This is to certify that the

dissertation entitled

Energies, polarizabilities, and forces of interacting molecules at long or intermediate range

presented by Ying Q. Liang

has been accepted towards fulfillment
of the requirements for

Ph.D degree in Chemical Physics

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Date 9/15/92

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

By

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A DISSERTATION

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1992

ABSTRACT

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

By

Ying Q. Liang

Collision-induced molecular phenomena are widely researched subjects. In complement with other research, deriving new results to understand the nature and effects of the interaction between molecules at long or intermediate range is the main goal of this thesis.

By applying Rayleigh-Schrödinger perturbation theory, we have obtained the molecular interaction energy to second order in terms of nonlocal polarizability densities. The derivation also includes the effects of an applied field.

The nonlocal polarizability density $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ plays a central role in this research. The polarizability density is a linear-response tensor that determines the electronic polarization induced at point $\mathbf{r}$ in a molecule, by an external electric field of frequency ω, acting at $\mathbf{r}'$. When a nuclear position in the molecule shifts infinitesimally, we find that the change in $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ is connected to the same hyperpolarizability $\beta_{\alpha\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0)$ that describes the electronic charge distribution's response to external fields, i.e.:

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

This is a generalization of the relationship between $\partial\alpha_{\beta\gamma}(0)/\partial R^I_{\alpha}$ and $\beta_{\beta\gamma\delta}(\mathbf{r}; \mathbf{r}', \mathbf{r}'')$.

Due to establishment of the relationships between $\partial\alpha_{\beta\gamma}/\partial R^I_{\alpha}$ and $\beta_{\beta\gamma\delta}$, we have obtained new analytical results for the forces acting on nuclei in a molecule. For the first

time, we have proven the equivalence of forces from interaction energy calculations and those obtained via the Hellmann-Feynman theorem, *order by order*. We are also able to separate forces on nuclei in one of the interacting molecules (A) into those due to its "own" electrons vs. forces due to the charge distribution of the collision partner, B.

By taking the long range limit of the new analytical results for forces acting on nuclei in a molecule, we express the electrical shielding effects in interacting molecules through nonlocal polarizability and hyperpolarizability densities. Intermolecular fields are screened via the same tensors that describe shielding of external fields.

An explicit expression for the momentum distribution of a particle in a one-dimensional box is also included in this thesis. It is a result from my work as a teaching assistant for the graduate course in quantum chemistry for several terms. The result corrects misconceptions about the momentum distribution in several quantum chemistry textbooks.

To All People Who Support, Direct and Cooperate with Me

in Scientific Research and Education, Among Them the Industrious

Family of Mine

ACKNOWLEDGMENTS

I offer my most grateful thanks to Dr. Katharine L. C. Hunt, whose guidance during the theoretical exploration led to the results of this research. She always shares her research experience and knowledge with me as well as her encouragement to smooth my transition in a research direction from pure physics to a combination of physics and chemistry. This also opened the door for my further research work.

My thanks are extended to the members of my guidance committee, Dr. Robert Cukier (who served as second reader), Dr. Subhendra Mahanti, Dr.Thomas A. Kaplan, and Dr. Jack Hetherington for their generous donation of time and assistance.

My thanks also go to Dr. K. M. Chen for his invitation for me to be a visiting researcher in his group for two years, where I obtained training in theoretical research and computational work. My gratitude must also be expressed to Dr. Henry Blosser and Dr. Sam Austin for introducing me to the physics graduate program in the National Superconducting Cyclotron Laboratory, from which I leaned much since they are exemplary scientists.

I thank Dr. George Leroi, Dr. Paul Hunt, and Dr. Thomas Atkinson for their administrative and computational support for my research.

I gratefully acknowledge financial support for this research from the National Science Foundation through grants to Dr. K. L. C. Hunt, and I am grateful for the award of a Summer Alumni Fellowship from Department of Chemistry, Michigan State University. I sincerely thank my family members for their understanding and encouragement,

especially my wife Ruiqun Xuan, whose constant love and great support are very truly appreciated. She also deserves as much credit as I for the completion of this dissertation.

I also express my thanks to all of my friends, whose help and assistance are very much appreciated.

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CHAPTER I

INTRODUCTION

This thesis is written so that each chapter is independent. However, there do exist internal logical relations between these chapters.

We consider two molecules interacting at long or intermediate range in an applied electro-static field. We assume that the intermolecular separation is sufficiently large that the overlap of molecular wave functions is weak and we neglect exchange of electrons between molecules.

We focus our attention on the changes of energy and polarization of the system, the forces acting on nuclei in each molecule, and the electrical shielding effects between them.

By applying Rayleigh-Schrödinger perturbation theory [1] to the system in Chapter II, we obtain the changes of energy to second order in terms of nonlocal polarizability densities. $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ is a linear-response tensor that determines the electronic polarization induced at point $\mathbf{r}$ in a molecule, by an external electric field of frequency ω, acting at $\mathbf{r}'$, which was introduced by Maaskant and Oosterhoff in a study of optical rotation in condensed media [2]. Hunt derived a simpler form suited for practical calculations in cases when the field acting on a molecule is derivable from a scalar potential [3]. The nonlocal polarizability density is discussed in Section 2.2. The results for energy changes in terms of the nonlocal polarizability densities are summarized in Section 2.3. Besides the inter action between applied field and each molecule, and the molecular pair interaction, there are trinary interactions among the applied field and the molecules, associated with the collision-induced dipole.

In Chapter III, it is shown that the change in frequency-dependent electronic polarizability densities due to shifts in nuclear positions depends upon the hyperpolarizability density.

This generalizes the relation initially established by Hunt [4] in the case when external field is static. By generalizing the relationship to the frequency-dependent case, we are able to give a new interpretation for integrated intensities of vibrational Raman bands as well as new analytical results for van der Waals' forces acting on nuclei in interacting molecules [5].

Chapter IV gives analytical results for the induced forces acting on nuclei in interacting molecules, in terms of nonlocal polarizability densities. We calculate these forces both by direct differentiation of the interaction energy and by use of the Hellmann-Feynman theorem [6]. By proving the equivalence order by order, we unify the two approaches.

Chapter V discusses the electrical shielding effects in interacting molecules at long range. By using the relationships initially established by Hunt [4] and generalized in Chapter III, and taking the long range limit of the forces acting on nuclei in interacting molecules obtained in Chapter IV, we prove that the same electrical shielding tensors describe not only the response to an external field, but also the response to local intermolecular fields.

Lastly, Chapter VI discusses a simple but general problem in quantum mechanics: the momentum distributions of a particle in a one-dimensional box. A simplified and explicit formula for this case is obtained and used to correct misconceptions in some quantum chemistry textbooks.

References

[1] See, for example, E. Merzbacher, *Quantum Mechanics* (Wiley, New York,1970), Chap. 17.

[2] W. J. A. Maaskant and L. J. Oosterhoff, Mol. Phys. **8**, 319 (1964).

[3] K. L. C. Hunt, J. Chem. Phys. **78**, 6149 (1983); **80**, 393 (1984).

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CHAPTER II

CHANGES OF ENERGY FOR INTERACTING MOLECULES AT INTERMEDIATE RANGE IN AN APPLIED ELECTROSTATIC FIELD

2.1The Perturbation Energy

The perturbation Hamiltonian for molecules interacting at intermediate or long range in an applied electrostatic field is

$$H' = \int \rho^A(\mathbf{r})\, \rho^B(\mathbf{r}')\, T(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' + \int \rho^A(\mathbf{r})\, \phi(\mathbf{r})\, d\mathbf{r} + \int \rho^B(\mathbf{r})\, \phi(\mathbf{r})\, d\mathbf{r}\ ,(1)$$

where $\rho^A(\mathbf{r})$ and $\rho^B(\mathbf{r})$ are the charge density operators for molecules A and B, respectively; $T(\mathbf{r} - \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$; and $\phi(\mathbf{r})$ is the scalar potential of the applied electrostatic field. The external field $\mathbf{F}^{ext}(\mathbf{r})$ is

$$\mathbf{F}^{ext}(\mathbf{r}) = -\nabla\, \phi(\mathbf{r}), \tag{2}$$

Assuming that the Rayleigh-Schrödinger perturbation theory [1] can be applied to this case, we obtain the change of energy for the system to first order as

$$\Delta E^{(1)} = \int \rho^A{}_0(\mathbf{r})\, T(\mathbf{r} - \mathbf{r}')\, \rho^B{}_0(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' + \int \rho^A{}_0(\mathbf{r})\, \phi(\mathbf{r})\, d\mathbf{r} + \int \rho^B{}_0(\mathbf{r})\, \phi(\mathbf{r})\, d\mathbf{r}, \tag{3}$$

where $\rho^A{}_0(\mathbf{r})$ and $\rho^B{}_0(\mathbf{r})$ are the unperturbed charge densities of A and B, respectively. The first term in Eq. 3 is the electrostatic interaction energy of the unperturbed charge distributions of the pair, while the second and third terms are the electrostatic interaction energies of the unperturbed charge distributions of molecules A and B with the external field.

The change of energy for the system to second order is

$$
\begin{aligned}
\Delta E^{(2)} = & - \sum_{k \neq g} \langle g^A g^B \,|H'|\, k^A g^B \rangle \langle k^A g^B \,|H'|\, g^A g^B \rangle / (E_k{}^A - E_g{}^A) \\
& - \sum_{j \neq g} \langle g^A g^B \,|H'|\, g^A j^B \rangle \langle g^A j^B \,|H'|\, g^A g^B \rangle / (E_j{}^B - E_g{}^B) \\
& - \sum_{j,k \neq g} \langle g^A g^B \,|H'|\, k^A j^B \rangle \langle k^A j^B \,|H'|\, g^A g^B \rangle / [(E_k{}^A - E_g{}^A) + (E_j{}^B - E_g{}^B)] \\
= & - \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \sum_k{}' \langle g^A \,|\rho^A(\mathbf{r})|\, k^A \rangle \langle k^A \,|\rho^A(\mathbf{r}'')|\, g^A \rangle / (E_k{}^A - E_g{}^A) \\
& \qquad \times \rho^B{}_0(\mathbf{r}') \,|\mathbf{r} - \mathbf{r}'|^{-1}\, \rho^B{}_0(\mathbf{r}''') \,|\mathbf{r}'' - \mathbf{r}'''|^{-1} \\
& - \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \sum_j{}' \langle g^B \,|\rho^B(\mathbf{r})|\, j^B \rangle \langle j^B \,|\rho^B(\mathbf{r}'')|\, g^B \rangle / (E_j{}^B - E_g{}^B) \\
& \qquad \times \rho^A{}_0(\mathbf{r}') \,|\mathbf{r} - \mathbf{r}'|^{-1}\, \rho^A{}_0(\mathbf{r}''') \,|\mathbf{r}'' - \mathbf{r}'''|^{-1} \\
& - \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \sum_k{}' \langle g^A \,|\rho^A(\mathbf{r})|\, k^A \rangle \langle k^A \,|\rho^A(\mathbf{r}'')|\, g^A \rangle \\
& \times \sum_j{}' \langle g^B \,|\rho^B(\mathbf{r}')|\, j^B \rangle \langle j^B \,|\rho^B(\mathbf{r}''')|\, g^B \rangle / [(E_k{}^A - E_g{}^A) + (E_j{}^B - E_g{}^B)] \\
& \times |\mathbf{r} - \mathbf{r}'|^{-1} \times |\mathbf{r}'' - \mathbf{r}'''|^{-1} \\
& - \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' \sum_k{}' \langle g^A \,|\rho^A(\mathbf{r})|\, k^A \rangle \langle k^A \,|\rho^A(\mathbf{r}'')|\, g^A \rangle / (E_k{}^A - E_g{}^A) \\
& \qquad \times \phi(\mathbf{r}) \rho^B{}_0(\mathbf{r}') \,|\mathbf{r}'' - \mathbf{r}'|^{-1} + \text{complex conjugate} \\
& - \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' \sum_j{}' \langle g^B \,|\rho^B(\mathbf{r})|\, j^B \rangle \langle j^B \,|\rho^B(\mathbf{r}'')|\, g^B \rangle / (E_j{}^B - E_g{}^B) \\
& \qquad \times \phi(\mathbf{r})\, \rho^A{}_0(\mathbf{r}') \,|\mathbf{r}'' - \mathbf{r}'|^{-1} + \text{complex conjugate} \\
& - \int d\mathbf{r}\, d\mathbf{r}' \sum_k{}' \langle g^A \,|\rho^A(\mathbf{r})|\, k^A \rangle \langle k^A \,|\rho^A(\mathbf{r}')|\, g^A \rangle / (E_k{}^A - E_g{}^A) \\
& \qquad \times \phi(\mathbf{r}) \phi(\mathbf{r}') \\
& - \int d\mathbf{r}\, d\mathbf{r}' \sum_j{}' \langle g^B \,|\rho^B(\mathbf{r})|\, j^B \rangle \langle j^B \,|\rho^B(\mathbf{r}')|\, g^B \rangle / (E_j{}^B - E_g{}^B) \\
& \qquad \times \phi(\mathbf{r})\, \phi(\mathbf{r}')
\end{aligned}
\tag{4}
$$

The first three terms in Eq. 4 give the interaction energy of the pair in the absence of the applied field. The first is the induction energy associated with the distortion of molecule A by the field due to the permanent charge distribution of B, the second is the induction energy associated with the distortion of B, and the third is termed the dispersion energy. The fourth and fifth terms give the interaction energy due to the applied field (to the leading order), while the sixth and seventh terms represent the effect of the applied field on each molecule.

2.2 The Nonlocal Polarizability Densities

Maaskant and Oosterhoff introduced the nonlocal polarizability densities in a study of optical rotation in condensed media [2]. They gave the nonlocal polarizability density in sum-over-states form, with each matrix element itself given as an infinite series. Hunt [3] derived a simple form that permits practical calculations in cases when the field acting on a molecule is derivable from a scalar potential.

The nonlocal polarizability density $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ is a linear-response tensor that determines the electronic polarization induced at point $\mathbf{r}$ in a molecule, by an external electric field of frequency ω, acting at $\mathbf{r}'$.

The polarizability density for a molecule in the ground state has the form

$$\alpha_{\alpha\beta}(\mathbf{r}; \mathbf{r}', \omega) = [1 + C(\omega \rightarrow -\omega)] \langle 0 \,|P_\alpha(\mathbf{r})\, G(\omega)\, P_\beta(\mathbf{r}')\,| 0 \rangle, \tag{5}$$

when the frequency ω is off-resonance with molecular transition frequencies. $C(\omega \rightarrow -\omega)$ designates the operator for complex conjugation and replacement of ω by $-\omega$, and

$$G(\omega) = (1 - \wp_0)\,(H - E_0 - \hbar\omega)^{-1}\,(1 - \wp_0), \tag{6}$$

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

The electronic polarization $\mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega)$ induced in a molecule by an external field $\mathbf{F}(\mathbf{r}, \omega)$ depends on the polarizability density $\alpha(\mathbf{r}; \mathbf{r}', \omega)$, the hyperpolarizability density $\beta(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', \omega'')$ and higher-order nonlinear response tensors

$$\mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega) = \int d\mathbf{r}' \; \alpha(\mathbf{r}; \mathbf{r}', \omega) \cdot \mathbf{F}(\mathbf{r}', \omega)$$

$$+ 1/2 \int_{-\infty}^{\infty} d\omega' \int d\mathbf{r}' d\mathbf{r}'' \beta(\mathbf{r}; \mathbf{r}', \omega - \omega', \mathbf{r}'', \omega') : \mathbf{F}(\mathbf{r}', \omega - \omega') \mathbf{F}(\mathbf{r}'', \omega')$$

$$+ \ldots .$$

$$= \mathbf{P}^{ind}(\mathbf{r}, \omega)^{(1)} + \mathbf{P}^{ind}(\mathbf{r}, \omega)^{(2)} + \ldots . \tag{7}$$

where $\mathbf{P}^{ind}(\mathbf{r}, \omega)^{(1)} = \int d\mathbf{r}' \ \alpha(\mathbf{r}; \mathbf{r}', \omega) \cdot \mathbf{F}(\mathbf{r}', \omega)$. $\mathbf{P}^{ind}(\mathbf{r}, \omega)^{(1)}$ gives the electronic polarization in a molecule by the external field to first order, and

$\mathbf{P}^{ind}(\mathbf{r}, \omega)^{(2)} = 1/2 \int_{-\infty}^{\infty} d\omega' \int d\mathbf{r}' d\mathbf{r}'' \beta(\mathbf{r}; \mathbf{r}', \omega - \omega', \mathbf{r}'', \omega') : \mathbf{F}(\mathbf{r}', \omega - \omega') \mathbf{F}(\mathbf{r}'', \omega')$. $\mathbf{P}^{ind}(\mathbf{r}, \omega)^{(2)}$ gives the second order term. $\beta(\mathbf{r}; \mathbf{r}', \omega - \omega', \mathbf{r}'', \omega')$ is the hyperpolarizability density; when $\omega' = 0$,

$$\begin{aligned}
\beta_{\alpha\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0) = {} & [1 + C(\omega \rightarrow -\omega)] \times \\
& \{\langle 0 | P_\alpha(\mathbf{r})\, G(\omega)\, [P_\gamma(\mathbf{r}'') - P_\gamma^{00}(\mathbf{r}'')]\, G(\omega)\, P_\beta(\mathbf{r}') | 0 \rangle \\
& + \langle 0 | P_\alpha(\mathbf{r})\, G(\omega)\, [P_\beta(\mathbf{r}') - P_\beta^{00}(\mathbf{r}')]\, G(0)\, P_\gamma(\mathbf{r}'') | 0 \rangle \\
& + \langle 0 | P_\gamma(\mathbf{r}'')\, G(0)\, [P_\alpha(\mathbf{r}) - P_\alpha^{00}(\mathbf{r})]\, G(\omega)\, P_\beta(\mathbf{r}') | 0 \rangle\} .
\end{aligned} \tag{8}$$

2.3 Analytical Results for the Perturbation Energy in terms of Nonlocal Polarizability Densities

We now rewrite the perturbation energy $\Delta E^{(2)}$ in terms of the nonlocal polarizability densities and obtain:

$$\begin{aligned}
\Delta E^{(2)} = & - \sum_{k \neq g} \langle g^A g^B | H' | k^A g^B \rangle \langle k^A g^B | H' | g^A g^B \rangle / (E_k^A - E_g^A) \\
& - \sum_{j \neq g} \langle g^A g^B | H' | g^A j^B \rangle \langle g^A j^B | H' | g^A g^B \rangle / (E_j^B - E_g^B) \\
& - \sum_{j,k \neq g} \langle g^A g^B | H' | k^A j^B \rangle \langle k^A j^B | H' | g^A g^B \rangle / [(E_k^A - E_g^A) + (E_j^B - E_g^B)]
\end{aligned}$$

$$\begin{aligned}
&= - 1/2 \int \mathbf{dr}\,\mathbf{dr}'\alpha^{A}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\ \mathcal{F}^{B}{}_{0\alpha}(\mathbf{r})\ \mathcal{F}^{B}{}_{0\beta}(\mathbf{r}') \\
&\quad - 1/2 \int \mathbf{dr}\,\mathbf{dr}'\alpha^{B}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\ \mathcal{F}^{A}{}_{0\alpha}(\mathbf{r})\ \mathcal{F}^{A}{}_{0\beta}(\mathbf{r}') \\
&\quad - h/4\pi^{2}\int_{0}^{\infty} d\omega \int \mathbf{dr}\,\mathbf{dr}'\mathbf{dr}''\mathbf{dr}'''\ \alpha^{A}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}''',i\omega)\ \alpha^{B}{}_{\gamma\delta}(\mathbf{r}'',\mathbf{r}',i\omega)T_{\alpha\delta}(\mathbf{r},\mathbf{r}') \\
&\qquad\qquad\qquad \mathrm{x}\ T_{\beta\gamma}(\mathbf{r}'',\mathbf{r}''') \\
&\quad - \int \mathbf{dr}\,\mathbf{dr}'\ \alpha^{A}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}')F_{\alpha}{}^{ext}(\mathbf{r})\ \mathcal{F}^{B}{}_{0\beta}(\mathbf{r}') \\
&\quad - \int \mathbf{dr}\,\mathbf{dr}'\ \alpha^{B}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}')F_{\alpha}{}^{ext}(\mathbf{r})\ \mathcal{F}^{A}{}_{0\beta}(\mathbf{r}') \\
&\quad - 1/2 \int \mathbf{dr}\,\mathbf{dr}'\alpha^{A}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}')F_{\alpha}{}^{ext}(\mathbf{r})F_{\beta}{}^{ext}(\mathbf{r}') \\
&\quad - 1/2 \int \mathbf{dr}\,\mathbf{dr}'\alpha^{B}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}')F_{\alpha}{}^{ext}(\mathbf{r})\ F_{\beta}{}^{ext}(\mathbf{r}') \qquad (9)
\end{aligned}$$

where

$$\mathcal{F}^{A}{}_{0\alpha}(\mathbf{r}) = -\int \mathbf{dr}'\rho^{A}{}_{0}(\mathbf{r}')\ T_{\alpha}(\mathbf{r}-\mathbf{r}')$$

is the field in molecule B produced by the unperturbed charge distribution of molecule A

and $\mathcal{F}^{B}{}_{0\alpha}(\mathbf{r}) = -\int \mathbf{dr}'\rho^{B}{}_{0}(\mathbf{r}')\ T_{\alpha}(\mathbf{r}-\mathbf{r}')$

is the field in molecule A produced by the unperturbed charge distribution of molecule B.

From Eq. 7, we can rewrite $\Delta E^{(2)}$ in terms of the induced polarization in molecules A and B:

$$\begin{aligned}
\Delta E^{(2)} &= -1/2 \int \mathbf{dr}\ P^{A}{}_{\alpha}(\mathbf{r})^{(1)}\ \mathcal{F}^{B}{}_{0\alpha}(\mathbf{r}) - 1/2 \int \mathbf{dr}\ P^{B}{}_{\alpha}(\mathbf{r})^{(1)}\ \mathcal{F}^{A}{}_{0\alpha}(\mathbf{r}) \\
&\quad - h/4\pi^{2}\int_{0}^{\infty} d\omega \int \mathbf{dr}\,\mathbf{dr}'\mathbf{dr}''\mathbf{dr}'''\ \alpha^{A}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}''',i\omega)\ \alpha^{B}{}_{\gamma\delta}(\mathbf{r}'',\mathbf{r}',i\omega) \\
&\qquad\qquad\qquad \mathrm{x}\ T_{\alpha\delta}(\mathbf{r},\mathbf{r}')T_{\beta\gamma}(\mathbf{r}'',\mathbf{r}''') \\
&\quad - \int \mathbf{dr}\ P^{A}{}_{\alpha}(\mathbf{r})^{(1)}\ F^{ext}{}_{\alpha}(\mathbf{r}) - \int \mathbf{dr}\ P^{B}{}_{\alpha}(\mathbf{r})^{(1)}\ F^{ext}{}_{\alpha}(\mathbf{r}) \\
&\quad - 1/2 \int \mathbf{dr}\ P^{Aext}{}_{\alpha}(\mathbf{r})^{(1)}\ F^{ext}{}_{\alpha}(\mathbf{r}) - 1/2 \int \mathbf{dr}\ P^{Bext}{}_{\alpha}(\mathbf{r})^{(1)}\ F^{ext}{}_{\alpha}(\mathbf{r}) \qquad (10)
\end{aligned}$$

where $P^{A}{}_{\alpha}(\mathbf{r})^{(1)} = \int \mathbf{dr}'\ \alpha^{A}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\ \mathcal{F}^{B}{}_{0\beta}(\mathbf{r}')$ (11)

is the first order polarization of molecule A induced by the field due to the unperturbed charge distribution of molecule B, while

$$p^{ext}_{\alpha}(\mathbf{r})^{(1)} = \int d\mathbf{r}'\, \alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, F^{ext}_{\beta}(\mathbf{r}') \qquad (12)$$

is the first order polarization of molecule A or B induced by the applied field.

From Eq. 9, we know that when two molecules interact with each other, there is not only the electrostatic interaction between their unperturbed charge distributions (in first order), but also the interaction between the induced charge density of one and the unperturbed charge distribution of the other (the first and second terms in Eq. 9, induction energy). Furthermore, there is a dispersion interaction between the two molecules, which comes from the fluctuations of the charge distributions of A and B, a purely quantum effect (the third term in Eq. 9, dispersion energy). When the molecules interact with an applied field, the external field affects the electrostatic and induction interactions between them, via the same polarizability density (the sixth and seventh terms in Eq. 9). The applied field acts on the interacting molecules not only directly with each, but also indirectly on one through the other. An alternative point of view is: each of the interacting molecules not only directly responds to the external field, but also does so indirecly through the other. For example, the field produced by the unperturbed charge distribution of B induces in A a polarization which interacts with the applied field (the fourth term in Eq. 9). An alternative point of view is: the applied field induces in A a polarization which interacts with the field produced by the unperturbed charge density of B. The same also happens for B (the fifth term in Eq. 9). We call this kind of interaction trinary.

References

[1] See, for example, E. Merzbacher, *Quantum Mechanics* (Wiley, New York,1970), Chap. 17.

[2] W. J. A. Maaskant and L. J. Oosterhoff, Mol. Phys. **8**, 319 (1964).

[3] K. L. C. Hunt, J. Chem. Phys. **78**, 6149 (1983); **80**, 393 (1984).

CHAPTER III

CHANGES IN ELECTRONIC POLARIZABILITY DENSITIES DUE TO SHIFTS IN NUCLEAR POSITIONS, AND A NEW INTERPRETATION FOR INTEGRATED INTENSITIES OF VIBRATIONAL RAMAN BANDS

Abstract:

The nonlocal polarizability density $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ is a linear-response tensor that determines the electronic polarization induced at point $\mathbf{r}$ in a molecule, by an external electric field of frequency ω, acting at $\mathbf{r}'$. This work focuses on the change in $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ when a nuclear position shifts infinitesimally. We prove directly that the electronic charge distribution responds to the change in Coulomb field due to the nucleus via the same hyperpolarizability density that describes its response to external fields. This generalizes a result established previously for the static ($\omega = 0$) polarizability density. The work also provides a new interpretation for the integrated intensities of vibrational Raman bands: it proves that the intensities depend on the hyperpolarizability densities and the dipole propagator.

3. 1. Introduction

The nonlocal polarizability density $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ gives the ω-frequency component of the polarization induced at point $\mathbf{r}$ in a molecule by an external electric field $\mathbf{F}(\mathbf{r}', \omega)$ acting at the point $\mathbf{r}'$, within linear response [1-5]. This property reflects the *distribution* of polarizable matter within the molecule; it represents the full response to external fields derived from scalar potentials of arbitrary spatial variation. Thus $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ is a fundamental molecular property. It has applications in theories of local fields and light scattering in condensed media [3,6], and in approximations for dispersion energies [4], collision-induced dipoles, and collision-induced polarizabilities [5,7] of molecules interacting at intermediate range. Recently, Hunt [8] has shown that $\alpha(\mathbf{r}; \mathbf{r}', 0)$ also determines the net field $\mathbf{F}^I$ acting on nucleus I of a molecule in a static, external field $\mathbf{F}^e(\mathbf{r})$:

$$\mathbf{F}^I = \mathbf{F}^{I(0)} + \mathbf{F}^e(\mathbf{R}^I) + \int d\mathbf{r}\, d\mathbf{r}'\; \mathrm{T}(\mathbf{R}^I, \mathbf{r}) \cdot \alpha(\mathbf{r}; \mathbf{r}', 0) \cdot \mathbf{F}^e(\mathbf{r}') + \dots, \qquad (1)$$

where $\mathbf{F}^{I(0)}$ is the field at nucleus I in the absence of the external perturbation, and $\mathrm{T}_{\alpha\beta}(\mathbf{R}^I, \mathbf{r})$ is the dipole propagator, i.e., $\mathrm{T}_{\alpha\beta}(\mathbf{R}^I, \mathbf{r}) = \nabla_\alpha \nabla_\beta (|\mathbf{R}^I - \mathbf{r}|^{-1})$. Specializing Eq. (1) to the case of a uniform external field leads to an expression for the linear electric field shielding tensor γ^I [9-15] in terms of $\alpha(\mathbf{r}; \mathbf{r}', 0)$. Further, the nonlocal polarizability density determines the derivative of the molecular dipole moment with respect to the position of each of the nuclei: If Z^I is the charge on the Ith nucleus, then [8]

$$\partial\mu_\alpha/\partial R^I{}_\beta = Z^I \delta_{\alpha\beta} + Z^I \int d\mathbf{r}\, d\mathbf{r}'\; \alpha_{\alpha\gamma}(\mathbf{r}; \mathbf{r}', 0)\, \mathrm{T}_{\gamma\beta}(\mathbf{r}', \mathbf{R}^I). \qquad (2)$$

This work focuses on the changes in the frequency-dependent molecular polarizability density when a nucleus shifts infinitesimally. The results are important because of the roles of the polarizability density noted above. In addition, the theory yields the derivatives of th polarizability $\alpha_{\alpha\beta}(\omega)$ with respect to the normal mode coordinates q_v, which determine the integrated intensities of vibrational Raman bands, within the Placzek approximation [16]. Earlier Hunt [8] has shown that the derivative of the static polarizability $\partial\alpha_{\alpha\beta}(0)/\partial R^I_\gamma$ is related to the nonlinear response tensor $\beta(\mathbf{r}; \mathbf{r}', 0, \mathbf{r}'', 0)$. This accounts for the connection between the polarizability derivative and the quadratic electric field shielding tensor (cf. Ref. 15).

The purpose of this work is to prove that the relation between $\partial\alpha_{\alpha\beta}(\mathbf{r}; \mathbf{r}', 0)/\partial R^I_\gamma$ and the nonlinear response tensors generalizes to the frequency-dependent case. The analysis in Ref. 8 employs the electrostatic Hellmann-Feynman theorem [9,17], and therefore does not apply to $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ with $\omega \neq 0$. A new approach is needed to prove the generalization. In this work, we have used direct differentiation to evaluate $\partial\alpha_{\alpha\beta}(\mathbf{r}; \mathbf{r}', \omega)/\partial R^I_\gamma$.

For the derivative of the total polarizability $\alpha(\omega)$, we obtain

$$\partial\alpha_{\beta\gamma}(\omega)/\partial R^I_\alpha = \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \beta_{\beta\gamma\delta}(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0)\; Z^I\; T_{\delta\alpha}(\mathbf{r}'', \mathbf{R}^I). \tag{3}$$

This result yields physical insight into the change in polarizability (at frequency ω) that results from an infinitesimal shift in the position of nucleus I. The molecule responds to the change in the Coulomb field of the nucleus via its hyperpolarizability density $\beta(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0)$. All of the quantum mechanical influences are contained within β, and the remainder of the calculation is classical. Eq. (3) also provides the basis for a new interpretation of integrated Raman band intensities, without requiring that $\alpha_{\alpha\beta}(\omega)$ be approximated by its zero-frequency limit.

3.2 Nonlocal Polarizability Densities and Polarization Induced by External Fields

The electronic polarization $\mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega)$ induced in a molecule by an external field $\mathbf{F}(\mathbf{r}, \omega)$ depends on the polarizability density $\alpha(\mathbf{r}; \mathbf{r}', \omega)$, the hyperpolarizability density $\beta(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', \omega'')$ and higher-order nonlinear response tensors:

$$\begin{aligned} \mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega) = & \int d\mathbf{r}' \; \alpha(\mathbf{r}; \mathbf{r}', \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \\ & + 1/2 \int_{-\infty}^{\infty} d\omega' \int d\mathbf{r}' d\mathbf{r}'' \, \beta(\mathbf{r}; \mathbf{r}', \omega - \omega', \mathbf{r}'', \omega') : \\ & \qquad \mathbf{F}(\mathbf{r}', \omega - \omega') \, \mathbf{F}(\mathbf{r}'', \omega') \\ & + \dots \, . \end{aligned} \tag{4}$$

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

$$\nabla \cdot \mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega) = -\rho^{\mathrm{ind}}(\mathbf{r}, \omega), \tag{5}$$

and the same relationship holds for the polarization and charge density operators, $\mathbf{P}(\mathbf{r})$ and $\rho(\mathbf{r})$ respectively.

The polarizability density for a molecule in the ground state has the form

$$\alpha_{\alpha\beta}(\mathbf{r}; \mathbf{r}', \omega) = [1 + C(\omega \rightarrow -\omega)] \langle 0 \,|\, P_{\alpha}(\mathbf{r}) \, G(\omega) \, P_{\beta}(\mathbf{r}') \,|\, 0 \rangle, \tag{6}$$

when the frequency ω is off-resonance with molecular transition frequencies. $C(\omega \rightarrow -\omega)$ designates the operator for complex conjugation and replacement of ω by $-\omega$, and

$$G(\omega) = (1 - \wp_0)(H - E_0 - \hbar\omega)^{-1}(1 - \wp_0), \tag{7}$$

where $\wp_0$ is the ground-state projection operator $|0\rangle\langle 0|$. It should be noted that the nonlocal polarizability density completely determines the electronic charge redistribution linear in a perturbing field $\mathbf{F}(\mathbf{r}, \omega)$, and not simply the dipolar component. Integration of $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ over all space with respect to $\mathbf{r}$ and $\mathbf{r}'$ gives the dipole polarizability $\alpha(\omega)$; but $\alpha(\mathbf{r}; \mathbf{r}', \omega)$ also determines all of the higher-multipole, linear-response tensors [5].

The hyperpolarizability density $\beta(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', \omega'')$ gives the polarization induced at **r** bythe lowest-order nonlinear response to a field of frequency ω' acting at $\mathbf{r}'$ and a field of frequency ω'' acting at $\mathbf{r}''$. Integrating $\beta_{\alpha\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', \omega'')$ with respect to **r**, $\mathbf{r}'$, and $\mathbf{r}''$ over all space yields $\beta_{\alpha\beta\gamma}(\omega', \omega'')$, while moment integrals of $\beta_{\alpha\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', \omega'')$ give all of the third-order higher multipole susceptibilities.

For the proof to be given here, we require the hyperpolarizability density $\beta_{\alpha\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0)$, which has the form

$$\begin{aligned}\beta_{\alpha\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0) = {} & [1 + C(\omega \to -\omega)] \times \\ & \{\langle 0 | P_\alpha(\mathbf{r})\, G(\omega)\, [P_\gamma(\mathbf{r}'') - P_\gamma^{00}(\mathbf{r}'')]\, G(\omega)\, P_\beta(\mathbf{r}') | 0 \rangle \\ & + \langle 0 | P_\alpha(\mathbf{r})\, G(\omega)\, [P_\beta(\mathbf{r}') - P_\beta^{00}(\mathbf{r}')]\, G(0)\, P_\gamma(\mathbf{r}'') | 0 \rangle \\ & + \langle 0 | P_\gamma(\mathbf{r}'')\, G(0)\, [P_\alpha(\mathbf{r}) - P_\alpha^{00}(\mathbf{r})]\, G(\omega)\, P_\beta(\mathbf{r}') | 0 \rangle\} \ .\end{aligned} \tag{8}$$

Eq. (8) is derived by analogy with Eq. (43b) in Ref. 18. For compactness, we have used the notation $P_\alpha^{00}(\mathbf{r}) = \langle 0 | P_\alpha(\mathbf{r}) | 0 \rangle$, and similarly for $P_\beta^{00}(\mathbf{r}')$ and $P_\gamma^{00}(\mathbf{r}'')$. Damping has been neglected in Eq. (8).

From Eq. (4), if a molecule is placed in a static external field $\mathbf{F}^s(\mathbf{r})$, its reaction to an additional external field $\mathbf{F}^e(\mathbf{r}, \omega)$ [19] can be characterized by the effective polarizability density $\alpha^e(\mathbf{r}; \mathbf{r}', \omega; \mathbf{F}^s)$, given by

$$\begin{aligned}\alpha^e(\mathbf{r}; \mathbf{r}', \omega; \mathbf{F}^s) = {} & \alpha(\mathbf{r}; \mathbf{r}', \omega; \mathbf{F}^s = 0) \\ & + \int d\mathbf{r}''\ \beta(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0) \cdot \mathbf{F}^s(\mathbf{r}'') \\ & + \ldots \ .\end{aligned} \tag{9}$$

The permutation symmetry of the β hyperpolarizability density has been employed to obtain this result.

3.3 Change in Polarizability Density due to an Infinitesimal Shift in Nuclear Position

A shift $\delta\mathbf{R}^I$ in the position of nucleus I in a molecule changes the nuclear Coulomb field acting on the electrons. In this section, we prove directly that the resulting change in polarizability density is determined by the same hyperpolarizability density $\beta_{\alpha\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', \omega'')$ that fixes the response to external fields. Specifically, we show

$$\partial\alpha_{\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega)/\partial R^I_{\alpha} = \int d\mathbf{r}'' \, \beta_{\beta\gamma\delta}(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0) \; Z^I \, T_{\delta\alpha}(\mathbf{r}'', \mathbf{R}^I), \tag{10}$$

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

The proof in this section is based on direct differentiation of the polarizability density $\alpha_{\alpha\beta}(\mathbf{r}; \mathbf{r}', \omega)$ with respect to R^I_{γ}. From Eq. (6),

$$\begin{aligned} \partial\alpha_{\alpha\beta}(\mathbf{r}; \mathbf{r}', \omega)/\partial R^I_{\gamma} = {} & [1 + C(\omega \rightarrow -\omega)] \times \\ & [\langle \partial 0/\partial R^I_{\gamma} \,|\, P_{\alpha}(\mathbf{r}) \, G(\omega) \, P_{\beta}(\mathbf{r}') \,|\, 0 \rangle \\ & + \langle 0 \,|\, P_{\alpha}(\mathbf{r}) \, \partial G(\omega)/\partial R^I_{\gamma} \, P_{\beta}(\mathbf{r}') \,|\, 0 \rangle \\ & + \langle 0 \,|\, P_{\alpha}(\mathbf{r}) \, G(\omega) \, P_{\beta}(\mathbf{r}') \,|\, \partial 0/\partial R^I_{\gamma} \rangle]. \end{aligned} \tag{11}$$

To convert Eq. (11) into Eq. (10), we first take the derivative of the ground state with respec to an arbitrary parameter η in the Hamiltonian,

$$|\, \partial 0/\partial\eta \,\rangle = - G(0) \;\; \partial H/\partial\eta \;\; |\, 0 \,\rangle . \tag{12}$$

We also require the derivative of the operator $G(\omega)$:

$$\begin{aligned} \partial G(\omega)/\partial\eta = {} & - G(\omega) \, \partial(H - E_0)/\partial\eta \;\; G(\omega) \\ & + \wp_0 \, \partial H/\partial\eta \, G(0) \, G(\omega) + G(\omega) \, G(0) \, \partial H/\partial\eta \; \wp_0 \; . \end{aligned} \tag{13}$$

Specializing Eqs. (12) and (13) to the case $\eta = R^I_{\gamma}$ gives the derivatives in Eq. (11).

The change in the Hamiltonian due to the shift δR^I_{γ} is given by

$$\partial H/\partial R^I_{\gamma} = \int d\mathbf{r} \quad Z^I \;\; \nabla^I_{\gamma} \, |\mathbf{r} - \mathbf{R}^I|^{-1} \;\; \rho(\mathbf{r}). \tag{14}$$

where ∇^I_{γ} denotes $\partial/\partial R^I_{\gamma}$. Eq. (14) for $\partial H/\partial R^I_{\gamma}$ can be rewritten in terms of the polarization operator $\mathbf{P}(\mathbf{r})$ by using Eq. (5) for $\mathbf{P}(\mathbf{r})$ and $\rho(\mathbf{r})$, integrating by parts with respect to $\mathbf{r}$, and using

$$\nabla_\alpha \, |\mathbf{r} - \mathbf{R}^I|^{-1} = - \nabla^I_\alpha \, |\mathbf{r} - \mathbf{R}^I|^{-1}. \tag{15}$$

This gives

$$\partial H/\partial R^I_\gamma = - \int d\mathbf{r}'' Z^I \, P_\delta(\mathbf{r}'') \, T_{\gamma\delta}(\mathbf{r}'', \mathbf{R}^I) \; . \tag{16}$$

Together, Eqs. (8), (11)-(13) and (16) prove Eq. (10) for $\partial\alpha_{\beta\gamma}(\mathbf{r}; \mathbf{r}', \omega)/\partial R^I_\alpha$. Equivalently, the polarizability density $\alpha^e_{\alpha\beta}(\mathbf{r}; \mathbf{r}', \omega)$ for the molecule perturbed by an infinitesimal shift of nucleus I satisfies Eq. (9), with $\mathbf{F}^s(\mathbf{r}'')$ replaced by $\delta f^I_\gamma(\mathbf{r}'')$, the infinitesimal change in the Coulomb field of nucleus I, due to its displacement by $\delta\mathbf{R}^I$. This shows that the molecule responds via to the change in the Coulomb field of nucleus I via the same hyperpolarizability density that governs its response to external fields.

Integrating Eq. (10) over all space with respect to $\mathbf{r}$ and $\mathbf{r}'$ gives the Eq. (3) for the derivative of the electronic polarizability $\alpha_{\beta\gamma}(\omega)$ with respect to R^I_α. Clearly the derivative of the polarizability $\alpha_{\alpha\beta}(\omega)$ with respect to the normal mode coordinate q_v is

$$\partial\alpha_{\alpha\beta}(\omega)/\partial q_v = \Sigma \, \partial\alpha_{\alpha\beta}(\omega)/\partial R^I_\gamma \;\; \partial R^I_\gamma/\partial q_v \, . \tag{17}$$

3.4 Discussion

This work has shown that the derivatives of the polarizability density with respect to nuclear coordinates depend upon the dipole propagator and the hyperpolarizability density $\beta(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', 0)$; the density β yields the lowest-order nonlinear response to imposed fields, on integration. Thus, we have generalized the relationship between static linear and nonlinear response tensors [8] to the frequency-dependent case.

Our work also gives a new expression for the second derivative of the dipole with respect to nuclear coordinates, for a molecule in any nuclear configuration. From Eq. (2) for $\partial\mu_\beta/\partial R^I{}_\alpha$ and Eq. (10),

$$\partial^2\mu_\gamma/\partial R^I{}_\alpha \partial R^J{}_\beta = Z^I Z^J \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \beta_{\gamma\delta\varepsilon}(\mathbf{r}; \mathbf{r}', 0, \mathbf{r}'', 0)\, T_{\varepsilon\beta}(\mathbf{r}'', \mathbf{R}^J)\, T_{\delta\alpha}(\mathbf{r}', \mathbf{R}^I)$$
$$+ Z^I \delta_{IJ} \int d\mathbf{r}\, d\mathbf{r}'\, \alpha_{\gamma\delta}(\mathbf{r}; \mathbf{r}', 0)\, T^J{}_{\delta\alpha\beta}(\mathbf{r}', \mathbf{R}^J), \tag{18}$$

where $T^J{}_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{R}^J) = -\nabla_\alpha \nabla_\beta \nabla_\gamma(\,|\mathbf{r} - \mathbf{R}^J|^{-1})$. (T tensors of odd orders are odd in the difference between the two arguments $\mathbf{r}$ and $\mathbf{R}^J$). A shift in the position of nucleus I from $\mathbf{R}^I$ to $\mathbf{R}^I + \delta\mathbf{R}^I$ changes the field at point $\mathbf{r}$, due to nucleus I, from

$$f^I{}_\alpha(\mathbf{r}) = -\nabla_\alpha Z^I(\,|\mathbf{r} - \mathbf{R}^I|^{-1})$$

fto

$$f^I{}_\alpha(\mathbf{r}) + \delta f^I{}_\alpha(\mathbf{r}) + 1/2\ \delta^2 f^I{}_\alpha(\mathbf{r}) + \ldots = -\nabla_\alpha Z^I(\,|\mathbf{r} - \mathbf{R}^I|^{-1}) + Z^I T_{\alpha\beta}(\mathbf{r}, \mathbf{R}^I)\,\delta R^I{}_\beta$$
$$+ 1/2\ Z^I T^I{}_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{R}^I)\,\delta R^I{}_\beta\,\delta R^I{}_\gamma + \ldots. \tag{19}$$

Thus the first term on the right in Eq. (18) represents the nonlinear response (via β) to the changes in the nuclear Coulomb field at $\mathbf{r}'$ and $\mathbf{r}''$, while the second term represents the linear response (via α) to the second variation in the field at $\mathbf{r}'$. Extensions of this analysis to find higher derivatives of the dipole and to find second and higher derivatives of the susceptibilities are straightforward. Immediate uses of the results from this work are conceptual rather than computational. Applied to single-molecule polarizabilities, our work provides a new physical interpretation for integrated intensities of vibrational Raman bands, by showing that the band intensity depends on the response of the molecule to the change in Coulomb fields of the nuclei, via the β hyperpolarizability density. For interacting molecules with nonoverlapping or weakly overlapping charge distributions, induction and dispersion energies, collision-induced dipoles and collision-induced polarizabilities are all related to the single-molecule polarizability densities. Thus, Eq. (10) determines in part the nuclear-coordinate dependence of these properties.

For computational purposes, methods of finding the required components of $\alpha(\mathbf{r}; \mathbf{r}', 0)$ are known (see Refs. 5 and 7, and references therein), and methods of approximating $\beta(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0)$ are currently under development. With information on $\beta(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0)$, it should be possible to identify the regions of the electronic charge dis tribution that make the principal contributions to the vibrational Raman band intensities for isolated molecules; and this would facilitate tests of atom- or group-additivity approximations. The dipole propagator tensors appearing in $\partial\alpha_{\beta\gamma}(\omega)/\partial R^I{}_\alpha$ weight the regions nearest to nucleus I. This tends to support additive approximations, provided that $\beta(\mathbf{r}; \mathbf{r}', \omega, \mathbf{r}'', 0)$ is largest for small $|\mathbf{r} - \mathbf{r}'|$ and $|\mathbf{r} - \mathbf{r}''|$.

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CHAPTER IV

FORCES ON NUCLEI IN INTERACTING MOLECULES

Abstract:

When the charge overlap between interacting molecules or ions A and B is weak or negligible, the first-order interaction energy depends only upon the molecular positions, orientations, and the *unperturbed* charge distributions of the molecules. In contrast, the first-order force on a nucleus in molecule A as computed from the Hellmann-Feynman theorem depends not only on the unperturbed charge distribution of molecule B, but also on the electronic polarization *induced* in A by the field from B. At second order, the interaction energy depends on the first-order, linear response of each molecule to its neighbor, while the Hellmann-Feynman force on a nucleus in A depends on second-order and nonlinear responses to B. One purpose of this work is to unify the physical interpretations of interaction energies and Hellmann-Feynman forces at each order, using nonlocal polarizability densities and connections that we have recently established among permanent mo ments, linear response, and nonlinear response tensors.

Our theory also yields new information on the origin of terms in the long-range forces on molecules, through second order in the interaction. One set of terms in the force on molecule A is produced by the field due to the unperturbed charge distribution of B and by the static reaction field from B, acting on the nuclear moments of A. This set originates in the direct interactions between the nuclei in A and the charge distribution of B. A second set of terms results from the permanent field and the reaction field of B acting on the permanent electronic moments of A.

This set results from the attraction of nuclei in A to the electronic charge in A itself, polarized by linear response to B. Finally, there are terms in the force on A due to the perturbation of B by the static reaction field from A; these terms stem from the attraction of nuclei in A to the electronic charge in A, hyperpolarized by the field from B.

For neutral, dipolar molecules A and B at long range, the forces on individual nuclei vary as R^{-3} in the intermolecular separation R, at long range; but when the forces are summed over all of the nuclei, the vector sum varies as R^{-4}. This result, an analogous conversion at second order (from R^{-6} forces on individual nuclei to an R^{-7} force when summed over the nuclei), and the longrange limiting forces on ions are all derived from new sum rules obtained in this work.

4.1 Introduction

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

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

where $\mathbf{R}^I$ is the position of nucleus I. Throughout this work, we use the Born-Oppenheimer approximation: we determine the forces on the nuclei as functions of the nuclear coordinates, fixed within individual calculations but not restricted to the equilibrium configuration. The electronic state is the fully perturbed ground state of the AB pair in the specified nuclear configuration.

For molecules with weak or negligible charge overlap, the first-order interaction energy, denoted by $\Delta E^{(1)}$, is determined completely by the molecular positions, the orientations, and the unperturbed charge distributions of molecules A and B. In contrast, the first-order interaction-induced force $\Delta\mathbf{F}^{I(1)}$ on nucleus I in molecule A, obtained directly from Eq. (1), depends not only on the interaction of that nucleus with the unperturbed charge distribution of B, but also on interaction-induced changes in the electronic charge distribution of A.

At second order in the A-B interaction, the induction energy $\Delta E^{(2)}{}_{\mathrm{ind}}$ is determined entirely by the first-order, linear response of each molecule to the field of its neighbor. Yet the associated induction force $\Delta\mathbf{F}^{I(2)}{}_{\mathrm{ind}}$ on nucleus I in molecule A does not originate solely in the first-order perturbed charge distributions of A and B. Instead, $\Delta\mathbf{F}^{I(2)}{}_{\mathrm{ind}}$ also depends on the hyperpolarization of the electronic charge in A by the field from B, and on the second-order change in the electronic charge density of A due to linear response to the perturbed charge distribution of B.

The results stated above appear counter-intuitive, although they are fully consistent with the Hellmann-Feynman theorem [1, 2] applied to compute forces on nuclei in interacting molecules, given the electronic charge distributions. One purpose of this paper is to connect the physical interpretations of interaction energies and Hellmann-Feynman forces, order by order. We allow for the possibility that A and B may be ionic. An important component in the analysis is the inter-relation that we have recently established among permanent moments, linear response, and nonlinear response tensors [3, 4].

In Sec. 4.2, we use nonlocal polarizability densities to find $\Delta F^{I(1)}$, $\Delta E^{(2)}{}_{ind}$, and $\Delta F^{I(2)}{}_{ind}$. The polarizability density tensors give the polarization produced at one point in a molecule due to the application of an external field at other points [3-12], and thus represent the distribution of polarizable matter throughout the interacting molecules. Quantum mechanical definitions for these tensors are given in Sec. 4.2. Earlier, it has been established that the nonlocal polarizability density determines the derivatives of the molecular dipole with respect to nuclear coordinates [3], and that the first hyperpolarizability density determines the derivatives of the polarizability with respect to nuclear coordinates [3, 4]. In each case, the molecule responds to the change in Coulomb field due to an infinitesimal shift in nuclear position via the *same* susceptibility density that determines its response to external fields.

Our approach, based on nonlocal polarizability densities, holds even when low-order, point-multipole models break down, provided that overlap and exchange between molecules A and B are minimal; for example, our analytical results apply to planar molecules in "sandwich" configurations and to long, chain-like molecules in configurations where appreciable charge overlap could be produced by rotation of either molecule. Our approach includes the direct effects of overlap on the electrostatic and inductive interactions, but it does not account for modifications of the classical interactions due to electron exchange or charge transfer between A and B. Overlap damping effects on dispersion energies have been studied extensively at this level of approximation [9, 12-27].

In Sec. 4.3, we take the long-range limits of the forces $\Delta F^{I(1)}$ and $\Delta F^{I(2)}{}_{ind}$, and express the results in terms of the field and field gradients due to molecule B, together with the screening tensors that represent the effects of electronic redistribution in molecule A [28-44]. We then sum over all nuclei in molecule A in order to find the total force on molecule A. In the process, we resolve a problem connected with the Hellmann-Feynman interpretation of the long-range forces. For specificity, we focus on the long-range forces on neutraldipolar molecules A and B: The lowest-order, long-range force on an individual nucleus in A varies as R^{-3} in the separation R between A and B--but when this force is summed over all of the nuclei in A, the R^{-3} component must drop out, leaving an R^{-4} force on the entire molecule, to leading order. Since the summation runs over nuclei only, elimination of the R^{-3} component is not a simple charge cancellation effect.

At second order, the leading term in the force $\Delta F^{I}{}_{\alpha}{}^{(2)}{}_{ind}$ on an individual nucleus in A depends in part on the attraction of the nucleus to the second-order perturbed electronic charge distribution of molecule A, and thus it varies as R^{-6}--but when the force is summed over all nuclei in molecule A, the result must vary as R^{-7}. The elimination of the R^{-3} and R^{-6} terms in the forces on molecule A follows from new sum rules that we derive in this work. The sum rules apply to integrals involving polarizability densities and dipole propagators from points in the electronic charge distribution to the nuclei, summed over the nuclei.

In Sec. 4.3, we also analyze the long-range, interaction-induced forces on molecule A into components originating in the interaction with the perturbed electronic charge distribution of A, or with the charge distribution of B, and we obtain new results at both first and second order. At first order, the interaction-induced force can be written as a sum of two sets of terms. One involves the net charge on all of the nuclei in A, and the nuclear contributions to the dipole, quadrupole, and higher moments, while the other involves the net electronic charge and the electronic contributions to the permanent charge moments. We show that all of the terms in $\Delta F^{A(1)}{}_{\alpha}$ containing the nuclear charge or nuclear moments of A result from the direct interaction between the nuclei in A and the unperturbed charge distribution of molecule B; the terms in $\Delta F^{A(1)}{}_{\alpha}$ containing permanent electronic moments of A result from the attraction of the nuclei to the electronic charge on A, perturbed to first order by interaction with B.

At second order, the induction energy $\Delta E^{(2)}{}_{\mathrm{ind}}$ is determined by the static "reaction fields" acting on molecules A and B. To lowest order, the static reaction field at A is the field resulting from the polarization of B by the permanent charge and moments of A (similarly for the reaction field at B). We show that interactions of A nuclei with the polarized charge distribution of B appear directly in the force, as terms involving reaction field effects on the nuclear moments of A. We also show that force terms involving reaction field effects on the electronic moments of A stem from the attraction of the A nuclei to the second-order, linear change in the electronic charge density of A itself. Finally, there are terms in the interaction-induced force on molecule A that are associated with the reaction field at B. These contain linear response tensors on A. We show that these terms stem from the attraction of nuclei in A to the electronic charge of A, hyperpolarized by the field from B.

At second order, the total interaction energy for molecules at long range is the sum of the induction energy $\Delta E^{(2)}_{ind}$ discussed above and the dispersion energy $\Delta E^{(2)}_{disp}$. 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. Previously, we have analyzed dispersion forces using nonlocal polarizability densities [45], and the results are summarized briefly below. Through second order in the molecular interaction, the total interaction-induced force is obtained by adding the forces $\Delta F^{I(1)}$ and $\Delta F^{I(2)}_{ind}$ determined in this work to the dispersion force found earlier.

We have shown that the dispersion force on molecule A results entirely from the attraction of nuclei in A to the dispersion-induced change in the electronic charge distribution on *A* [45]. In Ref. 45, a direct perturbative approach is used to find the dispersion terms in the charge densities of molecules A and B, through second order in the interaction. The polarization of A due to dispersion depends on the frequency-dependent hyperpolarizability density of A and the polarizability density of B, taken at imaginary frequencies. Separately, the nonlocal polarizability density theory gives the dispersion energy: Spontaneous fluctuations in the polarization of molecule A produce a field that polarizes B nonlocally. The induced polarization of B gives rise to a reaction field at A, with a resultant energy shift that depends on correlations of the fluctuating polarization of A at two points. Via the fluctuation-dissipation theorem, the correlations are connected to the imaginary part of the nonlocal polarizability density of A. The total dispersion energy is obtained by adding the energy shifts due to the reaction field effects at A and B, and then it is cast as an integral (over imaginary frequencies) of the product of the polarizability densities of the two inter acting molecules. Comparison of the dispersion force on a nucleus in A evaluated by differentiating the dispersion energy vs. that calculated from the dispersion-induced change in the polarization of A establishes the origin of the dispersion force.

Hunt [45] proved a conjecture by Feynman about the origin of forces between atom in S states [1], and generalized it to molecules of arbitrary symmetry. Feynman originally suggested that [1]:

> "The Schrödinger perturbation theory for two interacting atoms at a separation R, large compared to the radii of the atoms, leads to the result that the charge distribution of each is distorted from central symmetry, a dipole moment of order $1/R^7$ being induced in each atom. The negative charge distribution of each atom has its center of gravity moved slightly toward the other. It is not the interaction of these dipoles which leads to van der Waals' force, but rather the attraction of each nucleus for the distorted charge distribution of its *own* electrons that gives the attractive $1/R^7$ force."

Prior to Hunt's work, this conjecture had been proven by Hirschfelder and Eliason [46; see also 47], for the particular case of two hydrogen atoms, both in the 1s state. Hunt [45] provided the first explicit, general proof, and resolved two problems associated with the conjecture. First, the dispersion-induced change in charge density and the dispersion dipole both depend on *nonlinear* response tensors [10, 48-51] for molecules interacting at long range, while the dispersion energy and thus the dispersion forces depend on *linear* response [9, 12-27, 52], to leading order. The required connection between linear and nonlinear response is provided by our recent proof that the hyperpolarizability density determines the changes in the polarizability when nuclei shift [3, 4]. Second, while the dispersion dipole varies as R^{-7} for distinct, nonoverlapping atoms A and B in S states, the dispersion-induced change in charge density actually varies as R^{-6}. Therefore Feynman's electrostatic interpretation would predict an R^{-6} dispersion force in the absence of additional constraints.

A sum rule on the frequency-dependent hyperpolarizability density $\beta(\mathbf{r}, \mathbf{r}', \mathbf{r}''; i\omega, 0)$ [45] eliminates the net attraction of the nuclei to the R^{-6} component of the electronic charge distribution. This result is particularly striking for noncentrosymmetric molecules [45]. For these species, the long-range dispersion dipole varies as R^{-6}, while the net dispersion force varies as R^{-7}, as for heteroatoms. The rationale behind Feynman's conjecture fails--yet the electrostatic interpretation of the dispersion forces still holds, because of the sum rule on $\beta(\mathbf{r}, \mathbf{r}', \mathbf{r}''; i\omega, 0)$. This work is related to an electrostatic force theory based on the Hellmann-Feynman theorem, which has been developed by Nakatsuji and Koga [53; see also 54, 55] and applied to the special case of interactions between two atoms. Within this theory, a density matrix analysis is used to decompose the forces on nuclei into distinct terms, and only two forces--the atomic dipole (AD) force and the extended gross charge (EGC) force--act between atoms at long range. The atomic dipole force on the nucleus of atom A results from the polarization of A induced by interaction with B [53]. It corresponds to the attraction of the nucleus of A to the electronic polarization $P^A{}_\alpha(\mathbf{r})^{(n)}$ (with n > 1), in our approach (see Sec. 4.2). The extended gross charge force results from electrostatic interactions of the nucleus in A with the electrons and nucleus of atom B [53]; it corresponds to the force due to the charge distribution $\rho^B{}_0(\mathbf{r})$ and the polarization $P^B{}_\alpha(\mathbf{r})^{(n)}$ (with n > 1). We find the force on a nucleus in A in terms of $P^A{}_\alpha(\mathbf{r})^{(1)}$ and $\rho^B{}_0(\mathbf{r})$ at first order in the A-B interaction, and in terms of $P^A{}_\alpha(\mathbf{r})^{(2)}$ and $P^B{}_\alpha(\mathbf{r})^{(1)}$ at second order. This is consistent with the electrostatic force theory. Our approach differs from that in Ref. 53, however, since we use nonlocal polarizability densities to derive $P^A{}_\alpha(\mathbf{r})^{(n)}$ and $P^B{}_\alpha(\mathbf{r})^{(n)}$ and thus to deduce the forces, while Nakatsuji and Koga have given the AD and EGC forces in terms of density matrix elements that are not further specified, in general.

Based on the density-matrix analysis, Nakatsuji and Koga [53] have concluded that the electrostatic force theory of long-range interactions is "*quite different* from the traditional energetic theories in both theoretical and interpretative views." This conclusion also contrasts with our work. By use of relations we have recently derived among permanent moments, polarizability densities, and hyperpolarizability densities [3, 4], our work unifies the theories.This work is related in an indirect way to the incorporation of induction effects into density functional theory, carried out by Harris [56]. Our approach yields the mean-field interaction energy in terms of the unperturbed charge densities and the induced polarization, computed from the polarizability densities.

4.2 Forces on Nuclei in Interacting Molecules

In this section, we find the interaction-induced forces on nuclei in a pair of molecules A and B from the perturbation series for the interaction energy ΔE, and we establish the physical interpretation of the forces. The forces are determined for fixed nuclear configurations. The unperturbed electronic states of the A-B system are taken as direct prod ucts of states on A with states on B, under the assumption that overlap between the charge distributions of molecules A and B is weak or negligible. ΔE is expanded as a series in the perturbation V^{AB} [9, 12-27], given by

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

where $\rho^A(\mathbf{r})$ and $\rho^B(\mathbf{r}')$ are the molecular charge density operators:

$$\rho^A(\mathbf{r}) = \sum_j e\, \delta(\mathbf{r} - \mathbf{r}_j) + \sum_I Z^I\, \delta(\mathbf{r} - \mathbf{R}^I) \ ;(3)$$

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

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

For a nucleus I in molecule A, the force $\Delta F^I{}_\alpha{}^{(1)}$ derived from $\Delta E^{(1)}$ has two components: the first results from the change in the nuclear charge density of A when nucleus I shifts, while the second is due to the change in the permanent electronic charge density $\rho^{eA}{}_0(\mathbf{r})$ of molecule A (unperturbed by interactions with B) due to an infinitesimal shift of nucleus I:

$$\begin{aligned} \Delta F^I{}_\alpha{}^{(1)} = &- \int \partial\rho^{eA}{}_0(\mathbf{r})/\partial R^I{}_\alpha\ \rho^B{}_0(\mathbf{r}')\, |\mathbf{r} - \mathbf{r}'|^{-1}\, d\mathbf{r}\, d\mathbf{r}' \\ &- Z^I \int \partial\delta(\mathbf{r} - \mathbf{R}^I)/\partial R^I{}_\alpha\ \rho^B{}_0(\mathbf{r}')\, |\mathbf{r} - \mathbf{r}'|^{-1}\, d\mathbf{r}\, d\mathbf{r}' \ . \end{aligned} \tag{5}$$

The derivative of $\rho^{eA}{}_0(\mathbf{r})$ with respect to $R^I{}_\alpha$ satisfies

$$\begin{aligned} \partial\rho^{eA}{}_0(\mathbf{r})/\partial R^I{}_\alpha = &\int d\mathbf{r}''\, Z^I\, \nabla^I{}_\alpha\, |\mathbf{r}'' - \mathbf{R}^I|^{-1} \times \\ &\sum_k{}' [\langle g_A | \rho^{eA}(\mathbf{r}) | k_A \rangle \langle k_A | \rho^{eA}(\mathbf{r}'') | g_A \rangle \\ &+ \langle g_A | \rho^{eA}(\mathbf{r}'') | k_A \rangle \langle k_A | \rho^{eA}(\mathbf{r}) | g_A \rangle] / (E_g - E_k) \ , \end{aligned} \tag{6}$$

where $\nabla^I{}_\alpha$ denotes differentiation with respect to $R^I{}_\alpha$ and it operates only on $|\mathbf{r}'' - \mathbf{R}^I|^{-1}$. The prime on the summation indicates that the sum runs over the excited electronic states $|k_A\rangle$ of the unperturbed A molecule, omitting the ground state $|g_A\rangle$. The energies of the ground and excited states are E_g and E_k; and $\rho^{eA}(\mathbf{r})$ is the electronic charge density operator for A. Eq. (6) shows that the derivatives of the permanent charge density with respect to nuclear coordinates depend upon a molecular susceptibility. This observation is significant for the subsequent analysis.

The electronic charge density operator $\rho^e(\mathbf{r})$ is connected to the electronic polarization operator $\mathbf{P}^e(\mathbf{r})$ used in defining the nonlocal polarizability density by

$$\nabla \cdot \mathbf{P}^e(\mathbf{r}) = -\rho^e(\mathbf{r}) \ . \tag{7}$$

In sum-over-states form [9, 10], the nonlocal polarizability density $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ satisfies

$$\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = (1 + \wp_{\alpha\beta}) \sum_{k}{}' \langle g \,|\, P^e_{\alpha}(\mathbf{r}) \,|\, k \rangle \langle k \,|\, P^e_{\beta}(\mathbf{r}') \,|\, g \rangle / (E_k - E_g) \ , \tag{8}$$

where $\wp_{\alpha\beta}$ permutes the operators $P^e_{\alpha}(\mathbf{r})$ and $P^e_{\beta}(\mathbf{r}')$. The value of $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ is unchanged by substituting the full polarization operator $\mathbf{P}(\mathbf{r})$, including nuclear terms, for the electronic polarization operator $\mathbf{P}^e(\mathbf{r})$ in Eq. (8). The nonlocal polarizability density $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ represents the distribution of polarizable matter throughout a molecule, because it gives the polarization $P_{\alpha}(\mathbf{r})$ induced at point $\mathbf{r}$ by the application of a static external field $\mathcal{F}_{\beta}(\mathbf{r}')$ at another point $\mathbf{r}'$. Eq. (6) is equivalent to the following statement about the electronic polarization in terms of $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$: When a nucleus shifts infinitesimally within a molecule, the electrons respond to the change in the nuclear Coulomb field via the same nonlocal polarizability density $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ that describes the response to an external field.

Use of Eqs. (6)-(8) and integration by parts [57] transforms Eq. (5) for the force on nucleus I in molecule A into

$$\begin{aligned} \Delta F^{I}_{\alpha}{}^{(1)} = {} & Z^I \int (R^I_{\alpha} - r'_{\alpha}) \,|\mathbf{R}^I - \mathbf{r}'|^{-3} \, \rho^B_0(\mathbf{r}') \, d\mathbf{r}' \\ & + Z^I \int T_{\alpha\gamma}(\mathbf{R}^I, \mathbf{r}'') \, \alpha^A_{\beta\gamma}(\mathbf{r}, \mathbf{r}'') \, (r_{\beta} - r'_{\beta}) \, |\mathbf{r} - \mathbf{r}'|^{-3} \, \rho^B_0(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \, d\mathbf{r}''. \end{aligned} \tag{9}$$

Here $T_{\alpha\gamma}(\mathbf{R}^I, \mathbf{r}'')$ is the dipole propagator, defined by $T_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \nabla_{\alpha} \nabla_{\beta} \,|\mathbf{r} - \mathbf{r}'|^{-1}$. The Einstein convention of summation over repeated Greek indices is followed in Eq. (9) and below.

To lowest order in the A-B interaction, the polarization $P^A_{\gamma}(\mathbf{r}'')^{(1)}$ induced in molecule A by the permanent charge distribution of B satisfies

$$P^A_\gamma(\mathbf{r}'')^{(1)} = \int \alpha^A_{\gamma\beta}(\mathbf{r}'', \mathbf{r})\,(r_\beta - r'_\beta)\,|\mathbf{r} - \mathbf{r}'|^{-3}\,\rho^B_0(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' \tag{10}$$

The Born symmetry condition [10]

$$\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \alpha_{\beta\alpha}(\mathbf{r}', \mathbf{r}) \tag{11}$$

holds for the nonlocal polarizability density. From Eqs. (10)-(11), Eq. (9) is equivalent to

$$\Delta F^I_\alpha{}^{(1)} = Z^I \int (R^I_\alpha - r'_\alpha)\,|\mathbf{R}^I - \mathbf{r}'|^{-3}\,\rho^B_0(\mathbf{r}')\,d\mathbf{r}' + Z^I \int T_{\alpha\gamma}(\mathbf{R}^I, \mathbf{r}'')\,P^A_\gamma(\mathbf{r}'')^{(1)}\,d\mathbf{r}''. \tag{12}$$

Eq. (12) for $\Delta F^I_\alpha{}^{(1)}$ is identical to the lowest-order Hellmann-Feynman result; i.e., it gives the force obtained directly from the charge distributions $\rho^B_0(\mathbf{r}')$ and $\Delta\rho^{A(1)}(\mathbf{r}'')$. Since it has been derived here from $\Delta E^{(1)}$ in Eq. (4) via Eq. (1), we have proven that the energy-based theory and the electrostatic force theory give identical results for the interaction-induced force at first order, despite apparent differences in physical content. The interaction energy $\Delta E^{(1)}$ depends exclusively on the permanent charge distributions of the unperturbed molecules A and B, and not on the changes in the charge densities of A or B induced by interactions. From Eq. (12), though, the resultant force $\Delta F^I_\alpha{}^{(1)}$ exerted on nucleus I in molecule A depends on the electronic polarization *induced* in A by B. Thus Eqs. (1), (4), and (12) establish a new connection between pure electrostatic and induction effects. One key step in the proof involves relating linear response tensors--such as $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ or the charge-density susceptibility contained implicitly in Eq. (6)--to the derivatives of the permanent electronic charge density with respect to nuclear coordinates [3, 4]. A second key step relies on the Born symmetry of the nonlocal polarizability density [10].

At second order in V^{AB}, the interaction energy is a sum of induction and dispersion terms. Induction effects are classical, stemming from the polarization of each molecule by the field of the permanent charge distribution of the other. In contrast, dispersion effects (van der Waals attractions) are purely quantum mechanical, resulting from correlations between the spontaneously fluctuating charge distributions of molecules A and B [9, 12-27]. Within second-order perturbation theory, $\Delta E^{(2)}$ is obtained as a sum over states $| m^A n^B \rangle$ of the A-B pair, excluding $| g^A g^B \rangle$. Consequently, $\Delta E^{(2)}$ splits into three sets of terms, one with excited states confined to molecule A, a second with excited states confined to B, and a third with excited states on both molecules. The sum of the first two sets gives the induction energy, as analyzed below. The third set gives the dispersion (van der Waals) energy; in Ref. 45, dispersion forces have been analyzed using nonlocal polarizability densities.

The induction energy $\Delta E^{(2)}_{ind}$ depends on the polarizability densities of A and B, and on the fields $\mathcal{F}^A{}_0(\mathbf{r})$ and $\mathcal{F}^B{}_0(\mathbf{r})$ due to the permanent charge distributions of the un perturbed molecules A and B.

$$\begin{aligned}\Delta E^{(2)}_{ind} = &- 1/2 \int d\mathbf{r}\, d\mathbf{r}'\ \alpha^A{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathcal{F}^B{}_{0\alpha}(\mathbf{r})\, \mathcal{F}^B{}_{0\beta}(\mathbf{r}') \\ &- 1/2 \int d\mathbf{r}\, d\mathbf{r}'\ \alpha^B{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathcal{F}^A{}_{0\alpha}(\mathbf{r})\, \mathcal{F}^A{}_{0\beta}(\mathbf{r}')\ . \end{aligned} \tag{13}$$

Eq. (13) is derived as follows: Terms in $\Delta E^{(2)}$ with excitations confined to molecule A are:

$$\begin{aligned}\Delta E^{(2)}{}_A &= -\sum_{k \neq g} \langle g^A g^B | V^{AB} | k^A g^B \rangle \langle k^A g^B | V^{AB} | g^A g^B \rangle / (E_k - E_g) \\ &= - \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \sum_k{}' \langle g^A | \rho^A(\mathbf{r}) | k^A \rangle \langle k^A | \rho^A(\mathbf{r}'') | g^A \rangle / (E_k - E_g) \\ &\qquad \times \rho^B{}_0(\mathbf{r}')\ |\mathbf{r} - \mathbf{r}'|^{-1}\ \rho^B{}_0(\mathbf{r}''')\ |\mathbf{r}'' - \mathbf{r}'''|^{-1}\ . \end{aligned} \tag{14}$$

With Eq. (8) for the nonlocal polarizability density, successive integrations by parts [57] yield the first term in Eq. (13), and the second term is obtained by interchanging the roles of molecules A and B.

The induction force on nucleus K in molecule A is determined by the derivative of the polarizability density $\alpha^A{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ and by the derivative of the field $\mathcal{F}^A{}_{0\alpha}(\mathbf{r})$ with respect to the coordinates of K. In Refs. 3 and 4, we have shown that the derivative of the polarizability density with respect to $\mathbf{R}^K$ depends on the hyperpolarizability density $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, a nonlinear response tensor that gives the polarization $P_\alpha(\mathbf{r})$ induced at $\mathbf{r}$ by the concerted action of static electric fields $\mathcal{F}_\beta(\mathbf{r}')$ and $\mathcal{F}_\gamma(\mathbf{r}'')$. Explicitly, the static hyperpolarizability density is given by [58, 59]

$$\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \hbar^{-2} \wp_{\alpha\beta\gamma} \sum_{m,n}{}' \langle g | P_\alpha(\mathbf{r}) | m \rangle [\langle m | P_\beta(\mathbf{r}') | n \rangle - \delta_{mn} \langle g | P_\beta(\mathbf{r}') | g \rangle] \times \langle n | P_\gamma(\mathbf{r}'') | g \rangle / (\omega_{mg}\, \omega_{ng}) \;, \tag{15}$$

where the operator $\wp_{\alpha\beta\gamma}$ generates the sum of terms obtained by permuting $P_\alpha(\mathbf{r})$, $P_\beta(\mathbf{r}')$, and $P_\gamma(\mathbf{r}'')$ in the expression that follows, and $E_m - E_g = \hbar\omega_{mg}$. In terms of $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, the derivative of the polarizability density is [3]

$$\partial\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')/\partial R^K{}_\delta = \int d\mathbf{r}''\, \beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\, Z^K\, T_{\gamma\delta}(\mathbf{r}'', \mathbf{R}^K) \;. \tag{16}$$

As noted above, when a nucleus shifts, the electrons respond to the change in the nuclear Coulomb field via the same tensor that describes response to an external field. Response via $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ to an applied field, acting together with the change in the nuclear Coulomb field, yields a net effect that is linear in the applied field; and thus it determines the nuclear-coordinate dependence of $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$.

The static β-hyperpolarizability density has the permutation symmetry:

$$\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \beta_{\alpha\gamma\beta}(\mathbf{r}, \mathbf{r}'', \mathbf{r}') = \beta_{\gamma\beta\alpha}(\mathbf{r}'', \mathbf{r}', \mathbf{r}) \;. \tag{17}$$

From Eqs. (1), (13), and (16),

$$\Delta F^K{}_\varepsilon{}^{(2)}{}_{\text{ind}} = 1/2 \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\; \beta^A{}_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\, Z^K\, T_{\gamma\varepsilon}(\mathbf{r}'', \mathbf{R}^K)\, \mathcal{F}^B{}_{0\alpha}(\mathbf{r})\, \mathcal{F}^B{}_{0\beta}(\mathbf{r}') + \int d\mathbf{r}\, d\mathbf{r}'\; \alpha^B{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \partial\mathcal{F}^A{}_{0\alpha}(\mathbf{r})/\partial R^K{}_\varepsilon\, \mathcal{F}^A{}_{0\beta}(\mathbf{r}') \;. \tag{18}$$

The derivative of the field due to molecule A with respect to the coordinate of nucleus K in A satisfies

$$\begin{aligned}\partial \mathcal{F}^{A}{}_{0\alpha}(\mathbf{r})/\partial R^{K}{}_{\varepsilon} &= \int d\mathbf{r}' \left[(r_\alpha - r'_\alpha)\, |\mathbf{r} - \mathbf{r}'|^{-3}\, \partial \rho^{eA}{}_{0}(\mathbf{r}')/\partial R^{K}{}_{\varepsilon} \right] \\ &\quad + Z^{K}\, \nabla^{K}{}_{\varepsilon} (r_\alpha - R^{K}{}_{\alpha})\, |\mathbf{r} - \mathbf{R}^{K}|^{-3} \\ &= - \int d\mathbf{r}'\, d\mathbf{r}'' \left[\nabla'_\beta (r_\alpha - r'_\alpha)\, |\mathbf{r} - \mathbf{r}'|^{-3} \right. \\ &\quad \left. \times Z^{K}\, \nabla^{K}{}_{\varepsilon}\, \nabla''_\gamma\, |\mathbf{r}'' - \mathbf{R}^{K}|^{-1}\, \alpha^{A}{}_{\beta\gamma}(\mathbf{r}', \mathbf{r}'') \right] \\ &\quad + Z^{K}\, \nabla^{K}{}_{\varepsilon} (r_\alpha - R^{K}{}_{\alpha})\, |\mathbf{r} - \mathbf{R}^{K}|^{-3} \ ,\end{aligned} \tag{19}$$

where ∇'_β denotes differentiation with respect to r'_β, and similarly for ∇''_γ. From Eqs. (17)-(19), we obtain

$$\begin{aligned}\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{ind} = {} & 1/2 \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}''\ Z^{K}\, T_{\varepsilon\gamma}(\mathbf{R}^{K}, \mathbf{r}'')\, \beta^{A}{}_{\gamma\alpha\beta}(\mathbf{r}'', \mathbf{r}, \mathbf{r}')\ \mathcal{F}^{B}{}_{0\alpha}(\mathbf{r})\, \mathcal{F}^{B}{}_{0\beta}(\mathbf{r}') \\ & + \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}'''\ Z^{K}\, T_{\varepsilon\gamma}(\mathbf{R}^{K}, \mathbf{r}''')\, \alpha^{A}{}_{\gamma\delta}(\mathbf{r}''', \mathbf{r}'') \\ & \times T_{\delta\alpha}(\mathbf{r}'', \mathbf{r})\, \alpha^{B}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathcal{F}^{A}{}_{0\beta}(\mathbf{r}') \\ & + \int d\mathbf{r}\, d\mathbf{r}'\ Z^{K}\, T_{\varepsilon\alpha}(\mathbf{R}^{K}, \mathbf{r})\, \alpha^{B}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathcal{F}^{A}{}_{0\beta}(\mathbf{r}') \ .\end{aligned} \tag{20}$$

Eq. (20) has a simple physical interpretation in terms of the electronic polarization induced in B at first order, and the polarization induced in A at second order in the A-B interaction: At first order, the polarization induced in B by the permanent charge distribution of A is given by Eq. (10), or equivalently by

$$P^{B}{}_{\alpha}(\mathbf{r})^{(1)} = \int \alpha^{B}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathcal{F}^{A}{}_{0\beta}(\mathbf{r}')\, d\mathbf{r}' \ . \tag{21}$$

At second-order in the A-B interaction, there are two contributions to the polarization induced in A: (i) linear response to the field due to the induced polarization of B, $P^{B}{}_{\alpha}(\mathbf{r})^{(1)}$, and (ii) nonlinear response to the field $\mathcal{F}^{B}{}_{0\alpha}(\mathbf{r})$ due to the permanent charge distribution of B. Hence

$$\begin{aligned}P^{A}{}_{\alpha}(\mathbf{r})^{(2)} = {} & \int d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}'''\ \alpha^{A}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, T_{\beta\gamma}(\mathbf{r}', \mathbf{r}'')\, \alpha^{B}{}_{\gamma\delta}(\mathbf{r}'', \mathbf{r}''')\, \mathcal{F}^{A}{}_{0\delta}(\mathbf{r}''') \\ & + 1/2 \int d\mathbf{r}' d\mathbf{r}''\ \beta^{A}{}_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\ \mathcal{F}^{B}{}_{0\beta}(\mathbf{r}')\, \mathcal{F}^{B}{}_{0\gamma}(\mathbf{r}'') \ .\end{aligned} \tag{22}$$

Thus, from Eqs. (20)-(22),

$$\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{ind} = \int dr\ Z^{K}\, T_{\varepsilon\alpha}(R^{K}, r)\,[\, P^{A}{}_{\alpha}(r)^{(2)} + P^{B}{}_{\alpha}(r)^{(1)}\,]\ . \tag{23}$$

As given in Eq. (13), $\Delta E^{(2)}{}_{ind}$ depends solely on the linear response of each molecule to the field from the unperturbed (zeroth-order) charge distribution of the other--but as shown in Eqs. (21)-(23), the associated force on nucleus K in molecule A depends on the *nonlinear* response of A to the permanent charge distribution of B, and on the linear response of A to the induced polarization of B (as well as the linear response by B to A). This is a consequence of the connection between linear and nonlinear response in Eq. (16), the permutation symmetry of the hyperpolarizability density in Eq. (17), and Eqs. (6) and (11).

Eq. (23) for $\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{ind}$ is identical to the second-order Hellmann-Feynman result; thus it establishes the identity of the energy-based theory and the electrostatic force theory at second order. In Eq. (23), the force on nucleus K due to the nonlinear term in $P^{A}{}_{\alpha}(r)^{(2)}$ (i.e., the term containing β^{A}) arises from the dependence of $\alpha^{A}{}_{\alpha\beta}(r, r')$ on the position of K; the force due to the linear-response term in $P^{A}{}_{\alpha}(r)^{(2)}$ arises from the dependence of $\rho^{eA}{}_{0}(r')$ on the position of K; and the force due to $P^{B}{}_{\alpha}(r)^{(1)}$ results directly from the dependence of the nuclear Coulomb field on the position of K. It is also interesting to compare Eq. (23) with the corresponding result for the dispersion force on nucleus K, $\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{disp}$. The dispersion force on a nucleus K in A contains no contributions from the polarization of B [45]; it results solely from the attraction of K to the dispersion-induced change in the electronic charge distribution of A, and this depends upon the hyperpolarizability density of molecule A.

4.3 The Long-Range Limit, and New Sum Rules for Polarizability and Hyperpolarizability Densities

In the long-range limit, for a pair of molecules with charges Z^A and Z^B, permanent dipoles μ^A and μ^B, and permanent quadrupoles Θ^A and Θ^B, the force on the entire A molecule, taken to first order in the A-B interaction, simplifies to [60]

$$\begin{aligned} F^{A(1)}_{\alpha} = {} & -Z^A T_{\alpha} Z^B + Z^A T_{\alpha\beta} \mu^B_{\beta} - Z^B T_{\alpha\beta} \mu^A_{\beta} - 1/3\ Z^A T_{\alpha\beta\gamma} \Theta^B_{\beta\gamma} \\ & + \mu^A_{\beta} T_{\alpha\beta\gamma} \mu^B_{\gamma} - 1/3\ Z^B T_{\alpha\beta\gamma} \Theta^A_{\beta\gamma} + \dots , \end{aligned} \tag{24}$$

with the T tensors taken as functions of the vector $(\mathbf{R}^A - \mathbf{R}^B)$ between molecular origins, here and below; $T_{\alpha}(\mathbf{r}, \mathbf{r}') = \nabla_{\alpha} |\mathbf{r} - \mathbf{r}'|^{-1}$, $T_{\alpha\beta}$ has been defined following Eq. (9), and $T_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}') = \nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} |\mathbf{r} - \mathbf{r}'|^{-1}$. At second order in the interaction, the long-range limiting force on a pair of neutral dipolar molecules is [60]

$$F^{A(2)}_{\text{ind},\alpha} = \alpha^A_{\beta\gamma} T_{\beta\delta} \mu^B_{\delta} T_{\alpha\gamma\varepsilon} \mu^B_{\varepsilon} + \alpha^B_{\beta\gamma} T_{\beta\delta} \mu^A_{\delta} T_{\alpha\gamma\varepsilon} \mu^A_{\varepsilon} , \tag{25}$$

to order R^{-7} in the separation between molecular centers. For ions A and B, to order R^{-6} the net induction force is [60]

$$\begin{aligned} F^{A(2)}_{\text{ind},\alpha} = {} & \alpha^A_{\beta\gamma} T_{\beta}\ Z^B T_{\alpha\gamma} Z^B + \alpha^B_{\beta\gamma} T_{\beta}\ Z^A T_{\alpha\gamma} Z^A \\ & - \alpha^A_{\beta\gamma} (T_{\beta} T_{\alpha\gamma\delta} + T_{\alpha\beta} T_{\gamma\delta}) Z^B \mu^B_{\delta} \\ & + \alpha^B_{\beta\gamma} (T_{\beta} T_{\alpha\gamma\delta} + T_{\alpha\beta} T_{\gamma\delta}) Z^A \mu^A_{\delta} \\ & + 1/3\ A^A_{\beta,\gamma\delta} (T_{\beta} T_{\alpha\gamma\delta} + T_{\alpha\beta} T_{\gamma\delta}) Z^B Z^B \\ & - 1/3\ A^B_{\beta,\gamma\delta} (T_{\beta} T_{\alpha\gamma\delta} + T_{\alpha\beta} T_{\gamma\delta}) Z^A Z^A + \dots , \end{aligned} \tag{26}$$

where $A^A_{\beta,\gamma\delta}$ is the dipole-quadrupole polarizability, a linear response tensor that determines the dipole induced by a uniform field gradient, and the quadrupole induced by a uniform field [60]. It is not obvious how the results in Eqs. (24)-(26) emerge from the polarizability density theory developed in Sec. 4.2. For example, the result for $F^{A(1)}_{\alpha}$

from Eqs. (10) and (12) depends on the polarizability density of molecule A, as well as the permanent charge distribution of B; and the result for $\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{ind}$ from Eqs. (21)-(23) depends on the hyperpolarizability of A. One purpose of this section is to prove that the forces $\Delta F^{K}{}_{\alpha}{}^{(1)}$ and $\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{ind}$ in Eqs. (12) and (23) take on the long-range limiting forms in Eqs. (24)-(26), when summed over nuclei K. In the process, we gain new information on the physical origin of terms in Eqs. (24)-(26). We also derive new sum rules that apply to $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ and $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, in broad analogy to the Thomas-Reiche-Kuhn sum rule [61] for oscillator strengths.

To first order in the A-B interaction, the induced force $\Delta F^{K}{}_{\alpha}{}^{(1)}$ on nucleus K satisfies

$$\begin{aligned}\Delta F^{K}{}_{\alpha}{}^{(1)} = &-Z^{K} \int T_{\alpha}(\mathbf{R}^{K} - \mathbf{r}')\ \rho^{B}{}_{0}(\mathbf{r}')\, d\mathbf{r}' \\ &- Z^{K} \int T_{\alpha\beta}(\mathbf{R}^{K} - \mathbf{r}'')\, \alpha^{A}{}_{\beta\gamma}(\mathbf{r}'', \mathbf{r})\, T_{\gamma}(\mathbf{r} - \mathbf{r}')\, \rho^{B}{}_{0}(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'d\mathbf{r}'' . \quad (27)\end{aligned}$$

To find the long-range limit, it is convenient first to expand $\mathbf{r}'$ about the origin $\mathbf{R}^{B}$ in molecule B. This yields

$$\begin{aligned}\Delta F^{K}{}_{\alpha}{}^{(1)} = &- Z^{K}\ T_{\alpha}(\mathbf{R}^{K} - \mathbf{R}^{B})\, Z^{B} + Z^{K} T_{\alpha\beta}(\mathbf{R}^{K} - \mathbf{R}^{B})\, \mu^{B}{}_{\beta} \\ &- 1/3\ Z^{K}\ T_{\alpha\beta\gamma}(\mathbf{R}^{K} - \mathbf{R}^{B})\, \Theta^{B}{}_{\beta\gamma} + \ldots \\ &- Z^{K} \int T_{\alpha\beta}(\mathbf{R}^{K} - \mathbf{r}'')\, \alpha^{A}{}_{\beta\gamma}(\mathbf{r}'', \mathbf{r})\, T_{\gamma}(\mathbf{r} - \mathbf{R}^{B})\, Z^{B}\ d\mathbf{r}\, d\mathbf{r}'' \\ &+ Z^{K} \int T_{\alpha\beta}(\mathbf{R}^{K} - \mathbf{r}'')\, \alpha^{A}{}_{\beta\gamma}(\mathbf{r}'', \mathbf{r})\, T_{\gamma\delta}(\mathbf{r} - \mathbf{R}^{B})\, \mu^{B}{}_{\delta}\ d\mathbf{r}\, d\mathbf{r}'' \\ &- 1/3\ Z^{K} \int T_{\alpha\beta}(\mathbf{R}^{K} - \mathbf{r}'')\, \alpha^{A}{}_{\beta\gamma}(\mathbf{r}'', \mathbf{r})\, T_{\gamma\delta\varepsilon}(\mathbf{r} - \mathbf{R}^{B})\, \Theta^{B}{}_{\delta\varepsilon}\ d\mathbf{r}\, d\mathbf{r}'' + \ldots . \\ &\qquad (28)\end{aligned}$$

Next, we expand the T tensors in the integrands about $\mathbf{r} = \mathbf{R}^{K}$. This gives

$$\begin{aligned}\Delta F^{K}{}_{\alpha}{}^{(1)} = &- Z^{K} (\delta_{\alpha\beta} - \gamma^{K}{}_{\alpha\beta})\, [\, T_{\beta}(\mathbf{R}^{K} - \mathbf{R}^{B})\, Z^{B} - T_{\beta\gamma}(\mathbf{R}^{K} - \mathbf{R}^{B})\, \mu^{B}{}_{\gamma} \\ &+ 1/3\, T_{\beta\gamma\delta}(\mathbf{R}^{K} - \mathbf{R}^{B})\, \Theta^{B}{}_{\gamma\delta} + \ldots] \\ &- Z^{K} \phi^{K}{}_{\alpha\beta\gamma}\, [\, T_{\beta\gamma}(\mathbf{R}^{K} - \mathbf{R}^{B})\, Z^{B} - T_{\beta\gamma\delta}(\mathbf{R}^{K} - \mathbf{R}^{B})\, \mu^{B}{}_{\delta} + \ldots]\end{aligned}$$

$$- Z^K \kappa^K{}_{\alpha\beta\gamma\delta} [\, T_{\beta\gamma\delta}(\mathbf{R}^K - \mathbf{R}^B) Z^B + \ldots \,] \ , \tag{29}$$

where

$$\gamma^K{}_{\alpha\beta} = - \int T_{\alpha\gamma}(\mathbf{R}^K - \mathbf{r}) \, \alpha^A{}_{\gamma\beta}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \ , \tag{30}$$

$$\phi^K{}_{\alpha\beta\gamma} = \int T_{\alpha\delta}(\mathbf{R}^K - \mathbf{r}) \, \alpha^A{}_{\delta\beta}(\mathbf{r}, \mathbf{r}') \, (\mathbf{r}' - \mathbf{R}^K)_\gamma \, d\mathbf{r} \, d\mathbf{r}' \ , \tag{31}$$

and

$$\kappa^K{}_{\alpha\beta\gamma\delta} = 1/2 \int T_{\alpha\varepsilon}(\mathbf{R}^K - \mathbf{r}) \, \alpha^A{}_{\varepsilon\beta}(\mathbf{r}, \mathbf{r}') \, (\mathbf{r}' - \mathbf{R}^K)_\gamma \, (\mathbf{r}' - \mathbf{R}^K)_\delta \, d\mathbf{r} \, d\mathbf{r}' \ . \tag{32}$$

Equivalently, in terms of the long-range field $\mathcal{F}^B{}_\alpha(\mathbf{R}^K)$ at $\mathbf{R}^K$ due to molecule B, the field gradient $\mathcal{F}^{B\prime}{}_{\alpha\beta}(\mathbf{R}^K)$, and its gradient $\mathcal{F}^{B\prime\prime}{}_{\alpha\beta\gamma}(\mathbf{R}^K)$, Eq. (29) for the force on nucleus K is

$$\begin{aligned} \Delta F^K{}_\alpha{}^{(1)} = \ & Z^K (\delta_{\alpha\beta} - \gamma^K{}_{\alpha\beta}) \, \mathcal{F}^B{}_\beta(\mathbf{R}^K) + Z^K \phi^K{}_{\alpha\beta\gamma} \, \mathcal{F}^{B\prime}{}_{\beta\gamma}(\mathbf{R}^K) \\ & + Z^K \kappa^K{}_{\alpha\beta\gamma\delta} \, \mathcal{F}^{B\prime\prime}{}_{\beta\gamma\delta}(\mathbf{R}^K) - \ldots \ . \end{aligned} \tag{33}$$

The tensor $\gamma^K{}_{\alpha\beta}$ is the standard Sternheimer shielding tensor for nucleus K [3, 28-44]: If molecule A is placed in a uniform, applied electric field $\mathcal{F}^e$, electronic charge redistribution induced by the applied field changes the effective field at the nucleus from $\mathcal{F}^e$ to $(1 - \gamma^K) \cdot \mathcal{F}^e$, to first order in $\mathcal{F}^e$. Thus γ^K is the electric-field analogue of the chemical shift tensor. The relationship in Eq. (30) between the nonlocal polarizability density, the dipole propagator, and the shielding tensor γ^K has been proven in Ref. 3 (for related work, see Refs. 34, 40, and 62). Electronic charge redistribution in a nonuniform applied field differs from that in a uniform field, and the tensors $\phi^K{}_{\alpha\beta\gamma}$ [63] and $\kappa^K{}_{\alpha\beta\gamma\delta}$ reflect the corresponding modifications of the shielding, due to the nonuniformity of the field at $\mathbf{R}^K$.

In order to obtain the long-range force on the entire molecule A, we return to Eq. (28), expand the T tensors about $\mathbf{R}^K = \mathbf{R}^A$ and $\mathbf{r} = \mathbf{R}^A$, and sum over nuclei K. In earlier work, we have derived a condition on integrals of the polarizability density and dipole propagators for neutral molecules [3]; as modified for species which may have a non-zero net charge, that condition is:

$$Z^{eA}\,\delta_{\alpha\beta} = \sum_{K} Z^{K} \int T_{\alpha\gamma}(\mathbf{R}^{K}, \mathbf{r})\,\alpha^{A}{}_{\gamma\beta}(\mathbf{r}, \mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' \,, \tag{34}$$

where Z^{eA} is the total *electronic* charge in molecule A. The sum rule in Eq. (34) is derived by considering the ground-state expectation value of the commutator between the momentum operator p_α and the dipole μ_β (see [61]). New sum rules can be derived starting from the commutators of p_α with higher electronic moments, e.g., $q_{\beta\gamma}$ defined by

$$q_{\beta\gamma} = e \sum_{j} r_{\beta j}\, r_{\gamma j} \,, \tag{35}$$

where the sum runs over the electrons j, and $\mathbf{r}_j$ gives the electronic position relative to the origin $\mathbf{R}^A$. The ground-state expectation value of the commutator $[p_\alpha, q_{\beta\gamma}]$ is

$$\langle g \,|\, [p_\alpha, q_{\beta\gamma}] \,|\, g \rangle = (\hbar/i)\,\mu^{e}{}_{\gamma}\,\delta_{\alpha\beta} + (\hbar/i)\,\mu^{e}{}_{\beta}\,\delta_{\alpha\gamma} \,. \tag{36}$$

In Eq. (36), μ^e denotes the electronic part of the ground-state dipole, relative to $\mathbf{R}^A$. Since the ground-state expectation value of the momentum operator vanishes, $\langle g \,|\, [p_\alpha, q_{\beta\gamma}] \,|\, g \rangle$ also satisfies

$$\langle g \,|\, [p_\alpha, q_{\beta\gamma}] \,|\, g \rangle = \sum_{k}{}' \left[\langle g \,|\, p_\alpha \,|\, k \rangle \langle k \,|\, q_{\beta\gamma} \,|\, g \rangle - \langle g \,|\, q_{\beta\gamma} \,|\, k \rangle \langle k \,|\, p_\alpha \,|\, g \rangle \right]$$

$$= 2\,i\,\operatorname{Im} \sum_{k}{}' \langle g \,|\, [p_\alpha, H_0] \,|\, k \rangle \langle k \,|\, q_{\beta\gamma} \,|\, g \rangle / (E_k - E_g) \,. \tag{37}$$

where Im denotes the imaginary component of the expression that follows. Matrix elements for the commutator between $p_\alpha{}^j$ for the jth electron and the unperturbed Hamiltonian H_0 are determined by the force on the jth electron; and

$$\langle g \,|\, [p_\alpha, H_0] \,|\, k \rangle = i\hbar \,\langle g \,|\, \sum_{I=1}^{N} \sum_{j} F^{I\to j}{}_{\alpha} \,|\, k \rangle, \tag{38}$$

where $\mathbf{F}^{I\to j}$ denotes the force on electron j due to nucleus I, and the sum runs over all N nuclei. Eq. (38) holds because the sum over electrons j of the force due to the other electrons i ≠ j vanishes (cf. [3]).

The matrix elements for the net force on the electrons can also be cast in terms of the matrix elements for the electronic charge density operator as:

$$\langle g \,|\sum_{I}\sum_{j} F^{I\to j}{}_{\alpha}\,| k \rangle = \langle g\,| -\sum_{I} Z^{I} \int d\mathbf{r}\, \rho(\mathbf{r})\, \nabla_{\alpha}(|\mathbf{R}^{I} - \mathbf{r}|^{-1})\,| k \rangle \,. \tag{39}$$

With Eqs. (8), (36)-(39), the relation of the operator $q_{\beta\gamma}$ to the polarization operator via

$$q_{\beta\gamma} = \int d\mathbf{r}' \, [\, P_{\beta}(\mathbf{r}')\, r'_{\gamma} + P_{\gamma}(\mathbf{r}')\, r_{\beta}' \,] \,, \tag{40}$$

and an integration by parts, we obtain the new sum rule:

$$\begin{aligned}\sum_{K} Z^{K} \int T_{\alpha\delta}(\mathbf{R}^{K}, \mathbf{r})\, [\, \alpha^{A}{}_{\delta\beta}(\mathbf{r}, \mathbf{r}')\,(r'_{\gamma} - R^{A}{}_{\gamma}) + \alpha^{A}{}_{\delta\gamma}(\mathbf{r}, \mathbf{r}')\,(r'_{\beta} - R^{A}{}_{\beta})\,]\, d\mathbf{r}\, d\mathbf{r}' \\ = \mu^{eA}{}_{\gamma}\, \delta_{\alpha\beta} + \mu^{eA}{}_{\beta}\, \delta_{\alpha\gamma} \,.\end{aligned} \tag{41}$$

From an analogous proof, with $q_{\beta\gamma}$ replaced by the third-moment operator $t_{\beta\gamma\delta}$ defined by

$$t_{\beta\gamma\delta} = e\sum_{j} r_{\beta j}\, r_{\gamma j}\, r_{\delta j} = \int d\mathbf{r}' \, [\, P_{\beta}(\mathbf{r}')\, r'_{\gamma} r'_{\delta} + P_{\gamma}(\mathbf{r}')\, r_{\beta}' r'_{\delta} + P_{\delta}(\mathbf{r}')\, r'_{\beta}\, r'_{\gamma}] \,, \tag{42}$$

and the commutation relation

$$\begin{aligned}\langle g \,|[p_{\alpha}, t_{\beta\gamma\delta}]\,| g \rangle = (2\hbar/3i)\, [\, \Theta^{e}{}_{\gamma\delta}\, \delta_{\alpha\beta} + \Theta^{e}{}_{\beta\delta}\, \delta_{\alpha\gamma} + \Theta^{e}{}_{\beta\gamma}\, \delta_{\alpha\delta}\,] \\ + (\hbar/3i)\, q_{\varepsilon\varepsilon}\, (\delta_{\alpha\beta}\, \delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\, \delta_{\beta\gamma}) \,,\end{aligned} \tag{43}$$

we obtain a second new sum rule,

$$\begin{aligned}\sum_{K} Z^{K} \int T_{\alpha\phi}(\mathbf{R}^{K}, \mathbf{r})\, [\, &\alpha^{A}{}_{\phi\beta}(\mathbf{r}, \mathbf{r}')\,(r'_{\gamma} - R^{A}{}_{\gamma})\,(r'_{\delta} - R^{A}{}_{\delta}) \\ &+ \alpha^{A}{}_{\phi\gamma}(\mathbf{r}, \mathbf{r}')\,(r'_{\beta} - R^{A}{}_{\beta})\,(r'_{\delta} - R^{A}{}_{\delta}) \\ &+ \alpha^{A}{}_{\phi\delta}(\mathbf{r}, \mathbf{r}')\,(r'_{\beta} - R^{A}{}_{\beta})\,(r'_{\gamma} - R^{A}{}_{\gamma})\,]\, d\mathbf{r}\, d\mathbf{r}' \\ = 2/3\, [\, &\Theta^{eA}{}_{\gamma\delta}\, \delta_{\alpha\beta} + \Theta^{eA}{}_{\beta\delta}\, \delta_{\alpha\gamma} + \Theta^{eA}{}_{\beta\gamma}\, \delta_{\alpha\delta}\,] \\ &+ 1/3\, q^{A}{}_{\varepsilon\varepsilon}\, (\delta_{\alpha\beta}\, \delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\, \delta_{\beta\gamma}) \,,\end{aligned} \tag{44}$$

where Θ^{eA} and q^{A} are determined with $\mathbf{R}^{A}$ as the origin. With the sum rules in Eqs. (34), (41), and (44), the net long-range force on molecule A, obtained by summation of the forces in Eq. (28) over the nuclei K, reduces to Eq. (24). This is consistent with physical expectations. In addition, the work above makes it possible to draw a *new* conclusion about the nature of the first-order induction force at long range. If the charge, dipole, and quadrupole of molecule A are split into their electronic vs. nuclear contributions, Z^{eA}, μ^{eA}, and Θ^{eA} vs. Z^{nA}, μ^{nA}, and Θ^{nA}, then the first-order induction force on molecule A can be recast as

$$
\begin{aligned}
F^{A(1)}{}_{\alpha} = & -Z^{nA}\, T_{\alpha}\, Z^{B} + Z^{nA}\, T_{\alpha\beta}\, \mu^{B}{}_{\beta} - Z^{B}\, T_{\alpha\beta}\, \mu^{nA}{}_{\beta} - 1/3\ Z^{nA}\, T_{\alpha\beta\gamma}\, \Theta^{B}{}_{\beta\gamma} \\
& + \mu^{nA}{}_{\beta}\, T_{\alpha\beta\gamma}\, \mu^{B}{}_{\gamma} - 1/3\ Z^{B}\, T_{\alpha\beta\gamma}\, \Theta^{nA}{}_{\beta\gamma} + \ldots \\
& - Z^{eA}\, T_{\alpha}\, Z^{B} + Z^{eA}\, T_{\alpha\beta}\, \mu^{B}{}_{\beta} - Z^{B}\, T_{\alpha\beta}\, \mu^{eA}{}_{\beta} - 1/3\ Z^{eA}\, T_{\alpha\beta\gamma}\, \Theta^{B}{}_{\beta\gamma} \\
& + \mu^{eA}{}_{\beta}\, T_{\alpha\beta\gamma}\, \mu^{B}{}_{\gamma} - 1/3\ Z^{B}\, T_{\alpha\beta\gamma}\, \Theta^{eA}{}_{\beta\gamma} + \ldots\ .
\end{aligned}
\tag{45}
$$

From our analysis in Eqs. (27), (28), and (34)-(44), we conclude: each of the terms in Eq. (45) that contains the nuclear charge, dipole, or quadrupole moment on A originates in the direct interactions of the nuclear charge on A with the unperturbed charge distribution of B; each of the terms that contains the *permanent electronic* charge, dipole, or quadrupole moment on A originates in the attraction of the nuclei on A to the electrons on A, *perturbed* to first order by the interaction with B.

Next, we consider the long-range limit of the second-order induction force $F^{A(2)}{}_{ind,\alpha}$. For neutral, dipolar molecules, expansion of Eqs. (21)-(23) as above and elimination of terms that contain Z^{A} or Z^{B} leaves

$$
\begin{aligned}
F^{A(2)}{}_{ind,\varepsilon} = & \sum_{K} Z^{K}/2 \int dr\, dr'\, dr''\ T_{\varepsilon\phi}(R^{K}, r'')\, \beta^{A}{}_{\phi\alpha\beta}(r'', r, r') \\
& \times [\, T_{\alpha\eta}\, T_{\beta\lambda}\, \mu^{B}{}_{\eta}\, \mu^{B}{}_{\lambda} + T_{\alpha\eta}\, T_{\beta\lambda\kappa}\, \mu^{B}{}_{\eta}\, \mu^{B}{}_{\kappa}\, (r'_{\lambda} - R^{A}{}_{\lambda}) \\
& - 1/3\, T_{\alpha\eta}\, T_{\beta\lambda\kappa}\, \mu^{B}{}_{\eta}\, \Theta^{B}{}_{\lambda\kappa} + T_{\alpha\eta\kappa}\, T_{\beta\lambda}\, \mu^{B}{}_{\eta}\, \mu^{B}{}_{\lambda}\, (r_{\kappa} - R^{A}{}_{\kappa}) \\
& - 1/3\, T_{\alpha\eta\kappa}\, T_{\beta\lambda}\, \mu^{B}{}_{\lambda}\, \Theta^{B}{}_{\eta\kappa} + \ldots\,] \\
& + \sum_{K} Z^{K} \int dr\, dr'\, dr''\, dr'''\ T_{\varepsilon\gamma}(R^{K}, r''')\, \alpha^{A}{}_{\gamma\delta}(r''', r'')\, \alpha^{B}{}_{\alpha\beta}(r, r') \\
& \times [\, T_{\delta\alpha}\, T_{\beta\eta}\, \mu^{A}{}_{\eta} - T_{\delta\alpha}\, T_{\beta\eta\kappa}\, \mu^{A}{}_{\eta}\, (r'_{\kappa} - R^{B}{}_{\kappa}) \\
& + 1/3\, T_{\delta\alpha}\, T_{\beta\lambda\kappa}\, \Theta^{A}{}_{\lambda\kappa} + T_{\delta\alpha\lambda}\, T_{\beta\eta}\, \mu^{A}{}_{\eta}\, (r''_{\lambda} - R^{A}{}_{\lambda})
\end{aligned}
$$

$$
\begin{aligned}
& - T_{\delta\alpha\lambda}\, T_{\beta\eta}\, \mu^{A}{}_{\eta}\, (r_{\lambda} - R^{B}{}_{\lambda}) + \ldots\ ] \\
+ \quad & \sum_{K} Z^{K} \int dr\, dr'\ \alpha^{B}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \times [\, T_{\varepsilon\alpha}\, T_{\beta\lambda}\, \mu^{A}{}_{\lambda} + 1/3\, T_{\varepsilon\alpha}\, T_{\beta\lambda\kappa}\, \Theta^{A}{}_{\lambda\kappa} \\
& - T_{\varepsilon\alpha}\, T_{\beta\eta\kappa}\, \mu^{A}{}_{\eta}\, (r'_{\kappa} - R^{B}{}_{\kappa}) + T_{\varepsilon\alpha\lambda}\, T_{\beta\eta}\, \mu^{A}{}_{\eta}\, (R^{K}{}_{\lambda} - R^{A}{}_{\lambda}) \\
& - T_{\varepsilon\alpha\lambda}\, T_{\beta\eta}\, \mu^{A}{}_{\eta}\, (r_{\lambda} - R^{B}{}_{\lambda}) + \ldots\ ]\ , \qquad (46)
\end{aligned}
$$

complete to order R^{-7} in the A-B separation. The R^{-6} terms in Eq. (46) and the terms containing $\Theta^{A}{}_{\lambda\kappa}$ or $\Theta^{B}{}_{\lambda\kappa}$ vanish for neutral molecules because of the sum rule in Eq. (34) and the sum rule for the β hyperpolarizability [45],

$$\sum_{K} Z^{K} \int dr\, dr'dr''\ T_{\phi\varepsilon}(\mathbf{R}^{K}, \mathbf{r}'')\, \beta^{A}{}_{\phi\delta\alpha}(\mathbf{r}'', \mathbf{r}, \mathbf{r}') = 0\,. \qquad (47)$$

With the additional sum rule contained in Eq. (41), and the results [10]

$$\alpha^{B}{}_{\alpha\beta} = \int dr\, dr'\ \alpha^{B}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\ , \qquad (48)$$

and [45]

$$
\begin{aligned}
& 1/2 \sum_{K} Z^{K} \int dr\, dr'dr''\ T_{\phi\varepsilon}(\mathbf{R}^{K}, \mathbf{r}'')\, \beta^{A}{}_{\phi\delta\alpha}(\mathbf{r}'', \mathbf{r}, \mathbf{r}')\, (r_{\eta} - R^{A}{}_{\eta}) \\
& + 1/2 \sum_{K} Z^{K} \int dr\, dr'dr''\ T_{\phi\varepsilon}(\mathbf{R}^{K}, \mathbf{r}'')\, \beta^{A}{}_{\phi\eta\alpha}(\mathbf{r}'', \mathbf{r}, \mathbf{r}')\, (r_{\delta} - R^{A}{}_{\delta}) \\
& = 1/2\, [\alpha^{A}{}_{\alpha\delta}\, \delta_{\eta\varepsilon} + \alpha^{A}{}_{\alpha\eta}\, \delta_{\delta\varepsilon}]\ , \qquad (49)
\end{aligned}
$$

Eq. (46) reduces to Eq. (25), as required.

If $F^{A(2)}{}_{ind,\alpha}$ is written as a sum of three terms, $\mathfrak{S}_1$, $\mathfrak{S}_2$, and $\mathfrak{S}_3$, where

$$\mathfrak{S}_1 = \alpha^{A}{}_{\beta\gamma}\, T_{\beta\delta}\, \mu^{B}{}_{\delta}\, T_{\alpha\gamma\varepsilon}\, \mu^{B}{}_{\varepsilon}\ , \qquad (50)$$

$$\mathfrak{S}_2 = \alpha^{B}{}_{\beta\gamma}\, T_{\beta\delta}\, \mu^{A}{}_{\delta}\, T_{\alpha\gamma\varepsilon}\, \mu^{eA}{}_{\varepsilon}\ , \qquad (51)$$

and

$$\mathfrak{S}_3 = \alpha^{B}{}_{\beta\gamma}\, T_{\beta\delta}\, \mu^{A}{}_{\delta}\, T_{\alpha\gamma\varepsilon}\, \mu^{nA}{}_{\varepsilon}\ , \qquad (52)$$

then the analysis above provides a new physical interpretation, which is distinct for each term. (It should be noted that the electronic part of the dipole $\mu^{eA}{}_{\varepsilon}$ appears in $\mathfrak{S}_2$, while the nuclear part $\mu^{nA}{}_{\varepsilon}$ appears in $\mathfrak{S}_3$; the factor $\mu^{A}{}_{\delta}$ appearing in both $\mathfrak{S}_2$ and $\mathfrak{S}_3$ is the total dipole of molecule A.) The term $\mathfrak{S}_1$ originates in the attraction of the nuclei in A to the electronic charge distribution of A, hyperpolarized by the permanent dipolar field from molecule B. The term $\mathfrak{S}_2$ also stems from the attraction of the nuclei in A to the electronic charge distribution of A, in this case perturbed by linear response to the dipole induced in B by the permanent dipole of A. Finally, the term $\mathfrak{S}_3$ reflects the direct attraction of nuclei in A to the first-order perturbed charge distribution of molecule B, $P^{B}{}_{\alpha}(\mathbf{r})^{(1)}$ in Eq. (21)

A similar analysis holds for interacting ions A and B. To obtain results complete to order R^{-6}, we use [10]

$$A^{A}{}_{\alpha,\beta\gamma} = 3/2 \int d\mathbf{r}\, d\mathbf{r}' \,[\, \alpha^{A}{}_{\alpha\gamma}(\mathbf{r},\mathbf{r}')\,(r'_{\beta} - R^{A}{}_{\beta}) + \alpha^{A}{}_{\alpha\beta}(\mathbf{r},\mathbf{r}')\,(r'_{\gamma} - R^{A}{}_{\gamma})$$
$$- 2/3\, \delta_{\beta\gamma}\, \alpha^{A}{}_{\alpha\delta}(\mathbf{r},\mathbf{r}')\,(r'_{\delta} - R^{A}{}_{\delta})\,] \;, \tag{53}$$

and two new sum rules for the β hyperpolarizability density, derived next. We use Eqs. (15), (38), (39), and (42); we also use

$$\langle g \,|\, [p_{\alpha}, \mu_{\beta}] \,|\, n \rangle = \sum_{m}{}' \,[\, \langle g \,|\, p_{\alpha} \,|\, m \rangle \langle m \,|\, \mu_{\beta} \,|\, n \rangle - \langle g \,|\, \mu_{\beta} \,|\, m \rangle \langle m \,|\, p_{\alpha} \,|\, n \rangle \,]$$
$$- \langle g \,|\, \mu_{\beta} \,|\, g \rangle \langle g \,|\, p_{\alpha} \,|\, n \rangle \;, \tag{54}$$

the analogous relation for $\langle g \,|\, [p_{\alpha}, t_{\beta\gamma\delta}] \,|\, n \rangle$, the fact that $\langle g \,|\, [p_{\alpha}, \mu_{\beta}] \,|\, n \rangle$ vanishes for any $n \neq g$, and (assuming for simplicity that the molecular states are real)

$$\langle m \,|\, p_{\alpha} \,|\, n \rangle = -\langle n \,|\, p_{\alpha} \,|\, m \rangle \;. \tag{55}$$

Together, these results yield

$$\sum_{K} Z^{K} \int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\; T_{\varepsilon\phi}(\mathbf{R}^{K}, \mathbf{r}'')\, \beta^{A}{}_{\phi\alpha\beta}(\mathbf{r}'', \mathbf{r}, \mathbf{r}')\; T_{\alpha}\, T_{\beta\lambda\kappa}\, (r'_{\lambda} - R^{A}{}_{\lambda})\,(r'_{\kappa} - R^{A}{}_{\kappa})$$
$$= i/(3\hbar^{2})\, T_{\alpha}\, T_{\beta\lambda\kappa} \sum_{n}{}' \,[\, \langle g \,|\, [p_{\varepsilon}, t_{\beta\lambda\kappa}] \,|\, n \rangle \langle n \,|\, \mu_{\alpha} \,|\, g \rangle$$
$$+ \langle g \,|\, \mu_{\alpha} \,|\, n \rangle \langle n \,|\, [p_{\varepsilon}, t_{\beta\lambda\kappa}] \,|\, g \rangle \,] / \omega_{ng} \;. \tag{56}$$

From the analogue of Eq. (43) for transition matrix elements of the commutator $[p_{\varepsilon}, t_{\beta\lambda\kappa}]$, and the sum-over-states expression for $A_{\alpha,\beta\gamma}$ [60],

$$A_{\alpha,\beta\gamma} = \sum_{n}{}' \left[\langle g \,|\, \Theta_{\beta\gamma} \,|\, n \rangle \langle n \,|\, \mu_{\alpha} \,|\, g \rangle + \langle g \,|\, \mu_{\alpha} \,|\, n \rangle \langle n \,|\, \Theta_{\beta\gamma} \,|\, g \rangle \right] / \hbar\omega_{ng} , \tag{57}$$

we obtain

$$\begin{aligned} &\sum_{K} Z^{K} \int dr\, dr' dr''\ T_{\varepsilon\phi}(R^{K}, r'')\, \beta^{A}{}_{\phi\alpha\beta}(r'', r, r')\ T_{\alpha}\, T_{\beta\lambda\kappa}\, (r'_{\lambda} - R^{A}{}_{\lambda})\, (r'_{\kappa} - R^{A}{}_{\kappa}) \\ &\quad = 2/3\, T_{\alpha}\, T_{\beta\gamma\varepsilon}\, A^{A}{}_{\alpha,\beta\gamma} . \end{aligned} \tag{58}$$

The final sum rule is obtained similarly, using transition matrix elements of $[p_{\alpha}, q_{\beta\gamma}]$ in place of $[p_{\alpha}, t_{\beta\gamma\delta}]$, and using Eq. (40) for $q_{\beta\gamma}$; it is

$$\begin{aligned} &\sum_{K} Z^{K} \int dr\, dr' dr''\ T_{\varepsilon\phi}(R^{K}, r'')\, \beta^{A}{}_{\phi\alpha\beta}(r'', r, r')\ T_{\alpha\eta}\, T_{\beta\lambda}\, (r_{\eta} - R^{A}{}_{\eta})\, (r'_{\lambda} - R^{A}{}_{\lambda}) \\ &\quad = 2/3\, T_{\alpha\varepsilon}\, T_{\beta\gamma}\, A^{A}{}_{\alpha,\beta\gamma} . \end{aligned} \tag{59}$$

With Eqs. (47)-(49), (53), (58), and (59), for interacting ions A and B, we finally obtain the net long-range force $F^{A(2)}{}_{\mathrm{ind},\alpha}$ on A as a sum of terms $\mathfrak{I}'_{1}$, $\mathfrak{I}'_{2}$, and $\mathfrak{I}'_{3}$, where

$$\begin{aligned} \mathfrak{I}'_{1} = {} & \alpha^{A}{}_{\beta\gamma}\, T_{\beta}\ Z^{B}\, T_{\alpha\gamma}\, Z^{B} - \alpha^{A}{}_{\beta\gamma} (T_{\beta}\, T_{\alpha\gamma\delta} + T_{\alpha\beta}\, T_{\gamma\delta})\, Z^{B} \mu^{B}{}_{\delta} \\ & + 1/3\, A^{A}{}_{\beta,\gamma\delta} (T_{\beta}\, T_{\alpha\gamma\delta} + T_{\alpha\beta}\, T_{\gamma\delta})\, Z^{B} Z^{B} + \ldots , \end{aligned} \tag{60}$$

$$\begin{aligned} \mathfrak{I}'_{2} = {} & \alpha^{B}{}_{\beta\gamma}\, T_{\beta}\ Z^{A}\, T_{\alpha\gamma}\, Z^{eA} - 1/3\, A^{B}{}_{\beta,\gamma\delta} (T_{\beta}\, T_{\alpha\gamma\delta} + T_{\alpha\beta}\, T_{\gamma\delta})\, Z^{A} Z^{eA} \\ & + \alpha^{B}{}_{\beta\gamma}\, T_{\beta}\, T_{\alpha\gamma\delta}\, Z^{A} \mu^{eA}{}_{\delta} + \alpha^{B}{}_{\beta\gamma}\, T_{\alpha\beta}\, T_{\gamma\delta}\, \mu^{A}{}_{\delta}\, Z^{eA} + \ldots , \end{aligned} \tag{61}$$

and

$$\begin{aligned} \mathfrak{I}'_{3} = {} & \alpha^{B}{}_{\beta\gamma}\, T_{\beta}\ Z^{A}\, T_{\alpha\gamma}\, Z^{nA} - 1/3\, A^{B}{}_{\beta,\gamma\delta} (T_{\beta}\, T_{\alpha\gamma\delta} + T_{\alpha\beta}\, T_{\gamma\delta})\, Z^{A} Z^{nA} \\ & + \alpha^{B}{}_{\beta\gamma}\, T_{\beta}\, T_{\alpha\gamma\delta}\, Z^{A} \mu^{nA}{}_{\delta} + \alpha^{B}{}_{\beta\gamma}\, T_{\alpha\beta}\, T_{\gamma\delta}\, \mu^{A}{}_{\delta}\, Z^{nA} + \ldots . \end{aligned} \tag{62}$$

$\mathfrak{I}'_{1}$, $\mathfrak{I}'_{2}$, and $\mathfrak{I}'_{3}$ add to give $F^{A(2)}{}_{\mathrm{ind},\alpha}$ in Eq. (26), as required. As a significant new result from our analysis, we can explain the physical origin of each of the terms $\mathfrak{I}'_{1}$, $\mathfrak{I}'_{2}$, and $\mathfrak{I}'_{3}$ separately. The interpretation is analogous to that for the net forces on interacting neutral molecules. Terms in $\mathfrak{I}'_{1}$ contain *linear response* tensors of molecule A; they originate in the attraction of nuclei in A to the perturbed electronic charge distribution of A, *hyperpolarized* by interaction with the permanent moments of B. This interpretation reflects the deep connection between linear and nonlinear response; Eq. (16) gives one example. Terms in $\mathfrak{I}'_2$ contain the reaction field effects on the electronic charge and moments of A; these all originate in the attraction of nuclei in A to the perturbed electronic charge distribution on the same molecule--but in this case, the perturbation is produced by the field and field gradients due to the polarization induced in B, rather than the permanent polarization of B. Just as the interpretation of the first term relied on the connection between linear and nonlinear response [3, 4], the interpretation of $\mathfrak{I}'_2$ uses a similar connection between permanent moments and linear response tensors [3]. Finally, terms in $\mathfrak{I}'_3$ contain the reaction field effects on the nuclear charge distribution in A. These originate in the direct attraction of nuclei in A to the perturbed charge distribution of B.

4.4 Discussion and Summary

In this chapter, we have unified the seemingly disparate physical interpretations of Hellmann-Feynman forces on nuclei in interacting molecules vs. the forces obtained directly from interaction energies. Our results at first order are derived in Eqs. (4)-(12) of Sec. 4.2. They follow from two key relations: the connection between susceptibility densities and the derivatives of the permanent charge density with respect to nuclear coordinates [3], and the Born symmetry of the nonlocal polarizability density [10]. At second order, the results follow from the connection between linear and nonlinear response tensors contained in Eq. (16) [3, 4], the connection between permanent moments and linear response tensors [3], and the permutation symmetry of the hyperpolarizability density, Eq. (17). This is proven in Eqs. (13)-(23) of Sec. 4.2.

In Sec. 4.3, we have derived the lowest-order force on a nucleus in molecule A in terms of shielding tensors [3, 28-44] and the field and field gradients at the nucleus due to molecule B. In this section we have also derived new sum rules applicable to the polarizability and hyperpolarizability densities. Each of the new sum rules involves the dipole propagator from a point in the electronic charge distribution to the nuclear position $\mathbf{R}^K$, multiplied by the charge on nucleus K, and summed over nuclei. Our sum rules on the polarizability density $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$, Eqs. (41) and (44), have been derived from ground-state expectation values of the commutator of $\mathbf{p}$ with the second and third charge-moment operators $q_{\beta\gamma}$ and $t_{\beta\gamma\delta}$. It should be noted that the commutator of $\mathbf{p}$ with the charge moment of order n depends on the moment of order (n-1). The momentum operator $\mathbf{p}$ is the generator of infinitesimal translations, and the origin-dependence of the charge moment of order n is determined by all lower-order moments. New sum rules applicable to the hyperpolarizability density $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, Eqs. (58) and (59), have been derived starting from *transition* matrix elements of the commutators of $\mathbf{p}$ with charge moments. In general, the sum rules connect integrals of $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ and the dipole propagator with permanent charge moments, while they connect integrals of $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ and the dipole propagator to linear response tensors.

With the sum rules, we have obtained the long-range limiting results for the forces on molecule A at first and second order in the interaction. This analysis provides new information about contributions to the long-range force: If we split the charge, dipole, quadrupole, and higher moments on molecule A into their electronic and nuclear parts, then the first-order interaction-induced force $F^{A(1)}{}_{\alpha}$ can be separated into two sets of terms, one dependent on the nuclear moments of A and the other on the electronic moments of A, as in Eq. (45). All of the terms in $F^{A(1)}{}_{\alpha}$ that contain nuclear moments stem from the direct interactions between the nuclei in molecule A and the unperturbed charge distribution of molecule B, while all of the terms in $F^{A(1)}{}_{\alpha}$ that contain electronic moments originate in the interaction between the nuclei in A and the electronic charge distribution of A itself, polarized by B. It is important to note that the terms in the second set depend upon the permanent (unperturbed) electronic moments of A--yet they represent effects due to the polarization of A by B, as determined by linear response tensors of A. Our interpretation is pos sible because of the sum rules derived for $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$.

We have also obtained new information about the origin of contributions to the second-order force $\Delta F^{A}{}_{\varepsilon}{}^{(2)}{}_{ind}$ on the entire molecule A at long range. Each of the terms that contains a linear response tensor on molecule A stems from the attraction of nuclei in A to the component of the electronic charge distribution in A that has been hyperpolarized by fields from the permanent charge distribution of B. A second set of terms in $\Delta F^{A}{}_{\varepsilon}{}^{(2)}{}_{ind}$ represents the interactions of the reaction field at A with the electronic moments of A. These terms result from the attraction of nuclei in A to the electronic charge density of A, perturbed linearly, at second order by molecule B. The final set of terms in $\Delta F^{A}{}_{\varepsilon}{}^{(2)}{}_{ind}$ represents the interactions of the reaction field at A with the nuclear moments of A; and this set stems from the direct interaction between nuclei in A and the first-order polarized charge distribution of B.

For the specific case of two neutral, dipolar molecules A and B, the lowest-order, interaction-induced forces on individual nuclei vary as R^{-3} at long range, as shown by expansion of Eq. (27). The lowest-order force on the entire A molecule varies as R^{-4}, however, due to the sum rule in Eq. (34). This is not a simple charge cancellation effect, because the force on the entire A molecule is obtained by summing over the nuclei only; the net force on the electrons vanishes in the (perturbed) ground state. At second order force on nuclei in A stems from their attraction to the second-order perturbed charge distribution of A--yet this force varies as R^{-7}, rather than R^{-6} because of the sum rules in Eqs. (34) and (47).

The results obtained here hold the potential for computational applications, in analyzing intramolecular contributions to the net forces on nuclei in interacting molecules, and in analyzing collision-induced vibrational transitions. The polarizability density $\alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ can be computed with pseudo-state techniques [24], or via connections we have found [9] to auxiliary functions used in computing overlap-damped dispersion energies [21-25]. Related methods of computing the hyperpolarizability density $\beta_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, density-functional methods, direct perturbative approaches, and analytic differentiation techniques [64] are under investigation for computational tractability. At present, the new results from this work are important principally for the physical interpretation they offer for the forces on nuclei in interacting molecules.

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CHAPTER V

ELECTRIC FIELD SHIELDING EFFECTS IN INTERACTING MOLECULES

5.1 Chemical Shift and Electric Field Shielding at Nuclei

In nuclear magnetic resonance (NMR), the local magnetic field at a nucleus in a molecule is not exactly the applied one, rather

$$B^{loc}_{\alpha} = (\delta_{\alpha\beta} - \sigma_{\alpha\beta})\, B^{ext}_{\beta}\,, \tag{1}$$

where B^{ext} is the applied field, σ is called the shielding tensor or chemical shift. This is because the applied field induces a current in the electrons of the molecule, which produce an extra contribution in addition to the applied field [1].

Similarly when a molecule is placed in an applied electric field, according to Fowler and Buckingham [2], the local field acting on nucleus I satisfies:

$$\begin{aligned} F^{I}_{\alpha} = {} & F^{(0)}_{\alpha} + (\delta_{\alpha\beta} - \gamma^{I}_{\alpha\beta})\, F_{\beta} + 1/2\, \phi^{I}_{\alpha\beta\gamma} F_{\beta}\, F_{\gamma} + 1/6\, \eta^{I}_{\alpha\beta\gamma\delta} F_{\beta}\, F_{\gamma} F_{\delta} \\ & +1/3\, (3/2\, R^{I}_{\beta}\, \delta_{\alpha\gamma} + 3/2\, R^{I}_{\gamma}\, \delta_{\alpha\beta} - R^{I}_{\alpha} \delta_{\beta\gamma} + \nu^{I}_{\alpha\beta\gamma})\, F_{\beta\gamma} \\ & +1/3 \zeta^{I}_{\alpha\beta\gamma\delta} F_{\beta}\, F_{\gamma\delta} + \dots\,, \end{aligned} \tag{2}$$

where $\gamma^{I}, \phi^{I}, \eta^{I}, \nu^{I}, \zeta^{I}, \dots$ are response tensors, F_{β} is the β component of the applied field at the molecular origin, and $F_{\beta\gamma}$ is the field gradient at the molecular origin, while $F^{(0)}_{\alpha}$ represents the electric field at nucleus I in the absence of external fields. Usually γ^{I} is called the dipole electric shielding tensor and ϕ^{I} the quadratic dipole shielding tensor. This is because the applied electric field distorts the electron cloud around the nuclei in the molecule, which produces an extra contribution in addition to the applied field.

5.2 Relationships Between Electric Field Shielding Tensors, Dipole Derivatives, Polarizability Derivatives and Nonlocal Polarizability Densities

The relationship

$$\partial\mu_\beta/\partial R^I{}_\alpha = Z^I\,(\delta_{\alpha\beta} - \gamma^I{}_{\alpha\beta}) \qquad (3)$$

between the electric field shielding tensor $\gamma^I{}_{\alpha\beta}$, and the derivative of the dipole with respect to the coordinate of nucleus I, $\partial\mu_\beta/\partial R^I{}_\alpha$, was established by Sambe [3], Epstein [4], Lazzeretti and Zanasi [5,6], and Wolinski, *et al* [7]. Fowler and Buckingham [2] generalized the theory to treat molecules in nonuniform fields and to allow for nonlinear response to the applied field. The generalization provides a new relation between Raman (and hyper-Raman) intensities and higher order shielding tensors; e.g. :

$$\partial\alpha_{\beta\gamma}/\partial R^I{}_\alpha = Z^I\phi^I{}_{\alpha\beta\gamma} \qquad (4)$$

There are also relationships between derivatives of the quadrupole moment and quadrupole polarizabilities and the shielding tensors for molecules in a uniform field gradient [2, 8-11].

By use of nonlocal polarizability densities to analyze electronic charge redistribution in a molecule, Hunt [12] finds new expressions for $\gamma^I{}_{\alpha\beta}$ and $\phi^I{}_{\alpha\beta\gamma}$ in terms of nonlocal polarizability densities:

$$\gamma^I{}_{\alpha\beta} = -\int dr\, dr'\, T_{\alpha\gamma}(\mathbf{R}^I, \mathbf{r})\, \alpha^A{}_{\beta\gamma}(\mathbf{r}', \mathbf{r}) = (\delta_{\alpha\beta} - \partial\mu_\beta/\partial R^I{}_\alpha)\,/\,Z^I$$

or

$$\begin{aligned}\partial\mu_\beta/\partial R^I{}_\alpha &= Z^I\,(\delta_{\alpha\beta} - \gamma^I{}_{\alpha\beta}) \\ &= Z^I\,[\delta_{\alpha\beta} + \int dr\, dr'\, T_{\alpha\gamma}(\mathbf{R}^I, \mathbf{r})\, \alpha^A{}_{\beta\gamma}(\mathbf{r}', \mathbf{r})] \qquad (5)\end{aligned}$$

$$\phi^I{}_{\alpha\beta\gamma} = \int dr\, dr' dr''\, T_{\alpha\delta}(\mathbf{R}^I, \mathbf{r})\, \beta_{\delta\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \partial\alpha_{\beta\gamma}/\partial R^I{}_\alpha\,/\,Z^I$$

or

$$\partial\alpha_{\beta\gamma}/\partial R^I{}_\alpha = Z^I \int dr\, dr' dr''\, T_{\alpha\delta}(\mathbf{R}^I, \mathbf{r})\, \beta_{\delta\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \qquad (6)$$

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

$$T_{\alpha\beta}(\mathbf{r},\mathbf{r}') = T_{\alpha\beta}(\mathbf{r}-\mathbf{r}') = \nabla_\alpha\nabla_\beta(|\mathbf{r}-\mathbf{r}'|^{-1}) \tag{7}$$

$\alpha_{\beta\gamma}(\mathbf{r}', \mathbf{r})$ is the nonlocal polarizability density and $\beta_{\delta\beta\gamma}(\mathbf{r}'', \mathbf{r}', \mathbf{r})$ is nonlocal hyperpolarizability density. In all equations, the Einstein convention of summation over repeated Greek indices is employed.

Equation 5 gives an important new physical insight into the change in the molecular dipole moment that results from an infinitesimal shift in nuclear position. The electronic charge distribution responds to the change in field via the same nonlocal polarizability density $\alpha(\mathbf{r}, \mathbf{r}')$ that determines its reaction to an external field; and this response changes the electronic component of the molecular dipole.

Equation 6 explains the connection between $\phi^I{}_{\alpha\beta\gamma}$ and $\partial\alpha_{\beta\gamma}/\partial R^I{}_\alpha$: the effective polarizability of an electronic charge distribution in a perturbing field can be expanded as a series in the field, with a leading correction term that depends linearly on the perturbing field and the nonlocal hyperpolarizability density $\beta(\mathbf{r}'', \mathbf{r}', \mathbf{r})$.

These relationships give the possibility not only to find new results for the forces acting on nuclei, but also to find the electrical shielding effects in interacting molecules.

5.3 Electric Field Shielding Effects in Interacting Molecules

New analytical results for forces on nuclei in interacting molecules have been given in terms of nonlocal polarizability densities, in Chapter IV.

To first order in the A-B interaction, the induced force $\Delta F^{K}{}_{\alpha}{}^{(1)}$ on nucleus K in molecule A satisfies

$$\begin{aligned} \Delta F^{K}{}_{\alpha}{}^{(1)} &= -Z^{K} \int T_{\alpha}(\mathbf{R}^{K} - \mathbf{r}')\, \rho^{B}{}_{0}(\mathbf{r}')\, d\mathbf{r}' \\ &\quad - Z^{K} \int T_{\alpha\beta}(\mathbf{R}^{K} - \mathbf{r}'')\, \alpha^{A}{}_{\beta\gamma}(\mathbf{r}'', \mathbf{r})\, T_{\gamma}(\mathbf{r} - \mathbf{r}')\rho^{B}{}_{0}(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' \qquad (8) \end{aligned}$$

where Z^{K} and $\mathbf{R}^{K}$ are the charge and position of nucleus K, respectively, $T, T_{\alpha}, T_{\alpha\beta}, \ldots$ are propagator tensors, $\alpha^{A}(\mathbf{r}'', \mathbf{r})$ is the nonlocal polarizability density of molecule A, and $\rho^{B}{}_{0}$ is the unperturbed charge density of molecule B.

The second order induced force $\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{\text{ind}}$ on nucleus K is:

$$\begin{aligned} \Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{\text{ind}} &= 1/2 \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}''\; Z^{K} T_{\varepsilon\gamma}(\mathbf{R}^{K}, \mathbf{r}'')\, \beta^{A}{}_{\gamma\alpha\beta}(\mathbf{r}'', \mathbf{r}, \mathbf{r}')\; \mathcal{F}^{B}{}_{0\alpha}(\mathbf{r})\, \mathcal{F}^{B}{}_{0\beta}(\mathbf{r}') \\ &\quad + \int d\mathbf{r}\, d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}'''\; Z^{K}\, T_{\varepsilon\gamma}(\mathbf{R}^{K}, \mathbf{r}''')\, \alpha^{A}{}_{\gamma\delta}(\mathbf{r}''', \mathbf{r}'') \\ &\quad \times T_{\delta\alpha}(\mathbf{r}'', \mathbf{r})\, \alpha^{B}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathcal{F}^{A}{}_{0\beta}(\mathbf{r}') \\ &\quad + \int d\mathbf{r}\, d\mathbf{r}'\; Z^{K}\, T_{\varepsilon\alpha}(\mathbf{R}^{K}, \mathbf{r})\, \alpha^{B}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathcal{F}^{A}{}_{0\beta}(\mathbf{r}') . \qquad (9) \end{aligned}$$

where $\beta^{A}{}_{\gamma\alpha\beta}(\mathbf{r}'', \mathbf{r}, \mathbf{r}')$ is the nonlocal hyperpolarizability density, $\mathcal{F}^{A}{}_{0}$ is the field in molecule B produced by the unperturbed charge distribution of molecule A, and $\mathcal{F}^{B}{}_{0}$ is obtained by exchanging A, B in the above statement.

By taking the long-range limit of $\Delta F^{K}{}_{\alpha}{}^{(1)}$ and $\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{\text{ind}}$, we prove that intermolecular fields are screened via the same shielding tensors introduced in Sec. 5.1.

To find the long-range limit, it is convenient first to expand $\mathbf{r}'$ in T_α and T_γ about the origin $\mathbf{R}^B$ in molecule B. This yields

$$
\begin{aligned}
\Delta F^{K}{}_{\alpha}{}^{(1)} = & - Z^K\, T_\alpha(\mathbf{R}^K - \mathbf{R}^B)\, Z^B + Z^K\, T_{\alpha\beta}(\mathbf{R}^K - \mathbf{R}^B)\, \mu^B{}_\beta \\
& - 1/3\; Z^K\, T_{\alpha\beta\gamma}(\mathbf{R}^K - \mathbf{R}^B)\, \Theta^B{}_{\beta\gamma} + \ldots \\
& - Z^K \int T_{\alpha\beta}(\mathbf{R}^K - \mathbf{r}'')\, \alpha^A{}_{\beta\gamma}(\mathbf{r}'', \mathbf{r})\, T_\gamma(\mathbf{r} - \mathbf{R}^B)\, Z^B \; d\mathbf{r}\, d\mathbf{r}'' \\
& + Z^K \int T_{\alpha\beta}(\mathbf{R}^K - \mathbf{r}'')\, \alpha^A{}_{\beta\gamma}(\mathbf{r}'', \mathbf{r})\, T_{\gamma\delta}(\mathbf{r} - \mathbf{R}^B)\, \mu^B{}_\delta \; d\mathbf{r}\, d\mathbf{r}'' \\
& - 1/3\; Z^K \int T_{\alpha\beta}(\mathbf{R}^K - \mathbf{r}'')\, \alpha^A{}_{\beta\gamma}(\mathbf{r}'', \mathbf{r})\, T_{\gamma\delta\epsilon}(\mathbf{r} - \mathbf{R}^B)\, \Theta^B{}_{\delta\epsilon} \; d\mathbf{r}\, d\mathbf{r}'' + \ldots ,
\end{aligned}
\tag{10}
$$

where $Z^B = \int \rho^B{}_0(\mathbf{r}')\, d\mathbf{r}'$ ($Z^B = 0$, for neutral molecules) (11)

$$\mu^B{}_\beta = \int \rho^B{}_0(\mathbf{r}')\, (\mathbf{r}' - \mathbf{R}^B)_\beta\, d\mathbf{r}' , \tag{12}$$

and

$$\Theta^B{}_{\beta\gamma} = 1/2 \int \rho^B{}_0(\mathbf{r}')\, [3\, (\mathbf{r}' - \mathbf{R}^B)_\beta\, (\mathbf{r}' - \mathbf{R}^B)_\gamma - |\, \mathbf{r}' - \mathbf{R}^B\, |^2 \delta_{\beta\gamma}]\, d\mathbf{r}' . \tag{13}$$

Then by expanding $\mathbf{r}$ in the T tensors about $\mathbf{R}^K$, one obtains:

$$
\begin{aligned}
\Delta F^{K}{}_{\alpha}{}^{(1)} = & - Z^K (\delta_{\alpha\beta} - \gamma^K{}_{\alpha\beta})\, [T_\beta(\mathbf{R}^K - \mathbf{R}^B)\, Z^B - T_{\beta\gamma}(\mathbf{R}^K - \mathbf{R}^B)\, \mu^B{}_\gamma \\
& \quad + 1/3\, T_{\beta\gamma\delta}(\mathbf{R}^K - \mathbf{R}^B)\, \Theta^B{}_{\gamma\delta} + \ldots] \\
& - Z^K \lambda^K{}_{\alpha\beta\gamma}\, [\, T_{\beta\gamma}(\mathbf{R}^K - \mathbf{R}^B)\, Z^B - T_{\beta\gamma\delta}(\mathbf{R}^K - \mathbf{R}^B)\, \mu^B{}_\delta + \ldots] \\
& - Z^K \kappa^K{}_{\alpha\beta\gamma\delta}\, [\, T_{\beta\gamma\delta}(\mathbf{R}^K - \mathbf{R}^B)\, Z^B + \ldots] \\
= & \;\; Z^K (\delta_{\alpha\beta} - \gamma^K{}_{\alpha\beta})\, \mathcal{F}^B{}_{0\beta}(\mathbf{R}^K) \\
& + Z^K \lambda^K{}_{\alpha\beta\gamma}\, \mathcal{F}^B{}_{0}{}'{}_{\beta\gamma}(\mathbf{R}^K) \\
& + Z^K \kappa^K{}_{\alpha\beta\gamma\delta}\, \mathcal{F}^B{}_{0}{}''{}_{\beta\gamma\delta}(\mathbf{R}^K) + \ldots .
\end{aligned}
\tag{14}
$$

where $$\gamma^{K}_{\alpha\beta} = - \int T_{\alpha\gamma}(\mathbf{R}^{K} - \mathbf{r})\, \alpha^{A}_{\gamma\beta}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \; [4] \tag{15}$$

$$\lambda^{K}_{\alpha\beta\gamma} = \int T_{\alpha\delta}(\mathbf{R}^{K} - \mathbf{r})\, \alpha^{A}_{\delta\beta}(\mathbf{r}, \mathbf{r}')\, (\mathbf{r}' - \mathbf{R}^{K})_{\gamma}\, d\mathbf{r}\, d\mathbf{r}' \; [13] \tag{16}$$

$$\kappa^{K}_{\alpha\beta\gamma\delta} = 1/2 \int T_{\alpha\varepsilon}(\mathbf{R}^{K} - \mathbf{r})\, \alpha^{A}_{\varepsilon\beta}(\mathbf{r}, \mathbf{r}')\, (\mathbf{r}' - \mathbf{R}^{K})_{\gamma}\, (\mathbf{r}' - \mathbf{R}^{K})_{\delta}\, d\mathbf{r}\, d\mathbf{r}', \tag{17}$$

$$\mathcal{F}^{B}_{0\beta}(\mathbf{R}^{K}) = - T_{\beta}(\mathbf{R}^{K} - \mathbf{R}^{B})\, Z^{B} + T_{\beta\gamma}(\mathbf{R}^{K} - \mathbf{R}^{B})\, \mu^{B}_{\gamma} - 1/3\, T_{\beta\gamma\delta}(\mathbf{R}^{K} - \mathbf{R}^{B})\, \Theta^{B}_{\gamma\delta} + \ldots \tag{18}$$

$$\mathcal{F}^{B}{}_{0}{}'_{\beta\gamma}(\mathbf{R}^{K}) = - T_{\beta\gamma}(\mathbf{R}^{K} - \mathbf{R}^{B})\, Z^{B} + T_{\beta\gamma\delta}(\mathbf{R}^{K} - \mathbf{R}^{B})\, \mu^{B}_{\delta} - \ldots \tag{19}$$

and

$$\mathcal{F}^{B}{}_{0}{}''_{\beta\gamma\delta}(\mathbf{R}^{K}) = - T_{\beta\gamma\delta}(\mathbf{R}^{K} - \mathbf{R}^{B})\, Z^{B} + \ldots \tag{20}$$

The first order induced force $\Delta F^{K}_{\alpha}{}^{(1)}$ on nucleus K in molecule A at long range all comes from the screened field due to the unperturbed charge distribution of molecule B (the net charge Z^B, permanent dipole μ^B, quadrupole Θ^B, ...). Due to the electronic charge redistribution in molecule A, however, the effective field acting on nucleus K in A is not the total field of $\mathcal{F}^{B}_{0}$; instead, it is $(1 - \gamma^{K}).\mathcal{F}^{B}_{0}$ for the linear response to $\mathcal{F}^{B}_{0}$. It is $\lambda^{K}\vdots\,\mathcal{F}^{B}_{0}{}'$ for the linear response to the gradient of $\mathcal{F}^{B}_{0}$, $\kappa^{K}::\mathcal{F}^{B}_{0}{}''$ for the linear response to the gradient of the gradient of $\mathcal{F}^{B}_{0}$. That is, the tensors λ^{K} [13] and κ^{K} reflect the modifications of the shielding, due to the nonuniformity of the field at $\mathbf{R}^{K}$.

Similarly, for the second order force $\Delta F^{K}_{\varepsilon}{}^{(2)}_{\text{ind}}$, we expand $\mathbf{r}$ and $\mathbf{r}'$ in molecule A about the nuclear position of $\mathbf{R}^{K}$:

$$\mathcal{F}^{B}_{0\alpha}(\mathbf{r}) = \mathcal{F}^{B}_{\alpha}(\mathbf{R}^{K}) + (\mathbf{r}-\mathbf{R}^{K})_{\delta}\, \mathcal{F}^{B\prime}_{\alpha\delta}(\mathbf{R}^{K}) + 1/2\, (\mathbf{r}-\mathbf{R}^{K})_{\gamma}(\mathbf{r}-\mathbf{R}^{K})_{\delta}\, \mathcal{F}^{B\prime\prime}_{\alpha\gamma\delta}(\mathbf{R}^{K}) + \ldots \tag{21}$$

$$\mathcal{F}^{B}_{0\beta}(\mathbf{r}') = \mathcal{F}^{B}_{\beta}(\mathbf{R}^{K}) + (\mathbf{r}'-\mathbf{R}^{K})_{\delta}\, \mathcal{F}^{B\prime}_{\beta\delta}(\mathbf{R}^{K}) + 1/2\, (\mathbf{r}'-\mathbf{R}^{K})_{\gamma}(\mathbf{r}'-\mathbf{R}^{K})_{\delta}\, \mathcal{F}^{B\prime\prime}_{\beta\gamma\delta}(\mathbf{R}^{K}) + \ldots \tag{22}$$

and we define:

$$\mathcal{F}^{B}{}_{\delta}{}^{rea}(r'') = \int dr\, dr'\, T_{\delta\alpha}(r'', r)\, \alpha^{B}{}_{\alpha\beta}(r, r')\, \mathcal{F}^{A}{}_{0\beta}(r'). \tag{23}$$

Eq. 23 gives the reaction field from molecule B, due to its response to the field $\mathcal{F}^{A}{}_{0\beta}(r')$.

Then the first term in Eq. 9 becomes:

$$\begin{aligned}
&1/2 \int dr\, dr'dr''\ Z^K T_{\varepsilon\gamma}(R^K, r'')\, \beta^{A}{}_{\gamma\alpha\beta}(r'', r, r')\, \mathcal{F}^{B}{}_{0\alpha}(r)\, \mathcal{F}^{B}{}_{0\beta}(r') \\
&= 1/2 \int dr\, dr'dr''\ Z^K T_{\varepsilon\gamma}(R^K, r'')\, \beta^{A}{}_{\gamma\alpha\beta}(r'', r, r')\, \mathcal{F}^{B}{}_{\alpha}(R^K)\, \mathcal{F}^{B}{}_{\beta}(R^K) \\
&+ \int dr\, dr'dr''\ Z^K T_{\varepsilon\gamma}(R^K, r'')\, \beta^{A}{}_{\gamma\alpha\beta}(r'', r, r')\, (r-R^K)_{\delta}\, \mathcal{F}^{B}{}_{\alpha}(R^K)\, \mathcal{F}^{B'}{}_{\beta\delta}(R^K) \\
&+ \ldots, \\
&= 1/2\, Z^K \phi^K{}_{\varepsilon\alpha\beta}\ \mathcal{F}^{B}{}_{\alpha}(R^K)\, \mathcal{F}^{B}{}_{\beta}(R^K) \\
&+ 1/3\, Z^K \zeta^K{}_{\varepsilon\alpha\beta\delta}\, \mathcal{F}^{B}{}_{\alpha}(R^K)\, \mathcal{F}^{B'}{}_{\beta\delta}(R^K) \\
&+ \ldots,
\end{aligned} \tag{24}$$

where ϕ^K is the quadratic dipole shielding tensor defined in Eq. 6 and

$\zeta^K{}_{\varepsilon\alpha\beta\delta} = 3 \int dr\, dr'dr'' T_{\varepsilon\gamma}(R^K, r'')\, \beta^{A}{}_{\gamma\alpha\beta}(r'', r, r')\, (r-R^K)_{\delta}$, ζ^K is also a response tensor.

The second term in Eq. 9 becomes:

$$\begin{aligned}
&\int dr\, dr'dr''dr'''\ Z^K T_{\varepsilon\gamma}(R^K, r''')\, \alpha^{A}{}_{\gamma\delta}(r''', r'')\, T_{\delta\alpha}(r'', r)\, \alpha^{B}{}_{\alpha\beta}(r, r')\, \mathcal{F}^{A}{}_{0\beta}(r') \\
&= \int dr''dr'''\ Z^K T_{\varepsilon\gamma}(R^K, r''')\, \alpha^{A}{}_{\gamma\delta}(r''', r'')\, \mathcal{F}^{B}{}_{\delta}{}^{rea}(r'') \\
&= - Z^K [\, \gamma^K{}_{\varepsilon\delta}\, \mathcal{F}^{B}{}_{\delta}{}^{rea}(R^K) - \lambda^K{}_{\varepsilon\beta\delta}\, \mathcal{F}^{B'}{}_{\beta\delta}{}^{rea}(R^K) - \kappa^K{}_{\varepsilon\alpha\beta\delta} \mathcal{F}^{B''}{}_{\alpha\beta\delta}{}^{rea}(R^K) - \ldots\,]
\end{aligned} \tag{25}$$

where γ^K, λ^K, κ^K are the same as defined in Eq. 15, 16, 17 respectively.

The third term in Eq. 9 is:

$$\begin{aligned}
&\int dr\, dr'\ Z^K T_{\varepsilon\alpha}(R^K, r)\, \alpha^{B}{}_{\alpha\beta}(r, r')\, \mathcal{F}^{A}{}_{0\beta}(r') \\
&= Z^K\, \mathcal{F}^{B}{}_{\varepsilon}{}^{rea}(R^K)
\end{aligned} \tag{26}$$

Combining Eq. 24, 25, 26,

$$
\begin{aligned}
&\Delta F^{K}{}_{\varepsilon}{}^{(2)}{}_{\mathrm{ind}} \\
&= + Z^{K}\,[(\delta_{\alpha\beta} - \gamma^{K}{}_{\varepsilon\delta})\, \mathcal{F}^{B}{}_{\delta}{}^{\mathrm{rea}}(\mathbf{R}^{K}) + \lambda^{K}{}_{\varepsilon\beta\delta}\, \mathcal{F}^{B\prime}{}_{\beta\delta}{}^{\mathrm{rea}}(\mathbf{R}^{K}) + \kappa^{K}{}_{\varepsilon\alpha\beta\delta}\mathcal{F}^{B\prime\prime}{}_{\alpha\beta\delta}{}^{\mathrm{rea}}(\mathbf{R}^{K}) + \ldots\,] \\
&\quad +1/2\, Z^{K}\, \phi^{K}{}_{\varepsilon\alpha\beta}\ \mathcal{F}^{B}{}_{\alpha}(\mathbf{R}^{K})\, \mathcal{F}^{B}{}_{\beta}(\mathbf{R}^{K}) \\
&\quad + 1/3\, Z^{K}\, \zeta^{K}{}_{\varepsilon\alpha\beta\delta}\, \mathcal{F}^{B}{}_{\alpha}(\mathbf{R}^{K})\, \mathcal{F}^{B\prime}{}_{\beta\delta}(\mathbf{R}^{K}) \\
&\quad + \ldots\,, \qquad (27)
\end{aligned}
$$

Equation 27 shows how the field due to neighboring molecules and the reaction field are screened at second order in the molecular interaction.

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CHAPTER VI

QUANTUM THEORY OF THE MOMENTUM DISTRIBUTIONS FOR A PARTICLE IN A ONE-DIMENSIONAL BOX

A particle in a one-dimensional box is a widely used model system which appears in many textbooks of quantum mechanics [1-8] and quantum chemistry [9-13] as well as in the *Journal of Chemical Education* [14]. In most cases, however, it has been discussed only with regard to the position distributions of the particle. In this work, we emphasize the momentum distributions for which we obtain a simplified and explicit expression. We point out the nonclassical features of the momentum distributions, and show that the distribution bifurcates from unimodal to bimodal as the quantum number increases.

As is well known, quantum mechanics not only describes physical systems, such as an elementary particle in motion, but also specifies what an observer can know about the system. The limits on observations come from the famous uncertainty principle.

For a particle in a one-dimensional box, it is easy to solve the Schrödinger equation to obtain the wave function exactly. This model problem vividly demonstrates the principles of quantum mechanics, such as the uncertainty principle, and the connection between the space representation and momentum representation of the wave function [4].

The time-independent Schrödinger equation for a particle of mass m in a one-dimensional box of length a is:

$$d^2\Psi(x)/dx^2 + 8\pi^2 mE/h^2\Psi(x) = 0 \qquad (0 \leq x \leq a) \qquad (1)$$

Here $\Psi(x)$ is the wave function, h is Planck's constant, and E is the energy. The wave function satisfies the boundary conditions $\Psi(0) = \Psi(a) = 0$.

The normalized solutions are

$$\Psi_n(x) = \sqrt{2/a}\,\sin(n\pi x/a), \qquad (2)$$

where n=1, 2, 3, ...

The quantized energy levels obtained naturally from the boundary conditions are

$$E = h^2n^2/8ma^2 \quad n=1, 2, 3, ... \qquad (3)$$

Figure 1 shows the probability densities $\Psi_n(x)\,\Psi_n(x)$ for the position of the particle in the first several energy eigenstates.

Clearly the motion of a quantum particle in a box is very different from the classical motion. In a stationary state, the quantum particle cannot have any energy except the quantized values. In an energy eigenstate, the particle appears in various positions of the box with definite probabilities and there are special points (nodes) where $\Psi(x) = 0$ and the probability density to observe the particle drops to zero. Quantum mechanically, a standing probability wave is set up in the box [9]. When the energy quantum number n becomes large, the position distribution in the box becomes uniform. It approaches the classical limit of constant probability density in the box.

The average value of the position for the particle is

$$< x >_n = \int_{-\infty}^{\infty} \Psi_n(x)\, x\, \Psi_n(x)\, dx = 2/a \int_0^a x \sin^2(n\pi x/a)\, dx = a/2. \qquad (4)$$

The average value of x^2 is

$$<x^2>_n = \int_{-\infty}^{\infty} \Psi_n(x)\, x^2\, \Psi_n(x)\, dx$$

$$=2/a \int_0^a x^2 \sin^2(n\pi x/a)\, dx = (a/2n\pi)^2(4n^2\pi^2/3 - 2). \qquad (5)$$

Thus the root-mean-square deviation of the position for the particle is

$$\Delta x = \sqrt{<x^2>_n - <x>_n^2} = (a/2n\pi)\sqrt{(n^2\pi^2/3 - 2)}. \qquad (6)$$

The momentum distribution of a particle in a box is also very different from classical expectations. From a classical point of view, the particle should have a definite value of the momentum due to conservation of energy. Since $E = p^2/2m$, therefore $p = \pm\sqrt{2mE}$. Classically, the particle moves forward and backward in the box with constant speed.

Quantum mechanically, the energy eigenstate $\Psi_n(x) = \sqrt{2/a}\sin(n\pi x/a)$ is not an eigenstate of the momentum operator, because

$$\begin{aligned} p\sqrt{2/a}\sin(n\pi x/a) &= -i(h/2\pi)d/dx\,[\sqrt{2/a}\sin(n\pi x/a)] \\ &= -i(h/2\pi)(n\pi/a)\sqrt{2/a}\cos(n\pi x/a) \\ &\neq p_0\sqrt{2/a}\sin(n\pi x/a). \qquad (7) \end{aligned}$$

This means that the outcome from a momentum measurement for the particle cannot be predicte with certainty.

From the expression

$$\Psi_n(x) = \sqrt{2/a}\sin(n\pi x/a) = -i/\sqrt{2a}[\exp(in\pi x/a)-\exp(-in\pi x/a)]$$

$$(0 \le x \le a) \qquad (8)$$

it can be shown that the wavefunction inside the box is a superposition of traveling waves with equal and opposite momentum. However, it would be incorrect to jump to the conclusion that the state $\Psi_n(x)$ consists of two eigenstates of momentum operator with the same weighting factor, and therefore, the particle moves forward and backward uniformly in the box with a definite absolute value of the momentum $|p| = p_n = nh/2a$ [9-11]. This is identical to the classical point of view about the motion of a particle in a box.

The function $\exp(\pm i2\pi px/h)$ is an eigenstate of momentum operator when it is valid for all x, without spatial limitation. Only when a particle moves in free space can its momentum take on a definite value. This is easy to show [4]:

If a particle moves with a definite momentum p_0, its wave function in the momentum representation is

$$\Phi(p) = \delta(p-p_0); \tag{9}$$

Then by Fourier transformation, the wave function in the position representation is

$$\Psi(x) = 1/\sqrt{h}\int_{-\infty}^{\infty} \delta(p-p_0)\exp(2\pi ipx/h)\,dp = 1/\sqrt{h}\exp(2\pi ip_0x/h). \tag{10}$$

The probability density to find the particle within the infinitesimal range dx about x is

$$\rho(x) = |\Psi(x)|^2 = 1/h = \text{constant}. \tag{11}$$

This means that the particle can be found anywhere in space with the same probability. That is to say, if the momentum of a particle is fixed, its position is totally unknown.

In the opposite case, if a particle is fixed in space at $x = x_0$, its wave function in the position representation is

$$\Psi(x) = \delta(x-x_0); \tag{12}$$

Then by Fourier transformation, in the momentum representation the wave function is

$$\Phi(p) = 1/\sqrt{h}\int_{-\infty}^{\infty} \delta(x-x_0)\exp(-2\pi ipx/h)\,dx = 1/\sqrt{h}\exp(-2\pi ipx_0/h). \tag{13}$$

Hence the probability density to find the particle with a momentum in the infinitesimal range dp about p is

$$\rho(p) = |\Phi(p)|^2 = 1/h = \text{constant}. \tag{14}$$

This means that the particle has equal probability to be observed with any momentum value (relativistic effects are neglected). In other words, when the position of the particle is fixed, its momentum is totally unknown.

Between these two extremes, a particle in a one-dimensional box is spatially con strained (in the interval $0 \le x \le a$). The function $\Psi(x) = \exp(\pm in\pi x/a)$ for $0 \le x \le a$, but $\Psi(x) = 0$ otherwise, is not an eigenstate of momentum operator. The actual momentum distribution is found by transforming the energy eigenstate from the position representation to the momentum representation by Fourier transformation [6,15]:

$$
\begin{aligned}
\Phi_n(p) &= (1/\sqrt{h}) \int_{-\infty}^{\infty} \Psi_n(x) \exp(-2\pi ipx/h)\, dx \\
&= (1/\sqrt{h}) \int_0^a (\sqrt{2/a}) \sin(n\pi x/a) \exp(-2\pi ipx/h)\, dx \\
&= (-i/\sqrt{2ah}) \int_0^a [\exp(in\pi x/a)-\exp(-in\pi x/a)] \exp(-2\pi ipx/h)\, dx \\
&= (\sqrt{h/2\pi^2 a})\, p_n/(p_n^2-p^2)\, [1-(-1)^n \exp(-2\pi ipa/h)] \\
&= \begin{cases} (\sqrt{h/2\pi^2 a})\, p_n\, 2\, i \sin(pa\pi/h) \exp(-i\pi pa/h)/(p_n^2-p^2) & \text{(n even)} \\ (\sqrt{h/2\pi^2 a})\, p_n\, 2\cos(pa\pi/h) \exp(-i\pi pa/h)/(p_n^2-p^2) & \text{(n odd)} \end{cases}
\end{aligned}
$$

where $p_n = nh/2a,\ n = 1, 2, 3, ..$ (15)

Equation 15 gives an explicit, simplified expression for the wave function in the momentum representation, from which it is easily seen that the wave functions are amplitude-modulated and n-dependent also.

The corresponding probability densities to observe the momentum in the infinitesimal range dp about p are

$$
\begin{aligned}
\rho_{2k}(p) &= (2h/a\pi^2)\, p^2_{2k} \sin^2(p\pi a/h)/(p^2_{2k}-p^2)^2, && \text{(n even, n = 2k)} \\
\rho_{2k-1}(p) &= (2h/a\pi^2)\, p^2_{2k-1} \cos^2(p\pi a/h)/(p^2_{2k-1}-p^2)^2. && \text{(n odd, n = 2k-1)}
\end{aligned}
\tag{16}
$$

where $k = 1, 2, 3, ...$

Figure 2 shows the momentum probability densities for the particle in the first several energy eigenstates. This figure and Eq. 16 show clearly that there is a nonzero probability density to obtain many values other than $\pm nh/2a$ in a measurement of momentum for the particle in state n. This is very different from the classical behavior.

C. Cohen-Tannoudji, B. Diu, and F. Laloë, have analyzed the momentum probability density of a particle in a box in their textbook *Quantum Mechanics* [1]. In their expressions for the momentum wave functions and probability densities, they keep two terms separate as "diffraction functions" and this leads to a valuable physical interpretation of the momentum probability density distributions. But they did not simplify the expressions to the more explicit forms of our Eq. 15 and 16.

From Eq. 16, one can easily find all the maxima and minima of the momentum distribution. From $d\rho(p)/dp = 0$, the conditions for the maxima are

$$\cot(pa\pi/h) = -2\,(ph/a\pi)\,/\,(p^2_{2k} - p^2) \qquad (n\ \text{even},\ p \neq p_{2k}),$$

$$\tan(pa\pi/h) = 2\,(ph/a\pi)\,/\,(p^2_{2k-1} - p^2) \qquad (n\ \text{odd},\ p \neq p_{2k-1}). \qquad (17)$$

These equations can be solved numerically (see remark 3, below.)

The minima of the momentum distributions occur when $\rho(p) = 0$, i.e. when

$$\sin(pa\pi/h) = 0, \qquad (n\ \text{even},\ p \neq p_n)$$

and

$$\cos(pa\pi/h) = 0 \quad (n\ \text{odd},\ p \neq p_n). \qquad (18)$$

The separation between typical minima in the momentum distribution is obviously n-independent and equals h/a.

We make several observations:

1. The momentum distribution of a particle in a box gives a definite probability for observing values of p other than those corresponding to the eigenenergies of the particle. It is very interesting to note that, in analogy with the nodes in the position distribution of the particle (points in space where the particle has zero probability density to be found), the momentum distributions also have some zeroes at special values of the momentum. In even n states ($n=2k$), the particle cannot have the momentum values of $p = l\,h/a$, where $l \neq k$, while in odd n states ($n= 2k-1$), momentum values of $p = (2l-1)h/2a$ ($l \neq k$) cannot be measured. We could also regard the momentum wave function as a standing wave set up in the momentum space but it is amplitude-modulated.

2. The momentum of the particle in an eigenstate averages to zero due to the symmetry of momentum distribution: $\rho(p)$ is an even function of p, so

$$\langle p \rangle_n = \int_{-\infty}^{\infty} p\,\rho_n(p)\,dp = \int_{-\infty}^{\infty} \Psi_n(x)(-ih/2\pi\; d/dx)\,\Psi_n(x)\,dx=0. \qquad (19)$$

The probability densities at zero momentum are

$$\rho_{2k}(0)= 0, \qquad (n = 2k)$$

$$\rho_{2k-1}(0)=8a\,/\,(2k-1)^2\,h\pi^2. \qquad (n = 2k-1) \qquad (20)$$

In even n states, one cannot observe the particle with zero momentum (the probability is zero), while in odd n states, one does observe zero momentum of the particle with a certain probability. Surprisingly, in state $\Psi_1(x)$ ($n=1$), the most probable momentum is zero, rather than $p_1 = h/2a$. When odd n becomes larger, the probability of finding the particle with zero momentum decreases.

The mean value of p^2 is given by

$$\langle p^2 \rangle_n = \int_{-\infty}^{\infty} p^2\,\rho_n(p)\,dp = \int_{-\infty}^{\infty} \Psi_n(x)(-ih/2\pi\; d/dx)^2\,\Psi_n(x)\,dx = (nh/2a)^2 \qquad (21)$$

Thus the root-mean-square deviation of the momentum is

$$\Delta p = \sqrt{\langle p^2\rangle_n - \langle p\rangle_n{}^2} = nh/2a. \qquad (22)$$

Combining Eq. 22 with the root-mean-square deviation of the position for the particle, one obtains a result consistent with the uncertainty principle:

$$\Delta p \; \Delta x = (nh/2a)(a/2n\pi)\sqrt{(n^2\pi^2/3 - 2)} \geq h/4\pi. \qquad (23)$$

3. The probability density at $p = \pm p_n$ is a constant (n-independent):

$$\lim_{p \to p_n} \rho(p) = a/2h \qquad (24)$$

We note that the most probable momentum is not $\pm p_n$ when the particle in state $\Psi_n(x)$. Instead, by numerical calculations (Eq. 17) we find the following values for the most probable momentum p_m in different states:

n	p_m (±h/2a)
1	0.000
2	1.675
3	2.790
4	3.845
5	4.950
......	
10	9.985

From Fig. 2, it can be seen vividly that the distribution of the momentum for the particle bifurcates from a single peak (in the n=1 state) to two separate peaks near $p = \pm p_n$ (for all states $n \geq 2$). The most probable value of the momentum for the particle is n dependent. Only when n becomes large, does the probability density $\rho(p)$ reach its maximum at $p_m \cong \pm p_n$. This can be proven by taking the limit for $d\rho(p)/dp$ when $p \to p_n$:

$$\lim_{p \to p_n} d\rho(p)/dp \propto 1/n. \qquad (25)$$

We note that $\rho(\pm p_n)$ is n independent. This matches the classical description.

Acknowledgments

This work grew out of problem sets in CEM 991, Selected Topics in Quantum Chemistry taught by Prof. K. L. C. Hunt. The authors thank Prof. K. L. C. Hunt and Dr. V. Sethuraman for interesting discussions. YQL is grateful for a research assistantship, supported through NSF Grant CHE-9021912 to KLCH, and for a Summer Alumni Research Fellowship, from the Department of Chemistry, Michigan State University.

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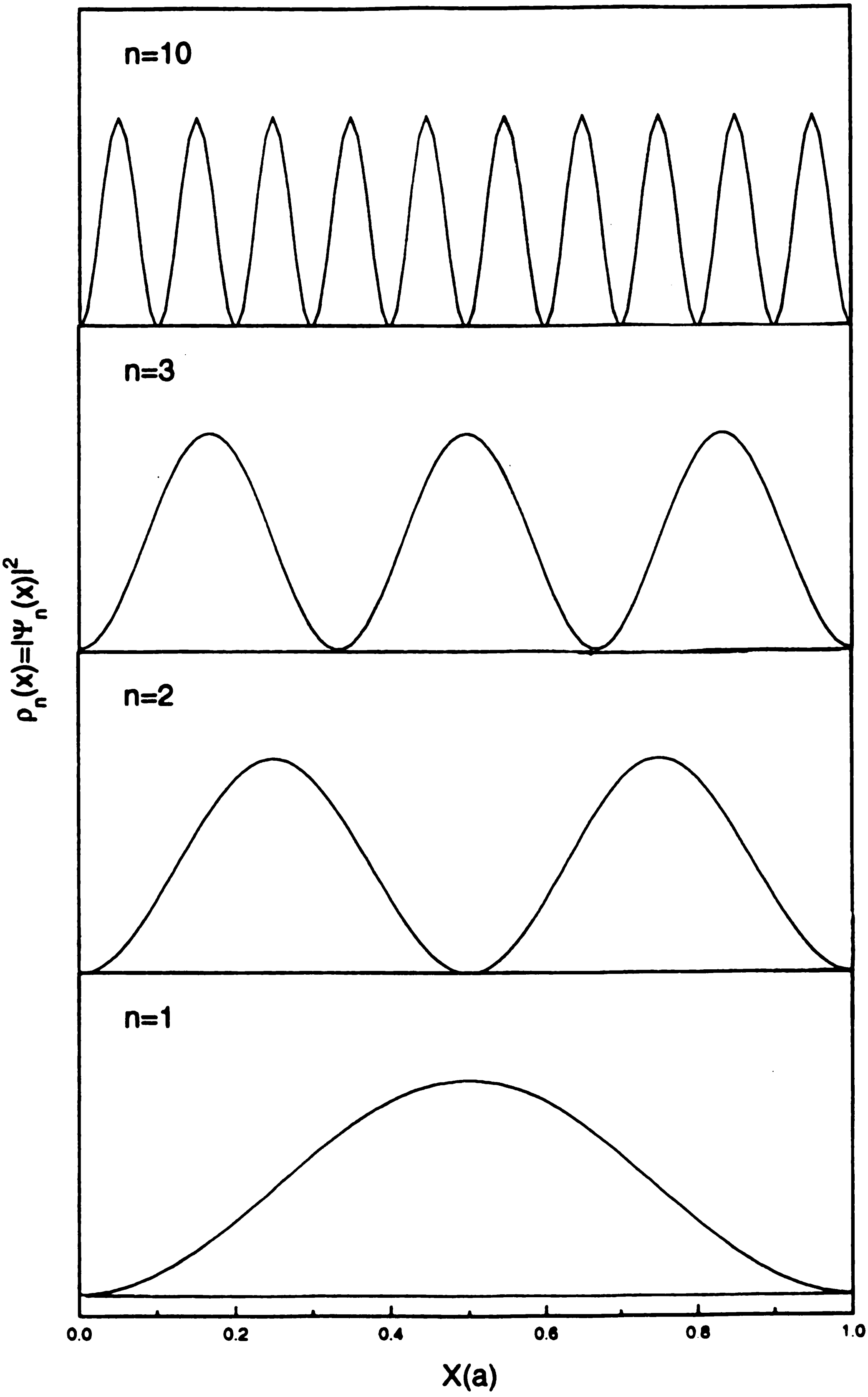

Figure 6.1 The position probability densities of a particle in a one-dimensional box; n indicates the energy levels of the particle (not to scale).

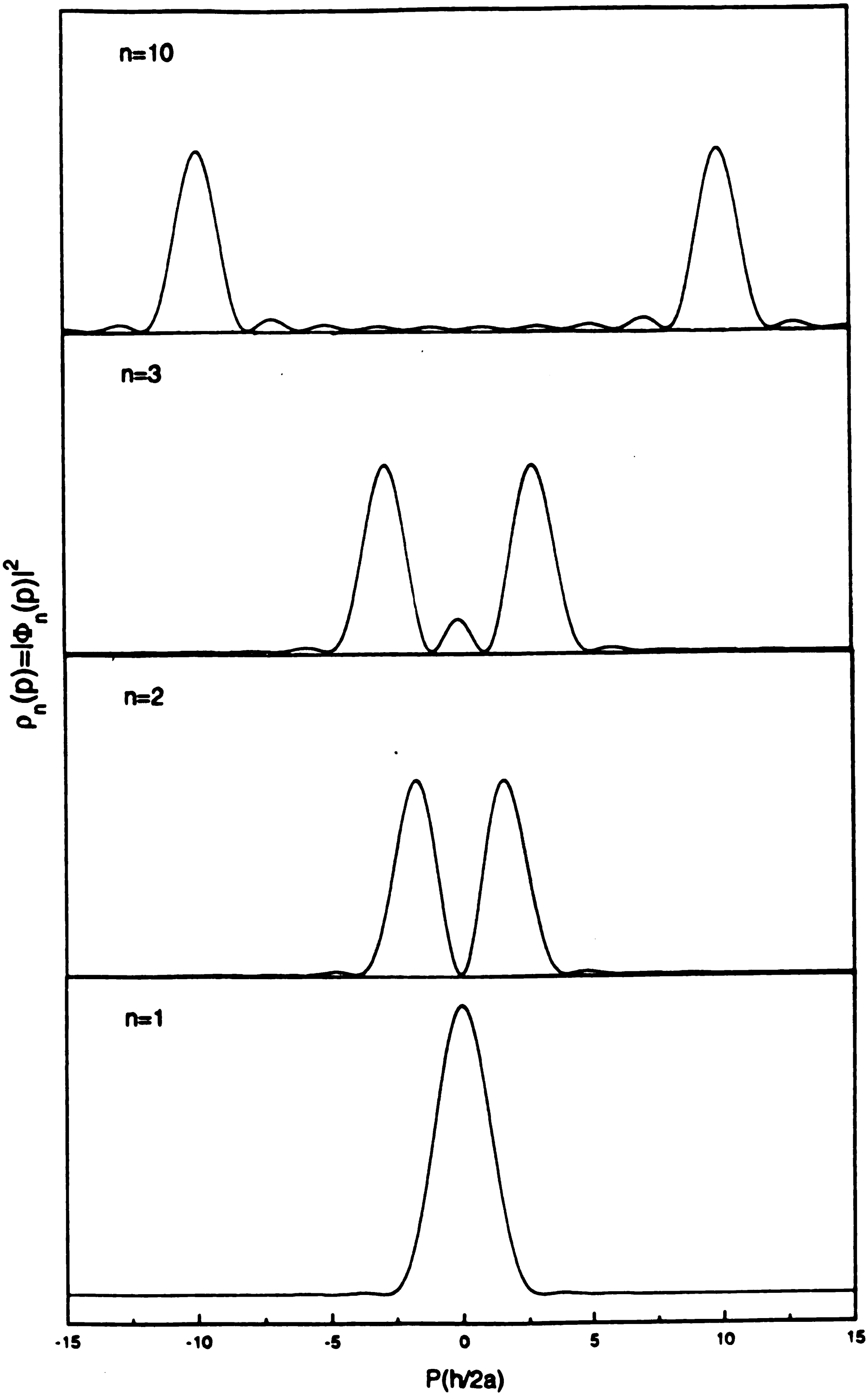

Figure 6.2 The momentum probability densities of a particle in a one-dimensional box; n indicates the energy levels of the particle (not to scale).

Figure 6.1 The position probability densities of a particle in a one-dimensional box; n indicates the energy levels of the particle (not to scale).

Figure 6.2 The momentum probability densities of a particle in a one-dimensional box; n indicates the energy levels of the particle (not to scale).