{r}'. \tag{7}$$

Comparison of Eqs. (5) and (7) shows that the first-order forces on *A* and B are equal and opposite, within the nonlocal response theory.

b. Force Balance for Second-Order Induction Forces

The sum of the second-order induction forces is

$$\sum_{I}\Delta\mathbf{F}^{I}{}_{2,\alpha,\mathrm{ind}} = \sum_{I} Z^{I}\int d\mathbf{r}\,T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\left[\mathbf{P}_{1,\beta}^{e,B}(\mathbf{r}) + \mathbf{P}_{2,\beta,\mathrm{ind}}^{e,A}(\mathbf{r})\right], \tag{8}$$

where

$$\mathbf{P}_{2,\beta,\mathrm{ind}}^{e,A}(\mathbf{r}) = \int d\mathbf{r}'d\mathbf{r}''d\mathbf{r}'''\alpha_{\beta\gamma}^{A}(\mathbf{r},\mathbf{r}')\,T_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')$$

$$\times\,\alpha_{\delta\varepsilon}^{B}(\mathbf{r}'',\mathbf{r}''')\,\Im_{0,\varepsilon}^{A}(\mathbf{r}''')$$

$$+\frac{1}{2}\int d\mathbf{r}'d\mathbf{r}''\beta_{\beta\gamma\delta}^{A}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,\Im^{B}{}_{0\gamma}(\mathbf{r}')\,\Im^{B}{}_{0\delta}(\mathbf{r}''). \tag{9}$$

Substitution of Eq. (2) into the first term of Eq. (8) gives

$$\sum_{I} Z^{I}\int d\mathbf{r}\,T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\,\mathbf{P}_{1,\beta}^{e,B}(\mathbf{r})$$

$$= \sum_{I} Z^{I}\int d\mathbf{r}\,d\mathbf{r}'T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\,\alpha_{\beta\gamma}^{B}(\mathbf{r},\mathbf{r}')\,\Im_{0,\gamma}^{A}(\mathbf{r}')$$

$$= \sum_{I} Z^{I}\,\Im_{1,\alpha}^{B}(\mathbf{R}^{I}), \tag{10}$$

where

$$\Im^{B}_{1,\alpha}(\mathbf{R}^{I}) = \int d\mathbf{r}\, d\mathbf{r}' T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\, \alpha^{B}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\, \Im^{A}_{0,\gamma}(\mathbf{r}') . \qquad (11)$$

Equation (10) gives the force on the nuclei of A, due to the first-order, interaction-induced field from molecule B, $\Im^{B}_{1,\alpha}(\mathbf{R}^{I})$, which depends on the change in charge density induced in B by the field from the entire unperturbed charge distribution of A.

The second term of Eq. (8) contains two parts

$$\sum_{I} Z^{I} \int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\, \mathbf{P}^{e,A}_{2,\beta,\mathrm{ind}}(\mathbf{r}) ,$$

$$= \sum_{I} Z^{I} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}''' T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\, \alpha^{A}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\, T_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')\, \alpha^{B}_{\delta\varepsilon}(\mathbf{r}'',\mathbf{r}''')\, \Im^{A}_{0,\varepsilon}(\mathbf{r}''')$$

$$+ \frac{1}{2} \sum_{I} Z^{I} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}'' T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\, \beta^{A}_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\, \Im^{B}{}_{0\gamma}(\mathbf{r}')\, \Im^{B}{}_{0\delta}(\mathbf{r}''). \qquad (12)$$

If one applies to Eq. (12) the same equations used to prove the force relay condition in Section 3.2, the first term in Eq. (12) becomes

$$\sum_{I} Z^{I} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}''' T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\, \alpha^{A}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\, T_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')\, \alpha^{B}_{\delta\varepsilon}(\mathbf{r}'',\mathbf{r}''')\, \Im^{A}_{0,\varepsilon}(\mathbf{r}''')$$

$$= T_{1} = \sum_{I} \int d\mathbf{r}' \frac{\partial \mathbf{P}^{e,A}_{0,\gamma}(\mathbf{r}')}{\partial \mathbf{R}^{I}_{\alpha}} \Im^{B}_{1,\gamma}(\mathbf{r}') . \qquad (13)$$

Then

$$T_{1} = \int d\mathbf{r}\, \rho^{e,A}{}_{0}(\mathbf{r})\, \Im^{B}_{1,\alpha}(\mathbf{r}) , \qquad (14)$$

where Eqs. (7)-(10) of Section 3.2 have been used to establish the equality of Eqs. (13)

and (14),

$$\frac{\partial \mathbf{P}^{e,A}_{0,\gamma}(\mathbf{r}')}{\partial \mathbf{R}^{I}_{\alpha}} = Z^{I}\int d\mathbf{r}\, T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\,\alpha^{A}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\,, \tag{15}$$

and

$$\Im^{B}_{1,\gamma}(\mathbf{r}') = \int d\mathbf{r}''d\mathbf{r}'''\,T_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')\,\alpha^{B}_{\delta\varepsilon}(\mathbf{r}'',\mathbf{r}''')\,\Im^{A}_{0,\varepsilon}(\mathbf{r}''')\,. \tag{16}$$

Equation (14) gives the force on the unperturbed electronic charge distribution of A due to the first-order correction to the field from B. The second term in Eq. (12) can also be rearranged by using the same procedure used to prove the force relay condition within the nonlocal polarizability density theory [see Section 3.2]:

$$\frac{1}{2}\sum_{I} Z^{I}\int d\mathbf{r}\,d\mathbf{r}'d\mathbf{r}''\,T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r})\,\beta^{A}_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,\Im^{B}{}_{0\gamma}(\mathbf{r}')\,\Im^{B}{}_{0\delta}(\mathbf{r}'')$$

$$= \frac{1}{2}\sum_{I}\int d\mathbf{r}'d\mathbf{r}''\frac{\partial \alpha^{A}_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')}{\partial \mathbf{R}^{I}_{\alpha}}\Im^{B}{}_{0\gamma}(\mathbf{r}')\,\Im^{B}{}_{0\delta}(\mathbf{r}'')\,. \tag{17}$$

Equation (17) is equal to $S_{\alpha}(n = 1)$ from Section 3.2, and it has already been proven in Eqs. (12)-(18) of Section 3.2 that

$$S_{\alpha}(n = 1) = \int d\mathbf{r}\,\rho^{e,A}_{n=1}(\mathbf{r})\,\Im^{B}_{0,\alpha}(\mathbf{r})\,. \tag{18}$$

Eq. (18) gives the force on the first-order correction to the electronic charge density of A, due to the unperturbed charge distribution of B. From Eqs. (10), (14) and (18), the sum of the second-order induction forces is

$$\sum_{I} \Delta \mathbf{F}^{I}{}_{2,\alpha,\mathrm{ind}} = \sum_{I} Z^{I} \mathfrak{I}^{B}_{1,\alpha}(\mathbf{R}^{I})$$

$$+\int d\mathbf{r}\left[\rho^{e,A}{}_{1}(\mathbf{r})\,\mathfrak{I}^{B}_{0,\alpha}(\mathbf{r}) + \rho^{e,A}{}_{0}(\mathbf{r})\,\mathfrak{I}^{B}_{1,\alpha}(\mathbf{r})\right]. \tag{19}$$

The first term in Eq. (19) is due to the direct force on the nuclei in A from the first-order, interaction-induced change in the charge density of B. The second term gives the induction force on nuclei in A due to the response of electrons in A to the field from B, at second order in the interaction. The second term is also obtained by direct evaluation of the induction terms in $\left[\rho^{e,A}(\mathbf{r})\,\mathfrak{I}^{B}(\mathbf{r})\right]_{1}$. Hence, the force relay condition is met for the second-order induction effects.

To show that the induction forces balance in the theory, it is useful to designate the force terms as $\mathbf{F}\left[\rho_{i}^{S,X} \rightarrow \rho_{j}^{O,Y}\right]$ according to their source S (electrons e or nuclei n) and molecule of origin X (A or B), and the object O in molecule Y, on which the source acts; i and j indicate the orders of the charge densities in the intermolecular interaction. Equation (19) implies

$$\sum_{I} \Delta \mathbf{F}^{I}{}_{2,\mathrm{ind}} = \mathbf{F}\left[\rho_{0}^{e,B} \rightarrow \rho_{1}^{e,A}\right] + \mathbf{F}\left[\rho_{0}^{n,B} \rightarrow \rho_{1}^{e,A}\right]$$

$$+\mathbf{F}\left[\rho_{1}^{e,B} \rightarrow \rho_{0}^{n,A}\right] + \mathbf{F}\left[\rho_{1}^{e,B} \rightarrow \rho_{0}^{e,A}\right]. \tag{20}$$

Similarly, for nuclei *J* in molecule B

$$\sum_{J} \Delta \mathbf{F}^{J}{}_{2,\mathrm{ind}} = \mathbf{F}\left[\rho_{0}^{e,A} \rightarrow \rho_{1}^{e,B}\right] + \mathbf{F}\left[\rho_{0}^{n,A} \rightarrow \rho_{1}^{e,B}\right]$$

$$+\mathbf{F}\left[\rho_{1}^{e,A} \rightarrow \rho_{0}^{n,B}\right] + \mathbf{F}\left[\rho_{1}^{e,A} \rightarrow \rho_{0}^{e,B}\right]. \tag{21}$$

The terms in Eq. (21) correspond one-to-one with the terms in Eq. (20), taken in reverse order. Then from the equalities

$$\mathbf{F}\left[\rho_0^{e,B} \rightarrow \rho_1^{e,A}\right] = -\mathbf{F}\left[\rho_1^{e,A} \rightarrow \rho_0^{e,B}\right], \tag{22}$$

$$\mathbf{F}\left[\rho_1^{e,B} \rightarrow \rho_0^{e,A}\right] = -\mathbf{F}\left[\rho_0^{e,A} \rightarrow \rho_1^{e,B}\right], \tag{23}$$

$$\mathbf{F}\left[\rho_0^{n,B} \rightarrow \rho_1^{e,A}\right] = -\mathbf{F}\left[\rho_1^{e,A} \rightarrow \rho_0^{n,B}\right], \tag{24}$$

and

$$\mathbf{F}\left[\rho_1^{e,B} \rightarrow \rho_0^{n,A}\right] = -\mathbf{F}\left[\rho_0^{n,A} \rightarrow \rho_1^{e,B}\right], \tag{25}$$

it follows that the induction forces balance within the nonlocal response theory.

c. Force Balance for Second-Order Dispersion Forces

The sum of the dispersion forces $\sum_I \Delta\mathbf{F}^I{}_{2,\mathrm{disp}}$ on the nuclei in A, due to the electrons in A, is obtained directly from Eqs. (16) and (17) in Section 2.3. To prove force balance, it is easier to use the derivative of Eq. (15) in Section 2.3 with respect to nuclear coordinates,

$$\sum_I \Delta\mathbf{F}^{I,A}{}_{2,\alpha,\mathrm{disp}} = (h/4\pi^2)\int_0^\infty d\omega \sum_I \int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}''' \frac{\partial \alpha^A{}_{\beta\gamma}(\mathbf{r},\mathbf{r}';-i\omega,i\omega)}{\partial \mathbf{R}^I_\alpha}$$

$$\times T_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')\,\alpha_{\delta\varepsilon}{}^B(\mathbf{r}'',\mathbf{r}''';-i\omega,i\omega)\,T_{\varepsilon\beta}(\mathbf{r}''',\mathbf{r})\,. \tag{26}$$

Equation (9) in Section 2.5 holds not only for the static response tensors, but also for the imaginary-frequency polarizability density $\alpha_{\beta\gamma}(\mathbf{r},\mathbf{r}';-i\omega,i\omega)$ [3]; that is

$$\sum_{I} \frac{\partial \alpha_{\beta\gamma}(\mathbf{r}, \mathbf{r}';i\omega)}{\partial \mathbf{R}_{\alpha}^{I}} = -\nabla_{\alpha}\alpha_{\beta\gamma}(\mathbf{r}, \mathbf{r}';-i\omega, i\omega) - \nabla_{\alpha}'\alpha_{\beta\gamma}(\mathbf{r}, \mathbf{r}';-i\omega, i\omega)\,, \tag{27}$$

Substitution of Eq. (27) into Eq. (26) shows that the sum of the dispersion forces on nuclei in A depends on the gradients of $\alpha_{\beta\gamma}^{A}(\mathbf{r}, \mathbf{r}';-i\omega, i\omega)$:

$$\begin{aligned}\sum_{I} \Delta \mathbf{F}^{I, A}{}_{2, \alpha, \mathrm{disp}} &= -(h/4\pi^2)\int_0^{\infty} d\omega \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}''' \\ &\quad \times \left[\nabla_{\alpha}\alpha_{\beta\gamma}^{A}(\mathbf{r}, \mathbf{r}';-i\omega, i\omega) + \nabla_{\alpha}'\alpha_{\beta\gamma}^{A}(\mathbf{r}, \mathbf{r}';-i\omega, i\omega)\right] \\ &\quad \times T_{\gamma\delta}(\mathbf{r}', \mathbf{r}'')\, \alpha_{\delta\varepsilon}{}^{B}(\mathbf{r}'', \mathbf{r}''';-i\omega, i\omega)\, T_{\varepsilon\beta}(\mathbf{r}''', \mathbf{r})\,. \end{aligned} \tag{28}$$

Equation (28) is used next to prove that the force relay condition is satisfied for dispersion, within the nonlocal polarizability density theory. The first-order dispersion term in the product of the external field and the charge-density operator for molecule A is:

$$\begin{aligned}&\int d\mathbf{r}\left[\rho^{e, A}(\mathbf{r})\, \mathfrak{I}^{B}(\mathbf{r})\right]_{1, \mathrm{disp}} \\ &\qquad = -(1 + C)\int d\mathbf{r}\, \langle \Psi_0 | \left[\hat{\rho}^{e, A}(\mathbf{r})\, \hat{\mathfrak{I}}^{B}(\mathbf{r})\right] G^{A \oplus B}(0)\, V^{AB} | \Psi_0 \rangle, \end{aligned} \tag{29}$$

where C denotes complex conjugation, Ψ_0 is the ground state of the unperturbed AB pair, V^{AB} is the perturbation due to the AB interaction, and $G^{A \oplus B}$ is a particular term in the reduced resolvent for the AB pair (cf. Eq. (4) in Section 2.1): states of the AB pair give a nonzero contribution to $G^{A \oplus B}$ only if both molecules A and B are excited. Eq. (29) transforms to

$$\int d\mathbf{r}\left[\rho^{e,A}(\mathbf{r})\,\Im^{B}(\mathbf{r})\right]_{1,\alpha,\mathrm{disp}}$$

$$= -(1+C)\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,T_{\delta\varepsilon}(\mathbf{r},\mathbf{r}')\,T_{\beta\gamma}(\mathbf{r}'',\mathbf{r}''')$$

$$\times \sum_{m}{}' \langle\, \Psi_{0}^{A} \,\big|\, \nabla_{\alpha}\hat{P}_{\delta}^{A}(\mathbf{r}) \,\big|\, \Psi_{m}^{A} \,\rangle\langle\, \Psi_{m}^{A} \,\big|\, \hat{P}_{\beta}^{A}(\mathbf{r}'') \,\big|\, \Psi_{0}^{A} \,\rangle$$

$$\times \sum_{n}{}' \langle\, \Psi_{0}^{B} \,\big|\, \hat{P}_{\varepsilon}^{B}(\mathbf{r}') \,\big|\, \Psi_{n}^{B} \,\rangle\langle\, \Psi_{n}^{B} \,\big|\, \hat{P}_{\gamma}^{B}(\mathbf{r}''') \,\big|\, \Psi_{0}^{B} \,\rangle$$

$$\times \left[\,(E_{m}^{A}-E_{0}^{A})+(E_{n}^{B}-E_{0}^{B})\right]^{-1}. \qquad (30)$$

For simplicity, it is assumed that the states of A and B are real. Then by use of standard integral identities, the definition of the nonlocal polarizability density [see Eq. (3) in Section 2.1], index relabeling, and the symmetry of the dipole propagator T, the right-hand side of Eq. (28) is obtained. Since Eq. (28) follows both from the standard perturbation theory [see Eqs. (16) and (17) in Section 2.3] and from Eq. (29), the force relay condition holds for dispersion, at leading order.

For force balance, Eq. (28) can be rewritten after an integration by parts

$$\sum_{I}\Delta\mathbf{F}^{I,A}{}_{2,\alpha,\mathrm{disp}} = (h/4\pi^{2})\int_{0}^{\infty}d\omega\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\left[\alpha_{\beta\gamma}^{A}(\mathbf{r},\mathbf{r}';-i\omega,i\omega)\right.$$

$$\times T_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')\,\alpha_{\delta\varepsilon}{}^{B}(\mathbf{r}'',\mathbf{r}''';-i\omega,i\omega)\,\nabla_{\alpha}T_{\varepsilon\beta}(\mathbf{r}''',\mathbf{r})$$

$$+\alpha_{\beta\gamma}^{A}(\mathbf{r},\mathbf{r}';-i\omega,i\omega)\,\nabla'_{\alpha}T_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')\,\alpha_{\delta\varepsilon}^{B}(\mathbf{r}'',\mathbf{r}''';-i\omega,i\omega)$$

$$\left.\times T_{\varepsilon\beta}(\mathbf{r}''',\mathbf{r})\,\right]. \qquad (31)$$

The same analysis, applied to nuclei *J* in molecule B gives the result on the right-hand of Eq. (31), but with $\nabla_\alpha T_{\varepsilon\beta}(\mathbf{r}''', \mathbf{r})$ replaced by $\nabla'''_\alpha T_{\varepsilon\beta}(\mathbf{r}''', \mathbf{r})$ and $\nabla'_\alpha T_{\gamma\delta}(\mathbf{r}', \mathbf{r}'')$ replaced by $\nabla''_\alpha T_{\gamma\delta}(\mathbf{r}', \mathbf{r}'')$. From the relations $\nabla_\alpha T_{\varepsilon\beta}(\mathbf{r}''', \mathbf{r}) = -\nabla'''_\alpha T_{\varepsilon\beta}(\mathbf{r}''', \mathbf{r})$ and $\nabla'_\alpha T_{\gamma\delta}(\mathbf{r}', \mathbf{r}'') = -\nabla''_\alpha T_{\gamma\delta}(\mathbf{r}', \mathbf{r}'')$, it is clear that dispersion forces balance in the nonlocal response theory.

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CHAPTER IV

MOLECULAR SOFTNESS FUNCTIONS

4.1 Introduction

Over the years scientists have tried to categorize the behavior of molecules under different circumstances. From the earliest observations of some metal oxides and sulfides, scientists are able to classify metal ions into two groups, hard and soft, by comparing the differences between their cohesive energies of the metal oxides and sulfides [1, 2]. Pearson [3] extended this work by adopting the generalized concept of acid and base introduced by G. N. Lewis to the entire range of chemistry.

The principle of hard and soft acids and bases [4] (HSAB), and the principle of electronegativity equalization [5] provide a framework for *simple* physical interpretations of complex phenomena. Parr and Yang [6] related the parameters associated with these principles, hardness[3, 4, 7, 8] and softness [9], and electronegativity with fundamental variables of density functional theory [10]. Through their work, a solid theoretical basis has been provided for these concepts, this allows us to build a bridge between these concepts and wavefunction theory which provide an accurate description of the electronic structure of chemical systems, but otherwise far from providing a framework for *simple* interpretations. This also makes it possible to transform the relevant information contained in the wavefunction into an almost pictorial representation, ready to be analyzed with the principles mentioned above [8, 10-20]. The purpose of this chapter is to provide an overview of the concepts of density functional theory needed for applications in Chapter V, and its relation with the nonlocal polarizability density theory.

a. Density Functional Theory

Density functional theory originated with a 1964 paper by Hohenberg and Kohn [21], and its chief method of implementation is described in a 1965 paper by Kohn and Sham [22]. An earlier model which is regarded as the source of modern density functional theory is the Thomas-Fermi model [23-26], from which originated the idea of an *"electron gas."* In this model all properties of a system are expressible in terms of the electron density $\rho(\mathbf{r})$, the number of electrons per unit volume, as it varies through space. The Thomas-Fermi model fails to give an accurate description of electronic systems of chemical interest; for example, it cannot account for chemical binding [27]. But it is now possible to characterize the properties of any system in terms of its electron density via the density functional description.

The Hohenberg-Kohn theorem ensures that the exact ground state density can be calculated from a variational principle involving only the electron density ρ, without solving the Schrödinger equation exactly. For any system, the ground-state electronic energy is a functional of the density, given by the formula

$$E[\rho] = \int \rho(1)\, v(1)\, d\tau_1 + F[\rho]. \tag{1}$$

Here v is the external one-particle potential (for example, $-Z/r$ for an isolated atom) and $F[\rho]$ is the sum [21]

$$F[\rho] = T[\rho] + V_{ee}[\rho], \tag{2}$$

where $T[\rho]$ is the electronic kinetic energy and $V_{ee}[\rho]$ is the electron-electron repulsion energy. Both $T[\rho]$ and $V_{ee}[\rho]$ are well-defined, universal, but unknown functionals of the density.

The spin-free density may be expressed in terms of the wavefunction,

$$\rho(1) = N\int|\Psi(1,2,\ldots,N)|^2 d\omega_1 dx_2 dx_3 \ldots dx_N, \tag{3}$$

where $dx_i = d\omega_i d\tau_i$ is a spin-space volume element, with $d\omega_i$ the spin part. The number of electrons is given by the formula

$$N = N[\rho] = \int\rho(1)d\tau_1. \tag{4}$$

The quantity N, like E, is a functional of ρ.

Suppose there is some ρ' from some approximation to the exact ground-state density ρ, normalized to the proper number of electrons, $N[\rho'] = N$. Using the same definition as Eq. (1), the energy associated with the electron density ρ' is given by

$$E_v[\rho'] = \int\rho'(1)v(1)d\tau_1 + F[\rho'], \tag{5}$$

and $E_v[\rho']$ obeys the inequality

$$E_v[\rho'] \geq E_v[\rho]; \tag{6}$$

when ρ' equals ρ, the equality holds and results in the true energy, $E[\rho]$. That is to say, the density ρ and energy E are determined from the stationary principle,

$$\delta\{E_v[\rho'] - \mu N[\rho']\} = 0, \tag{7}$$

where μ is a Lagrange multiplier. In Eq. (7) an arbitrary variation in ρ' is allowed; the potential v is fixed. If the solution making E an absolute minimum is selected from all possible solutions, the associated value of μ is characteristic of the system of interest [28] and is called the chemical potential of the system. The chemical potential is related to the Mulliken definition of electronegativity [29, 30] (χ_M) through

$$\mu = \mu\int d\mathbf{r}\frac{\partial\rho}{\partial N} = \int d\mathbf{r}\left(\frac{\delta E}{\delta\rho}\right)\left(\frac{\partial\rho}{\partial N}\right)$$

$$= \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \cong -\frac{I+A}{2} \cong -\chi_M, \tag{8}$$

where $v(\mathbf{r})$, I and A are the external potential, the ionization potential and the electron affinity, respectively.

From Eq. (7) and a theorem from the calculus of variations [31] it follows that

$$\mu = \left[\left(\frac{\delta E[\rho]}{\delta\rho(1)}\right)_v\right]_{\rho=\rho[v]} . \tag{9}$$

The quantity $\delta E/\delta\rho$ is the functional derivative of the Hohenberg-Kohn functional with respect to the electron density; it is evaluated at the correct ground-state density at an arbitrary point in space. The corresponding functional derivative with respect to the potential v may be determined from Eq. (1); it is

$$\rho(1) = \left(\frac{\delta E[\rho]}{\delta v(1)}\right)_\rho . \tag{10}$$

The total differential of $E = E(N, v)$ accordingly is given by the fundamental equation

$$dE = \mu\ dN + \int\rho(1)\,dv(1)\,d\tau_1 . \tag{11}$$

This is the generalization, to include change in the number of particles, of a formula from first-order perturbation theory (the Hellmann-Feynman formula) [38].

b. Chemical Hardness and Softness

Chemical hardness is a helpful concept for describing a variety of acid-base reactions. This idea has been in the chemical vocabulary for almost four decades [3, 7]. A wide variety of chemical reactions can be encompassed by general reaction scheme,

$$A + :B \rightarrow A:B \tag{12}$$

involving a Lewis acid (A) and a Lewis base (:B); electrons transfer from the base (:B) with an available pair of electrons to the generalized acid (A). Through study of the characteristics of acids and bases, both Lewis acids and bases have been divided into two categories, called hard and soft [3] based on the following properties:

a) Hard acid: high positive charge, low polarizability and small size, e.g., H^+, Li^+, Ca^{2+}.

b) Hard base: high electronegativity, difficult to oxidize and low polarizability, e.g., NH_3.

c) Soft acid: low positive charge, high polarizability, large size, e.g.,, Cu^+, Ag^+, Rs^+, I_2.

d) Soft base: low electronegativity, easily oxidizable, higher polarizability, e.g., bases containing P, Se, S, or I as donor atoms.

From the time hardness was first defined within density functional theory [8], various related concepts like softness, local hardness [32, 33] and local softness [9], hardness and softness kernels [34], and related hardness [35] have emerged to correlate and to analyze experiment information on the interactions between different chemical species in many different situation.

c. Density Functional Theory of Chemical Hardness and Softness

Equation (11) gives the differential energy change if the external potential or the number of electrons or both are varied slightly, and the chemical system moves from one ground state to another:

$$dE = \mu dN + \int \rho(\mathbf{r})\, dv(\mathbf{r})\,. \tag{13}$$

In order to understand the energy change to higher order, one would need to know how the chemical potential behaves as the external potential or the number of electrons is changed differentially. The variation in μ to first order is

$$d\mu = \left(\frac{\partial\mu}{\partial N}\right)_{v(\mathbf{r})} dN + \int\left[\frac{\delta\mu}{\delta v(\mathbf{r})}\right]_N dv(\mathbf{r})\, d\mathbf{r}. \qquad (14)$$

Both derivatives on the right hand side of Eq. (14) are chemically significant. The first derivative has been defined as chemical hardness η [8]

$$\eta = \frac{1}{2}\left(\frac{\partial\mu}{\partial N}\right)_{v(\mathbf{r})} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})}, \qquad (15)$$

and the second derivative is defined as the Fukui function f($\mathbf{r}$) [36]

$$f(\mathbf{r}) = \left[\frac{\delta\mu}{\delta v(\mathbf{r})}\right]_N = \left[\frac{\partial\rho}{\partial N}\right]_{v(\mathbf{r})}. \qquad (16)$$

With these definitions, Eq.(14) becomes

$$d\mu = 2\eta dN + \int f(\mathbf{r})\, dv(\mathbf{r})\, d\mathbf{r}. \qquad (17)$$

Equation (17) connects three important molecular properties: the chemical potential μ; the hardness η, and the Fukui function $f(\mathbf{r})$, whose rigorous, quantitative definitions are supplied by density functional theory. The parameters μ and η are global quantities which do not depend on spatial coordinates, whereas $f(\mathbf{r})$ is a local quantity varying from place to place in a molecule; $f(\mathbf{r})$ is useful for explaining the frontier-orbital theory of chemical reactivity in molecules.

Taking the finite difference approximation [11] for the curvature of the E vs. N curve one can obtain the following formula for hardness:

$$\eta = \frac{I - A}{2}. \tag{18}$$

Comparison of Eq. (18) with Eq. (8) shows that both global quantities, the chemical potential μ and the hardness η of a molecule, can be determined from the ionization potential and the electron affinity of the molecule, just as can the electronegativity.

From Eq. (15), another global quantity, softness, is defined in terms of the reciprocal of the hardness

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(\mathbf{r})}. \tag{19}$$

Generalizing to treat a chemical system (atom, molecule or solid) in the grand canonical ensemble, the softness in Eq. (19) may be also defined in terms of number fluctuations as [9]

$$S = \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{v,T} = \frac{1}{kT}[\langle N^2 \rangle - \langle N \rangle^2], \tag{20}$$

where k is the Boltzmann constant and the brackets < > designate ensemble averages at constant T, v and μ.

d. Local Quantities and Nonlocal Quantities

In order to measure the chemical reactivity of a particular site in a molecule, different local variables are defined. The local softness is introduced by combining two important quantities, η and $f(\mathbf{r})$ in Eq. (17):

$$s(\mathbf{r}) = \frac{f(\mathbf{r})}{2\eta} = f(\mathbf{r})S = \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_{v(\mathbf{r})} \left(\frac{\partial N}{\partial \mu}\right)_{v(\mathbf{r})} = \left[\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right]_{v(\mathbf{r})}. \tag{21}$$

Since the Fukui function is normalized (it integrates to unity), the local softness must yield the global softness on integration

$$\int s(\mathbf{r})\,d\mathbf{r} = S\int f(\mathbf{r})\,d\mathbf{r} = S. \tag{22}$$

A nonlocal quantity, the softness kernel [34] is defined by

$$s(\mathbf{r},\mathbf{r}') \equiv -\frac{\delta\rho(\mathbf{r})}{\delta u(\mathbf{r}')}, \tag{23}$$

where $u(\mathbf{r})$ is the difference between external and chemical potentials, i.e.

$$u(\mathbf{r}) = v(\mathbf{r}) - \mu. \tag{24}$$

The softness kernel integrates to the local softness [9]

$$\int s(\mathbf{r},\mathbf{r}')\,d\mathbf{r}' = s(\mathbf{r}), \tag{25}$$

Combination of the definitions of the global softness S, the local softness $s(\mathbf{r})$, and the softness kernel $s(\mathbf{r},\mathbf{r}')$ gives the linear density response function [34],

$$\frac{s(\mathbf{r})\,s(\mathbf{r}')}{S} - s(\mathbf{r},\mathbf{r}') = \left[\frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right]_N. \tag{26}$$

In more detail, from perturbation formula [33]

$$\left[\frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right]_N = 2\mathrm{Re}\sum_k{}' \frac{\langle \Psi_0 |\, \hat{\rho}(\mathbf{r}) \,| \Psi_k\rangle\langle \Psi_k |\, \hat{\rho}(\mathbf{r}') \,| \Psi_0\rangle}{E_k - E_0} \tag{27}$$

Equations (26) and (27) provide a route to connect softness functions and nonlocal polarizability densities; this will be discussed in the next section.

The fluctuation formulas for the local softness [9] and the softness kernel [37] are respectively given by

$$s(\mathbf{r}) = \frac{1}{kT}[\langle \rho(\mathbf{r}) N \rangle - \langle N \rangle \langle \rho(\mathbf{r}) \rangle], \tag{28}$$

and

$$s(\mathbf{r}, \mathbf{r}') = \frac{1}{kT}[\langle \rho(\mathbf{r}) \rho(\mathbf{r}') \rangle - \langle \rho(\mathbf{r}) \rangle \langle \rho(\mathbf{r}') \rangle] . \tag{29}$$

The hardness kernel [32] $\eta(\mathbf{r}, \mathbf{r}')$ is defined in terms of functional the inverse of the softness kernel,

$$2\eta(\mathbf{r}, \mathbf{r}') \equiv -\frac{\delta u(\mathbf{r})}{\delta \rho(\mathbf{r}')} = \frac{\delta^2 F[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')}, \tag{30}$$

where $F[\rho]$ is the universal functional of density functional theory [see Eq. (2)]. The hardness kernel integrates to the local hardness, $\eta(\mathbf{r})$, though not in the sense that the softness kernel integrates to local softness [Eq. (25)]. In this case

$$\eta(\mathbf{r}) \equiv \frac{1}{N}\int \eta(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}', \tag{31}$$

and the local hardness integrates to the global hardness,

$$\eta = \int \eta(\mathbf{r}) f(\mathbf{r}) d\mathbf{r}. \tag{32}$$

The reciprocal relations between local hardness and local softness, and between hardness and softness kernels [34] are

$$2\int s(\mathbf{r})\,\eta(\mathbf{r})\,d\mathbf{r} = 1 \tag{33}$$

and

$$2\int s(\mathbf{r},\mathbf{r}')\,\eta(\mathbf{r}',\mathbf{r}'')\,d\mathbf{r}' = \delta(\mathbf{r}-\mathbf{r}'') . \tag{34}$$

The local hardness involves the variation of $\rho(\mathbf{r})$ at constant external potential; this situation makes the definition of the local hardness [32] ambiguous [37, 38]. [Interestingly, the hardness kernel and the local softness do not suffer from this drawback]. This ambiguity stems from the interdependence of $v(\mathbf{r})$ and $\rho(\mathbf{r})$ as they appear in density functional theory [21]. To avoid this ambiguity and take advantage of the simpler interrelation of softness functions, it is easier to use the softness functions for the further derivations in the next chapter.

4.2 Relation between Molecular Softness and Nonlocal Polarizability Densities

Nonlocal polarizability densities and molecular softness functions are both related to the electronic charge density $\rho^e(\mathbf{r})$. Nonlocal polarizability densities represent the distribution of polarizable matter within a molecule; and softness functions represent the compressibility of the electronic charge cloud [33].

Within density functional theory, the nonlocality of molecular response to perturbations is expressed in terms of the softness kernel $s(\mathbf{r}, \mathbf{r}')$ [34] and the hypersoftness $\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ introduced in this section. The softness kernel $s(\mathbf{r}, \mathbf{r}')$ is a measure of the sensitivity of the electronic charge density $\rho^e(\mathbf{r})$ [1] to a change in the potential $v(\mathbf{r}')$ relative to the chemical potential μ. Here, the potential $v(\mathbf{r})$ is the sum of the potential $v^n(\mathbf{r})$ due to the nuclei and the potential $v^e(\mathbf{r})$ due to an external perturbation. The chemical potential μ [11, 32, 33, 39, 40] is determined by the change in total energy E with a change in the number of electrons N, at constant $v(\mathbf{r})$:

$$\mu = (\partial E/\partial N)_v; \qquad (1)$$

Parr, Donnelly, Levy and Palke [11] have shown that the electronegativity equals $-\mu$. It is convenient to define a modified potential $u(\mathbf{r}')$ by [34]

$$u(\mathbf{r}') = v(\mathbf{r}') - \mu. \qquad (2)$$

The softness and hypersoftness are derivatives of the electronic charge density with respect to the modified potential u(**r**). As shown by Berkowitz and Parr [34], u(**r**) deter-

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[1] The sign changes if the number density $\rho(\mathbf{r})$ is used instead of electronic charge density, in the definition of the softness kernel.

mines all properties, subject to the assumption that E is a convex function of N: Since v(**r**) vanishes as **r** → ∞, the long-range behavior of u(**r**) yields μ; then for finite **r**, v(**r**) follows by subtraction. Given μ and the convexity property of the energy, N is determined. Then the softness kernel is a functional derivative [34],

$$s(\mathbf{r}, \mathbf{r}') = \delta\rho^{e}(\mathbf{r}) / \delta u(\mathbf{r}') . \tag{3}$$

Integrating the softness kernel $s(\mathbf{r}, \mathbf{r}')$ over all space with respect to $\mathbf{r}'$ gives the local softness $s(\mathbf{r})$, [8, 9, 34, Eq. (24) in Section 4.1]

$$s(\mathbf{r}) = \int s(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}'; \tag{4}$$

where the local softness, $s(\mathbf{r})$, is defined by [8, 9, 34]

$$s(\mathbf{r}) = f(\mathbf{r})\, S = -\left[\frac{\partial\rho^{e}(\mathbf{r})}{\partial N}\right]_{v} \left(\frac{\partial N}{\partial\mu}\right)_{v} = -\left[\frac{\partial\rho^{e}(\mathbf{r})}{\partial\mu}\right]_{v} . \tag{5}$$

In Eq. (5), S is the global softness; $f(\mathbf{r})$ is the Fukui function [36], a normalized local softness, which is useful for explaining the frontier-orbital theory of chemical reactivity in molecules. A Maxwell relation yields [see Eqs. (27) and (28), below]

$$f(\mathbf{r}) = -\left[\frac{\partial\rho^{e}(\mathbf{r})}{\partial N}\right]_{v} = \left[\frac{\delta\mu}{\delta v(\mathbf{r})}\right]_{N} . \tag{6}$$

Since the Fukui function is normalized (it integrates to unity), the local softness must yield the global softness on integration [8, 9, 34]

$$\int s(\mathbf{r})\, d\mathbf{r} = S \int f(\mathbf{r})\, d\mathbf{r} = S. \tag{7}$$

The global softness, S, is reciprocally related to the hardness, η, as defined by Parr and Pearson [8]

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_v . \tag{8}$$

The molecular softness determines the change in the electronic charge density at **r** due to a change in the external potential $v^e(\mathbf{r}')$, for a system with a fixed number of electrons N, via

$$\left[\frac{\delta\rho^e(\mathbf{r})}{\delta v^e(\mathbf{r}')}\right]_N = s(\mathbf{r},\mathbf{r}') - s(\mathbf{r})\, s(\mathbf{r}')\, S^{-1}, \tag{9}$$

as proven by Berkowitz and Parr [34] (see also Handler and March [41]).

By definition, the derivative $[\delta\rho^e(\mathbf{r})/\delta v^e(\mathbf{r}')]_N$ is related to the static charge-density susceptibility $\chi(\mathbf{r},\mathbf{r}';0,0)$ by [42]

$$[\delta\rho^e(\mathbf{r})/\delta v^e(\mathbf{r}')]_N = \chi(\mathbf{r},\mathbf{r}';0,0) . \tag{10}$$

Equation (9) permits a connection of the softness kernel and the local softness to the nonlocal polarizability density, since the relation between the charge-density susceptibility $\chi(\mathbf{k},\mathbf{k}';0,0)$ in Fourier space and the longitudinal component $\alpha^L(\mathbf{k},\mathbf{k}';0,0)$ of the nonlocal polarizability density is known.

In terms of the polarization operators $\mathbf{P}_\alpha(\mathbf{r})$ and $\mathbf{P}_\beta(\mathbf{r}')$, the $\alpha\beta$-component of $\alpha(\mathbf{r},\mathbf{r}';-\omega,\omega)$ satisfies [43-47, Eq. (3) in Section 2.1]

$$\begin{aligned}\alpha_{\alpha\beta}(\mathbf{r},\mathbf{r}';-\omega,\omega) &= \langle 0 \,|\, \mathbf{P}_\alpha(\mathbf{r})\, G(\omega)\, \mathbf{P}_\beta(\mathbf{r}') \,|\, 0 \rangle \\ &\quad + \langle 0 \,|\, \mathbf{P}_\beta(\mathbf{r}')\, G^*(-\omega)\, \mathbf{P}_\alpha(\mathbf{r}) \,|\, 0 \rangle, \end{aligned} \tag{11}$$

where $G(\omega)$ is the reduced resolvent operator

$$G(\omega) = (1 - \wp_0)\,(H - E_0 - h\omega)^{-1}\,(1 - \wp_0), \tag{12}$$

$\wp_0$ is the ground-state projection operator $|0\rangle\langle 0|$, H is the unperturbed molecular Hamiltonian, and E_0 is the unperturbed ground-state energy.

After Fourier transformation into k-space, the *longitudinal* component of the static nonlocal polarizability density $\alpha^L(\mathbf{k}, \mathbf{k}';0, 0)$ is related to the charge-density susceptibility [47, 48]. Specifically, with the convention

$$\alpha(\mathbf{k}, \mathbf{k}';0, 0) = \int d\mathbf{r}d\mathbf{r}' \exp(-i\mathbf{k}\cdot\mathbf{r}) \exp(i\mathbf{k}'\cdot\mathbf{r}')\,\alpha(\mathbf{r}, \mathbf{r}';0, 0)\,. \tag{13}$$

and

$$\nabla\cdot\mathbf{P}(\mathbf{r}, \omega) = -\Delta\rho(\mathbf{r}, \omega)\,, \tag{14}$$

one obtains [47, 48]

$$\alpha^L(\mathbf{k}, \mathbf{k}';0, 0) = \vec{\mathbf{k}}\vec{\mathbf{k}}'\chi(\mathbf{k}, \mathbf{k}';0, 0)/kk'. \tag{15}$$

Then from Eqs. (9), (10) and (13), one can obtain

$$\alpha^L(\mathbf{k}, \mathbf{k}';0, 0) = \vec{\mathbf{k}}\vec{\mathbf{k}}'\left[s(\mathbf{k}, \mathbf{k}') - s(-\mathbf{k})\,s(\mathbf{k}')\,S^{-1}\right](kk')^{-1}. \tag{16}$$

The longitudinal component of the polarizability density $\alpha^L(\mathbf{k}, \mathbf{k}';0, 0)$ suffices to determine all of the physical properties considered in the next chapter. In **r** space Eq. (16) is

$$\nabla_\alpha\nabla'_\beta\,\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}';0, 0) = s(\mathbf{r}, \mathbf{r}') - s(\mathbf{r})\,s(\mathbf{r}')\,S^{-1}. \tag{17}$$

Equation (16) gives an exact formulation of the observed qualitative correlation between polarizability and softness; it is consistent with the result of Vela and Gázquez for the total polarizability [49]:

$$\alpha_{\alpha\beta} = \int d\mathbf{r}d\mathbf{r}' \left[s(\mathbf{r}, \mathbf{r}') - s(\mathbf{r})\, s(\mathbf{r}')\, S^{-1} \right] r_{\alpha} r'_{\beta}. \tag{18}$$

Vela and Gázquez have used Eq. (18) and a local approximation to the softness kernel to correlate the isotropically averaged polarizability α and the global softness S, in an approximate fashion [49]. The total polarizability can be obtained from Eq. (16) in the form

$$\alpha_{ij} = \left.\frac{\partial^2 s(\mathbf{k}\hat{\imath}, \mathbf{k}'\hat{\jmath})}{\partial k_i \partial k'_j}\right|_{k = k' = 0} - \left[\left.\frac{\partial s(-\mathbf{k}\hat{\imath})}{\partial k_i}\right|_{k = 0}\right]\left[\left.\frac{\partial s(\mathbf{k}'\hat{\jmath})}{\partial k'_j}\right|_{k' = 0}\right] S^{-1}, \tag{19}$$

in terms of the derivatives of the softness kernel with respect to $\mathbf{k}$ and $\mathbf{k}'$. In Eq. (19), $\hat{\imath}$ and $\hat{\jmath}$ denote unit vectors in the directions of the **i** and **j** axes.

Further, Eq. (16) suggests a generalization of softness to include frequency dependence, with $s(\mathbf{r}, \mathbf{r}'; -\omega, \omega)$ determined by the ω-frequency component of the change in electronic charge density $\rho^e(\mathbf{r}, \omega)$ induced by the ω-frequency component of the modified potential $u(\mathbf{r}', \omega)$, within linear response:

$$s(\mathbf{r}, \mathbf{r}'; -\omega, \omega) = \frac{\delta\rho^e(\mathbf{r}, \omega)}{\delta u(\mathbf{r}', \omega)}. \tag{20}$$

To extend the density-functional analysis to nonlinear response, Fuentealba and Parr [50] have used higher-order derivatives of the molecular hardness $\eta(\mathbf{r})$ [8]. Here, we introduce a hypersoftness $\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, which permits a more direct relation to the hyperpolarizability density. The hypersoftness $\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ is defined by

$$\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \left[\frac{\delta^2\rho^e(\mathbf{r})}{\delta u(\mathbf{r}')\, \delta u(\mathbf{r}'')}\right] = \frac{\delta s(\mathbf{r}, \mathbf{r}')}{\delta u(\mathbf{r}'')}. \tag{21}$$

From Eq. (21) and the symmetry of $s(\mathbf{r}, \mathbf{r}')$, $\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ is symmetric in all three variables $\mathbf{r}$, $\mathbf{r}'$ and $\mathbf{r}''$. The analysis below requires contracted versions of the hypersoftness, obtained by integration with respect to one or more of the spatial variables:

$$\sigma(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}''\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \int d\mathbf{r}''\sigma(\mathbf{r}', \mathbf{r}'', \mathbf{r}) = \int d\mathbf{r}''\sigma(\mathbf{r}'', \mathbf{r}, \mathbf{r}'), \tag{22}$$

and

$$\sigma(\mathbf{r}) = \int d\mathbf{r}'d\mathbf{r}''\sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \int d\mathbf{r}'d\mathbf{r}''\sigma(\mathbf{r}', \mathbf{r}'', \mathbf{r}) = \int d\mathbf{r}'d\mathbf{r}''\sigma(\mathbf{r}'', \mathbf{r}, \mathbf{r}'). \tag{23}$$

When the external potential $v^e(\mathbf{r})$ changes while the number of electrons N is held constant, the change $\Delta\rho^e(\mathbf{r})$ in the electronic charge density at point **r** satisfies

$$\begin{aligned}\Delta\rho^e(\mathbf{r}) &= \delta\rho^e(\mathbf{r}) + \frac{1}{2}\delta^2\rho^e(\mathbf{r}) + \ldots \\ &= \int d\mathbf{r}'\chi(\mathbf{r}, \mathbf{r}')\delta v^e(\mathbf{r}') + \frac{1}{2}\int d\mathbf{r}'d\mathbf{r}''\chi^{(2)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\delta v^e(\mathbf{r}')\delta v^e(\mathbf{r}'') + \ldots \end{aligned} \tag{24}$$

where $\chi^{(2)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ is the nonlinear charge-density susceptibility (at lowest order). For comparison, within the density functional framework, $\Delta\rho^e(\mathbf{r})$ is obtained from [see Appendix B]

$$\begin{aligned}\Delta\rho^e(\mathbf{r}) = &\int d\mathbf{r}'\left[\frac{\delta\rho^e(\mathbf{r})}{\delta u(\mathbf{r}')}\right]\delta u(\mathbf{r}') \\ &+\frac{1}{2}\int d\mathbf{r}'d\mathbf{r}''\left[\frac{\delta^2\rho^e(\mathbf{r})}{\delta u(\mathbf{r}')\delta u(\mathbf{r}'')}\right]\delta u(\mathbf{r}')\delta u(\mathbf{r}'') \\ &+\frac{1}{2}\int d\mathbf{r}'\left[\frac{\delta\rho^e(\mathbf{r})}{\delta u(\mathbf{r}')}\right]\delta^2 u(\mathbf{r}') + \ldots\end{aligned} \tag{25}$$

to second order. When $v^e(\mathbf{r})$ is changed but N is held constant, there is a non-zero second variation in u(**r**), due to the second variation in μ. The first variation in μ at constant N is specified by the Fukui function f(**r**):

$$\delta\mu_N = \int d\mathbf{r}\ f(\mathbf{r})\, v^e(\mathbf{r})\,, \tag{26}$$

where [34, 51]

$$f(\mathbf{r}) = -\left[\frac{\partial\rho^e(\mathbf{r})}{\partial N}\right]_v = \left[\frac{\delta\mu}{\delta v^e(\mathbf{r})}\right]_N . \tag{27}$$

The equality of the two derivatives in Eq. (27) follows from a Maxwell relation [52] for the mixed second partial derivatives of the energy E, with N and $v^e(\mathbf{r})$ taken as the independent variables:

$$dE = \mu dN - \int d\mathbf{r}\rho^e(\mathbf{r})\, v^e(\mathbf{r}). \tag{28}$$

The second variation in μ stems from nonlinear response to the external potential:

$$\delta^2\mu_N = \int d\mathbf{r}d\mathbf{r}'\left[\frac{\delta f(\mathbf{r})}{\delta v^e(\mathbf{r}')}\right]_N \delta v^e(\mathbf{r})\,\delta v^e(\mathbf{r}')\,. \tag{29}$$

From Eqs. (2) and (3), within the density functional framework the change in charge density is

$$\begin{aligned}\Delta\rho^e(\mathbf{r}) &= \int d\mathbf{r}' s(\mathbf{r},\mathbf{r}')\ [\delta v^e(\mathbf{r}') - \delta\mu] \\ &\quad + \frac{1}{2}\int d\mathbf{r}'d\mathbf{r}''\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'')\ [\delta v^e(\mathbf{r}') - \delta\mu]\ [\delta v^e(\mathbf{r}'') - \delta\mu] \\ &\quad - \frac{1}{2}\int d\mathbf{r}' s(\mathbf{r},\mathbf{r}')\,\delta^2\mu + \ldots\end{aligned} \tag{30}$$

Then from Eqs. (26) and (29)

$$\begin{aligned}\Delta\rho^e(\mathbf{r}) = {} & \int d\mathbf{r}' s(\mathbf{r},\mathbf{r}')\,\delta v^e(\mathbf{r}') - \int d\mathbf{r}'' s(\mathbf{r},\mathbf{r}'') \int d\mathbf{r}' f(\mathbf{r}')\,\delta v^e(\mathbf{r}') \\ & + \frac{1}{2}\int d\mathbf{r}' d\mathbf{r}'' \sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,\delta v^e(\mathbf{r}')\,\delta v^e(\mathbf{r}'') \\ & - \frac{1}{2}\int d\mathbf{r}' d\mathbf{r}''' \sigma(\mathbf{r},\mathbf{r}',\mathbf{r}''')\,\delta v^e(\mathbf{r}') \int d\mathbf{r}'' f(\mathbf{r}'')\,\delta v^e(\mathbf{r}'') \\ & - \frac{1}{2}\int d\mathbf{r}'' d\mathbf{r}''' \sigma(\mathbf{r},\mathbf{r}''',\mathbf{r}'')\,\delta v^e(\mathbf{r}'') \int d\mathbf{r}' f(\mathbf{r}')\,\delta v^e(\mathbf{r}') \\ & + \frac{1}{2}\int d\mathbf{r}''' d\mathbf{r}^{iv} \sigma(\mathbf{r},\mathbf{r}''',\mathbf{r}^{iv}) \int d\mathbf{r}' f(\mathbf{r}')\,\delta v^e(\mathbf{r}') \int d\mathbf{r}'' f(\mathbf{r}'')\,\delta v^e(\mathbf{r}'') \\ & - \frac{1}{2}\int d\mathbf{r}''' s(\mathbf{r},\mathbf{r}''') \int d\mathbf{r}' d\mathbf{r}'' \left[\frac{\delta f(\mathbf{r}')}{\delta v^e(\mathbf{r}'')}\right] \delta v^e(\mathbf{r}')\,\delta v^e(\mathbf{r}'') + \ldots \end{aligned} \tag{31}$$

From Eqs. (2), (22), and (23), Eq. (31) becomes

$$\begin{aligned}\Delta\rho^e(\mathbf{r}) = {} & \int d\mathbf{r}' [s(\mathbf{r},\mathbf{r}') - s(\mathbf{r}) f(\mathbf{r}')]\,\delta v^e(\mathbf{r}') \\ & + \frac{1}{2}\int d\mathbf{r}' d\mathbf{r}'' \{\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'') - \sigma(\mathbf{r},\mathbf{r}') f(\mathbf{r}'') - \sigma(\mathbf{r},\mathbf{r}'') f(\mathbf{r}') \\ & + \sigma(\mathbf{r}) f(\mathbf{r}') f(\mathbf{r}'') - s(\mathbf{r}) \left[\frac{\delta f(\mathbf{r}')}{\delta v^e(\mathbf{r}'')}\right] \}\,\delta v^e(\mathbf{r}')\,\delta v^e(\mathbf{r}'') \\ & + \ldots \end{aligned} \tag{32}$$

The Fukui function f(**r**) is related to the local softness s(**r**) via the global softness S,

$$f(\mathbf{r}) = s(\mathbf{r}) S^{-1}. \tag{33}$$

Then

$$\begin{aligned}\Delta\rho^{e}(\mathbf{r}) = {} & \int d\mathbf{r}'\,[s(\mathbf{r},\mathbf{r}') - s(\mathbf{r})\,s(\mathbf{r}')\,S^{-1}]\,\delta v^{e}(\mathbf{r}') \\ & + \frac{1}{2}\int d\mathbf{r}'d\mathbf{r}''\,\{\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'') - \sigma(\mathbf{r},\mathbf{r}')\,s(\mathbf{r}'')\,S^{-1} - \sigma(\mathbf{r},\mathbf{r}'')\,s(\mathbf{r}')\,S^{-1} \\ & + \sigma(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-2} - s(\mathbf{r})\left[\frac{\delta f(\mathbf{r}')}{\delta v^{e}(\mathbf{r}'')}\right]\} \\ & \times \delta v^{e}(\mathbf{r}')\,\delta v^{e}(\mathbf{r}'') + \ldots \end{aligned} \tag{34}$$

The final term in Eq. (34) can be further simplified as [see Appendix C]

$$\begin{aligned}\left[\frac{\delta f(\mathbf{r}')}{\delta v^{e}(\mathbf{r}'')}\right]_{N} = {} & \sigma(\mathbf{r}',\mathbf{r}'')\,S^{-1} - \sigma(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-2} \\ & - \sigma(\mathbf{r}'')\,s(\mathbf{r}')\,S^{-2} + \sigma s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-3}. \end{aligned} \tag{35}$$

Substitution of Eq. (35) into Eq. (34) gives

$$\begin{aligned}\Delta\rho^{e}(\mathbf{r}) = {} & \int d\mathbf{r}'\,[s(\mathbf{r},\mathbf{r}') - s(\mathbf{r})\,s(\mathbf{r}')\,S^{-1}]\,\delta v^{e}(\mathbf{r}') \\ & + \frac{1}{2}\int d\mathbf{r}'d\mathbf{r}''\,\{\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'') - [\sigma(\mathbf{r},\mathbf{r}')\,s(\mathbf{r}'') + \sigma(\mathbf{r},\mathbf{r}'')\,s(\mathbf{r}') + \sigma(\mathbf{r}',\mathbf{r}'')\,s(\mathbf{r})]\,S^{-1} \\ & + [\sigma(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'') + \sigma(\mathbf{r}')\,s(\mathbf{r})\,s(\mathbf{r}'') + \sigma(\mathbf{r}'')\,s(\mathbf{r})\,s(\mathbf{r}')]\,S^{-2} \\ & - \sigma\; s(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-3}\}\,\delta v^{e}(\mathbf{r}')\,\delta v^{e}(\mathbf{r}'') + \ldots \end{aligned} \tag{36}$$

Then by comparison with Eqs. (24) and (36), the lowest order nonlinear charge-density susceptibility $\chi^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ in terms of molecular softness and hypersoftness is

$$\begin{aligned}
&\chi^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'') \\
&= \sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'') - [\sigma(\mathbf{r},\mathbf{r}')\,s(\mathbf{r}'') + \sigma(\mathbf{r},\mathbf{r}'')\,s(\mathbf{r}') + \sigma(\mathbf{r}',\mathbf{r}'')\,s(\mathbf{r})]\,S^{-1} \\
&\qquad + [\sigma(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'') + \sigma(\mathbf{r}')\,s(\mathbf{r})\,s(\mathbf{r}'') + \sigma(\mathbf{r}'')\,s(\mathbf{r})\,s(\mathbf{r}')]\,S^{-2} \\
&\qquad - \sigma\; s(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-3} \qquad (37) \\
&= C(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,[1/3\;\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'') - \sigma(\mathbf{r},\mathbf{r}')\,s(\mathbf{r}'')\,S^{-1} \\
&\qquad + \sigma(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-2} - 1/3\;\sigma\; s(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-3}\,], \qquad (38)
\end{aligned}$$

where σ is obtained by integrating over $\mathbf{r}$ in Eq. (23), and $C(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ denotes the operator that sums the cyclic permutations of $\mathbf{r}$, $\mathbf{r}'$ and $\mathbf{r}''$ in the expression that follows it. The symmetries of $\chi^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ and $\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ with respect to $\mathbf{r}$, $\mathbf{r}'$ and $\mathbf{r}''$ are evident in Eq. (38). The lowest order nonlinear charge-density susceptibility $\chi^{(2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ is related to the longitudinal component of the β hyperpolarizability density in k-space, via

$$\beta^{L}(\mathbf{k},\mathbf{k}',\mathbf{k}'') = i\vec{\mathbf{k}}\vec{\mathbf{k}}'\vec{\mathbf{k}}''\chi^{(2)}(\mathbf{k},\mathbf{k}',\mathbf{k}'')\,(kk'k'')^{-1}. \qquad (39)$$

Thus, the relation between $\beta^{L}(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ and the hypersoftness is

$$\beta^{L}(\mathbf{k}, \mathbf{k}', \mathbf{k}'')$$

$$= i\vec{\mathbf{k}}\vec{\mathbf{k}}'\vec{\mathbf{k}}''C(\mathbf{k}, \mathbf{k}', \mathbf{k}'')\,[1/3\ \sigma(\mathbf{k}, \mathbf{k}', \mathbf{k}'') - \sigma(\mathbf{k}, \mathbf{k}')\,s(\mathbf{k}'')\,S^{-1}$$

$$+\sigma(\mathbf{k})\,s(\mathbf{k}')\,s(\mathbf{k}'')\,S^{-2} - 1/3\ \sigma\ s(\mathbf{k})\,s(\mathbf{k}')\,s(\mathbf{k}'')\,S^{-3}\,]\,(kk'k'')^{-1}. \quad (40)$$

For comparison, a perturbation analysis gives the hyperpolarizability density in the form [48, 52]

$$\begin{aligned}
&\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}''; -\omega_\sigma, \omega_1, \omega_2) \\
&\quad = \wp_{\beta\gamma}\,[\,\langle 0\,|\,\mathbf{P}_\alpha(\mathbf{r})\,G(\omega_\sigma)\,\mathbf{P}^{\emptyset}{}_\gamma(\mathbf{r}'')\,G(\omega_1)\,\mathbf{P}_\beta(\mathbf{r}')\,|\,0\,\rangle \\
&\qquad + \langle 0\,|\,\mathbf{P}_\gamma(\mathbf{r}'')\,G(-\omega_2)\,\mathbf{P}^{\emptyset}{}_\beta(\mathbf{r}')\,G(-\omega_\sigma)\,\mathbf{P}_\alpha(\mathbf{r})\,|\,0\,\rangle \\
&\qquad + \langle 0\,|\,\mathbf{P}_\gamma(\mathbf{r}'')\,G(-\omega_2)\,\mathbf{P}^{\emptyset}{}_\alpha(\mathbf{r})\,G(\omega_1)\,\mathbf{P}_\beta(\mathbf{r}')\,|\,0\,\rangle\,], \qquad (41)
\end{aligned}$$

where the operator $\wp_{\beta\gamma}$ denotes the sum of all terms obtained by permuting $\mathbf{P}_\beta(\mathbf{r}')$ and $\mathbf{P}_\gamma(\mathbf{r}'')$ and simultaneously permuting the associated frequencies ω_1 and ω_2, in the expression following the operator; and $\omega_\sigma = \omega_1 + \omega_2$. The operator $\mathbf{P}^{\emptyset}{}_\alpha(\mathbf{r})$ is defined by $\mathbf{P}^{\emptyset}{}_\alpha(\mathbf{r}) = \mathbf{P}_\alpha(\mathbf{r}) - \langle 0\,|\,\mathbf{P}_\alpha(\mathbf{r})\,|\,0\,\rangle$.

4.3 Density of States and Nonlocal Polarizability Densities for Metals at Absolute Zero

In the Kohn-Sham [53] formulation of finite-temperature density functional theory, one has the self-consistent equations

$$\left[-\frac{1}{2}\nabla^2+v_{\text{eff}}(\mathbf{r})-\mu\right]\psi_i = \varepsilon_i\psi_i, \tag{1}$$

$$\rho(\mathbf{r}) = \sum_i|\psi_i(\mathbf{r})|^2 f(\varepsilon_i-\mu), \tag{2}$$

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r})+\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\frac{\delta F_{xc}[\rho]}{\delta\rho(\mathbf{r})}, \tag{3}$$

where $f(\varepsilon_i-\mu)$ is the Fermi function,

$$f(\varepsilon_i-\mu) = \frac{1}{1+\exp[\beta(\varepsilon_i-\mu)]} \tag{4}$$

and the $\psi_i(\mathbf{r})$ are the normalized Kohn-Sham orbitals. $F_{xc}[n]$ is the exchange-correlation free-energy functional.

Equations (1) to (4) hold for molecules or solids, for the specific case of solids,

$$\begin{aligned} N = \int d\mathbf{r}\rho(\mathbf{r}) &= \sum_i f(\varepsilon_i-\mu) \\ &= \frac{2V}{(2\pi)^3}\int d\mathbf{k}\ f[\varepsilon_i(\mathbf{k})-\mu], \end{aligned} \tag{5}$$

where the discrete sum has been replaced by an integral; a sum over the band index is assumed here and in the formulas below. Alternatively [9, 54, 55],

$$N = \int d\varepsilon \; g(\varepsilon) f[\varepsilon - \mu], \tag{6}$$

where $g(\varepsilon)$, the density of states at energy ε, is given by

$$\begin{aligned} g(\varepsilon) &= \sum_i \delta(\varepsilon_i - \varepsilon) \\ &= \frac{2V}{(2\pi)^3} \int d\mathbf{k} \; \delta[\varepsilon(\mathbf{k}) - \varepsilon]. \end{aligned} \tag{7}$$

At $T = 0$, μ is equal to the Fermi energy ε_F and

$$f(\varepsilon_i - \mu) = \begin{cases} 1 & \varepsilon_i < \mu \\ 0 & \varepsilon_i > \mu \end{cases} \tag{8}$$

At $T = 0$ one therefore has

$$N = \int_0^{\mu} d\varepsilon \; g(\varepsilon) \tag{9}$$

and hence

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{1}{2\eta} = S = g(\varepsilon_F), \tag{10}$$

where the volume V and the lattice structure, remain fixed through all the differentiations here and later. For a metal at absolute zero, the global softness is the density of states at the Fermi level.

The local density of states $g(\varepsilon, \mathbf{r})$ is defined by

$$g(\varepsilon, \mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \delta(\varepsilon_i - \varepsilon)$$

$$= \frac{2V}{(2\pi)^3}\int d\mathbf{k}\ |\psi_k(\mathbf{r})|^2\ \delta[\varepsilon(\mathbf{k}) - \varepsilon]\,. \tag{11}$$

In analogy with Eq.(9), the electron density is given at absolute zero temperature by

$$\rho(\mathbf{r}) = \int_0^{\mu} d\varepsilon\ g(\varepsilon, \mathbf{r})\,. \tag{12}$$

Consequently, using Eq. (10) and Eq. (16) in Section 4.1, one can connect the Fukui function [36] with the density of states $g(\varepsilon)$ and the local density states $g(\varepsilon, \mathbf{r})$:

$$\begin{aligned} f(\mathbf{r}) &= \left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_{T,V} = \left[\frac{\partial\rho(\mathbf{r})}{\partial\mu}\right]_{T,V}\left(\frac{\partial\mu}{\partial N}\right)_{T,V} \\ &= 2\eta g(\varepsilon_F, \mathbf{r}) = \frac{g(\varepsilon_F, \mathbf{r})}{g(\varepsilon_F)}\,. \end{aligned} \tag{13}$$

The Fukui function is the normalized local density of states at the Fermi level; the normalization $\int f(\mathbf{r})\,d\mathbf{r} = 1$ corresponds to $\int g(\varepsilon_F, \mathbf{r})\,d\mathbf{r} = g(\varepsilon_F)$.

Equations (10) and (13) give the product of the global softness S and Fukui function, that is the definition of the local softness $s(\mathbf{r})$ [see Eq. (21) in Section 4.1]

$$s(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial\mu}\right)_{T,v(\mathbf{r})} = Sf(\mathbf{r}) = g(\varepsilon_F, \mathbf{r})\,. \tag{14}$$

Equations (10) and (14) extend the application of the molecular softness functions to metals at T = 0:

$$S = g(\varepsilon_F)\,, \tag{15}$$

$$s(\mathbf{r}) = g(\varepsilon_F, \mathbf{r})\,, \tag{16}$$

The integration relation also holds for Eqs. (15) and (16), thus

$$S = \int d\mathbf{r} s(\mathbf{r}) . \quad (17)$$

Chemisorption and catalytic reactions on metals can be regarded as soft-soft chemical reactions. Falicov and Somorjai [54] have pointed out that $f(\mathbf{r})$ or $g(\varepsilon, \mathbf{r})$ appears to determines site selectivity for metals in chemisorption and catalysis. In general metals are soft [4], with large $g(\varepsilon)$ [9], and transition metals are particular active because of their high $g(\varepsilon)$.

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CHAPTER V

MOLECULAR SOFTNESS, INFRARED ABSORPTION, AND VIBRATIONAL RAMAN SCATTERING: RELATIONS DERIVED FROM NONLOCAL POLARIZABILITY DENSITIES

5.1 Vibrational Force Constants and Anharmonicities in Terms of Molecular Softness

When a nucleus shifts position infinitesimally, the change in energy quadratic in the nuclear displacement depends on the gradients of the field at the nucleus due to the unperturbed electronic and nuclear charge distribution, and on the electronic induction energy associated with the change in the nuclear Coulomb field. The electronic charge distribution responds to the change in the nuclear Coulomb field due to the shift in the nuclear position via the same susceptibilities that describe its response to external fields. Force constants and anharmonicities depend respectively on the second and third derivatives of the molecular potential energy function V with respect to nuclear coordinates (within the Born-Oppenheimer approximation). By the Hohenberg-Kohn theorem [1], the electronic energy is a functional of the electron density, $E = E[\rho^e(\mathbf{r})]$. For a specified nuclear configuration $\{\mathbf{R}\}$, within the Born-Oppenheimer approximation, the force on nucleus I is obtained by differentiating the effective potential $V(\{\mathbf{R}\})$, the sum of $E[\rho^e(\mathbf{r})]$ and the nuclear Coulomb potential:

$$-\frac{\partial V(\{\mathbf{R}\})}{\partial \mathbf{R}_\alpha^I} = -\int d\mathbf{r}\left[\frac{\delta E}{\delta \rho^e(\mathbf{r})}\right]\frac{\partial \rho^e(\mathbf{r})}{\partial \mathbf{R}_\alpha^I}$$

$$-Z^{I}\int d\mathbf{r}\ \rho^{e}(\mathbf{r})\,\nabla^{I}_{\alpha}|\mathbf{r}-\mathbf{R}^{I}|^{-1}$$

$$-Z^{I}\sum_{J\neq I} Z^{J}\nabla^{I}_{\alpha}|\mathbf{R}^{I}-\mathbf{R}^{J}|^{-1}, \tag{1}$$

where $\delta E/\delta\rho^{e}(\mathbf{r})$ denotes the functional derivative of the energy with respect to the electronic charge density; equivalently, $-\delta E/\delta\rho^{e}(\mathbf{r})$ is the chemical potential for the electrons [2-4]. ∇^{I}_{α} denotes the derivative with respect to $\mathbf{R}^{I}_{\alpha}$. Since $\delta E/\delta\rho^{e}(\mathbf{r})$ is independent of $\mathbf{r}$ [2-5], the first term in Eq. (1) vanishes, to give the Hellmann-Feynman result [6] for the force.

The second derivatives of $V(\{\mathbf{R}\})$ with respect to the normal mode coordinates q_n, evaluated at the equilibrium nuclear configuration, determine the vibrational force constants k_n, as $k_n = \partial^2 V(\{\mathbf{R}_{eq}\})/\partial q_n^2$. Differentiating Eq. (1) directly gives:

$$\frac{\partial^2 V}{\partial \mathbf{R}^{I}_{\alpha}\partial \mathbf{R}^{J}_{\beta}} = Z^{I}\int d\mathbf{r}\frac{\partial\rho^{e}(\mathbf{r})}{\partial \mathbf{R}^{J}_{\beta}}\nabla^{I}_{\alpha}|\mathbf{r}-\mathbf{R}^{I}|^{-1}$$

$$+\int d\mathbf{r}\rho^{e}(\mathbf{r})\frac{\partial\left[Z^{I}\nabla^{I}_{\alpha}|\mathbf{r}-\mathbf{R}^{I}|^{-1}\right]}{\partial \mathbf{R}^{J}_{\beta}}$$

$$+\frac{\partial}{\partial \mathbf{R}^{J}_{\beta}}\left[Z^{I}\sum_{K\neq I} Z^{K}\nabla^{I}_{\alpha}|\mathbf{R}^{I}-\mathbf{R}^{K}|^{-1}\right]. \tag{2}$$

By using Eq. (3) in Section 2.3, assuming that the electronic ground state adjusts adiabatically to the shift in nuclear coordinates, one finds

$$\frac{\partial\rho^{e,A}{}_{0}(\mathbf{r})}{\partial \mathbf{R}^{I}{}_{\alpha}} = -\frac{\partial\nabla_{\beta}\mathbf{P}_{0,\beta}{}^{e,A}(\mathbf{r})}{\partial \mathbf{R}^{I}{}_{\alpha}}$$

$$= -\nabla_{\beta}Z^{I}\int d\mathbf{r}'\alpha^{A}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\,T_{\gamma\alpha}(\mathbf{r}',\mathbf{R}^{I}), \tag{3}$$

which permits the transformation of Eq. (2) into an *analytic* expression for the second derivatives of the potential [7]:

$$\frac{\partial^2 V}{\partial \mathbf{R}^I_\alpha \partial \mathbf{R}^J_\beta} = -Z^I Z^J \int d\mathbf{r} d\mathbf{r}' \alpha_{\gamma\delta}(\mathbf{r}, \mathbf{r}')\, T_{\alpha\gamma}(\mathbf{r}, \mathbf{R}^I)\, T_{\beta\delta}(\mathbf{r}', \mathbf{R}^J)$$

$$+\delta_{IJ} Z^I \left[\int d\mathbf{r} \rho^e(\mathbf{r})\, T_{\alpha\beta}(\mathbf{r}, \mathbf{R}^I) + \sum_{K \neq I} Z^K T_{\alpha\beta}(\mathbf{R}^I, \mathbf{R}^K) \right]$$

$$-(1 - \delta_{IJ})\, Z^I Z^J T_{\alpha\beta}(\mathbf{R}^I, \mathbf{R}^J)\,. \tag{4}$$

In Eq. (4), $T_{\alpha\beta}(\mathbf{R}^I, \mathbf{R}^J) = \nabla^I_\alpha \nabla^I_\beta |\mathbf{R}^I - \mathbf{R}^J|^{-1}$. Equation (4) holds for arbitrary nuclear configurations $\{\mathbf{R}\}$, not restricted to the equilibrium nuclear configuration, $\{\mathbf{R}_{eq}\}$. In interpreting Eq. (4), it is useful to focus on the quadratic energy shifts $1/2\,[\partial^2 V(\{\mathbf{R}\})/\partial \mathbf{R}^I_\alpha \partial \mathbf{R}^J_\beta]\, \delta R^I_\alpha \delta R^J_\beta$ associated with small nuclear displacements δR^I_α and δR^J_β. Then the first term on the right in Eq. (4) gives the second-order *induction energy* of the electrons in the internal fields $\delta \mathfrak{I}^I_\gamma$ and $\delta \mathfrak{I}^J_\delta$, where $\delta \mathfrak{I}^I_\gamma$ is the change in the nuclear Coulomb field due to the shift δR^I_α. Equivalently, the change in field satisfies $\delta \mathfrak{I}^I_\gamma = Z^I\, T_{\gamma\alpha}(\mathbf{r}, \mathbf{R}^I)\, \delta R^I_\alpha$. When $I = J$, the remaining terms give the negative of the field gradient due to the other charge; for $I \neq J$, the remaining terms gives the change in the I - J nuclear Coulomb potential due to the shifts δR^I_α, δR^J_β [8].

From Eq. (17) in Section 4.2,

$$\nabla_\alpha \nabla'_\beta\, \alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; 0, 0) = -s(\mathbf{r}, \mathbf{r}') + s(\mathbf{r})\, s(\mathbf{r}')\, S^{-1}, \tag{5}$$

and a double integration by parts in Eq. (4), one obtains

$$\begin{aligned}\frac{\partial^2 V}{\partial \mathbf{R}^I_\alpha \partial \mathbf{R}^J_\beta} &= -Z^I Z^J \int d\mathbf{r}\, d\mathbf{r}' \left[s(\mathbf{r},\mathbf{r}') - s(\mathbf{r})\, s(\mathbf{r}')\, S^{-1} \right] T_\alpha(\mathbf{r},\mathbf{R}^I)\, T_\beta(\mathbf{r}',\mathbf{R}^J) \\ &\quad + \delta_{IJ} Z^I \left[\int d\mathbf{r}\, \rho^e(\mathbf{r})\, T_{\alpha\beta}(\mathbf{r},\mathbf{R}^I) + \sum_{K \neq I} Z^K T_{\alpha\beta}(\mathbf{R}^I,\mathbf{R}^K) \right] \\ &\quad - (1-\delta_{IJ})\, Z^I Z^J T_{\alpha\beta}(\mathbf{R}^I,\mathbf{R}^J), \qquad (6)\end{aligned}$$

where $T_\alpha(\mathbf{r},\mathbf{R}^I) = \nabla_\alpha \left| \mathbf{r} - \mathbf{R}^I \right|^{-1}$.

At the next order, differentiating Eq. (4) directly gives:

$$\begin{aligned}\frac{\partial^3 V}{\partial \mathbf{R}^I_\alpha \partial \mathbf{R}^J_\beta \partial \mathbf{R}^K_\gamma} &= -Z^I Z^J \int d\mathbf{r}\, d\mathbf{r}' \frac{\partial \alpha_{\delta\varepsilon}(\mathbf{r},\mathbf{r}')}{\partial \mathbf{R}^K_\gamma} T_{\alpha\delta}(\mathbf{r},\mathbf{R}^I)\, T_{\beta\varepsilon}(\mathbf{r}',\mathbf{R}^J) \\ &\quad - \int d\mathbf{r}\, d\mathbf{r}'\, \alpha_{\delta\varepsilon}(\mathbf{r},\mathbf{r}') \frac{\partial \left[Z^I Z^J T_{\alpha\delta}(\mathbf{r},\mathbf{R}^I)\, T_{\beta\varepsilon}(\mathbf{r}',\mathbf{R}^J) \right]}{\partial \mathbf{R}^K_\gamma} \\ &\quad + \frac{\partial}{\partial \mathbf{R}^K_\gamma} \left\{ \delta_{IJ} Z^I \left[\int d\mathbf{r}\, \rho^e(\mathbf{r})\, T_{\alpha\beta}(\mathbf{r},\mathbf{R}^I) + \sum_{L \neq I} Z^L T_{\alpha\beta}(\mathbf{R}^I,\mathbf{R}^L) \right] \right\} \\ &\quad - \frac{\partial \left[(1-\delta_{IJ})\, Z^I Z^J T_{\alpha\beta}(\mathbf{R}^I,\mathbf{R}^J) \right]}{\partial \mathbf{R}^K_\gamma}. \qquad (7)\end{aligned}$$

Using the same assumptions as for Eq. (3), one needs the derivatives of the polarizability density with respect to nuclear coordinates, which are determined by the hyperpolarizability density and the dipole propagator [9],

$$\frac{\partial \alpha_{\beta\gamma}(\mathbf{r},\mathbf{r}')}{\partial \mathbf{R}^I_\alpha} = Z^I \int d\mathbf{r}\, \beta_{\beta\gamma\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\, T_{\delta\alpha}(\mathbf{r}'',\mathbf{R}^I). \qquad (8)$$

to lead to an analytic expression for the third derivatives of $V(\{\mathbf{R}\})$, and hence the anharmonic force constants, $\partial^3 V(\{\mathbf{R}\})/\partial \mathbf{R}^I_\alpha \partial \mathbf{R}^J_\beta \partial \mathbf{R}^K_\gamma$. These quantities depend on the first and second derivatives of $\rho^e(\mathbf{r})$ with respect to the nuclear coordinates:

$$\frac{\partial^3 V}{\partial \mathbf{R}^I_\alpha \partial \mathbf{R}^J_\beta \partial \mathbf{R}^K_\gamma}$$

$$= -Z^I Z^J Z^K \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \beta_{\delta\varepsilon\xi}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\, T_{\alpha\delta}(\mathbf{r}, \mathbf{R}^I)\, T_{\beta\varepsilon}(\mathbf{r}', \mathbf{R}^J)\, T_{\gamma\xi}(\mathbf{r}'', \mathbf{R}^K)$$

$$+ C_{IJK}\delta_{IJ} Z^I Z^K \int d\mathbf{r}\, d\mathbf{r}'\, \alpha_{\delta\varepsilon}(\mathbf{r}, \mathbf{r}')\, T_{\alpha\beta\delta}(\mathbf{r}, \mathbf{R}^I)\, T_{\gamma\varepsilon}(\mathbf{r}', \mathbf{R}^K)$$

$$+ \delta_{IJ}\delta_{JK} Z^I \left[\int d\mathbf{r}\, \rho^e(\mathbf{r})\, T_{\alpha\beta\gamma}(\mathbf{R}^I, \mathbf{r}) + \sum_{M \neq I} Z^M T_{\alpha\beta\gamma}(\mathbf{R}^M, \mathbf{R}^I) \right]$$

$$- C_{IJK}\delta_{IJ}(1 - \delta_{JK}) Z^I Z^K T_{\alpha\beta\gamma}(\mathbf{R}^I, \mathbf{R}^K), \tag{9}$$

where C_{IJK} denotes the sum over the three cyclic permutations of $\{I,\alpha\}$, $\{J,\beta\}$ and $\{K,\gamma\}$, and $T_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}') \equiv \nabla_\alpha \nabla_\beta \nabla_\gamma |\mathbf{r} - \mathbf{r}'|^{-1}$. Equation (9) leads to a physical interpretation of the cubic energy shifts $1/6\, [\partial^3 V(\{\mathbf{R}\})/\partial \mathbf{R}^I_\alpha \partial \mathbf{R}^J_\beta \partial \mathbf{R}^K_\gamma]\, \delta R^I_\alpha \delta R^J_\beta \partial R^K_\gamma$. The first term gives the energy of hyperpolarization of the electronic charge distribution in the fields $\delta\mathfrak{I}^I_\delta$, $\delta\mathfrak{I}^J_\varepsilon$, and $\delta\mathfrak{I}^K_\xi$. The second term on the right gives the induction energy bilinear in the first-order change $\delta\mathfrak{I}^K_\varepsilon$ in the Coulomb field due to nucleus K and the *second-order* change $\delta^2\mathfrak{I}^I_\delta$ in the Coulomb field due to nucleus I (plus the terms associated with permutations of the nuclear labels). Here $\delta^2\mathfrak{I}^I_\delta = 1/2\; Z^I T_{\alpha\beta\delta}(\mathbf{R}^I, \mathbf{r})\, \delta R^I_\alpha \delta R^I_\beta$. Hence the second term vanishes unless at least two of I, J, and K are identical. When I = J = K, the remaining terms give $(-Z^I) \times$ the derivative of the field gradient due to the other charges; when two of the nuclei are identical but distinct from the third, the contribution is the third-order change in the nuclear Coulomb interaction between the two distinct nuclei;

and when I, J, and K are all distinct, the remaining terms vanish.

The hyperpolarizability is related to molecular softness and hypersoftness:

$$-\nabla_\alpha \nabla'_\beta \nabla''_\gamma \beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$$

$$= \sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'') - [\sigma(\mathbf{r}, \mathbf{r}')\, s(\mathbf{r}'') + \sigma(\mathbf{r}, \mathbf{r}'')\, s(\mathbf{r}') + \sigma(\mathbf{r}', \mathbf{r}'')\, s(\mathbf{r})]\, S^{-1}$$

$$+ [\sigma(\mathbf{r})\, s(\mathbf{r}')\, s(\mathbf{r}'') + \sigma(\mathbf{r}')\, s(\mathbf{r})\, s(\mathbf{r}'') + \sigma(\mathbf{r}'')\, s(\mathbf{r})\, s(\mathbf{r}')]\, S^{-2}$$

$$-\sigma\ s(\mathbf{r})\, s(\mathbf{r}')\, s(\mathbf{r}'')\, S^{-3}$$

$$= C(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\Big[1/3\ \sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'') - \sigma(\mathbf{r}, \mathbf{r}')\, s(\mathbf{r}'')\, S^{-1}$$

$$+\sigma(\mathbf{r})\, s(\mathbf{r}')\, s(\mathbf{r}'')\, S^{-2} - 1/3\ \sigma\ s(\mathbf{r})\, s(\mathbf{r}')\, s(\mathbf{r}'')\, S^{-3}\Big], \qquad (10)$$

Again by repeated integration by parts and substitution of Eqs. (5) and (10) into Eq. (9), one can show that anharmonicity constants depend on molecular softness and hypersoftness:

$$\frac{\partial^3 V}{\partial R^I_\alpha \partial R^J_\beta \partial R^K_\gamma}$$

$$= -Z^I Z^J Z^K \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, T_\alpha(\mathbf{r}, \mathbf{R}^I)\, T_\beta(\mathbf{r}', \mathbf{R}^J)\, T_\gamma(\mathbf{r}'', \mathbf{R}^K)$$

$$\times C(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\Big[1/3\ \sigma(\mathbf{r}, \mathbf{r}', \mathbf{r}'') - \sigma(\mathbf{r}, \mathbf{r}')\, s(\mathbf{r}'')\, S^{-1}$$

$$+\sigma(\mathbf{r})\, s(\mathbf{r}')\, s(\mathbf{r}'')\, S^{-2} - 1/3\ \sigma\ s(\mathbf{r})\, s(\mathbf{r}')\, s(\mathbf{r}'')\, S^{-3}\Big]$$

$$+C_{IJK}\delta_{IJ}Z^{I}Z^{K}\int d\mathbf{r}d\mathbf{r}'\left[s(\mathbf{r},\mathbf{r}') - s(\mathbf{r})\,s(\mathbf{r}')\,S^{-1}\right]T_{\alpha\beta}(\mathbf{r},\mathbf{R}^{I})\,T_{\gamma}(\mathbf{r}',\mathbf{R}^{K})$$

$$-\delta_{IJ}\delta_{JK}Z^{I}\left[\int d\mathbf{r}\rho^{e}(\mathbf{r})\,T_{\alpha\beta\gamma}(\mathbf{r},\mathbf{R}^{I}) + \sum_{M\neq I} Z^{M}T_{\alpha\beta\gamma}(\mathbf{R}^{M},\mathbf{R}^{I})\right]$$

$$-C_{IJK}\delta_{IJ}(1-\delta_{JK})\,Z^{I}Z^{K}T_{\alpha\beta\gamma}(\mathbf{R}^{I},\mathbf{R}^{K})\,. \qquad (11)$$

5.2 Electric Field Shielding Tensors, Infrared and Vibrational Raman Band Intensities in Terms of Molecular Softness

When a uniform external field $\mathbf{F}^e$ is applied to a molecule, the net field $\mathbf{F}^K$ acting at nucleus K is

$$\mathbf{F}^K = \mathbf{F}_0^K + (\mathbf{1} - \gamma^K) \cdot \mathbf{F}^e + \frac{1}{2}\phi^K : \mathbf{F}^e\mathbf{F}^e + \ldots, \tag{1}$$

where $\mathbf{F}_0^K$ is the field at nucleus K in the absence of the external perturbation, **1** denotes the unit tensor, γ^K is the Sternheimer (linear) shielding tensor [9-13], and ϕ^K is the nonlinear shielding tensor. As shown by Sambe [9], Epstein [14, 15], and Lazzeretti and Zanasi [16], a molecule with internal vibrational degrees of freedom may couple to the external field through the derivatives of the moments and polarizabilities with respect to nuclear motion[1]. Thus, in general, "a molecule in an external field distorts by an amount depending on the dipole moment and other derivatives to reach a new equilibrium geometry in which the electric field at each nucleus is again zero" [17]. This physical explanation of the connection between γ^K and the atomic polar tensor P was also pointed out by Lazzeretti and Zanasi [16]:

$$\gamma^K_{\alpha\beta} = \delta_{\alpha\beta} - \mathbf{P}_{\alpha\beta}/Z^K, \tag{2}$$

where

$$\mathbf{P}_{\alpha\beta} = \partial\mu_\beta/\partial\mathbf{R}^K_\alpha. \tag{3}$$

Here Z^K is the charge of nucleus K, $\mathbf{R}^K$ is its position vector in a space-fixed frame, and μ is the molecular dipole moment.

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[1] This can also apply to the force relay discussed in Section 3.1.

For clamped nuclei the polarizability $\alpha_{\alpha\beta}$ and the higher polarizabilities such as $\beta_{\alpha\beta\gamma}$ are purely electronic. From Eqs. (2) and (3), the dipole derivative $\partial\mu_\alpha/\partial\mathbf{R}^K_\beta$ is given in terms of γ^K by

$$\partial\mu_\alpha/\partial\mathbf{R}^K_\beta = \mathbf{P}_{\beta\alpha} = Z^K(\delta_{\alpha\beta} - \gamma^K_{\beta\alpha})\,. \tag{4}$$

Buckingham and Fowler [17] have proven that

$$\partial\alpha_{\alpha\beta}/\partial\mathbf{R}^K_\gamma = Z^K\phi^K_{\gamma\alpha\beta}. \tag{5}$$

By use of nonlocal polarizability densities to analyze electronic charge redistribution induced in a molecule by an external field, Hunt [18] has found new expressions for γ^K and ϕ^K in terms of nonlocal polarizability densities $\alpha(\mathbf{r},\mathbf{r}')$ and $\beta(\mathbf{r},\mathbf{r}',\mathbf{r}'')$:

$$\gamma^K_{\beta\alpha} = -\int d\mathbf{r}d\mathbf{r}'\ \alpha_{\alpha\gamma}(\mathbf{r},\mathbf{r}')\,T_{\gamma\beta}(\mathbf{r}',\mathbf{R}^K)\,, \tag{6}$$

and

$$\phi^K_{\gamma\alpha\beta} = \int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''\ \beta_{\alpha\beta\delta}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,T_{\delta\gamma}(\mathbf{r}'',\mathbf{R}^K)\,. \tag{7}$$

By Integrating by parts and substituting Eqs. (5) and (10) in Section 5.1 into Eqs. (6) and (7), one can find the shielding tensor γ^K in terms of the softness, and the quadratic shielding tensor ϕ^K in terms of the softness and hypersoftness:

$$\gamma^K_{\beta\alpha} = -\int d\mathbf{r}d\mathbf{r}'\left[s(\mathbf{r},\mathbf{r}') - s(\mathbf{r})\,s(\mathbf{r}')\,S^{-1}\right]r_\alpha T_\beta(\mathbf{r}',\mathbf{R}^K)\,, \tag{8}$$

$$\phi^K_{\alpha\beta\gamma} = \int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''T_\alpha(\mathbf{r},\mathbf{R}^K)\,r'_\beta r''_\gamma C(\mathbf{r},\mathbf{r}',\mathbf{r}'')\ \{\,[\,1/3\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'')$$

$$-\sigma(\mathbf{r},\mathbf{r}')\,s(\mathbf{r}'')\,S^{-1}+\sigma(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-2}$$

$$-1/3\ \sigma\ s(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-3}\big]\,\}\,. \tag{9}$$

By substituting Eq. (8) into Eq. (4), and Eq. (9) into Eq. (5), one can derive the property derivatives that determine infrared and vibrational Raman band intensities in terms of the molecular softness:

$$\partial\mu_\alpha/\partial\mathbf{R}^K_\beta = Z^K\{\delta_{\alpha\beta}+\int d\mathbf{r}d\mathbf{r}'\big[s(\mathbf{r},\mathbf{r}')-s(\mathbf{r})\,s(\mathbf{r}')\,S^{-1}\big]r_\alpha T_\beta(\mathbf{r}',\mathbf{R}^K)\,\} \tag{10}$$

and

$$\partial\alpha_{\alpha\beta}/\partial\mathbf{R}^K_\gamma = Z^K\int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''r_\alpha r'_\beta T_\gamma(\mathbf{r}'',\mathbf{R}^K)\,C(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,\{\big[1/3\ \sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'')$$

$$-\sigma(\mathbf{r},\mathbf{r}')\,s(\mathbf{r}'')\,S^{-1}+\sigma(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-2}$$

$$-1/3\ \sigma\ s(\mathbf{r})\,s(\mathbf{r}')\,s(\mathbf{r}'')\,S^{-3}\big]\,\}\,. \tag{11}$$

5.3 Interaction Energies and Intermolecular Forces in Terms of Molecular Softness

In addition to single-molecule spectroscopic properties, the long-range interaction energy for a pair of molecules A and B can be expressed in terms of the softness kernels. Gázquez [19] has established a relation that can be used to connect the second-order induction energy to the softness kernel. Here, by using the results of Section 4.2, the intermolecular forces at both first and second order are related to softness and hypersoftness. The first-order interaction energy for a pair of molecules A and B is

$$\Delta E^{(1)} = \int \rho^{A}{}_{0}(\mathbf{r})\,\rho^{B}{}_{0}(\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1}d\mathbf{r}d\mathbf{r}'. \tag{1}$$

The first-order induction force on nucleus K in molecule A is

$$\begin{aligned}\Delta \mathbf{F}^{K}{}_{1,\alpha} &= -\partial\Delta E^{(1)}/\partial \mathbf{R}^{K}{}_{\alpha} \\ &= -\int \frac{\partial \rho^{A}{}_{0}(\mathbf{r})}{\partial \mathbf{R}^{K}{}_{\alpha}}\,\rho^{B}{}_{0}(\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1}d\mathbf{r}d\mathbf{r}' \\ &= -\int \left[\frac{\partial \rho^{n,A}{}_{0}(\mathbf{r})}{\partial \mathbf{R}^{K}_{\alpha}} + \frac{\partial \rho^{e,A}{}_{0}(\mathbf{r})}{\partial \mathbf{R}^{K}_{\alpha}}\right]\rho^{B}{}_{0}(\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1}d\mathbf{r}d\mathbf{r}',\end{aligned} \tag{2}$$

where $\rho^{n,A}{}_{0}(\mathbf{r}')$ is the nuclear charge density, and $\rho^{e,A}{}_{0}(\mathbf{r}')$ is the electronic charge density. From Eq. (3) of Section 2.3

$$\frac{\partial \rho^{e,A}{}_{0}(\mathbf{r})}{\partial \mathbf{R}^{K}_{\delta}} = -\nabla_{\beta} Z^{K}\int d\mathbf{r}'\alpha^{A}_{\beta\gamma}(\mathbf{r},\mathbf{r}')\,T_{\gamma\delta}(\mathbf{r}',\mathbf{R}^{K})$$

$$= Z^K \int d\mathbf{r}' \left[\nabla_\beta \nabla'_\gamma \alpha^A_{\beta\gamma}(\mathbf{r},\mathbf{r}') \right] T_\delta(\mathbf{r}', \mathbf{R}^K)$$

$$= Z^K \int d\mathbf{r}' [s^A(\mathbf{r}, \mathbf{r}') - s^A(\mathbf{r}) s^A(\mathbf{r}') / S^A] T_\delta(\mathbf{r}', \mathbf{R}^K) \qquad (3)$$

and

$$\frac{\partial \rho^{n,A}{}_0(\mathbf{r})}{\partial \mathbf{R}^K_\delta} = Z^K \frac{\partial \delta(\mathbf{r} - \mathbf{R}^K)}{\partial \mathbf{R}^K_\delta}. \qquad (4)$$

From Eqs. (3) and (4), one can derive the *first-order* induction force in terms of the softness function:

$$\Delta F^K_{1,\alpha} = Z^K \int (\mathbf{R}^K - \mathbf{r})_\alpha |\mathbf{R}^K - \mathbf{r}|^{-3} \rho^B{}_0(\mathbf{r}) d\mathbf{r}$$

$$-Z^K \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' [s^A(\mathbf{r}, \mathbf{r}') - s^A(\mathbf{r}) s^A(\mathbf{r}') / S^A]$$

$$\times T_\alpha(\mathbf{r}', \mathbf{R}^K) \rho^B{}_0(\mathbf{r}'') |\mathbf{r} - \mathbf{r}''|^{-1}. \qquad (5)$$

The second-order interaction energy for a pair of molecules A and B is

$$\Delta E^{(2)}{}_{\text{ind}} = -1/2 \int d\mathbf{r} d\mathbf{r}' \alpha^A{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \Im^B{}_{0\alpha}(\mathbf{r}) \Im^B{}_{0\beta}(\mathbf{r}')$$

$$-1/2 \int d\mathbf{r} d\mathbf{r}' \alpha^B{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \Im^A{}_{0\alpha}(\mathbf{r}) \Im^A{}_{0\beta}(\mathbf{r}') \qquad (6)$$

$$= -1/2 \int d\mathbf{r} d\mathbf{r}' [s^A(\mathbf{r}, \mathbf{r}') - s^A(\mathbf{r}) s^A(\mathbf{r}') / S^A] \phi^B{}_0(\mathbf{r}) \phi^B{}_0(\mathbf{r}')$$

$$-1/2 \int d\mathbf{r} d\mathbf{r}' [s^B(\mathbf{r}, \mathbf{r}') - s^B(\mathbf{r}) s^B(\mathbf{r}') / S^B] \phi^A{}_0(\mathbf{r}) \phi^A{}_0(\mathbf{r}'), \qquad (7)$$

where s^A is the softness function associated with molecule A, and the α component of the electric field of the unperturbed molecule A satisfies $\mathfrak{E}^{A}{}_{0\alpha}(\mathbf{r}) = -\nabla_\alpha \phi^{A}{}_{0}(\mathbf{r})$. Equation (7) is the same as Gázquez's result [19].

From Eq. (7), one can derive the second-order induction force by differentiating Eq. (7) with respect to the coordinates of a nucleus in molecule A

$$\begin{aligned}
\Delta F^{K}_{2,\delta,\mathrm{ind}} &= -\frac{\partial E^{(2)}_{\mathrm{ind}}}{\partial \mathbf{R}^{K}_{\delta}} \\
&= 1/2\int d\mathbf{r}d\mathbf{r}'\frac{\partial}{\partial \mathbf{R}^{K}_{\delta}}[s^{A}(\mathbf{r},\mathbf{r}') - s^{A}(\mathbf{r})s^{A}(\mathbf{r}')/S^{A}]\,\phi^{B}{}_{0}(\mathbf{r})\,\phi^{B}{}_{0}(\mathbf{r}') \\
&\quad + 1/2\int d\mathbf{r}d\mathbf{r}'[s^{B}(\mathbf{r},\mathbf{r}') - s^{B}(\mathbf{r})s^{B}(\mathbf{r}')/S^{B}]\frac{\partial}{\partial \mathbf{R}^{K}_{\delta}}\left[\phi^{A}{}_{0}(\mathbf{r})\,\phi^{A}{}_{0}(\mathbf{r}')\right].
\end{aligned} \tag{8}$$

In Section 1.3, Eq. (10) can be rewritten as follows:

$$\begin{aligned}
\frac{\partial \alpha_{\beta\gamma}(\mathbf{r},\mathbf{r}')}{\partial \mathbf{R}^{K}_{\delta}} &= Z^{K}\int d\mathbf{r}''\beta_{\beta\gamma\varepsilon}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,T_{\varepsilon\delta}(\mathbf{r}'',\mathbf{R}^{K}) \\
&= -Z^{K}\int d\mathbf{r}''\nabla''_{\varepsilon}\beta_{\beta\gamma\varepsilon}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,T_{\delta}(\mathbf{r}'',\mathbf{R}^{K}),
\end{aligned} \tag{9}$$

then the derivative in the first term on the right in Eq. (8) is related to hyperpolarizability density β

$$\begin{aligned}
&\frac{\partial}{\partial \mathbf{R}^{K}_{\delta}}[s^{A}(\mathbf{r},\mathbf{r}') - s^{A}(\mathbf{r})s^{A}(\mathbf{r}')/S^{A}] \\
&\qquad = \frac{\partial \nabla_{\beta}\nabla'_{\gamma}\alpha^{A}{}_{\beta\gamma}(\mathbf{r},\mathbf{r}')}{\partial \mathbf{R}^{K}_{\delta}} \\
&\qquad = Z^{K}\int d\mathbf{r}''\left[-\nabla_{\beta}\nabla'_{\gamma}\nabla''_{\varepsilon}\beta^{A}{}_{\beta\gamma\varepsilon}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\right]T_{\delta}(\mathbf{r}'',\mathbf{R}^{K})
\end{aligned}$$

$$= Z^K\int dr''T_\delta(\mathbf{r}'',\mathbf{R}^K)\,C(\mathbf{r},\mathbf{r}',\mathbf{r}'')\,[1/3\;\sigma^A(\mathbf{r},\mathbf{r}',\mathbf{r}'')$$

$$-\sigma^A(\mathbf{r},\mathbf{r}')\,s^A(\mathbf{r}'')\,(S^A)^{-1}+\sigma^A(\mathbf{r})\,s^A(\mathbf{r}')\,s^A(\mathbf{r}'')\,(S^A)^{-2}$$

$$-1/3\;\sigma^A s^A(\mathbf{r})\,s^A(\mathbf{r}')\,s^A(\mathbf{r}'')\,(S^A)^{-3}\Big]. \tag{10}$$

The derivative in the second term of Eq. (8) satisfies

$$\frac{\partial}{\partial \mathbf{R}^K_\delta}\left[\phi^A{}_0(\mathbf{r})\,\phi^A{}_0(\mathbf{r}')\right]$$

$$= \frac{\partial\phi^A{}_0(\mathbf{r})}{\partial \mathbf{R}^K_\delta}\left[\phi^A{}_0(\mathbf{r}')\right]+\frac{\partial\phi^A{}_0(\mathbf{r}')}{\partial \mathbf{R}^K_\delta}\left[\phi^A{}_0(\mathbf{r})\right], \tag{11}$$

where

$$\frac{\partial\phi^A{}_0(\mathbf{r})}{\partial \mathbf{R}^K_\delta} = \int d\mathbf{r}'|\mathbf{r}-\mathbf{r}'|^{-1}\frac{\partial\rho^A{}_0(\mathbf{r}')}{\partial \mathbf{R}^K_\delta}$$

$$= \int d\mathbf{r}'|\mathbf{r}-\mathbf{r}'|^{-1}\left[\frac{\partial\rho^{n,A}{}_0(\mathbf{r}')}{\partial \mathbf{R}^K_\delta}+\frac{\partial\rho^{e,A}{}_0(\mathbf{r}')}{\partial \mathbf{R}^K_\delta}\right]. \tag{12}$$

From Eqs. (3), (4), (11) and (12), the second term in Eq. (8) becomes

$$1/2\int d\mathbf{r}\,d\mathbf{r}'[s^B(\mathbf{r},\mathbf{r}')-s^B(\mathbf{r})\,s^B(\mathbf{r}')/S^B]\frac{\partial}{\partial \mathbf{R}^K_\delta}\left[\phi^A{}_0(\mathbf{r})\,\phi^A{}_0(\mathbf{r}')\right]$$

$$= \frac{1}{2}Z^K\int d\mathbf{r}\,d\mathbf{r}'[s^B(\mathbf{r},\mathbf{r}')-s^B(\mathbf{r})\,s^B(\mathbf{r}')/S^B]$$

$$\times\{\phi^A{}_0(\mathbf{r})\,Z^K\nabla^K_\delta|\mathbf{r}'-\mathbf{R}^K|^{-1}+\phi^A{}_0(\mathbf{r})\,Z^K\int d\mathbf{r}''d\mathbf{r}'''T_\delta(\mathbf{r}''',\mathbf{R}^K)\,|\mathbf{r}'-\mathbf{r}''|^{-1}$$

$$\times\, [s^A(\mathbf{r}'',\mathbf{r}''') - s^A(\mathbf{r}'')\, s^A(\mathbf{r}''')/S^A]$$

$$+\phi^A{}_0(\mathbf{r}')\, Z^K \nabla^K_\delta |\mathbf{r}-\mathbf{R}^K|^{-1} + \phi^A{}_0(\mathbf{r}')\, Z^K \int d\mathbf{r}''d\mathbf{r}'''\, T_\delta(\mathbf{r}''',\mathbf{R}^K)\, |\mathbf{r}-\mathbf{r}''|^{-1}$$

$$\times\, [s^A(\mathbf{r}'',\mathbf{r}''') - s^A(\mathbf{r}'')\, s^A(\mathbf{r}''')/S^A]\ \} . \tag{13}$$

From Eqs. (8), (10), and (13), the second-order induction force is

$$\Delta F^K_{2,\delta,\mathrm{ind}}$$

$$= \frac{1}{2} Z^K \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, T_\delta(\mathbf{r}'',\mathbf{R}^K)\, \phi^B{}_0(\mathbf{r})\, \phi^B{}_0(\mathbf{r}')$$

$$\times\, C(\mathbf{r},\mathbf{r}',\mathbf{r}'')\ [1/3\ \sigma^A(\mathbf{r},\mathbf{r}',\mathbf{r}'')$$

$$-\sigma^A(\mathbf{r},\mathbf{r}')\, s^A(\mathbf{r}'')\ (S^A)^{-1} + \sigma^A(\mathbf{r})\, s^A(\mathbf{r}')\, s^A(\mathbf{r}'')\ (S^A)^{-2}$$

$$-1/3\ \sigma^A\, s^A(\mathbf{r})\, s^A(\mathbf{r}')\, s^A(\mathbf{r}'')\ (S^A)^{-3}\Big]$$

$$+\frac{1}{2} Z^K \int d\mathbf{r}\, d\mathbf{r}'\, [s^B(\mathbf{r},\mathbf{r}') - s^B(\mathbf{r})\, s^B(\mathbf{r}')/S^B]$$

$$\times\, \{\phi^A{}_0(\mathbf{r})\, Z^K \nabla^K_\delta |\mathbf{r}'-\mathbf{R}^K|^{-1} + \phi^A{}_0(\mathbf{r})\, Z^K \int d\mathbf{r}''d\mathbf{r}'''\, T_\delta(\mathbf{r}''',\mathbf{R}^K)\, |\mathbf{r}'-\mathbf{r}''|^{-1}$$

$$\times\, [s^A(\mathbf{r}'',\mathbf{r}''') - s^A(\mathbf{r}'')\, s^A(\mathbf{r}''')/S^A]$$

$$+\phi^A{}_0(\mathbf{r}')\, Z^K \nabla^K_\delta |\mathbf{r}-\mathbf{R}^K|^{-1} + \phi^A{}_0(\mathbf{r}')\, Z^K \int d\mathbf{r}''d\mathbf{r}'''\, T_\delta(\mathbf{r}''',\mathbf{R}^K)\, |\mathbf{r}-\mathbf{r}''|^{-1}$$

$$\times\, [s^A(\mathbf{r}'',\mathbf{r}''') - s^A(\mathbf{r}'')\, s^A(\mathbf{r}''')/S^A]\ \} . \tag{14}$$

The dispersion energy can be expressed in terms of softness functions, generalized to imaginary frequencies.

$$\Delta E^{(2)}_{\text{disp}} = -(h/4\pi^2)\int_0^\infty d\omega \int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,\alpha^{A}_{\alpha\beta}(\mathbf{r},\mathbf{r}';-i\omega,i\omega)$$

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

$$= -\frac{h}{4\pi^2}\int_0^\infty d\omega \int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''\,[s^{A}(\mathbf{r},\mathbf{r}';-i\omega,i\omega) - s^{A}(\mathbf{r};i\omega)\,s^{A}(\mathbf{r}';i\omega)/S^{A}(i\omega)]$$

$$\times\,[s^{B}(\mathbf{r}'',\mathbf{r}''';-i\omega,i\omega) - s^{B}(\mathbf{r}'';i\omega)\,s^{B}(\mathbf{r}''';i\omega)/S^{B}(i\omega)]$$

$$\times\,|\mathbf{r}-\mathbf{r}'''|^{-1}|\mathbf{r}''-\mathbf{r}'|^{-1}. \qquad (15)$$

In Eq. (15), the softness kernel $s(\mathbf{r},\mathbf{r}';i\omega)$ is obtained by first generalizing $s(\mathbf{r},\mathbf{r}') = \delta\rho^{e}(\mathbf{r})/\delta u(\mathbf{r}')$ to the ω-frequency component of the change in electronic charge density produced by a potential of frequency ω, and then analytically continuing into the complex plane. In terms of transition matrix elements between the ground state $|\,0\,\rangle$ and excited states $|\,k\,\rangle$.

$$[s^{A}(\mathbf{r},\mathbf{r}';-i\omega,i\omega) - s^{A}(\mathbf{r};i\omega)\,s^{A}(\mathbf{r}';i\omega)/S^{A}(i\omega)]$$

$$= (4\pi^2/h)\sum_{k\neq 0}\omega_{k0}(\omega_{k0}^2+\omega^2)^{-1}\langle\,0\,|\,\rho(\mathbf{r})|\,k\,\rangle\langle\,k\,|\,\rho(\mathbf{r}')|\,0\,\rangle. \qquad (16)$$

The second-order dispersion force is

$$\Delta\mathbf{F}^{K}_{2,\delta,\text{disp}} = -\frac{\partial\Delta E^{(2)}_{\text{disp}}}{\partial\mathbf{R}^{K}_{\delta}}$$

$$= (h/4\pi^2)\int_0^\infty d\omega \int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}''' \frac{\partial [s^A(\mathbf{r},\mathbf{r}';-i\omega,i\omega) - s^A(\mathbf{r};i\omega)\,s^A(\mathbf{r}';i\omega)/S^A(i\omega)]}{\partial \mathbf{R}^K{}_\delta}$$

$$\times [s^B(\mathbf{r}'',\mathbf{r}''';-i\omega,i\omega) - s^B(\mathbf{r}'';i\omega)\,s^B(\mathbf{r}''';i\omega)/S^B(i\omega)]$$

$$\times |\mathbf{r}-\mathbf{r}'''|^{-1}|\mathbf{r}''-\mathbf{r}'|^{-1}. \qquad (17)$$

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APPENDIX

Appendix A

Force Theorems[1]

Let $\mathbf{F}_e$ be the total force operator on N electrons. That is,

$$\mathbf{F}_e = \sum_{s=1}^{N} \sum_{a} Z_a \frac{(\mathbf{R}_a - \mathbf{r}_s)}{|\mathbf{R}_a - \mathbf{r}_s|^3} - \sum_{s=1}^{N} \Im(\mathbf{r}_s) \equiv \mathbf{F}_{eN} + \mathbf{F}_{e\Im}, \tag{A1}$$

also

$$\mathbf{F}_e = -\sum_{s} (\partial \mathrm{H} / \partial \mathbf{r}_s) = i[\mathrm{H}, \mathbf{P}] \tag{A2}$$

where $\mathbf{P}$ is the total electronic momentum operator, H is the Hamiltonian operator. Z_a is the electron charge of the nucleus a. In Eq. (A1) the double sum yielding the force on the electrons is due to the nuclei and the single sum is the force due to an applied electric field, $\Im$ (if any). The electron-electron force cancels. From Eq. (A2) if the hypervirial theorem for $\mathbf{P}$ is satisfied, i.e., if $\langle [\mathrm{H}, \mathbf{P}] \rangle = 0$, then the average of $\mathbf{F}_e$ vanishes.

As an interesting application of the force theorem, consider the average total force on all the nuclei. Since the operator for this total force is

$$\mathbf{F}_n = \sum_{s=1}^{N} \sum_{a} Z_a \frac{(\mathbf{r}_s - \mathbf{R}_a)}{|\mathbf{r}_s - \mathbf{R}_a|^3} + \sum_{a} Z_a \Im(\mathbf{R}_a) \equiv \mathbf{F}_{Ne} + \mathbf{F}_{N\Im}, \tag{A3}$$

and since

$$\mathbf{F}_{Ne} = -\mathbf{F}_{eN}, \tag{A4}$$

if follows that

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[1] From S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic Press, N.Y., 1974)

$$\langle \mathbf{F}_n \rangle = -\langle \mathbf{F}_{eN} \rangle + \langle \mathbf{F}_{N\mathfrak{Z}} \rangle. \tag{A5}$$

However, if the force theorems are satisfied, then

$$0 = \langle \mathbf{F}_{eN} \rangle + \langle \mathbf{F}_{e\mathfrak{Z}} \rangle = \langle \mathbf{F}_e \rangle = \langle\, i\,[\mathrm{H}, \mathbf{P}]\, \rangle, \tag{A6}$$

and Eq. (A5) can be rewritten as

$$\langle \mathbf{F}_n \rangle = -\langle \mathbf{F}_{eN} \rangle + \langle \mathbf{F}_{N\mathfrak{Z}} \rangle = \langle \mathbf{F}_{e\mathfrak{Z}} \rangle + \langle \mathbf{F}_{N\mathfrak{Z}} \rangle; \tag{A7}$$

or in words

average total force on the nuclei

= force on the nuclei due to the external field

+ average force on the electrons due to the external field. (A8)

Appendix B

Assume that f is a function of g(x),

$$f = f[g(x)]. \tag{B1}$$

Then the first-order, second-order, third-order and fourth-order differentials of f with respect to x are

$$\Delta^1 f = \frac{df}{dg}\frac{dg}{dx}\Delta x, \tag{B2}$$

$$\Delta^2 f = \frac{d^2f}{dg^2}\left(\frac{dg}{dx}\right)^2 \Delta x^2 + \frac{df}{dg}\frac{d^2g}{dx^2}\Delta x^2, \tag{B3}$$

$$\Delta^3 f = \frac{d^3f}{dg^3}\left(\frac{dg}{dx}\right)^3 \Delta x^3 + 3\frac{d^2f}{dg^2}\left(\frac{dg}{dx}\right)\frac{d^2g}{dx^2}\Delta x^3 + \frac{df}{dg}\frac{d^3g}{dx^3}\Delta x^3, \tag{B4}$$

$$\begin{aligned}\Delta^4 f = {} & \frac{d^4f}{dg^4}\left(\frac{dg}{dx}\right)^4 \Delta x^4 + 6\frac{d^3f}{dg^3}\left(\frac{dg}{dx}\right)^2\frac{d^2g}{dx^2}\Delta x^4 + 3\frac{d^2f}{dg^2}\left(\frac{d^2g}{dx^2}\right)^2 \Delta x^4 \\ & + 4\frac{d^2f}{dg^2}\left(\frac{dg}{dx}\right)\frac{d^3g}{dx^3}\Delta x^4 + \frac{df}{dg}\left(\frac{d^4g}{dx^4}\right)\Delta x^4. \end{aligned} \tag{B5}$$

Substitution of Eqs. (B2) to (B5) into a Taylor expansion gives

$$\begin{aligned}\Delta f = {} & \frac{df}{dg}\frac{dg}{dx}\Delta x + \frac{1}{2}\left[\frac{d^2f}{dg^2}\left(\frac{dg}{dx}\right)^2 + \frac{df}{dg}\frac{d^2g}{dx^2}\right]\Delta x^2 \\ & + \frac{1}{3!}\left[\frac{d^3f}{dg^3}\left(\frac{dg}{dx}\right)^3 + 3\frac{d^2f}{dg^2}\left(\frac{dg}{dx}\right)\frac{d^2g}{dx^2} + \frac{df}{dg}\frac{d^3g}{dx^3}\right]\Delta x^3 \end{aligned}$$

$$+\frac{1}{4!}\left[\frac{d^4f}{dg^4}\left(\frac{dg}{dx}\right)^4+6\frac{d^3f}{dg^3}\left(\frac{dg}{dx}\right)^2\frac{d^2g}{dx^2}\right.$$

$$\left.+3\frac{d^2f}{dg^2}\left(\frac{d^2g}{dx^2}\right)^2+4\frac{d^2f}{dg^2}\left(\frac{dg}{dx}\right)\frac{d^3g}{dx^3}+\frac{df}{dg}\left(\frac{d^4g}{dx^4}\right)\right]\Delta x^4+\ldots \tag{B6}$$

Rearranging Eq. (B6) according to the order of the differential of f with respect to g gives

$$\Delta f = \frac{df}{dg}\left[\delta g+\frac{1}{2}\delta^2 g+\frac{1}{3!}\delta^3 g+\frac{1}{4!}\delta^4 g+\ldots\right]$$

$$+\frac{1}{2}\frac{d^2f}{dg^2}\left[(\delta g)^2+\delta g\cdot\delta^2 g+\frac{1}{4}(\delta^2 g)^2+\frac{1}{3}\delta g\cdot\delta^3 g+\ldots\right]$$

$$+\frac{1}{3!}\frac{d^3f}{dg^3}\left[(\delta g)^3+\frac{3}{2}(\delta g)^2\cdot\delta^2 g+\ldots\right]$$

$$+\frac{1}{4!}\frac{d^4f}{dg^4}\left[(\delta g)^4+\ldots\right], \tag{B7}$$

where $\delta g = \frac{dg}{dx}\Delta x$, $\delta^2 g = \frac{d^2g}{dx^2}\Delta x^2$, etc. If the electronic charge density $\rho^e(\mathbf{r})$ is identified as the function f and the modified potential $u(\mathbf{r}')$ is identified as the function g of a continuous variable $\mathbf{r}$, then Eq. (B7) corresponds to the functional relation

$$\Delta\rho^e(\mathbf{r}) = \int d\mathbf{r}'\frac{\delta\rho^e(\mathbf{r})}{\delta u(\mathbf{r}')}\left[\delta u(\mathbf{r}')+\frac{1}{2}\delta^2 u(\mathbf{r}')+\frac{1}{3!}\delta^3 u(\mathbf{r}')+\frac{1}{4!}\delta^4 u(\mathbf{r}')+\ldots\right]$$

$$+\frac{1}{2}\int d\mathbf{r}'d\mathbf{r}''\frac{\delta^2\rho^e(\mathbf{r})}{\delta u(\mathbf{r}')\,\delta u(\mathbf{r}'')}\left[\delta u(\mathbf{r}')\,\delta u(\mathbf{r}'')+\delta u(\mathbf{r}')\cdot\delta^2 u(\mathbf{r}'')\right.$$

$$\left.+\frac{1}{4}\delta^2 u(\mathbf{r}')\,\delta^2 u(\mathbf{r}'')+\frac{1}{3}\delta u(\mathbf{r}')\cdot\delta^3 u(\mathbf{r}'')+\ldots\right]$$

$$+\frac{1}{3!}\int d\mathbf{r}'d\mathbf{r}''d\mathbf{r}'''\frac{\delta^3\rho^e(\mathbf{r})}{\delta u(\mathbf{r}')\,\delta u(\mathbf{r}'')\,\delta u(\mathbf{r}''')}\left[\delta u(\mathbf{r}')\,\delta u(\mathbf{r}'')\,\delta u(\mathbf{r}''')\right.$$

$$+\frac{3}{2}\delta u(\mathbf{r}')\,\delta u(\mathbf{r}'')\cdot\delta^2 u(\mathbf{r}''')+\ldots\Bigg].\qquad\text{(B8)}$$

Equation (B8) is similar to the result from differential expansions in density functional theory, but with higher-order variations in the modified potential.

Appendix C

The Fukui function $f(\mathbf{r})$ is related to the local softness $s(\mathbf{r})$ via the global softness S

$$f(\mathbf{r}) = s(\mathbf{r})S^{-1}. \tag{C1}$$

To simplify the final term in Eq. (34) in Section 4.2, the following expansion is used:

$$\begin{aligned}\left[\frac{\delta f(\mathbf{r})}{\delta v^e(\mathbf{r}')}\right]_N &= S^{-1}\left[\frac{\delta s(\mathbf{r})}{\delta v^e(\mathbf{r}')}\right]_N + s(\mathbf{r})\left[\frac{\delta S^{-1}}{\delta v^e(\mathbf{r}')}\right]_N \\ &= S^{-1}\int d\mathbf{r}''\left[\frac{\delta s(\mathbf{r})}{\delta u(\mathbf{r}'')}\right]\left[\frac{\delta u(\mathbf{r}'')}{\delta v^e(\mathbf{r}')}\right]_N \\ &= S^{-2}s(\mathbf{r})\int d\mathbf{r}''\left[\frac{\delta S}{\delta u(\mathbf{r}'')}\right]\left[\frac{\delta u(\mathbf{r}'')}{\delta v^e(\mathbf{r}')}\right]_N,\end{aligned} \tag{C2}$$

where

$$\frac{\delta s(\mathbf{r})}{\delta u(\mathbf{r}'')} = \int d\mathbf{r}'\left[\frac{\delta s(\mathbf{r},\mathbf{r}')}{\delta u(\mathbf{r}'')}\right] = \int d\mathbf{r}'\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'') = \sigma(\mathbf{r},\mathbf{r}''), \tag{C3}$$

$$\begin{aligned}\left[\frac{\delta u(\mathbf{r}'')}{\delta v^e(\mathbf{r}')}\right]_N &= \left\{\frac{\delta[v^e(\mathbf{r}'') - \mu]}{\delta v^e(\mathbf{r}')}\right\}_N \\ &= \delta(\mathbf{r}''-\mathbf{r}') - \frac{\delta\mu}{\delta v^e(\mathbf{r}')} = \delta(\mathbf{r}''-\mathbf{r}') - f(\mathbf{r}')\end{aligned} \tag{C4}$$

and

$$\frac{\delta S}{\delta u(\mathbf{r}'')} = \int d\mathbf{r}d\mathbf{r}'\left[\frac{\delta s(\mathbf{r},\mathbf{r}')}{\delta u(\mathbf{r}'')}\right] = \int d\mathbf{r}d\mathbf{r}'\sigma(\mathbf{r},\mathbf{r}',\mathbf{r}'') = \sigma(\mathbf{r}''). \tag{C5}$$

From Eqs. (C1) and (C3)-(C5), Eq.(C2) simplifies to

$$\left[\frac{\delta f(\mathbf{r})}{\delta v^{e}(\mathbf{r}')}\right]_N = \sigma(\mathbf{r},\mathbf{r}')\,S^{-1} - \sigma(\mathbf{r})\,s(\mathbf{r}')\,S^{-2} - \sigma(\mathbf{r}')\,s(\mathbf{r})\,S^{-2} + \sigma\;s(\mathbf{r})\,s(\mathbf{r}')\,S^{-3}. \tag{C6}$$