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# INTERACTION-INDUCED PROPERTIES
# AND
# PERTURBATION THEORY

By

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# ABSTRACT

# INTERACTION-INDUCED PROPERTIES
# AND
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The perturbation expansions obtained from Löwdin's projection-operator formalism are derived in a new way, using Kato's formulation of perturbation theory. This formulation does not involve the symbolic use of the inverse of singular operators. Kato's approach provides a convenient algebraic alternative to diagrammatic techniques for obtaining eigenvalues and eigenvectors. Different normalization criteria imposable on the wave function are easily visualized in terms of the operator that yields the perturbed state vector when it acts upon the unperturbed wave function.

We use a label-free exchange perturbation method to calculate the dipole moment of interacting He and H atoms as function of internuclear separation. In the label-free formalism, the unperturbed Hamiltonian and perturbation terms are constructed so that each is invariant with respect to exchange of electrons between the interacting atoms; then a Rayleigh-Schrödinger perturbation expansion with a fully antisymmetrized set of zeroth-order wave functions yields the interaction energy and collision-induced properties. Good agreement with <u>ab initio</u> results for the He...H dipole is obtained when a long-range dispersion contribution is added to the first-order overlap and exchange contributions.

Jesús Juanós i Timoneda

We calculate the dipole moment for the quartet state of $H_3$ in its linear and right triangular configurations and we find that the first-order overlap-exchange and the long-range contributions are about the same order of magnitude at intermediate range. We prove that a system of n atoms in any spatial configuration has zero dipole moment when the electrons are described by s-type functions (Slater or Gaussian) and the dipole moment is calculated as the expectation value of the corresponding operator with an unperturbed, but fully antisymmetrized wave function.

An analytic expression for the damped pair dipole moment is calculated in terms of Clebsch-Gordan coefficients and reduced matrix elements. We show explicitly with the first nonlocal hyperpolarizability how susceptibility densities may be cast in a form without secular divergences. The theory of generalized functions is applied to calculate the limits in the expressions for susceptibility densities and tensors.

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The computations involved in this research have been carried out at a time of expansion of the computational facilites in the Chemistry Department. My thanks to those who helped me in making efficient use of them.

## TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

| FIGURE | CHAPTER | |
|---|---|---|
| 1 | 3 | Collision-induced dipole of He...H as a function of the internuclear separation R in the range from 4.0 to 11.0 a.u. Curve A shows the <u>ab initio</u> results obtained by Meyer, and Curve B the <u>ab initio</u> results of Ulrich <u>et</u> <u>al</u>. Curves C and D have been obtained by adding the long-range dispersion dipole to the exchange-overlap dipole computed form the energy derivative (Eq. 13). Curve C shows the dipole in the Gaussian basis, and D the dipole in the Slater basis. Curves E and F have been obtained similarly, but the exchange-overlap dipole has been computed as an expectation value from Eq. 12; Curve E shows results from the Gaussian basis, F from the Slater basis. Curve G is a plot on the leading term of the dispersion dipole, $D_7R^{-7}$. The ordinate is scaled logarithmically and the dipole $\mu(R)$ is given in a.u. |
| 2 | 3 | Collision-induced dipole of He...H as a function of internuclear separation R in the range from 0 to 4.0 a.u. Curve A shows the <u>ab initio</u> results of Ulrich <u>et</u> <u>al</u>. Curve B and C show the lowest-order |

# CHAPTER 1.

# INTRODUCTION.

A major part of this work is devoted to the analysis of interactions between atoms or molecules at separations such that the overlap is not negligible. From this analysis we derive methods to calculate interaction-induced properties. These properties allow us to predict the behavior of matter interacting with radiation; alternatively the calculated properties may be compared with those computed from experimental data. We have also worked on several theoretical aspects of the methods used in our study.

Perturbation theory is the framework within which most of our work has been performed. The next chapter is devoted to a theoretical analysis of perturbation theory. On the basis of an entirely algebraic formalism, we present formulae to calculate corrections to the perturbed wave function and eigenvalue to any order. Several normalization criteria are associated with the way in which different projection operators are manipulated. We use a reduced resolvent for which no problem about singularities arises. This powerful technique allows us to establish consistency with other formalisms and developments in perturbation theory. We conclude the second chapter by presenting a unification of several different formalisms, with common principles.

In chapter 3 we use a special form of perturbation theory, viz., exchange perturbation theory in label-free form, to calculate interaction-induced dipole moments. In particular, the collision-induced dipole moment of a diaton is computed. We compare our method with other perturbation theories and we analyze an approximation employing additive long- and short-range contributions to the pair dipole moment. Since the

Hellmann-Feynman theorem is not satisfied at the level of approximation used in our calculations, the dipole moment is calculated both as the expectation value of the corresponding operator and as the field derivative of the energy. The results that each strategy yields and comparison with accurate ab initio calculations are used to assess the reliability of different methods in computing pair dipoles. Our computations have been performed with Gaussisan- and Slater-type orbitals. The work with Slater-type orbitals required us to augment the contents of the standard tables in order to calculate one of the integrals over these functions.

The same perturbation method as in Chapter 3 is used in Chapter 4. We derive an expression for the overlap-exchange contribution to the triplet dipole moment. The significance of the results of this chapter for studies of many-body effects is twofold: We prove that some methods used to calculate interaction-induced properties are not reliable. Second, we show that the results for the three-body long-range and exchange-overlap contributions to the pair dipole of quartet $H_3$ are comparable in order of magnitude at intermediate range. This result is known to hold also for the energy.

The exchange-overlap dipole (upon which Chapters 3 and 4 focus) vasishes when the separation becomes very large. The dispersion dipole moment as calculated in the region where overlap and exchange effects are negligible diverges when the separation approaches zero. In chapter 5 we calculate the overlap damped dispersion dipole moment, which remains finite. Also, we present a general treatment of susceptibility densities and tensors of potential use in the study of nonlinear phenomena. We treat the problem of secular divergencies, and we give an analytic expression for the first nonlocal hyperpolarizability density, needed to compute several damped properties, including the dispersion dipole.

# CHAPTER 2

## 2.1. - INTRODUCTION

Perturbation techniques are widely used ([1,2] and refs. therein) in the study of intermolecular interactions and their effects on supermolecular system properties. The wave operator that generates the perturbed state vector from the unperturbed wave function is important within this context, and in a general treatment of self-consistent field theory [3].

Löwdin has developed a projection operator formalism [3,5] that gives the wave operator in terms of a reduced resolvent operator T. Within Löwdin's formalism, proof of the existence of T hinges on proofs of operator invertibility. Wilson and Sharma [6,7] have analysed the invertibility requirements for one form of the T operator. By relating T to an "outer projection" of the Hamiltonian, Löwdin has recently shown that the operator T remains regular as needed for the construction of perturbed eigenfunctions [4]; he has also applied the partitioning method to derive rational perturbation approximations [4].

An alternative derivation of Löwdin's perturbation expansions is presented in this chapter, based on Kato's theory. This approach does not involve manipulation of inverse operators, although it does require proper manipulation of resolvents and consideration of their domains. In section 2.2 we review the aspects of Löwdin's work necessary for comparisons [3,5], with brief reference to other work in this field [8]. In section 2.3 the calculation of the perturbed eigenvectors and eigenfunctions is treated from the viewpoint of complex variable and Hilbert space theories [9-13]. Expansions are developed in section 2.3 for perturbed Hamiltonians with arbitrary dependence on a perturbation parameter $\kappa$. The Hamiltonians considered by Löwdin (in Refs. 4, p. 79 and 5) can be understood as one-parameter dependent expansions in which only the first-order correction term is present. The results and conclusions from section 2.3 are discussed in section 2.4, while section 2.5 contains a digression on the interrelation among several perturbative treatments used in quantum mechanics.

## 2.2. - ON LÖWDIN'S STUDIES IN PERTURBATION THEORY

The Hamiltonian H of the system under consideration is expressed in terms of the Hamiltonian $H_0$ for the unperturbed system and the correction term $H^{(1)}$ as $H = H_0 + H^{(1)}$. The wave operator U relates the perturbed eigenfunction $\psi$ to the unperturbed eigenfunction $\psi_0$:

$$\psi = U\psi_0. \tag{1}$$

When the operator t is constructed from the reduced resolvent T and the perturbation term $H^{(1)}$ as

$$t = H^{(1)} + H^{(1)}TH^{(1)} = H^{(1)}U \quad , \tag{2}$$

where

$$U = 1 + TH^{(1)} \tag{3}$$

the eigenvalue $\lambda$ associated with $\psi$ may be written as

$$\lambda = \lambda_0 + \langle t\rangle_0 \quad , \tag{4}$$

where the brackets with subscript zero denote an expectation value in the state $\psi_0$.

It is useful to express T in terms of the projection operator P that projects out the eigenfunction $\psi_0$ of $H_0$ from an arbitrary function. P projects onto a one-dimensional subspace of $\mathcal{H}$, the separable Hilbert space taken as the set of functions that are square-integrable and complex-valued on the configuration space of the Hamiltonian operator H. The projector onto the orthogonal complement with respect to the range of P is (1-P).

The reduced resolvent T in Eq. 3 is the operator

$$T(\epsilon) = [\epsilon - (1-P)H]^{-1}\,(1-P) \tag{5}$$

evaluated at $\epsilon = \lambda$ (in general $\epsilon$ is a complex variable). $T(\epsilon)$ may be expressed equivalently in terms of the resolvent $\bar{R} = (\epsilon-\bar{H})^{-1}$ of the outer projection $\bar{H} = (1-P)H(1-P)$ of the Hamiltonian $H$:

$$T(\epsilon) = (1-P)\,(\epsilon-\bar{H})^{-1}\,(1-P)\ . \qquad (6)$$

In general we may assume $\exists(\lambda-\bar{H})^{-1}$ only when $\lambda\notin\sigma(\bar{H})$, where $\sigma(\bar{H})$ is the discrete or point spectrum of $\bar{H}$, even though $\lambda$ may be a point of constancy of $E(\lambda)$ or a point of continuity of $E(\lambda)$, where $E(\lambda)$ stands for a resolution of the identity [14]. In deriving conventional perturbation theory formulae, we may take $T(\epsilon)$ with $\epsilon$ in the spectrum of $H$, provided that $\epsilon$ is not in the spectrum of $\bar{H}$; in particular, we may set $\epsilon=\lambda$, because $\langle\psi|\psi_0\rangle\neq0$ ensures that $T(\epsilon)$ remains regular at $\lambda$ [4].

Series for t and U [5] may be derived by using the unperturbed reduced resolvent $T_0(\epsilon)$, defined as $T_0(\epsilon) = [\epsilon-(1-P)H_0]^{-1}\,(1-P)$, with appropriate choice of $\epsilon$ to obtain Brillouin-Wigner, Rayleigh-Schrödinger or "intermediary" perturbation expansions [4].

With the reduced resolvent $S = [\lambda_0-(1-P)H_0]^{-1}(1-P)$, if $|\langle SV'\rangle| < 1$, where

$$V' = H^{(1)} - \langle\psi_0|t|\psi_0\rangle = H^{(1)} - \langle t\rangle_0\ , \qquad (7)$$

the following expansion is obtained for t:

$$t = H^{(1)} + H^{(1)}SH^{(1)} + H^{(1)}SV'SH^{(1)} + H^{(1)}SV'SV'SH^{(1)} + \cdots\ . \qquad (8)$$

Hence

$$V' = H^{(1)} - \langle H^{(1)}\rangle_0 - \langle H^{(1)}SH^{(1)}\rangle_0 - \langle H^{(1)}SH^{(1)}SH^{(1)}\rangle_0 +$$

$$+ \langle H^{(1)}\,S\langle H^{(1)}\rangle_0 SH^{(1)}\rangle_0 + \langle H^{(1)}S\langle H^{(1)}SH^{(1)}\rangle_0 SH^{(1)}\rangle_0 + \cdots\ , \qquad (9)$$

and so

$$t = [H^{(1)}] + [H^{(1)}SH^{(1)}] + [H^{(1)}S(H^{(1)} - \langle H^{(1)}_0 \rangle)SH^{(1)}] +$$

$$[H^{(1)}S(H^{(1)} - \langle H^{(1)}\rangle_0)S(H^{(1)} - \langle H^{(1)}\rangle_0)SH^{(1)} -$$

$$- \langle H^{(1)}\, SH^{(1)}\rangle_0 SSH^{(1)}] + \cdots \equiv t_1 + t_2 + t_3 + \cdots \qquad (10)$$

$$U = 1 + [SH^{(1)}] + [S(H^{(1)} - \langle H^{(1)}\rangle_0)SH^{(1)}] +$$

$$+ [S(H^{(1)} - \langle H^{(1)}\rangle_0)S(H^{(1)} - \langle H^{(1)}\rangle_0)SH^{(1)} \qquad (11)$$

$$- \langle H^{(1)}SH^{(1)}\rangle_0 S^2H^{(1)}] + \cdots \equiv 1 + U_1 + U_2 + U_3 + \cdots$$

where the i$^{th}$ term in square brackets has been identified with $t_i$ in expression (10) or with $U_i$ in (11). The expansions for t and U given in (10) and (11) let us calculate corrections to $\psi_0$ and $\lambda_0$ consistently with the choice of H.

A related perturbation formalism has been developed by Speisman [8], using the operator

$$\tilde{T} = \frac{(1-P)}{H_0-\lambda_0} \; . \qquad (12)$$

We should emphasize, though, the essentially symbolic character of this expression in his work. This character becomes evident when, after taking $\lambda_0$ as an isolated eigenvalue of $H_0$, Speisman in fact equates (12) to the reduced resolvent, i.e., $\int'(\lambda - \lambda_0)^{-1}\, dE(\lambda)$, where the prime in the integration means that it is performed in the whole range of $\lambda$ except within a properly defined neighbourhood of $\lambda_0$.

## 2.3. - THEORETICAL ANALYSIS

This section begins with a brief review of the aspects of Kato's perturbation theory that are central in this analysis. Rigorous treatments of the perturbation methods, regular or asymptotic expansions and convergence properties may be found in Kato's original papers [9-12,15]. The derivation of the perturbation series is carried out and the connection with Löwdin's work [4,5] is established.

Following Kato, let us consider $H_\kappa$ a self-adjoint or hypermaximal, but not necessarily bounded operator such that

$$H_\kappa = \int_{-\infty}^{\infty} \lambda dE_\kappa(\lambda) \tag{13}$$

where the system of projections $E_\kappa(\lambda)$ is the resolution of the identity corresponding to $H_\kappa$ and the sub-index $\kappa$ stands for the dependence on a parameter $\kappa \in \mathbb{R}$. For $\ell \in \Lambda(H_\kappa)$, the resolvent $R_\kappa(\ell)$ is defined by

$$R_\kappa(\ell) = (H_\kappa - \ell)^{-1} = \int_{-\infty}^{\infty} (\lambda - \ell)^{-1} \, dE_\kappa(\lambda) \ , \tag{14}$$

and it is a bounded analytic function of $\ell$. $\Lambda(H_\kappa)$ is the resolvent set of $H_\kappa$, *i.e.*, the set of real numbers not belonging to the spectrum of $H_\kappa$, and the non-real complex numbers.

When $\lambda_0$ is an isolated eigenvalue (in general with finite multiplicity m) of $H_0$ within a properly chosen closed curve $\Gamma$ belonging to $\Lambda(H_0)$, we shall write

$$R_\kappa(\ell) = (\lambda_0 - \ell)^{-1} E_0 + S_\kappa(\ell) \ , \tag{15}$$

where

$$S_\kappa(\ell) = \int' (\lambda-\ell)^{-1}\, dE_\kappa(\lambda) \quad . \tag{16}$$

($\int'$ stands for an integration except at the point $\lambda=\lambda_0$, [12]).

$S_\kappa(\ell)$ given by (16) is the reduced resolvent with respect to $\lambda_0$, and $E_0$ is the projection operator onto the space associated with $\lambda_0$. It should be emphasized that $S_\kappa(\ell)$ has a singularity at $\ell=\lambda_0$.

Let $\kappa H^{(1)}$ be a regular perturbation and

$$E_\kappa = \frac{-1}{2\pi i} \oint_\Gamma R_\kappa(\ell)d\ell \ . \tag{17}$$

Since

$$R_\kappa(\ell) = R_0(\ell) \sum_{n=0}^{\infty} (-1)^n \kappa^n [H^{(1)} R_0(\ell)]^n \ , \tag{18}$$

we obtain

$$E_\kappa = E_0 + \sum_{n=1}^{\infty} \kappa^n A^{(n)} \ , \tag{19}$$

where

$$A^{(n)} = (-1)^{n-1} \frac{1}{2\pi i} \oint_\Gamma R_0(\ell)H^{(1)} \overset{n}{\cdots} R_0(\ell)d\ell \tag{20}$$

with $H^{(1)}$ appearing n times in the integrand.

We take from Kato's papers the expression for $A^{(n)}$ :

$$A^{(n)} = (-1)^{n-1} \sum_{i=1}^{\text{card }(L)} (S^{k_1} H^{(1)} S^{k_2} \overset{n}{\cdots} H^{(1)} S^{k_{n+1}})_i \tag{21}$$

where card(L) = number of elements in L, and

$$L = \{ (k_1, \ldots, k_{n+1}) : \sum_{j=1}^{n+1} k_j = n \wedge k_j \geq 0,\ \forall j : 1 \leq j \leq n+1\} \quad (22)$$

$$S^0 \equiv -E_0\,, \quad S \equiv S_0(\lambda_0) \quad (23)$$

(An explicit derivation is given in Appendix A.)

In the more general case

$$H_\kappa = H_0 + \kappa H^{(1)} + \kappa^2 H^{(2)} + \cdots , \quad (24)$$

we obtain

$$A^{(n)} = - \sum_{i=1}^{\mathrm{card}\,(I)} (-1)^p \sum_{j=1}^{\mathrm{card}\,(J)} (S^{k_1} H^{(\nu_1)} S^{k_2} \cdots S^{k_p} H^{(\nu_p)} S^{k_{p+1}})_{ij}\,, \quad (25)$$

where card(I) = number of elements in

$$I = \{(\nu_1, \cdots, \nu_p) : \sum_{j=1}^{p} \nu_j = n \wedge \nu_j \geq 1,\ \forall j : 1 \leq j \leq p\}$$

and card(J) = number of elements in

$$J = \{(k_1, \ldots, k_{p+1}) : \sum_{j=1}^{p+1} k_j = p \wedge k_j \geq 0, \forall j : 1 \leq j \leq p+1\}$$

It has been proven [10] that there exists a unitary operator $U_\kappa$ such that

a) $U_0 = 1$,

b) $U_\kappa E_0$ is regular wherever $E_\kappa$ is regular,

and c) $E_\kappa = U_\kappa E_0 U_\kappa^{-1}$ .

Let us now consider explicitly the terms $A^{(n)}$, for n = 1 and 2

$$A^{(1)} = -E_0H^{(1)}S - SH^{(1)}E_0$$

$$A^{(2)} = E_0H^{(1)}SH^{(1)}S + SH^{(1)}E_0H^{(1)}S + SH^{(1)}SH^{(1)}E_0 -$$

$$- E_0H_0^{(1)}E_0H^{(1)}S^2 - E_0H^{(1)}S^2H^{(1)}E_0 - S^2H^{(1)}E_0H^{(1)}E_0 - E_0H^{(2)}S -$$

$$-SH^{(2)}E_0 \ . \qquad (26)$$

If we define

$$a_1^{(1)} \equiv -SH^{(1)}E_0$$

$$a_2^{(1)} \equiv - E_0H^{(1)}S$$

$$a_1^{(2)} \equiv SH^{(1)}SH^{(1)}E_0 - S^2H^{(1)}E_0H^{(1)}E_0 - SH^{(2)}E_0$$

$$a_2^{(2)} \equiv E_0H^{(1)}SH^{(1)}S - E_0H^{(1)}E_0H^{(1)}S^2 - E_0H^{(2)}S \qquad (27)$$

then from (26) and (27)

$$A^{(1)} = a_1^{(1)} + a_2^{(1)}$$

$$A^{(2)} = a_1^{(2)} + a_2^{(2)} + SH^{(1)}E_0H^{(1)}S - E_0H^{(1)}S^2H^{(1)}E_0 \ . \qquad (28)$$

Substitution of (28) into (19) yields

$$E_\kappa = E_0 + \kappa[a_1^{(1)} + a_2^{(1)}] + \kappa^2[a_1^{(2)} + a_2^{(2)}] + \ldots + \kappa^2[SH^{(1)}E_0H^{(1)}S -$$

$$-E_0H^{(1)}S^2H^{(1)}E_0] + \cdots =$$

$$= E_0 + \kappa[a_1^{(1)} + a_2^{(1)}] + \kappa^2[a_1^{(2)} + a_2^{(2)}] + \ldots + \{\mathcal{O}(\kappa^2)\mathrm{Tr}=0\} \qquad (29)$$

where the braces in (29) include all those terms whose order in $\kappa$ is equal or greater than 2 and whose trace vanishes, the first of which is $SH^{(1)}E_0H^{(1)}S - E_0H^{(1)}S^2H^{(1)}E_0$.

Let us denote by $\bar{E}_\kappa$ the operator obtained by removing from $E_\kappa$ all those terms whose trace vanishes. We may take

$$\bar{E}_\kappa = e_{\kappa 1} + e_{\kappa 2} \qquad (30)$$

where

$$\begin{aligned} e_{\kappa 1} &= E_0 + \kappa a_1^{(1)} + \kappa^2 a_1^{(2)} + \ldots \\ e_{\kappa 2} &= \kappa a_2^{(1)} + \kappa^2 a_2^{(2)} + \ldots \end{aligned} \qquad (31)$$

Rearrangement of the terms in the series (19) is justified by the fact that the expansions (19) and (29) are absolutely convergent when $|\kappa|$ is less than a bound that must be determined in each particular case [12]. Also

$$e_{\kappa 2}\psi_0 = 0 \text{ and } \bar{E}_\kappa\psi_0 = \bar{\psi}_\kappa \qquad (32)$$

Using for the unitary operator the same notation for removal of terms with vanishing trace, we write

$$\bar{E}_\kappa = \bar{U}_\kappa E_0 \bar{U}_\kappa^{-1} = (\bar{U}_\kappa E_0)(E_0\bar{U}_\kappa^{-1}) \ . \qquad (33)$$

The following relationship is trivially fulfilled when

$A = 1 + \sum_{i=1}^{\infty} a_i$ and $B = 1 + \sum_{i=1}^{\infty} b_i$ :

$$A \cdot B = A + B + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} a_i b_j - 1 \tag{34}$$

provided that A and B are absolutely convergent.

Since

$$\bar{U}_\kappa = 1 + \kappa \bar{U}^{(1)} + \kappa^2 \bar{U}^{(2)} + \ldots , \tag{35}$$

$$\bar{E}_\kappa = \bar{U}_\kappa E_0 + E_0 \bar{U}_\kappa^{-1} + [\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \kappa^{(i+j)} \bar{U}^{(i)} E_0 \bar{U}^{(j)\dagger}] - E_0 \tag{36}$$

as may easily be deduced by using (34).

Comparing (36) and (30), we identify

$$e_{\kappa 1} = \bar{U}_\kappa E_0 = E_0 + \kappa a_1^{(1)} + \kappa^2 a_1^{(2)} + \ldots \tag{37}$$

The expansion for $\bar{U}_\kappa$ may be written from (37) and (27) as

$$\begin{aligned} \bar{U}_\kappa &= 1 - \kappa S H^{(1)} + \kappa^2 [S H^{(1)} S H^{(1)} - S^2 H^{(1)} E_0 H^{(1)} - S H^{(2)}] + \ldots \\ &= 1 + [-\kappa S + \kappa^2 (S H^{(1)} S - S^2 H^{(1)} E_0) + \ldots] H^{(1)} + \\ &\quad + [\kappa^2 (-S) + \ldots] H^{(2)} + \ldots = \\ &= 1 + f_1(\kappa) H^{(1)} + f_2(\kappa) H^{(2)} + \ldots = 1 + \sum_{n=1}^{\infty} f_n(\kappa) H^{(n)} , \end{aligned} \tag{38}$$

where $f_n(\kappa)$ stands for an expansion in powers of $\kappa$, the first term being of order n. It contains the operators $H^{(1)}$, $H^{(2)}$, . . .

According to (32),

$$\bar{\psi}_\kappa = \bar{U}_\kappa \psi_0 \qquad (39)$$

If the traceless terms in $E_\kappa$ had not been omitted, a different $U_\kappa$ would have been obtained, and it would yield (see (39)) a wave function that would satisfy the normalization criterion $\langle\psi_\kappa|\psi_\kappa\rangle = 1$, rather than $\langle\psi_0|\bar{\psi}_\kappa\rangle = 1$ .

When only one perturbative term is present in the Hamiltonian, $\bar{U}_\kappa$ becomes

$$\bar{U}_\kappa = 1 + f_1(\kappa)H^{(1)} \qquad (40)$$

and

$$\bar{\psi}_\kappa = \bar{U}_\kappa E_0\psi_0 = \bar{U}_\kappa\psi_0 = \psi_0 + f_1(\kappa)H^{(1)}\psi_0 \qquad (41)$$

where

$$f_1(\kappa) = -\kappa S + \kappa^2(SH^{(1)}S - S^2H^{(1)}E_0) + . . . \qquad (42)$$

Let

$$T \equiv f_1(\kappa=1) = -S+SH^{(1)}S-S^2H^{(1)}E_0+... = S'+SH^{(1)}S-S^2H^{(1)}E_0+ ... \qquad (43)$$

where $S' \equiv -S$. Now

$$W = (1 + TH^{(1)})E_0 = (1 + w^{(1)} + w^{(2)} + ... ) E_0 \qquad (44)$$

where $w^{(1)} = S'H^{(1)}E_0$

$$W^{(2)} = SH^{(1)}SH^{(1)}E_0 - S^2H^{(1)}E_0H^{(1)}E_0 . \tag{45}$$

Formulae (45) are exactly the same as those given by Löwdin, as may be seen in a straightforward way, once (37) has been slightly transformed by using

$$S^2H^{(1)}E_0H^{(1)}E_0 = S^2H^{(1)}E_0H^{(1)}E_0E_0 = S^2H^{(1)}\langle H^{(1)}\rangle_0 E_0 , \tag{46}$$

and by substituting $S^2H^{(1)}\langle H^{(1)}\rangle_0$ for $S^2H^{(1)}E_0H^{(1)}$ in $\bar{U}_\kappa$.

Let us now compare our results with the expression for the energy given in ref. [5]. If $\kappa = 1$,

$$\begin{aligned}
\lambda &= \lambda_0 + \langle\psi_0|H^{(1)}W|\psi_0\rangle = \lambda_0 + \langle\psi_0|H^{(1)}(1 + TH^{(1)})|\psi^{(0)}\rangle \\
&= \lambda_0 + \langle\psi_0|H^{(1)}|\psi_0\rangle + \langle\psi_0|H^{(1)}TH^{(1)}|\psi_0\rangle \\
&= \lambda_0 + [\langle\psi_0|H^{(1)}|\psi_0\rangle] + [\langle\psi_0|H^{(1)}S'H^{(1)}|\psi_0\rangle] + \\
&\qquad [\langle\psi_0|H^{(1)}SH^{(1)}SH^{(1)}|\psi_0\rangle - \langle\psi_0|H^{(1)}S^2H^{(1)}E_0H^{(1)}|\psi_0\rangle] + \dots \\
&\equiv \lambda_0 + \langle t_1\rangle_0 + \langle t_2\rangle_0 + \langle t_3\rangle_0 + \dots
\end{aligned} \tag{47}$$

where $\langle t_i\rangle_0$ has been identified with the i^th^ term in square brackets.

According to (24) and (38), we may write in general

$$t = \sum_{n=1}^{\infty} \kappa^n H^{(n)} [1 + \sum_{m=1}^{\infty} f_m(\kappa)\, H^{(m)}] \tag{48}$$

and if, in particular, we take only $n = 1$ and $\kappa = 1$

$$t = H^{(1)}[1 + f_1(\kappa=1)H^{(1)}] = H^{(1)}[1 + TH^{(1)}] = H^{(1)}U \qquad (49)$$

The last expression above is identical to the expression given by Löwdin for the reaction operator t.

Kato [12] found the expansion of $\psi_\kappa$ in a slightly different way. He considered the adiabatic transformation $W_\kappa$ that allows us to obtain $\psi_\kappa$ from $\psi_0$,

$$\psi_\kappa = W_\kappa \psi_0 \qquad (50)$$

where $W_\kappa$ is taken as $U_\kappa \cdot E_0$ and

$$\frac{dW_\kappa}{d\kappa} = \frac{dE_\kappa}{d\kappa} W_\kappa \qquad (51)$$

The formulae to be substituted in an expansion of $W_\kappa$ at $\kappa = 0$ are found by calculating the $q^{th}$ derivative of $W_\kappa$ with respect to $\kappa$ at $\kappa = 0$ and by comparing with (19),

$$W_\kappa = \sum_{q=0}^{\infty} \frac{1}{q!} [\frac{d^q}{d\kappa^q} W_\kappa]_{\kappa=0} q! \kappa^q = E_0 + \kappa A^{(1)} E_0 +$$

$$+ \kappa^2 \{ E_0 + \frac{1}{2} (A^{(1)})^2 E_0 \} + \ldots \qquad (52)$$

where

$$\left[ \frac{dE_\kappa}{d\kappa} \right]_{\kappa=0} = A^{(1)}$$

$$\left[ \frac{d^2E_\kappa}{d\kappa^2} \right]_{\kappa=0} = 2A^{(2)} \qquad (53)$$

. . . , have been used.

The perturbed wave function is obtained from (50).

$$\psi_\kappa = \psi_0 - \kappa SH^{(1)}\psi_0 + \kappa^2 \{SH^{(1)}SH^{(1)}\psi_0 - \langle H^{(1)}\rangle_0 S^2H^{(1)}\psi_0$$
$$- \frac{1}{2} ||SH^{(1)}\psi_0||^2\psi_0 - SH^{(2)}\psi_0\} + . . . \qquad (54)$$

Derivations of the expressions equivalent to $A^{(n)}$ for the energy are analogous (<u>cf</u>. [9,12]).

## 2.4. - DISCUSSION

Several authors ([16] and references therein) have formulated diagrammatic representations of the Rayleigh-Schrödinger perturbation theory. The use of the rules from such techniques is a convenient way to write to any order the correction to both the energy and the wave function, without requiring an explicit calculation when the expressions are needed. Similarly we point out that the sum rules in expressions for $A^{(n)}$ and its equivalent correction terms to $\lambda_0$ are not particularly complicated. Once these expressions have been written, it is a straightforward matter to obtain correction terms directly either by introducing $A^{(n)}$ in the expansion of $W_\kappa$ to obtain the wave function or by calculating several traces to obtain the eigenvalue.

The method has the advantage that we may keep consistency between the order of the correction in our expansions for $\lambda_\kappa$ and $\psi_\kappa$ and the order in $\kappa$ kept in the expansion for $H_\kappa$, since we have formulae that are general enough for both $A^{(n)}$ and its equivalent form for $\lambda_\kappa$; i.e., the formulae are not restricted to Hamiltonians like $H_\kappa = H_0 + \kappa H^{(1)}$, but $H_\kappa$ may be taken to the desired order in $\kappa$.

Another significant aspect within this context is that $\psi_\kappa$ is obtained from $\psi_0$ as the result of an adiabatic transformation, $W_\kappa$ or $U_\kappa \cdot E_0$. The operator that carries out this transformation acting on an arbitrary function yields an eigenfunction of $H_\kappa$. The unitary operator, $U_\kappa$ or $\bar{U}_\kappa$, represents how the function describing the state of the system evolves as the effects of the perturbation change it.

The relationship with the variational principle has been discussed by Kato in his original papers. The degenerate case is also treated in the references given to Kato's work.

Following Kato's original work, the usual series in perturbation theory have been deduced, with the same normalization criterion as in Löwdin's work [3-5]. The series have been written in terms of a reduced resolvent, for which no problem about singularities arises. This work establishes the consistency between results obtained from Löwdin's method and expressions developed strictly within the framework of complex-variable perturbation methods applicable for Hilbert spaces.

A different method from that used by Kato [12] has been given to derive an expansion for the wave operator. It allows us to visualize different ways to obtain the perturbed wave function and its different normalization conditions.

## 2.5 - RELATIONSHIPS AMONG PERTURBATION METHODS.

This section should be regarded as a complement to the main contents of this chapter. We include it here because we have seldom encountered references to Kato's work in the literature on perturbation theory; yet Kato's rigorous treatment of perturbation theory provides a reliable and powerful algebraic language to deal with perturbative problems. The diversity of perturbative treatments in textbooks and research papers and their apparent independence and specialized character make it difficult to develop a unified conception of several areas of nuclear, atomic and molecular quantum mechanics because of an apparent lack of common principles. We therefore present in this section the underlying fundamentals, which interrelate different mathematical formalisms through a common background.

It is customary to regard interactions as corrections to an unperturbed Hamiltonian, $H_0$. The total Hamiltonian $H_\kappa$ is decomposed into $H_0$ and the perturbation $\kappa H^{(1)}$ associated with the interaction. The limit $\kappa = 0$ correspondents to the unperturbed system whereas $\kappa = 1$ corresponds to the real system. In the study of atoms, for instance, $H_0$ may include the kinetic energy, nuclear attraction and central potential terms; $H^{(1)}$ would include the Coulomb repulsion minus the central potential terms, and perhaps magnetic interactions or interactions with an external field. The whole Hamiltonian is thus split into two terms formulated according to the independent-particle model.

Kato's formalism, as formulated in the references given in this chapter, yields expansions commonly called Ragleigh-Schrödinger expansions for the perturbed eigenvalues and eigenfunctions. Besides mathematical rigour, Kato's treatment has the strength of dealing with projection operators, $E_\kappa$ or $E_0$, which are uniquely determined, whereas eigenvectors lack this property. Some of the results of this chapter have been obtained because of this feature, e.g., different normalization criteria imposable on the wave function are easily visualized in terms of the operator that yields the perturbed state vector when it acts upon the unperturbed wave function. The exact energy, $\lambda_\kappa$, does not appear explicity in the expansions. This fact renders the expansions for the exact eigenvalues and eigenfunctions very useful for calculations. Size consistency is another interesting feature of the expansion for the exact energy given by Eq. (47). Brueckner [17] considered the Rayleigh-Schrödinger expansion and showed that the terms having a non-linear (aphysical) dependence on the number of particles of the system cancel with each other. The linked-cluster diagram theorem was later proven by time-dependent [18] and time-independent [19] methods. This theorem states that the aphysical terms cancel through all orders of diagrammatic perturbation theory, only linked diagrams appear in the series for $\lambda_\kappa$.

Although it is not conventional in the theory of operators on the Hilbert space, we could consider the inverse $(\lambda_\kappa - H_0)^{-1}$ instead of the resolvents of either $H_0$ or $H_\kappa$, as taken previously. We would thus generate expansions analogous to those given in previous sections of this chapter, but they would have $\lambda_\kappa$ instead of $\lambda_0$ in the resolvents. The perturbation expansions with explicit dependence on the perturbed eigenvalue $\lambda_\kappa$ are known as the Brillouin-Wigner expansions. The analogue to Eq. (47) so constructed is the Brillouin-Wigner expansion for the energy, and that of Eq. (49) is designed the transition matrix or T-matrix [20-22] in scattering theory, whereas its expanded form is known as the Born (or Newmann) series [20-22]. "Reaction matrix" or "K-matrix" replaces the term "transition matrix" in studies on nuclear matter [23]. Eq. (47) with $\lambda_0$ in the resolvents replaced by $\lambda_\kappa$ may provide a justification for the terminology "effective interaction", as t is sometimes called.

The sum of the zeroth- and first-order correction energies is the expectation value of $H_\kappa$ in the state represented by the model function $\psi_0$ in both the Brillouin-Wigner and the Rayleigh-Schrödinger perturbation expansions (see Eq. (47)). When $H_0$ is the central-field Hamiltonian and $H^{(1)}$ includes at least the noncentral electrostatic interaction, the sum $\lambda_0 + \langle\psi_0 \mid H^{(1)} \mid\psi_0\rangle$ is called the Hartree-Fock energy because this is the quantity minimized in a Hartree-Fock procedure [24-27]. The remaining part of the energy is the correlation energy. Methods such as CI, MCSCF, electron-pair theories,..., [28] are employed to obtain quantitative information on the terms in Eq. (47) beyond the first two. The terms in Eq. (47) of second order and beyond represent true many-body effects, for the Hartree-Fock approximation only takes into account the effects on each electron of the average field of the remaining electrons and nuclei. Thus, the electrons move independently of each other and the instantaneous motion of the electrons or the correlation between them in their mutual Coulomb field is not taken into account as such [29].

Size consistency is a desirable property of any method used in computations in chemistry because it is the differences between two quantities what are often most interesting. In contrast to the Rayleigh-Schrödinger perturbation expansion however, the Brillouin-Wigner expansion for the energy is not size consistent. Nevertheless, we know [9] that the eigenvalue $\lambda_\kappa$ of the perturbed Hamiltonian is regular in $\kappa$ and power-series expandable with a non-vanishing convergence radius. The eigenvalue is an analytic function of $\kappa$ and $\lambda_\kappa \rightarrow \lambda_0$ as $\kappa \rightarrow 0$. Therefore, it is legitimate to think of an expansion about $\lambda_\kappa = \lambda_0$ of the resolvents in the Brillouin-Wigner series. Such an expansion allows us to recast the Brillouin-Wigner series in the Rayleigh-Schrödinger form. Furthermore, Brandow proved [31,32] that this procedure allows for cancellation of all the unlinked terms in the Brillouin-Wigner series, as should be expected because the Rayleigh-Schrödinger series is size consistent.

Feshbach's operator [34,35] in nuclear physics is an effective operator that yields the exact energy when operating on a model function. Löwdin's [3,5] treatment of the partitioning technique may be considered a development of Feshbach's previous work.

Finally, the resolvent operator (14) may be written as

$$R_\kappa(\ell) = (H_\kappa - \ell)^{-1} = -(\xi - H_\kappa + i\eta)^{-1} \equiv -G^+(\xi) \tag{55}$$

with $\xi$, $\eta \in \mathbb{R}$ and $\ell \equiv \xi + i\eta$. The zeroth-order Green's function operator or propagator $G_0^+(\xi)$ is obtained from $G^+(\xi)$ by replacing $H_\kappa$ by $H_0$. Now

$$(\xi - H_0 + i\eta) = (\xi - H_\kappa + i\eta) + H^{(1)} \tag{56}$$

from which it is a simple matter to obtain the Dyson equation

$$G^+(\xi) = G_0^+(\xi) + G_0^+(\xi)H^{(1)}G^+(\xi) \tag{57}$$

closely related to the wave-operator relationship (40). The limit of $\xi \rightarrow \lambda_\kappa$ and $\eta \rightarrow 0$ yields a distribution which establishes the connection between the Green's function-opeator notation of the resolvent and the singular (or Sochozki's) generalized functions [36] of use in scattering theory.

# CHAPTER 3.

## 3.1. INTRODUCTION

Interactions between colliding molecules in gases or liquids cause shifts in the charge distributions of the collision partners. These shifts result in differences between the net dipoles of colliding pairs (or clusters) and the vector sums of the dipoles of the molecular constituents, if unperturbed. Collision-induced changes in dipole moments are manifested in the dielectric and spectroscopic properties of bulk samples. For example, infrared and far infrared absorption processes that are single-molecule forbidden may be observed in compressed gases and liquids as a consequence of transient, collision-induced dipoles. Such pressure-induced far IR absorption has been observed experimentally in inert-gas mixtures [37-39], $H_2$ [38], $N_2$ [38,40-42], $O_2$ [38,40,41], $CH_4$ [43], and $SF_6$ [44] and forbidden near IR spectra have been studied for the diatomics, triatomics such as $CS_2$ [45], and other polyatomics. Useful information on dynamics in dense gases and liquids can be obtained by analyzing the lineshapes for single-molecule forbidden spectra (and for collision-induced contributions to allowed spectra), if the collision-induced dipoles are known as functions of intermolecular separation and relative orientation. In analyses to date, collision-induced dipoles for small molecule pairs have often been approximated as sums of classical multipolar contributions, with short-range anisotropic overlap corrections represented by parametrized exponential functions. At this stage, direct calculations of overlap effects on pair dipoles are needed in spectroscopic applications. It is also of interest to compare the calculated dipoles of van der Waals complexes in their equilibrium configurations with the dipoles determined experimentally by molecular beam electric resonance studies of the Stark effect on rotational transition frequencies characteristic of the complex [46,47]. Calculations or measurements of collision-induced dipoles provide information on molecular interactions complementary to that obtained from potential energy surfaces, and may indicate the relative importance of classical electrostatic interactions, charge transfer, and short-range overlap and exchange effects [48].

For molecules interacting at long range, only classical-multipole polarization (cf. [48]) and dispersion effects [49] contribute to the collision-induced change in dipole moment. The net dipole for well separated molecules can therefore be determined if values of the single-molecule multipole moments, polarizabilities, and nonlinear response tensors are known [50-55]. For molecules interacting at short range, definitive results can only be obtained by ab initio calculation [56-62]. Calculations including correlation effects have been performed for the pair dipoles of He...H [57,59,60], He...Ar, He...$H_2$, and $H_2$...$H_2$ [57], while calculations restricted to self-consistent field level are available for the dipoles of the inert-gas heterodiatoms Ne...Ar, Ne...Kr, and Ar...Kr [56,58], and for the Ne...HF dipole [48]. Quite large basis sets are usually needed in pair property calculations [61], with the consequence that the computational requirements are substantial. This prompts interest in approximations that yield good results in the region where overlap is small, but nonnegligible. Since numerical precision is most difficult to attain in ab initio calculations on molecules at intermediate and long range, approximations applicable near the van der Waals minimum may be used to join the known long-range forms of the interaction-induced dipole to ab initio results at short range. Additionally, quantum mechanical approximations for collision-induced properties provide information on the effects of long-range electrostatic interactions, overlap, exchange, hyperpolarization, and dispersion, which may prove useful in selecting basis sets for subsequent ab initio work.

To evaluate proposed approximations for pair properties, it is necessary to compare the results with the accurate ab initio results available for properties of small molecular pairs. Comparisons of ab initio and approximate collision-induced polarizabilities of H...H in the triplet state [62] and He...He [61] have been used to test electrostatic overlap models [63], exchange perturbation methods [62,64-66], polarizability density models [67-69], and exchange antisymmetrization approximations [70,71].

In this chapter, we report a calculation of the collision-induced dipole moment of He...H as a test of label-free exchange perturbation theory [72-75] at lowest order. The label-free exchange perturbation method constitutes a direct Rayleigh-Schrödinger perturbation theory with fully antisymmetrized zeroth-order wavefunctions. By construction in terms of projection operators, the unperturbed Hamiltonian and the perturbation term are individually invariant with respect to exchange of electrons between the interacting molecules. The label-free exchange perturbation formalism is reviewed briefly in section 3.2, for application in computing collision-induced dipoles. In section 3.3 the label-free theory is related to other exchange perturbation approximations, and the collision-induced dipole is shown to separate into polarization and exchange contributions. It is also shown that results for the pair dipole at zeroth-order in the label-free theory are identical to the results of an exchange-antisymmetrization approximation developed by Lacey and Byers Brown [70].

We have calculated the He...H dipole moment in two ways: first, by evaluating the expectation value of the dipole operator with the zeroth-order pair wavefunction; and second, by computing the energy for He...H in the presence of a uniform applied electric field and then differentiating with respect to the field to obtain the dipole. Also, we have carried out the calculations at two levels of approximation for the single-atom wavefunctions. In the first, 1s Slater orbitals are used on each center; and in the second, an extended Gaussian basis is used at each center. Evaluation of the dipole expectation value in the Slater basis has been reported previously by Buckingham [49] and by Mahanty and Majumdar [76]; we obtain identical results in this case and new results from the other three calculations. The methods of calculation and the selection of basis sets are described in section 3.4. Results are presented in section 3.5. We find that closest agreement with accurate *ab initio* results [57] is obtained from the Gaussian-basis calculations of the dipole as an energy derivative. Errors in the overlap dipole are typically 20-30% at this level of approximation. Significantly, the errors in this approximation appear to be smaller than the discrepancies between the two reported *ab initio* calculations of the He...H dipole [57,60].

## 3.2 EXCHANGE PERTURBATION THEORY IN LABEL-FREE FORM

For molecules interacting at short range, both polarization and exchange effects contribute significantly to the interaction energy and to interaction-induced changes in electric properties. The label-free exchange perturbation theory developed by Jansen [72-75] treats these effects within a direct Rayleigh-Schrödinger formalism. Projection operators are used to define an unperturbed Hamiltonian and a perturbation term that are separately invariant with respect to electron permutation. Also, within this formalism the expectation value of any dynamical variable for a cluster of interacting molecules can be separated into additive contributions from each of the molecules in the cluster.

The Hamiltonian H for interacting molecules A and B with a total of N electrons is

$$H = \sum_{j=1}^{N} \left( \frac{-\nabla_j^2}{2} - \sum_{a} \frac{Z_a}{r_{aj}} - \sum_{b} \frac{Z_b}{r_{bj}} \right) + \sum_{k<j} \frac{1}{r_{kj}} \qquad (1)$$

where $Z_a$ is the charge of nucleus a in molecule A, $Z_b$ is the charge of nucleus b in B, j and k are electron indices and $r_{qj}$ is the distance from electron j to nucleus q. Atomic units are used throughout this work, and the nuclear positions are assumed to be fixed.

To carry out a Rayleigh-Schrödinger perturbation expansion with a fully antisymmetrized pair wavefunction as the unperturbed wavefunction, an appropriate partitioning of the pair Hamiltonian into an unperturbed operator and a perturbation term must be found--but the electron labels (j = 1 to N) are not assigned exclusively to molecule A or to molecule B, and the antisymmetrized wavefunction is not an eigenfunction of the single-molecule

Hamiltonian corresponding to any fixed electron assignment. Within the label-free exchange perturbation formalism, this problem is resolved by splitting H into the unperturbed Hamiltonian

$$\hat{H}_0 = \sum_{i=1}^{p} \hat{H}_{0i} = \sum_{i=1}^{p} \left[H_{Ai}^{(0)} + H_{Bi}^{(0)}\right] \Lambda_i \ , \tag{2}$$

and the perturbation $\hat{V}$ due to molecular interactions,

$$\hat{V} = \sum_{i=1}^{p} V_i \Lambda_i . \tag{3}$$

In these equations $H_{Ai}^{(0)}$ is the Hamiltonian for the isolated molecule A, given that A has been assigned the $i^{th}$ possible set of $N_A$ electrons selected from the total of N (and similarly for $H_{Bi}^{(0)}$; $V_i$ represents the interaction-energy operator for the $i^{th}$ assignment of electrons to molecules A and B. The number of ways of assigning $N_A$ electrons to molecule A and $N_B$ to molecule B, from a total of $N_A + N_B$, is

$$p = \frac{(N_A + N_B)!}{N_A! \ N_B!} \tag{4}$$

The operator $\Lambda_i$ projects out the simple product term for the $i^{th}$ electron assignment, when applied to an antisymmetrized pair wavefunction. The zeroth-order wavefunction $\Psi_0$ is constructed by antisymmetrizing the product of the ground-state wavefunctions $\psi_A$ and $\psi_B$ for isolated A and B molecules:

$$\Psi_0 = f \sum_i \sigma_{P_i} P_i \left[\psi_A \psi_B\right] = f \sum_{i=1}^{p} \Phi_i \tag{5}$$

where f is a normalization constant and $\sum_i \sigma_{P_i} P_i$ is the intersystem antisymmetrizer. By definition the projection operator $\Lambda_i$ acting on $\Psi_0$ yields $f\Phi_i$.

If a uniform, static electric field $\underset{\sim}{F}$ is applied to the A B pair, the full Hamiltonian $\hat{H}_F$ is

$$\hat{H}_F = \hat{H}\ (\underset{\sim}{F} = 0) + \hat{H}'\ (\underset{\sim}{F}) \tag{6}$$

where $\hat{H}\ (\underset{\sim}{F}=0)$ is given by Eq. 1 and

$$\hat{H}'(\underset{\sim}{F}) = -\hat{\underset{\sim}{\mu}} \cdot \underset{\sim}{F} = -\underset{\sim}{F} \cdot \sum_{i=1}^{P} \underset{\sim}{\mu}_i \Lambda_i = -\underset{\sim}{F} \cdot \sum_{i=1}^{P} (\underset{\sim}{\mu}_i^A + \underset{\sim}{\mu}_i^B) \Lambda_i \tag{7}$$

The dipole operator $\underset{\sim}{\mu}_i$ is the same for all electron assignments i, but the dipole operators $\underset{\sim}{\mu}_i^A$ and $\underset{\sim}{\mu}_i^B$ for A and B depend upon the electron assignment.

At self-consistent field (SCF) level, the wave function for molecules A and B is given to first order in an applied field $\underset{\sim}{F}$ and zeroth order in the molecular interaction by

$$\Psi_0 = c_1^{-1/2}\ \tilde{\Phi}^{(0)} + \underset{\sim}{F} \cdot [\ c_1^{-1/2} \sum_{i=1}^{N} \underset{\sim}{\tilde{\Phi}}_i^{(1)} - \frac{1}{2}\ \underset{\sim}{c}_2 c_1^{-3/2}\ \tilde{\Phi}^{(0)}] \ . \tag{8}$$

The constants $c_1$ and $\underset{\sim}{c}_2$ are

$$c_1 = \langle \tilde{\Phi}^{(0)} |\ \tilde{\Phi}^{(0)} \rangle \tag{9}$$

$$c_{2\alpha} = 2 \sum_{i=1}^{N} \langle \tilde{\Phi}^{(0)} | \tilde{\Phi}_{i\alpha}^{(1)} \rangle \ . \tag{10}$$

$\tilde{\Phi}^{(0)}$ is an antisymmetrized product of unperturbed orbitals centered on A and B, and the tilde superscript indicates that the function has not been normalized. $\tilde{\Phi}_{i\alpha}^{(1)}$ is the antisymmetrized product with the unperturbed orbital i replaced by the first order correction to orbital i in an applied field $F_\alpha$ in the $\alpha$ direction. The vector $\underset{\sim}{\tilde{\Phi}}_i^{(1)}$ has components

$\tilde{\Phi}_{ix}^{(1)}$, $\tilde{\Phi}_{iy}^{(1)}$, and $\tilde{\Phi}_{iz}^{(1)}$.

To lowest order in the interaction, the total energy E of the A-B pair is

$$E = \langle\Psi_0|H|\Psi_0\rangle = E_A^{(0)} + E_B^{(0)} + c_1^{-1}\,\langle\tilde{\Phi}^{(0)}|\sum_{i=1}^{P} V_i\Lambda_i|\tilde{\Phi}^{(0)}\rangle +$$

$$+\underset{\sim}{F}\cdot\{2c_1^{-1}\langle\tilde{\Phi}^{(0)}|\hat{H}(\underset{\sim}{F}=0)|\sum_{j=1}^{N}\underset{\sim}{\tilde{\Phi}}_j^{(1)}\rangle - \underset{\sim}{c}_2 c_1^{-2}\langle\tilde{\Phi}^{(0)}|\hat{H}(\underset{\sim}{F}=0)|\tilde{\Phi}^{(0)}\rangle - \bar{\underset{\sim}{\mu}}\,\} \qquad (11)$$

where

$$\bar{\underset{\sim}{\mu}} = \langle\tilde{\Phi}^{(0)}|\sum_{i=1}^{P}\underset{\sim}{\mu}_i\;{}_i|\tilde{\Phi}^{(0)}\rangle c_1^{-1} \qquad (12)$$

Thus, to lowest order, the energy is the sum of three terms: first, the total energy $E_A^{(0)} + E_B^{(0)}$ for molecules A and B at infinite separation and in the absence of the applied electric field; second, a field-independent term equal to the A-B interaction energy to lowest order if exact wavefunctions $\Psi_A$ and $\Psi_B$ are used to construct $\Psi_0$ [77,78]; and third, a term linear in the applied field.

From the energy expression, the dipole moment may be obtained by differentiating with respect to the applied field:

$$\underset{\sim}{\mu} = \frac{-\partial E}{\partial\underset{\sim}{F}}\bigg|_{\underset{\sim}{F}=0} = \frac{-\partial}{\partial\underset{\sim}{F}}\langle\Psi_0|H|\Psi_0\rangle\bigg|_{\underset{\sim}{F}=0} = -\Big[\langle\frac{\partial\Psi_0}{\partial\underset{\sim}{F}}|H|\Psi_0\rangle +$$

$$+ \langle\Psi_0|\frac{\partial H}{\partial \underset{\sim}{F}}|\Psi_0\rangle + \langle\Psi_0|H|\frac{\partial\Psi}{\partial \underset{\sim}{F}}\rangle]_{\underset{\sim}{F}} = 0$$

$$= \bar{\underset{\sim}{\mu}} - 2c_1^{-1}\langle\tilde{\Phi}^{(0)}|\hat{H}(\underset{\sim}{F}=0)|\sum_{i=1}^{N}\tilde{\underset{\sim}{\Phi}}_i^{(1)}\rangle + c_1^{-2}\underset{\sim}{c}_2\langle\tilde{\Phi}^{(0)}|\hat{H}(\underset{\sim}{F}=0)|\tilde{\Phi}^{(0)}\rangle. \quad (13)$$

In Eq. (13) $\bar{\underset{\sim}{\mu}}$ is the dipole moment calculated directly as the expectation value of the dipole operator with the zeroth-order, zero-field wavefunction, as in Eq. 12. The remaining terms in Eq. (13) represent the non-Hellmann-Feynman contribution, which would vanish if $\Psi_0$ were exact.

In the label-free perturbation formalism, the operators $\hat{H}_0$ and $\hat{V}$ are not Hermitian individually, although the sum of the operators is Hermitian. As a result, the pair energy at first order in the interaction formally includes the correction term $\langle\Psi_0|H_0|\Psi_1\rangle$, which depends on the first-order change $\Psi_1$ in the pair wavefunction due to the perturbation V. Since this term is expected to be substantially smaller than the standard first-order energy shift $\langle\Psi_0|V|\Psi_0\rangle$ included in Eq. 11, the correction $\langle\Psi_0|H_0|\Psi_1\rangle$ is usually grouped with the leading second-order terms [72,73].

To second order, the interaction energy may be computed from $\Psi_1$ in a sum-over-states form [72], with contributions from the continuum generally nonnegligible [79]. Alternatively $\Psi_1$ may be approximated by finding the stationary vector of the functional (cf. [80])

$$J[\Psi] = \langle\Psi|H_0-E_0|\Psi\rangle + \langle\Psi_0|V^{\dagger}-E_1|\Psi\rangle + \langle\Psi|V-E_1|\Psi_0\rangle \quad (14)$$

subject to $\langle\Psi|\Psi_0\rangle = 0$. If $\delta J$ vanishes with an arbitrary variation $\delta\Psi$ of $\Psi$ away from the stationary vector $\tilde{\Psi}_1$, then the expansion coefficients $a_k$ for $\tilde{\Psi}_1$ satisfy

$$a_k = \frac{\langle \Phi_k | V | \Psi_0 \rangle + \frac{1}{2} \sum_{\ell \neq 0,k} a_\ell \left[ \langle \Phi_k | H_0 | \Phi_\ell \rangle + \langle \Phi_\ell | H_0 | \Phi_k \rangle \right]}{E_0 - E_k} \qquad (15)$$

in the basis $\Phi_k$ of orthogonalized, antisymmetrized product states for A and B at infinite separation. In the approximation that the sum on the right-hand side of Eq. 16 is negligible, $\tilde{\Psi}_1 = \Psi_1$. An equivalent approximation has been made by Jansen in a direct expansion of $\Psi_1$ in the basis $\Phi_k$ [72].

If $\Psi_0$ and $\Psi_1$ have been determined, then the sum of the unperturbed energy $E_0$, the full first-order energy $E_1$ (including the correction term $\langle \Psi_0 | H_0 | \Psi_1 \rangle$), and an approximate second-order energy $\tilde{E}_2$ for the A-B pair in an external field can be obtained from

$$E_0 + E_1 + \tilde{E}_2 = \langle \Psi_0 | H\,(\underset{\sim}{F} = 0) - \underset{\sim}{\mu} \cdot \underset{\sim}{F} \mid \Psi_0 \rangle + \langle \Psi_1 | V | \Psi_0 \rangle \ . \qquad (16)$$

The interaction-induced dipole may then be computed from the derivative of Eq. 16 with respect to $\underset{\sim}{F}$, as in Eq. 13.

In this work, the calculation of exchange-overlap contributions to the He...H pair dipole is based on Eqs. 11 and 12, which represent the lowest-order effects. The exchange-overlap terms fall off exponentially with increasing R. In contrast, the second-order dispersion contribution to the He...H dipole (present in $\underset{\sim}{\mu}$ derived from Eq. 16) varies as $R^{-7}$ at long range. This contribution originates in the correlations between the fluctuating charge moments on the H and He atoms, and it dominates the exchange-overlap contribution for sufficiently large R. Accordingly, in calculating the He...H dipole for internuclear distances R > 4.0 a.u., we have added the leading dispersion dipole to the lowest-order exchange-overlap dipole from Eq. 11 or 12. Higher-order polarization and exchange effects are neglected at this level of approximation for the pair dipole; overlap damping of the dispersion contribution and the effects of He-electron correlation on the He-H correlation and exchange energies are also neglected.

## 3.3. COMPARISON WITH OTHER EXCHANGE PERTURBATION METHODS

In this section the label-free exchange perturbation theory of interaction-induced properties is related to other exchange perturbation approaches. We show that the results from the label-free theory can be separated into polarization and exchange contributions [2,81-83]. We also show that the zeroth-order expression for the pair dipole in the label-free theory is identical to the exchange-antisymmetrization approximation used by Lacey and Byers Brown in calculations of inert-gas heterodiatom dipoles [70].

### 3.3.1 Exchange perturbation theory: Polarization and exchange contributions to interaction energies and pair properties

In one standard form of exchange-perturbation theory [81] the $n^{th}$ approximation to the wavefunction $\Psi_n$ and the $n^{th}$ approximation to the interaction energy $E_n$ of an A-B pair are obtained iteratively from

$$\Psi_n = \Phi_0 + R_0\,(E_n - V_1)\,\Psi_{n-1} \tag{17}$$

and

$$E_n = \langle\Phi_0|V_1|\Psi_{n-1}\rangle , \tag{18}$$

where $\Phi_0$ is the simple product of the ground-state wavefunctions $\psi_A$ and $\psi_B$, $V_1$ is the perturbation term for the assignment of the first $N_A$ electrons to molecule A and the remainder to B, and $R_0$ is the reduced resolvent

$$R_0 = \sum_{k\neq0} \frac{|\Phi_k\rangle\langle\Phi_k|}{E_k - E_0} . \tag{19}$$

The function $\Phi_k$ is the $k^{th}$ simple-product excited state of A and B at infinite separation and $E_k$ is the corresponding energy. The intermediate normalization $\langle\Phi_0|\Psi\rangle = 1$ has been imposed. Symmetry forcing is accomplished by choosing the normalized antisymmetrized product of $\psi_A$ and $\psi_B$ as the zeroth-order approximation $\Psi_0$ [2,65,66]. At first order the A-B interaction energy is the sum of a polarization term $E_1^{pol}$ and an exchange term $E_1^{exch}$:

$$E_1 = E_1^{pol} + E_1^{exch} = \langle\Phi_0|V_1|\Phi_0\rangle + \frac{\langle\Phi_0|V_1|P\Phi_0\rangle - \langle\Phi_0|V_1|\Phi_0\rangle\langle\Phi_0|P|\Phi_0\rangle}{1 + \langle\Phi_0|P\Phi_0\rangle}$$

$$= \frac{\langle\Phi_0|V_1|\Phi_0\rangle + \langle\Phi_0|V_1|P\Phi_0\rangle}{1 + \langle\Phi_0|P\Phi_0\rangle} , \qquad (20)$$

where P is the intersystem antisymmetrizer (see Appendix B).

In the label-free exchange perturbation theory, the interaction energy at first order is

$$E_1 = \langle\Psi_0|\sum_{i=1}^{P} V_i\Lambda_i|\Psi_0\rangle . \qquad (21)$$

This expression for $E_1$ may be simplified by splitting the full antisymmetrizer in $\Psi_0$ into terms that involve electron permutations within A, within B, and between A and B. In Appendix B, the permutation invariance of V is used to obtain

$$E_1 = \frac{1}{s}\left[\langle\psi_A\psi_B|V_1|\psi_A\psi_B\rangle + \langle\psi_A\psi_B|\sum_{i=2}^{P} V_i\Lambda_i|\mathcal{A}_A\mathcal{A}_B\sum_{j=1}^{\ell}\sigma_j P_j^{AB}\{\chi_1\ldots\chi_N\}\rangle\right] \quad (22)$$

The expressions for $\psi_A$ and $\psi_B$ have been restricted to the self-consistent field level, and the set $\{\chi_1\ldots\chi_N\}$ contains the orbitals occupied in the ground states of isolated A and B molecules. The operators $P_i^{AB}$ acting on $\{\chi_1\ldots\chi_N\}$ perform intersystem permutations only. In Eq. 22, $\mathcal{A}_A$ is the antisymmetrizer for electrons assigned to molecule A, $\mathcal{A}_B$ is the antisymmetrizer for B, $\sigma_i$ is the parity of the $i^{th}$ permutation among the total of $\ell$, and

$$s = 1 + \langle \Phi_0 | P\Phi_0 \rangle . \tag{23}$$

Thus the interaction energy at first order is given as the sum of the polarization contribution $\langle \Phi_0 | V_1 | \Phi_0 \rangle$ and an exchange correction. Each of the operators $\Lambda_i$ in the second term of Eq. 22 projects out the single term from the ket for which the assignment of electrons to A and B is consistent with the form $V_i$ for the perturbation. In the product $\psi_A \psi_B$ the first $N_A$ electrons are assigned to A and the remainder to B. Relabelling of dummy indices suffices to show that Eqs. 20 and 22 are identical. At first order, equivalent results are also obtained from variants of exchange-perturbation theory with stronger symmetry forcing [2,84-87].

The one-particle density matrix [88-90] can also be separated into two terms, one without electron exchange between A and B and a second with one or more interchange contributions. Consequently the expectation value of any single-particle operator decomposes into polarization contributions and exchange-overlap contributions [2]. McWeeny and Sutcliffe [89] and Magnasco, Musso, and McWeeny [91] have performed the separation explicitly for the one-electron part of the Hamiltonian for two interacting molecules. The analysis for the dipole moment operator is analogous.

### 3.3.2 Density-matrix perturbation theory

Lacey and Byers Brown have evaluated the dipole moments of several diatoms by first finding the density matrix associated with the normalized, antisymmetrized product $c_1^{-1/2}\,\tilde{\Phi}^{(0)}$ of the isolated atom wavefunctions [70]. The spinless electron density $\rho^{(0)}(\underset{\sim}{r})$ in the absence of an applied field is obtained from

$$\rho^{(0)}(\underset{\sim}{r}_1) = Nc_1^{-1} \int ds_1 \int d\underset{\sim}{x}_2 \ldots d\underset{\sim}{x}_N \, \tilde{\Phi}^{(o)}(\underset{\sim}{x}_1, \underset{\sim}{x}_2 \ldots \underset{\sim}{x}_N) \tilde{\Phi}^{(0)*}(\underset{\sim}{x}_1, \underset{\sim}{x}_2 \ldots \underset{\sim}{x}_N) \quad (24)$$

where $\tilde{\Phi}^{(0)}$ and $c_1$ are defined as in section 3.2, and $\underset{\sim}{r}$, s, and $\underset{\sim}{x}$ denote spatial variables, spin variables, and collective space-spin variables, respectively. The exchange-overlap dipole of the atom pair AB is then

$$\underset{\sim}{\mu} = - \int \underset{\sim}{r} \, \rho^{(0)}(\underset{\sim}{r}) \, d^3\underset{\sim}{r} + Z_A \underset{\sim}{r}_A + Z_B \underset{\sim}{r}_B . \quad (25)$$

At lowest order in the label-free perturbation theory, the expectation value of the dipole is identical to the Lacey-Byers Brown result. This equivalence can be shown explicitly starting from

$$\underset{\sim}{\mu} = \langle \Psi \mid \sum_{i=1}^{P} \underset{\sim}{\mu}_i \Lambda_i \mid \Psi \rangle \quad (26)$$

with the pair wavefunction $\Psi$ from Eq. 8. The operator $\underset{\sim}{\mu}_i$ is the same for each of the electron assignments i and

$$\sum_{i=1}^{P} \Lambda_i = 1 . \quad (27)$$

Thus

$$\underset{\sim}{\mu} = \langle \Psi \mid \underset{\sim}{\mu}_1 \mid \Psi \rangle$$

$$= - \int \underset{\sim}{r} \, \rho(\underset{\sim}{r}) \, d^3\underset{\sim}{r} + Z_A \underset{\sim}{r}_A + Z_B \underset{\sim}{r}_B \quad (28)$$

In terms of the applied field $\underset{\sim}{F}$

$$\rho(\underset{\sim}{r}) = \rho^{(0)}(\underset{\sim}{r}) + \underset{\sim}{F} \cdot \underset{\sim}{\rho}^{(1)}(\underset{\sim}{r}) + \mathcal{O}(F^2) \quad (29)$$

The electron density $\rho^{(0)}(\boldsymbol{r})$ for the AB pair in the absence of an applied field (determined from $\Psi$) is identical to $\rho^{(0)}(\boldsymbol{r})$ from Eq. 24, so the field-independent dipole is equal to $\boldsymbol{\mu}$ from Eq. 25.

It should be noted that this approach yields only the term $\bar{\boldsymbol{\mu}}$ in Eq. 13. At this level of approximation the Hellmann-Feynman theorem is not satisfied, and the pair dipole moment obtained by differentiating the energy differs from $\bar{\boldsymbol{\mu}}$.

The lowest-order correction to the pair electron density in an applied field satisfies

$$\boldsymbol{\rho}^{(1)}(\boldsymbol{r}_1) = N c_1^{-1} \sum_{i=1}^{N} \int ds_1 \int d\boldsymbol{x}_2 \ldots d\boldsymbol{x}_N \Big[ \tilde{\Phi}^{(0)}(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N)\, \tilde{\boldsymbol{\Phi}}_i^{(1)*}(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N) + \tilde{\boldsymbol{\Phi}}_i^{(1)}(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N)\, \tilde{\Phi}^{(0)*}(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N) \Big]$$

$$- N \boldsymbol{c}_2 c_1^{-2} \int ds_1 \int d\boldsymbol{x}_2 \ldots d\boldsymbol{x}_N\, \tilde{\Phi}^{(0)}(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N)\, \tilde{\Phi}^{(0)*}(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N) \;. \quad (30)$$

Substitution of this result for $\boldsymbol{\rho}^{(1)}(\boldsymbol{r})$ into Eqs. 28 and 29 gives an approximation for the exchange-overlap contribution to the pair polarizability.

## 3.4. COMPUTATIONAL METHODS.

In this section the methods used to approximate the He...H wavefunction and to calculate the pair dipole are described. In each of the calculations we have employed a wavefunction of the form given in Eq. 8 for the He-H pair in an applied field in the z direction

$$\tilde{\Psi} = \tilde{\Phi}^{(0)} + F_z \sum_{i=1}^{3} \tilde{\Phi}_i \qquad (31)$$

with $$\tilde{\Phi}^{(0)} = \frac{1}{\sqrt{2}} \sum_P \sigma_P P\{\chi_H^{(0)}(1)\, \chi_{He}^{(0)}(2)\, \bar{\chi}_{He}^{(0)}(3)\} \qquad (32)$$

prior to normalization. P runs over all the elements of the symmetric group $S_3$ and $\sigma_P = \pm 1$ depending on the parity of P. The functions $\tilde{\Phi}_i$ are defined by

$$\tilde{\Phi}_1^{(1)} = \chi_H^{(1)}(1)\psi^{(0)}(2,3) - \chi_H^{(1)}(2)\, \psi^{(0)}(1,3) + \chi_H^{(1)}(3)\, \psi^{(0)}(1,2) \qquad (33.a)$$

$$\tilde{\Phi}_2^{(1)} = \chi_H^{(0)}(1)\, \Psi_1^{(1)}(2,3) - \chi_H^{(0)}(2)\, \psi_1^{(1)}(1,3) + \chi_H^{(0)}(3)\, \psi_1^{(1)}(1,2) \qquad (33.b)$$

$$\tilde{\Phi}_3^{(1)} = \chi_H^{(0)}(1)\, \psi_2^{(1)}(2,3) - \chi_H^{(0)}(2)\, \psi_2^{(1)}(1,3) + \chi_H^{(0)}(3)\, \psi_2^{(1)}(1,2) \qquad (33.c)$$

$$\psi^{(0)}(1,2) = \frac{1}{\sqrt{2}} \{ \chi_{He}^{(0)}(1)\, \bar{\chi}_{He}^{(0)}(2) - \bar{\chi}_{He}^{(0)}(1)\, \chi_{He}^{(0)}(2) \} \qquad (34.a)$$

$$\psi_1^{(1)} = \frac{1}{\sqrt{2}} \{\chi_{He}^{(1)}(1)\, \bar{\chi}_{He}^{(0)}(2) - \bar{\chi}_{He}^{(0)}(1)\, \chi_{He}^{(1)}(2)\} \qquad (34.b)$$

$$\psi_2^{(1)} = \frac{1}{\sqrt{2}} \{\chi_{He}^{(0)}(1)\bar{\chi}_{He}^{(1)}(2) - \bar{\chi}_{He}^{(1)}(1)\chi_{He}^{(0)}(2)\} \qquad (34.c)$$

In each of the terms above, $\chi(i)$ represents $\chi(\underset{\sim}{r}_i)\alpha(i)$ and $\bar{\chi}(i)$ represents $\chi(\underset{\sim}{r}_i)\beta(i)$, where $\alpha$ and $\beta$ denote spin states. $\chi_q^{(0)}$ is the lowest-energy atomic orbital for an isolated atom q and $\chi_q^{(1)}$ is the first-order correction to $\chi_q^{(0)}$ for a single q atom in an applied field in the z direction.

Within the label-free exchange perturbation theory, the z component of the He...H pair dipole can be expressed as a sum of H-atom and He-atom dipoles:

$$\langle\mu_z\rangle = \langle\mu_z^{H}\rangle + \langle\mu_z^{He}\rangle \; . \tag{35}$$

To lowest order in the atomic interaction and to first order in the applied field $F_z$,

$$\langle\mu_z^{H}\rangle = N^2(F_z)\;\{\langle\tilde{\Phi}^{(0)}|\hat{\mu}_z^{H}|\tilde{\Phi}^{(0)}\rangle + F_z\sum_{j=1}^{3}\langle\tilde{\Phi}^{(0)}|\hat{\mu}_z^{H}|\tilde{\Phi}_j^{(1)}\rangle + F_z\sum_{j=1}^{3}\langle\tilde{\Phi}_j^{(1)}|\hat{\mu}_z^{H}|\tilde{\Phi}^{(0)}\rangle\} \tag{36}$$

and

$$\langle\mu_z^{He}\rangle = N^2(F_z)\;\{\langle\tilde{\Phi}^{(0)}|\hat{\mu}_z^{He}|\tilde{\Phi}^{(0)}\rangle + F_z\sum_{j=1}^{3}\langle\tilde{\Phi}^{(0)}|\hat{\mu}_z^{He}|\tilde{\Phi}_j^{(1)}\rangle\;\} + F_z\sum_{j=1}^{3}\langle\tilde{\Phi}_j^{(1)}|\hat{\mu}_z^{He}|\tilde{\Phi}^{(0)}\rangle\} \tag{37}$$

where $N^2(F_z) = c_1^{-1}(1 - F_z c_{2z} c_1^{-1})$ and $c_{2z}$ is the z component of $\underset{\sim}{c}_2$ given by Eq. 10 with N=3. If the origin of the coordinate system coincides with the H nucleus and the He nucleus is located at R on the +z axis,

$$\hat{\mu}_z^{H} = -\sum_i z_i \Lambda_i \tag{38}$$

and

$$\hat{\mu}_z^{He} = -\;[\;(z_2 + z_3 - 2R)\,\Lambda_1 + (z_1 + z_3 - 2R)\,\Lambda_2 + (z_1 + z_2 - 2R)\,\Lambda_3\;]. \tag{39}$$

The result for $\langle\mu_z\rangle$ is then

$$\langle\mu_z\rangle=\frac{S_{HHe}^{00}}{1-S_{HHe}^{00\,2}}[2z_{HHe}^{00}-RS_{HHe}^{00}]+F_z\frac{2}{1-S_{HeH}^{00\,2}}[-RS_{HHe}^{00}(S_{HHe}^{01}+S_{HHe}^{10})+$$

$$+z_{HeH}^{00}(S_{HeH}^{01}+S_{HeH}^{10})-z_{HH}^{10}+$$

$$+z_{HHe}^{10}S_{HeH}^{00}-z_{HeHe}^{10}(2-S_{HHe}^{00\,2})$$

$$+z_{HeH}^{10}S_{HHe}^{00}+\frac{S_{HHe}^{00}}{1-S_{HHe}^{00\,2}}[2z_{HHe}^{00}-RS_{HHe}^{00}](S_{HeH}^{01}+S_{HeH}^{10})S_{HeH}^{00}\ \} \qquad (40)$$

where

$S_{ab}^{ts}=\langle\chi_a^{(t)}|\chi_b^{(s)}\rangle$ and $z_{ab}^{ts}=\langle\chi_a^{(t)}|z|\chi_b^{(s)}\rangle$ ; $t,s = 0$ or $1$; $a,b =$ H or He .

The field-independent term yields the approximate zero-field pair dipole (and the term linear in $F_z$ approximates the exchange-overlap contribution to the zz component of the pair polarizability tensor.

It has been suggested [92] that calculating the energy of the He-H pair in an applied field $F_z$ and then differentiating with respect to $F_z$ in order to find the dipole (Eq. 13) should yield more accurate results than a direct calculation as an expectation value (from the field-independent term of Eq. 28). In general, though, no a priori choice between the two methods is possible, and we have performed calculations to test each of the methods. The explicit expression obtained from Eq. 11 for the He-H pair energy (to first order in the atomic interaction and first order in the applied field $F_z$) is given in Appendix C.

We have obtained wave functions for the isolated atoms in an external field at two levels of approximation. The A.O.'s $\chi$ are constructed with

Slater bases in the first approximation and with Gaussian bases in the second. In the Slater basis, $\chi_H^{(0)}$ is the H-atom 1s orbital, and the first order correction to the hydrogenic wave function $\chi_H^{(1)}$ is found analytically[93]. $\chi_H^{(1)}$ can be expressed in terms of modified $2p_z$ and $3p_z$ Slater orbitals:

$$\tilde{\chi}_H^{(1)} = \frac{-1}{\sqrt{\pi}} e^{-r} (1+\frac{r}{2}) r \cos\theta \tag{41}$$

In the first approximation for He [76], we use the optimal 1s Slater-orbital for $\chi_{He}^{(0)}$ and the unperturbed wave function $\psi_{He}^{(0)}$ satisfies

$$\psi_{He}^{(0)} = \frac{1}{\pi\sqrt{2}} \zeta^3 \exp[-\zeta(r_1+r_2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)] \tag{42}$$

with $\zeta = 27/16$. The first order correction to the He wave function is approximated variationally by minimizing

$$I=\int d^3r_1 d^3r_2 [\frac{1}{4} \underset{\sim}{\nabla}_1 \psi_{He}^{(1)} \cdot \underset{\sim}{\nabla}_1 \psi_{He}^{(1)} + \frac{1}{4} \underset{\sim}{\nabla}_2 \psi_{He}^{(1)} \cdot \underset{\sim}{\nabla}_2 \psi_{He}^{(1)} + (\frac{1}{2r_{12}} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{2} (\frac{27}{16})^2) \psi_{He}^{(1)^2}$$

$$+(z_1+z_2)F_z \psi_{He}^{(0)} \psi_{He}^{(1)}] \tag{43}$$

using a trial wave function of the form $\psi_{He}^{(1)} = \xi H^{(1)} \psi_{He}^{(0)}$

with $H^{(1)} = (z_1+z_2)F_z$.

(The subscripts 1 and 2 in the functional I refer to the electrons in the He atom.) The value obtained for the variational parameter is $\xi = -0.72231$, and

$$\tilde{\chi}_{He}^{(1)} = \zeta z \chi_{He}^{(0)} \tag{44}$$

In the calculations at this level of approximation, the matrix elements appearing in Eqs. C.1-C.11 for the pair energy and in Eq. 40 for the pair dipole were evaluated by use of standard formulas for integrals involving Slater orbitals [94-102] (see Appendix D for a hybrid integral involving the modified Slater orbital $3p_z$).

In the second approximation SCF calculations were performed for He and H using uncontracted bases of ten s Gaussian functions to determinc $\chi^{(0)}$. The Gaussian orbital exponents [103] and the calculated coefficients for each of the functions are given in the Table. The calculated ground state energies are -2.8616692 a.u. for the He atom and -0.49999862 a.u. for the H atom. As outlined below, $\chi_H^{(1)}$ was determined from a series of SCF calculations on the H atom, with a bare positive electric charge placed on the z axis at a distance ranging from 45 a.u. to 60 a.u. from the H nucleus [104]; $\chi_{He}^{(1)}$ was determined in the same way. An uncontracted Gaussian basis set of six p functions was used for each atom, together with a single contracted function $\chi^{(0)}$ formed from the ten s functions with contraction coefficients from the Table. The orbital exponents of the p Gaussian functions for hydrogen [105] and helium [62] are also listed in this Table. The p function coefficients obtained directly from the SCF calculation reflect linear and nonlinear polarization of the atoms by the field $\underset{\sim}{F}$ and field gradients $\underset{\approx}{F}'$, $\underset{\approx}{F}''$... of the point charge. To fix $\chi^{(1)}$, it is necessary to determine the contribution to each coefficient that is first order in the electric field $F_z$. This contribution was obtained by fitting each contraction coefficient $c_i$ to the expansion

$$c_i = c_i^{(1)} F_z + c_i^{(2)} F_z^3 + c_i^{(3)} F_z F'_{zz}. \tag{45}$$

The resulting $c_i^{(1)}$ values are listed as the p contraction coefficients in the Table .

As a check on the quality of the Gaussian bases, we have calculated the atomic polarizabilities of H and He. For the H atom the Gaussian basis yields $\alpha = 4.4989$ a.u., while the exact value is $\alpha = 9/2$. For He, in the Gaussian basis $\alpha = 1.3087$ a.u. More accurate values for the He polarizability from near Hartree-Fock calculations differ by less than 2% from this result [61,106,107].

The integrals needed in the Gaussian basis calculations were performed using the program SOINTS, written by R. Pitzer (Ohio State University) and maintained by the Argonne National Laboratory Theoretical Chemistry Group.

## TABLE 1

Orbital exponents and contraction coefficients of the Gaussian basis (10s 6p) on each atom

| | | H | | He | |
|---|---|---|---|---|---|
| Function | Type | Exponent | Coefficient (Normalized) | Exponent | Coefficient (Normalized) |
| 1 | s | 1170.498 | $7.37776139.10^{-5}$ | 3293.694 | $9.59977811\cdot10^{-5}$ |
| 2 | s | 173.5822 | $5.83581828\cdot10^{-4}$ | 488.8941 | $7.61241309\cdot10^{4}$ |
| 3 | s | 38.65163 | $3.18288336\cdot10^{-3}$ | 108.772 | $4.11477457\cdot10^{-3}$ |
| 4 | s | 10.60720 | $1.38031549\cdot10^{-2}$ | 30.1799 | $1.72174980\cdot10^{-2}$ |
| 5 | s | 3.379649 | $4.89937724\cdot10^{-2}$ | 9.789653 | $5.70398703\cdot10^{-2}$ |
| 6 | s | 1.202518 | $1.42487999\cdot10^{-1}$ | 3.522610 | $1.49210258\cdot10^{-1}$ |
| 7 | s | 0.463925 | $3.12524622\cdot10^{-1}$ | 1.35436 | $2.82269836\cdot10^{-1}$ |
| 8 | s | 0.190537 | $4.13000752\cdot10^{-1}$ | 0.5561 | $3.59695130\cdot10^{-1}$ |
| 9 | s | 0.0812406 | $2.02671433\cdot10^{-1}$ | 0.2409 | $2.51503899\cdot10^{-1}$ |
| 10 | s | 0.0285649 | $7.74758325\cdot10^{-3}$ | 0.10795 | $5.17599605\cdot10^{-2}$ |
| 11 | p | 3.009711 | $-1.5993250\cdot10^{-2}$ | 6.6 | $-2.4617864\cdot10^{-3}$ |
| 12 | p | 0.710128 | $-1.4338116\cdot10^{-1}$ | 2.1957216 | $-1.9220719\cdot10^{-2}$ |
| 13 | p | 0.227763 | $-8.7766919\cdot10^{-1}$ | 0.5693178 | $-1.4916053\cdot10^{-1}$ |
| 14 | p | 0.0812406 | $-1.4154398$ | 0.4223072 | $-2.4362999\cdot10^{-3}$ |
| 15 | p | 0.0356520 | $-1.3241078\cdot10^{-1}$ | 0.2007022 | $-3.4883846\cdot10^{-1}$ |
| 16 | p | 0.0154420 | $-3.0605474\cdot10^{-2}$ | 0.0799030 | $-1.0301889\cdot10^{-1}$ |

## 3.5. - RESULTS AND DISCUSSION

The He...H dipole obtained by differentiating the interaction energy with respect to an applied field (Eq. 13) shows a roughly exponential dependence on internuclear separation in the range 4 a.u. $\lesssim$ R $\lesssim$ 8 a.u. This range extends beyond the van der Waals minimum near 7 a.u. [60]. In the Gaussian basis, the dipole from Eq. 13 reaches a local maximum at very short range (R ~ 0.6 a.u.), and vanishes as R approaches zero, as expected. At short range, where the dipole is determined primarily by overlap and exchange effects, the polarity is $He^+H^-$, consistent with the rule that the larger atom is negative [49]. At long range, the pair dipole results entirely from dispersion effects, and its sign changes to $He^-H^+$. Asymptotically [49,53,54]

$$\mu(R) = D_7R^{-7} + D_9R^{-9} + . . . \tag{46}$$

As noted in section 3.3, we have approximated the pair dipole by adding the leading dispersion term (with $D_7$ = 120 a.u. [53,54]) to the exchange-overlap dipole calculated from Eq. 13 or from Eq. 12 (i.e., by direct calculation of $\bar{\underset{\sim}{\mu}}$ alone). In the Gaussian-basis calculations using Eq. 13, the dipole changes sign at R ~ 8.7 a.u.

Ab initio calculations of the He...H dipole including correlation effects have been reported by Bender and Davidson for the single internuclear distance R = 3.0 a.u. [59], by Ulrich, Ford and Browne for the R range from 0.5 to 20.0 a.u. [60]; and by Meyer for R between 5.0 and 11.0 a.u. [57]. At intermediate and long range, there are substantial differences between the available ab initio results. The dipole calculated by Ulrich et al. changes sign at R ~ 7 a.u., while the dipole obtained by Meyer does not change sign until R reaches ~ 8.5 a.u. Between 9.5 and 11.0

a.u., Meyer's results approach the known long-range form of the dipole closely. In contrast, the dipole calculated by Ulrich et al. exceeds the leading dispersion dipole by a factor of ~ 6 in this R range. For He-H distances between 6.0 a.u. and 11.0 a.u., Meyer's results are used as the basis for assessing our approximations, and the results of Ulrich et al. are used at shorter range.

Our results for the He...H dipole are plotted for comparison with the ab initio dipole in Figs. 1 and 2. The long-range form is also shown in Fig. 1. Our approximation exhibits the same qualitative features as the ab initio dipole. Fig. 1 shows that the results obtained by differentiating the interaction energy with respect to the applied field to find the overlap dipole (Eq. 13) and then adding the asymptotic dispersion correction agree quite closely with Meyer's results in the range from 4 a.u. to 11 a.u. In fact, the discrepancies between Meyer's results and this approximation are smaller than the discrepancies between the two sets of ab initio results [57,60]. Relative to Meyer's values, our closest approximation is typically in error by 20-30% over the range from 4 a.u. to 11 a.u. The remaining differences result from neglect of the higher-order exchange, dispersion, and orbital distortion effects, overlap damping of dispersion (cf. [108-111]), and the effects of intra-atomic correlation in He on the He-H exchange and dispersion dipole. Some cancellation of error occurs, since the omitted effects are not all of the same sign. The error is $\lesssim$ 5% at R = 4.0 a.u., ~20% at R = 7.0 a.u. (the van der Waals minimum), and $\lesssim$ 5% at R = 11.0 a.u. It is large (roughly a factor of 2) at R = 8.0 a.u., but near this point large relative error can result from a slight displacement of the zero of $\mu(R)$ between the accurate and approximate analyses.

Computing the expectation value of the dipole with the zeroth-order antisymmetrized wavefunction (Eq. 12) gives a smaller exchange-overlap dipole than that found by differentiating the energy with respect to an applied field (Eq. 13). The latter approach yields better results. It is interesting that the ab initio value of the pair dipole lies between the Gaussian-basis values obtained from Eq. 12 and those obtained from Eq. 13 for exchange-overlap effects, (with the dispersion correction added in each case), when $R<9.5$a.u.

As R decreases from 5.0 to 1.0 a.u., the dipole moment increases rapidly. Low-order perturbation theory breaks down at short range, and the exchange-overlap contribution to the dipole is overestimated by Eq. 13. The level of agreement between the results of Eq. 13, evaluated either with the Slater basis or with the Gaussian basis, and the results of Ulrich et al. for $R < 4$ a.u. is surprisingly high, as Fig. 2 shows. This agreement must be fortuitous. The local maximum in $\mu(R)$ occurs at larger R (near 1.0 a.u.) in the ab initio calculations than in the approximate work, and the value of $\mu(R)$ from Eq. 13 is smaller at the maximum. In the Slater-basis calculations with Eq. 13, we did not find a local maximum in $\mu(R)$ over the range of R values studied. At short range, the dipole computed from Eq. 12 is substantially smaller than the ab initio dipole. On the scale of Fig. 2, results from Eq. 12 are essentially unaffected by the choice of the Slater or Gaussian basis.

The dipole obtained by differentiating the energy with respect to an applied field (Eq. 13) differs from the expectation value of the dipole moment (Eq. 12) by the correction term $\Delta\mu_z$ [112]

$$\Delta\mu_z = \frac{\partial E}{\partial F_z}\bigg|_{\underset{\sim}{F}=\underset{\sim}{0}} - \langle\Psi_0|\frac{\partial H}{\partial F_z}|\Psi_0\rangle\bigg|_{\underset{\sim}{F}=\underset{\sim}{0}} \tag{39}$$

This term is nonvanishing because the Hellmann-Feynman theorem is not satisfied at lowest order in label-free exchange perturbation theory. The ratio of the correction term $\Delta\mu_z$ to the total dipole calculated from Eq. 13 is plotted in Fig. 3 for both the Gaussian basis and for the Slater basis. Comparison of the dipoles calculated with Eqs. 12 and 13 provides one indicator of the uncertainty in the results. Calculations of $\Delta\mu_z$ have been used previously to indicate uncertainties in the correlation contributions to molecular dipoles, in cases where the wavefunction at self-consistent field level approaches the Hartree-Fock limit. In this work, $\Delta\mu_z$ is definitely smaller for the Slater basis (see Fig. 3), but the results from the Gaussian basis and Eq. 13 agree more closely with Meyer's work.

At lowest order in the label-free exchange perturbation theory, for the He...H dipole we have found better agreement with accurate ab initio results when the dipole is determined by differentiating the pair energy with respect to an applied field than when the dipole is computed directly as an expectation value. The dipole calculated as an energy derivative is significantly larger than the dipole calculated from the expectation value (by factors as large as 4 for Gaussian-basis calculations in the range 4.0 a.u. $< R <$ 7.0 a.u.). In this context, it is interesting to compare recent self-consistent field (SCF) results [56] for inert-gas heterodiatom dipoles with estimates based on the exchange-antisymmetrization approximation developed by Lacey and Byers Brown, since the exchange-antisymmetrization approximation is equivalent to a direct calculation of the dipole expectation value with the zeroth-order wavefunction. The SCF results exceed the exchange-antisymmetrization estimates by ~ 60% for Ne...Ar for internuclear distances between 4.0 and 6.0 a.u., and by ~ 50% for Ne...Kr (with smaller differences for other pairs). Although the discrepancies are significantly smaller than for He...H, they are of the same sign. Improved agreement with SCF results might be obtained from exchange-perturbation calculations that employ energy derivatives. Results for the He...H dipole suggest that the label-free exchange perturbation method can provide a useful approximation for collision-induced properties in the region of charge overlap.

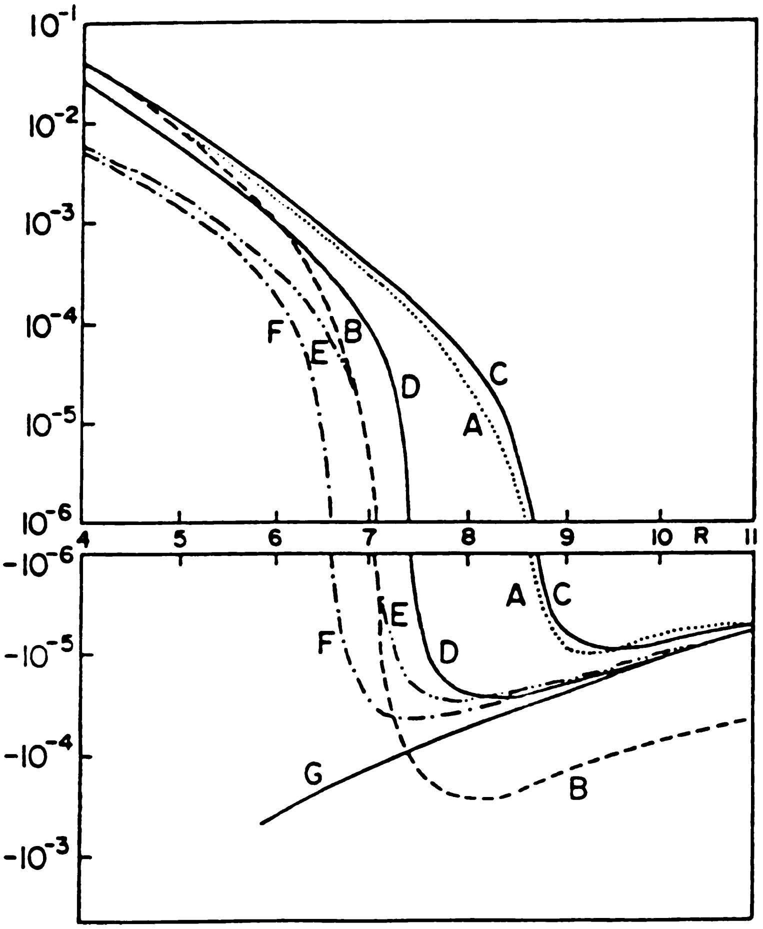

Fig. 1. Collision-induced dipole of He...H as a function of the internuclear separation R in the range from 4.0 to 11.0 a.u. Curve A shows the <u>ab initio</u> results obtained by Meyer, and Curve B the <u>ab initio</u> results of Ulrich <u>et</u> <u>al</u>. Curves C and D have been obtained by adding the long-range dispersion dipole to the exchange-overlap dipole computed form the energy derivative (Eq. 13). Curve C shows the dipole in the Gaussian basis, and D the dipole in the Slater basis. Curves E and F have been obtained similarly, but the exchange-overlap dipole has been computed as an expectation value from Eq. 12; Curve E shows results from the Gaussian basis, F from the Slater basis. Curve G is a plot on the leading term of the dispersion dipole, $D_7R^{-7}$. The ordinate is scaled logarithmically and the dipole $\mu(R)$ is given in a.u.

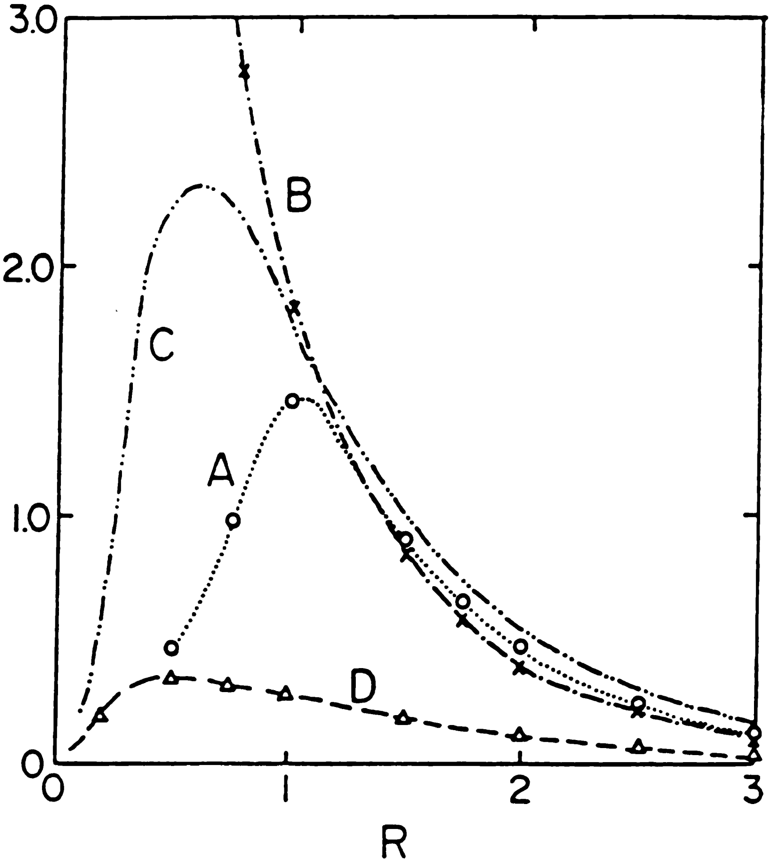

Fig. 2. Collision-induced dipole of He...H as a function of internuclear separation R in the range from 0 to 4.0 a.u. Curve A shows the *ab initio* results of Ulrich *et al*. Curve B and C show the lowest-order exchange-overlap dipole, obtained from Eq. 13, B in Slater basis and C in Gaussian basis. Curve D shows the exchange-overlap dipole computed as an expectation value with the zeroth-order wavefunction; results from the Gaussian and Slater bases superimpose on this scale. The dipole $\mu(R)$ is given in a.u.

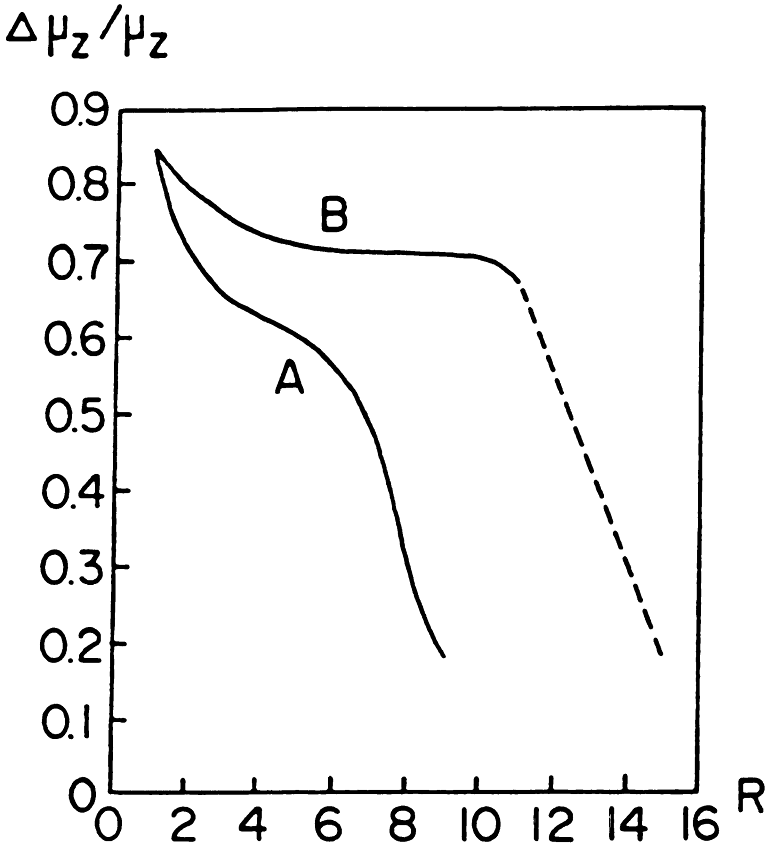

Fig. 3. Ratio of the correction term $\Delta\mu_z$ to the exchange-overlap dipole for He...H, plotted as a function of the internuclear separation R (in a.u.). The exchange-overlap dipole has been computed as the derivative of the first-order interaction energy with respect to an applied field. Curve A shows the results from the Slater-basis calculation, and Curve B the results from the Gaussian basis.

# CHAPTER 4.

## 4.1. INTRODUCTION

Absorption in the IR region of the spectrum by non-polar fluids is a collision-induced phenomenon [115], and a number of molecular properties may be determined from the spectra [116]. Collision-induced IR spectra have been studied for atoms and non-polar molecules [37-38, 40-41, 117-119]. Furthermore, cooperative many-particle effects in polar fluids affect the absorption line shape in this region of the spectrum. Experiments have been performed [120] in order to ascertain the importance of the collision-induced absorption relative to the absorption associated with the permanent dipole.

Both the intermolecular potential and the interaction-induced dipole are needed [121] as functions of the intermolecular separation and relative orientation in the calculation of the absorption line shape. Pairwise additivity of the potential is usually assumed [122] in the simulation of collision dynamics, but higher order or nonadditive effects [81,123-124] play an important rôle in many physical situations. For example, the inclusion of three-body forces is known [125-126] to bring results of molecular dynamics simulations into closer agreement with experimental data. Molecular dynamics simulations with many-body potential functions have been suggested [127]. Some calculations [73,128] have been reported with long-range triple dipole potentials [129-130]. When the intermolecular interaction is expanded in a Taylor series, the first nonadditive part of the third-order perturbation energy of three nonoverlapping molecules is the triple-dipole potential. Nonpolar species can have a triple-dipole potential; if we consider three indentical rare gas atoms a, b and c, an instantaneous dipole on atom a polarizes b, whose dipolar field perturbs c, and the dipole on c interacts with a. The long-range triple-dipole energy may be written as a sum-over-states expression [129] or as an integral over imaginary frequencies [130]. Bounds to the three-body long-range interaction coefficients have been obtained [131] for a number of atoms. It was established [132c] in the Drude model approximation that the triple-dipole energy term is a good approximation to the long-range nonadditive energy for the rare gas crystals, for the many-body terms that involve more than three bodies in the dipole interaction approximately cancel the remaining three-body multiple interaction terms. Nevertheless, the addition of higher order contributions than the triple-dipole term was later claimed [133] to be necessary for Xe. A combination of two-body Lennard-Jones and three-body triple-dipole and experimental exchange-overlap potentials has been used [134] in the study of atomic cluster growth. The relevance of nonadditive interactions has prompted the generalization [135] of the correction to the basis-set-superposition error for the calculation of many-body effects [136-138]. Also, nonadditive effects in the potential have been studied for hydrogen [129,139-140] and rare gases [73,135,137,141-153].

Barker <u>et</u> <u>al</u>. [154-158] have claimed with the support of experimental data that overlap-dependent many-body interactions in rare gases must be irrelevant. However, the fact that the addition of long-range three-body interactions to the pair potential brings calculated properties of rare gases into agreement with experimental data does not in itself provide a high degree of physical insight [159] into the nature of the interactions. While the three-body exchange terms are considerably smaller than the two-body [132d] at distances corresponding to the minimum of the van der Waals potentials, the three-body exchange contribution is significant [137,160-161] when it is compared with the triple-dipole energy [129]. Although an overlap-dependent modification of the long-range forces [132a,162-163] has been used to explain the stability of the different rare gas solid structures, three-body exchange energy had earlier been considered crucial by Jansen et al. [164-171] in explaining the polymorphism of the rare gas and another isoelectronic solids. In spite of points made [172] in reply to criticisms [173], it has been suggested later [132a-b, 174] that Jansen et al. overestimated the nonadditive exchange contributions. The unavailability of reliable information on many body forces has prompted their accurate quantum mechanical computation [156,174], consistently to some specified order of magnitude [174]. Despite Barker's remarks [157-158] and the interpretive challenge posed [158] by the agreement of experimental data and results of calculations that omit three-body exchange effects, it is believed [127, 153, 174-177] that overlap-dependent three-body forces cannot be fully disregarded and that they alone or in combination with other many-body effects may be the cause of discrepancies between experimental data and calculations of the dynamic structure factor and other properties [127,178]. Furthermore, it does not seem totally convincing to argue that overlap-dependent contributions are made irrelevant by the small statistical weight of regions where overlap is important, given that these contributions may be very large in those regions (orders of magnitude larger than in the statistically favored regions).

The moment induced in a group of three atoms or molecules introduces three-body effects in the ternary absorption coefficient [115,179]. This coefficient has been calculated [180] from experimental data for $CO_2$. Pair additivity in the dipole moment is usually assumed in dynamics calculations [39,181], but it has been suggested that many-body effects associated with the irreducible triplet dipole moment must be included in order for the calculated collision-induced absorption to reproduce the experimental line shapes [39,182]. Although binary collisions are the most important [183] at sufficiently low densities, the irreducible triplet dipole moment must make the leading contribution to absorption by monatomic unicomponent gases. Buckingham stated [184] that a set of three spherically symmetrical charge distributions should be polar due to induced moments, hence capable of absorbing electromagnetic radiation in the IR region of the spectrum. A model has been proposed [185] to calculate the spectrum due to ternary collisions in pure rare gases. Studies on the triplet dipole moment [186] have yielded the long range contribution as a power series of the internuclear distances. The coefficients of the leading terms have been calculated [187-188] for three hydrogen and three helium atoms, and the dispersion triplet dipole moment has been evaluated [189] for the Drude model. A variational method has been used [190] in order to explore the dipole moment of a hypothetical model neutral system with one electron in the field of three identical nuclei with a fractional charge each. The effects of applied pressure [191] and many-body effects [181,192-195] on interaction-induced depolarized light scattering [196] have also been discussed and calculations have been performed [197] to determine the triplet polarizability of helium.

A system of three hydrogen atoms in its quartet state is a good candidate to study three-body effects on the dipole moment with no interference from two-body contributions, and, in general to model interaction-related properties or potentials for three closed shell atoms. Nonadditivity in the potential energy has been studied [140,198-201] for spin-polarized $H_3$, and the potential energy curves [199,201-204] and the Axilrod-Teller triple-dipole term [139,205] have been calculated at different levels of approximation. Hecht [206] predicted that gas or liquid completely spin polarized hydrogen would be endowed with superfluid behavior, and that it would recombine at densities where the three-body collisions became important unless an external magnetic field precluded such recombination. Monte Carlo calculations of bulk properties showed [207-208] that the system would exist as a gas ($^1H$,$^2H$) or liquid ($^3H$), and liquid-to-gas and solid-to-gas phase transitions were studied [209-211] subsequently. Measurements on completely polarized atomic hydrogen at low temperatures have been reported [212-218], transport properties [219-220] have been determined, and the quantum Boltzmann equation [221] has been established for the gas in a regime where only binary collisions are important. Three-particle recombination has been considered [222] in the kinetics studies of the polarized gas, and experimental evidence for such a process has been reported [223-225]. In order to achieve Bose-Einstein condensation, magnetic confinement of the gas is under investigation [226].

Label-free exchange perturbation theory [74-75,168,172,227] has been applied to the study of interaction energies [73,168,171-172], interaction-induced molecular properties [76,228], and hyperfine structre spectral line shifts [75]. A reformulation of the label-free exchange perturbation theory has been proposed [229] since model calculations for a non-interacting system [230] suggested that the original formulation [227] could not be satisfactory in practice. Further calculations [75,228] have shown that this method can be useful in approximating interaction-induced properties when overlap is non-negligible. We derive in Section 4.2 the expression for the dipole moment of $H_3$ in its quartet spin state. Although the Hellmann-Feynman theorem is not satisfied at this level of approximation, for this system it can be shown that the dipole moment calculated as an energy derivative will be more accurate than the dipole calculated as an expectation value (section 4.2). It has been established [228] that the Lacey and Byers Brown method [70], which gives the lowest-order expectation value, accounts for only a small part of the exchange-overlap pair dipole moment. We conclude on the grounds of the treatment given in Section 4.2 that the Lacey-Byers Brown method provides no information at all about the dipole moment of certain triplets of identical atoms. Furthermore, the Gaussian model yields in both its original [164,166,231] and modified [232] forms an electron density which renders the exchange-antisymmetrization dipole moment [70] equal to zero for any cluster of identical atoms. The second-order dispersion triplet dipole moment has already been calculated [187-188]; the question then arises whether the total dipole can be approximated simply by adding the first-order exchange contribution. The issue of approximating interaction energies as the sum of second-order dispersion and first-order exchange contribution has been addressed by Margenau [233]. The calculations that he performed with a rather simple wave function showed that the approximation was not acceptable for hydrogen, but it was almost correct for helium and it should be legitimate for heavier structures. Second-order nonadditive overlap-dependent contributions to the energy have been studied [166,170] in the Gaussian effective electron model, but it has already been established [132a,174] that this approximation overestimates the second-order energies. The results of more accurate calculations [234] on hydrogen have shown that the first-order exchange energy between two 1s atomic orbitals accounts for ~90% of the difference between the energies of the lowest singlet and triplet states. Second-order interaction energies involving exchange are considerably smaller than the first-order exchange contribution in the He...He interactions [235]. Higher-order exchange energies are expected to be a small percentage of the first-order exchange energy unless a strong bond is formed [132d]. Furthermore, it has been claimed that it is legitimate to calculate induction and first-order exchange energies independently, and this procedure has been used in the computation of interatomic interactions [236]; the results seem to support the validity of the approximation [236]. The same approximation for the second-order exchange contribution to the triplet dipole moment is adopted here. The results of our calculations discussed in Section 4.3 show that the exchange-overlap contribution to the triplet dipole moment cannot be disregarded in comparison with the long-range dispersion contribution.

## 4.2. DIPOLE MOMENT CALCULATIONS.

In this section, the dipole moment for a system of three interacting hydrogen atoms in the lowest quartet state is obtained in the label-free exchange perturbation formalism.

The Hamiltonian, H, for the system in a uniform static electric field is

$$H = H(\underset{\sim}{F}=\underset{\sim}{0}) + H(\underset{\sim}{F}) = \hat{H}_o + \hat{V} - \underset{\sim}{F} \cdot \hat{\underset{\sim}{\mu}} \tag{1}$$

$H(\underset{\sim}{F})$ is associated with the interaction of the external electric field $\underset{\sim}{F}$ and the hydrogen triplet. $H(\underset{\sim}{F}=\underset{\sim}{0})$ is the sum of the Hamiltonian operators for the three non-interacting hydrogen atoms plus a term, $\hat{V}$, which contains all the electrostatic interatomic electron- nucleus attractions, and nucleus-nucleus as well as electron-electron repulsions.

Each term in the Hamiltonian may be written in a form which is invariant with respect to assignment of the electrons to the interacting atoms:

$$\hat{O} = \sum_{i=i}^{P} O_i \Lambda_i \quad , \tag{2}$$

where $\hat{O}$ represents one of the operators $\hat{H}_o$, $\hat{V}$ or $\hat{\underset{\sim}{\mu}}$ in (1), and

$$\hat{O} = \sum_{i=1}^{P} \sum_{\rho} O_{\rho i} \Lambda_i \quad . \tag{3}$$

The subscript $\rho$=a, b, c labels each hydrogen nucleus in the triplet system. The number of ways $N_\rho$ electrons from a total of $N = \sum_\rho N_\rho$ may be assigned to three different centers is

$$p = \frac{(N_a+N_b+N_c)!}{N_a!N_b!N_c!} \qquad (4)$$

so in this case, $p = 6$.

When applied to an antisymmetrized triplet wave function $\Psi$, $\Lambda_i$ projects out the simple product term for the ith electron assignment. If the zeroth order save function, $\Psi_o$, is constructed as an antisymmetrized product of the ground-state save functions $\Psi_a$, $\Psi_b$ and $\Psi_c$ for the isolated atoms:

$$\Psi_0 = f \sum_{i=1}^{p} \sigma_{P_i} P_i \left[\Psi_a\Psi_b\Psi_c\right] = f \sum_{i=1}^{p} \phi i \quad , \qquad (5)$$

where f is a normalization constant and $\sum_{i=1}^{p} \sigma_{P_i} P_i$ is the intersystem antisymmetrizer. Thus, $\Lambda i$ is not self-adjoint and $\Lambda_i\Psi_0 = f\Phi_i$.

The triplet wave function to first order in the applied field $\underset{\sim}{F}$ and zeroth order in the interatomic interaction is given by

$$\Psi_0 = c_1^{-1/2}\Phi^{(0)} + \underset{\sim}{F}\cdot\left[c_1^{-1/2} \sum_{i=1}^{3} \underset{\sim}{\Phi}{}_i^{(1)} - \frac{1}{2}\, \underset{\sim}{c}_2 c_1^{-3/2}\Phi^{(0)}\right] \qquad (6)$$

The constants $c_1$ and $\underset{\sim}{c}_2$ are

$$c_1 = \langle\Phi^{(0)} | \Phi^{(0)}\rangle \qquad (7)$$

and

$$C_{2\alpha} = 2 \sum_{i=1}^{3} \langle\Phi^{(0)} | \Phi_{i\alpha}^{(1)}\rangle \quad . \qquad (8)$$

$\Phi^{(0)}$ is an antisymmetrized product of unperturbed orbitals $\chi_\rho^{(o)}$ centered on $\rho = a,b,c$ and $\Phi_{i\alpha}^{(1)}$ is the antisymmetrized product with the unperturbed orbital i replaced by the first-order correction to orbital i in an applied field $F_\alpha$ in the $\alpha$ direction. The vector $\underset{\sim}{\Phi}{}_i^{(1)}$ has components

$\Phi_{ix}^{(1)}$, $\Phi_{iy}^{(1)}$, $\Phi_{iz}^{(1)}$. To lowest order in the interaction, the triplet energy E is [228]

$$E = \langle\Psi_0|H|\Psi_0\rangle = 3E_H^{(0)} = c_1^{-1}\,\langle\Phi^{(0)}|\sum_{i=1}^{6} V_i\Lambda_i|\Phi^{(0)}\rangle +$$

$$+\underset{\sim}{F}\cdot\left\{2c_1^{-1}\langle\Phi^{(0)}|\hat{H}(\underset{\sim}{F}=0)|\sum_{j=1}^{3}\underset{\sim}{\Phi}_j^{(1)}\rangle - \underset{\sim}{c}_2 c_1^{-2}\langle\Phi^{(0)}|\hat{H}(\underset{\sim}{F}=0)|\Phi^{(0)}\rangle - \bar{\underset{\sim}{\mu}}\right\}\quad, \tag{9}$$

where

$$\bar{\underset{\sim}{\mu}} = \langle\Phi^{(0)}|\sum_{i=1}^{6}\mu_i\Lambda_i|\Phi^{(0)}\rangle c_1^{-1} \tag{10}$$

With possible basis-set-dependent effects [81] confined to second and higher orders [228], the energy is given by the sum of three terms: the total energy of the three non-interacting atoms $3E_H^{(0)}$; the zero-field triplet interaction energy to the lowest order, and a term linear in the electric field.

The dipole moment may be obtained as a field derivative of the energy (9):

$$\underset{\sim}{\mu} = -\left.\frac{\partial E}{\partial\underset{\sim}{F}}\right]_{\underset{\sim}{F}=0} = -\left\{\langle\frac{\partial\Psi_0}{\partial\underset{\sim}{F}}|\hat{H}|\Psi_0\rangle + \langle\Psi_0|\frac{\partial\hat{H}}{\partial\underset{\sim}{F}}|\Psi_0\rangle + \langle\Psi_0|\hat{H}|\frac{\partial\Psi_0}{\partial\underset{\sim}{F}}\rangle\right\}_{F=\underset{\sim}{0}} =$$

$$= \bar{\underset{\sim}{\mu}} - 2c_1^{-1}\,\langle\Phi^{(0)}|\hat{H}(\underset{\sim}{F}=0)|\sum_{i=1}^{3}\underset{\sim}{\Phi}_i^{(1)}\rangle + c_1^{-2}\underset{\sim}{c}_2\langle\Phi^{(0)}|\hat{H}(\underset{\sim}{F}=0)|\Phi^{(0)}\rangle\quad. \tag{11}$$

For the three H-atom problem, if the term $\hat{V}$ were removed from the Hamiltonian H in (1) at $\underset{\sim}{F}=0$, an exact eigenfunction could then be calculated. Moreover, even if an external electric field were turned on, an exact wave function could still be obtained to any desired order in the electric field. The presence of $\hat{V}$ in the Hamiltonian introduces an error $\delta\Psi_0$ in the zeroth-order wave function when $\underset{\sim}{F}=\underset{\sim}{0}$. Therefore, when an electric field is applied the error has the form $\delta\Psi_0(\underset{\sim}{F})=\delta\Psi_0(1+g(\underset{\sim}{F}))$ where $g(\underset{\sim}{F})$ is some function of the electric field. The error in the dipole moment calculated as

$$\bar{\underset{\sim}{\mu}} = - \langle \Psi_0 | \frac{\partial \hat{H}}{\partial \underset{\sim}{F}} | \Psi_0 \rangle \Big]_{\underset{\sim}{F}=0} \tag{12}$$

is first order in $\delta\Psi_0$. Generally, the error in the field derivative of the energy may be first or second order in $\delta\Psi_0$. When $\delta\Psi_0(\underset{\sim}{F})$ is of the form considered above though, $(\partial E/\partial \underset{\sim}{F})_{\underset{\sim}{F}=0}$ is second order in $\delta\Psi_0$ [237]. Hence, the dipole moment as given by Eq. (11) is in this case more accurate than the expectation value of the corresponding operator, as in (12).

The AO's $\chi$ in the wave function $\Psi$ are constructed with Slater bases; $\chi_H^{(0)}$ is the H-atom 1s orbital and the first-order correction to the hydrogenic wave function $\chi_H^{(1)}$ is found analytically [93] and written in terms of modified p-Slater orbitals. We find that $\underset{\sim}{c}_2=\underset{\sim}{0}$, according to the properties of overlap integrals with Slater orbitals on identical centers.

The exchange-overlap contribution [70] to the dipole moment given by Eq. (12) may be analysed as follows. Let us consider a system of p identical atoms with a total of N electrons. Let us assign the set $P_1 = \{\chi_1, \ldots, \chi_{N/p}\}$ of AO's to the first atom, the set

$$P_2 = \{\chi_{\frac{N}{p}+1}, \ldots, \chi_{\frac{2N}{p}}\}$$

to the second atom, and so forth. The set $P_p = \{\chi_{\frac{(p-1)N}{p}+1}, \ldots, {}_n\chi\}$ is assigned to the $p^{\underline{th}}$ atom. The atomic orbitals of the non-interacting atoms satisfy

$$\langle (\chi^i)_\rho | (\chi_j)_{\rho'} \rangle = (\delta^i{}_j - S^i{}_j)\delta_{\rho\rho'} + S^i{}_j \quad ; \; \rho,\rho' = 1, \ldots, p \; . \tag{13}$$

Thus, there are $p^2$ $(\frac{N}{p} \times \frac{N}{p})$-dimensional blocks in the overlap matrix S.

All the diagonal blocks are $(\frac{N}{p} \times \frac{N}{p})$-unit matrices. Consequently, we can decompose S as the sum of the unit matrix $\Delta$ and a matrix T which contains p $(\frac{N}{p} \times \frac{N}{p})$-diagonal blocks whose elements are identically equal to zero. The inverse of the overlap matrix may be expanded in a power series (below, the implicit summation convention applies to the contracted covariant and contravariant indices, but Eq. 14c does not involve summation over i values):

$$S^{-1} = (\Delta+T)^{-1} = \Delta - T + T^2 - T^3 + \ldots \tag{14a}$$

$$(S^{-1})^i{}_j = - T^i{}_j + T^i{}_k T^k{}_j - T^i{}_k \tau^k{}_\ell T^\ell{}_j \qquad , \; i \neq j \tag{14b}$$

$$(S^{-1})^i{}_i = 1 + T^i{}_k T^k{}_i - T^i{}_k \tau^k{}_\ell \, T^\ell{}_i \tag{14c}$$

$$\tau^k{}_\ell \equiv T^k{}_\ell - T^k{}_m T^m{}_\ell + T^k{}_m T^m{}_n T^n{}_\ell - \ldots \tag{14d}$$

All the contracted indices are distinct from i (diagonal and off-diagonal matrix elements) and from j (off-diagonal matrix elements). If

$$\rho(1,1') = |\chi_i(1)\rangle (S^{-1})^i{}_j \langle \chi^j(1')| \tag{15}$$

is the first-order reduced density matrix, the $\alpha$-component of the electronic contribution to the dipole moment $\bar{\mu}^{el}_\alpha$ [70] is given [228] by

$$\bar{\mu}^{el}_\alpha = - \int_{1' \leftarrow 1} dv_1 \, \rho(1,1') \, q_\alpha = - (S^{-1})^i{}_j \langle \chi^j | q_\alpha | \chi_i \rangle \equiv -(S^{-1})^i{}_j (q_\alpha)^j{}_i \; . \tag{16}$$

Hence

$$\bar{\mu}^{e\ell}_\alpha = - \left[\delta^i{}_i + T^i{}_k T^k{}_i \;\; \tau^k{}_\ell T^\ell{}_i\right] (q_\alpha)^i{}_i - \left[-T^i{}_j + T^i{}_k T^k{}_j - T^i{}_k \tau^k{}_\ell T^\ell{}_j\right] (q_\alpha)^j{}_i \; . \tag{17}$$

Now

$$(q_\alpha)^i{}_i = \langle \chi^i | q_\alpha | \chi_i \rangle = \langle \chi^i | q_\alpha{}^\rho | \chi_i \rangle + \langle \chi^i | \chi_i \rangle R_{\alpha\rho} = 0 + R_{\alpha\rho} \delta^i{}_i \; , \tag{18}$$

where $q_\alpha^\rho$ is referred to the $\rho$-nucleus and $R_{\alpha\rho}$ is the coordinate of the $\rho$-nucleus in a given reference frame. Then

$$\delta^{i}{}_{i}(q_\alpha)^{i}{}_{i} = \sum_{\rho} R_{\alpha\rho} \sum_{i\in P_\rho} \delta^{i}{}_{i} = \frac{N}{p} \sum_{\rho} R_{\alpha\rho} \quad . \tag{19}$$

The product of a component of the dipole moment and an atomic orbital in Eq. (17) is expressed in terms of modified AO's, and the spherical harmonics are transformed to the forms referred to canonical axes by means of the corresponding rotation matrices. The use of orthogonality relationships and specialization to s-type atomic orbitals let us write (see Appendix E)

$$\bar{\mu}_\alpha^{el} = \sum_{\rho} \left(\frac{-N}{p}\right) R_{\alpha\rho} \tag{20}$$

The nuclear $\alpha$-component is

$$\bar{\mu}_\alpha^{nuc} = \sum_{\rho} \frac{N}{p} R_{\alpha\rho} \frac{1}{N} \int_{1'\leftarrow 1} dv_1 \; \rho(1,1') = \sum_{\rho} \frac{N}{p} R_{\alpha\rho} \quad ; \tag{21}$$

so

$$\bar{\mu}_\alpha = \bar{\mu}_\alpha^{el} + \bar{\mu}_\alpha^{nuc} = 0 \quad , \quad \forall\alpha \tag{22}$$

Therefore, the exchange-overlap contribution [70] to the dipole moment given by Eq. (12) vanishes when a cluster of hydrogen atoms is described by an approximate wave function such as $\Psi_o$. Furthermore, this result applies to any spatial arrangement of any number of atoms whose electrons are described by zeroth order s-orbitals, or by an effective s Gaussian function [164,166,231-232,242]. Thus, the dipole moment is given by

$$\underset{\sim}{\mu} = -2c_1^{-1} \langle \Phi^{(0)} | \hat{H} \, (\underset{\sim}{F}=\underset{\sim}{0}) | \sum_{i=1}^{3} \underset{\sim}{\Phi}_i^{(1)} \rangle \tag{23}$$

Further elementary consideration on the properties of integrals involving Slater orbitals on identical atoms allow for additional simplification in the expression of $\mu$, namely, Eq. (23) becomes

$$\mu = -2c_1^{-1} \langle \Phi^{(0)} | \hat{V}' | \sum_{i=1}^{3} \underset{\sim}{\Phi}_i^{(1)} \rangle \tag{24}$$

where $\hat{V}'$ is the operator $\hat{V}$ after removal of the terms which involve nucleus-nucleus repulsions. The constant $c_1$ is given by

$$c_1 = 6\left[1-S_{ab}^2-S_{ac}^2-S_{bc}^2+2S_{ab}S_{ac}S_{bc}\right] , \tag{25}$$

where $S_{\rho\rho'}$ is the overlap integral between two ls hydrogen orbitals on $\rho,\rho'$ = a, b, or c. The explicit formula for $\mu_\alpha$ is given in Appendix F. Modified Slater-type orbitals for $\chi_H^{(1)}$ have been taken in the directions z and x for $\alpha$ = z, x, respectively. The total dipole moment has been computed as the sum of the overlap-exhcange (Eq. (24)) and the long-range dispersion [187-188] contributions. Overlap damping, orbital distortion and higher-order effects are neglected. The calculations have been carried out for several values of R and Q (or $X_c$ for the right triangle configuration) between 3.0 a.u. and 10.0 a.u.; R, Q and $X_c$ are defined in Fig. 1 in the linear and equilateral, isosceles and right triangular configurations of the three hydrogen atoms a, b, c. This range of internuclear separations includes the van der Waals minimum of ${}^3\Sigma_u^+$ $H_2$ [243-244] and it covers the region where the pair distribution function is appreciably different from 0 and 1 [208].

All the integrals over Gaussian expansions [245] of the Slater-type orbitals which appear in the expression for the triplet dipole moment have been computed with the program ARGOS [246-248] maintained by R. Shepard (Argonne National Laboratory).

## 4.3. RESULTS AND DISCUSSION.

We have proven that the Lacey and Byers Brown [70] approximation yields zero for the triplet dipole moment when the calculation is performed for identical, spherically symmetric, neutral charge distributions described by s-type functions. This result generalizes to any number of such systems in any spatial configuration.

Overlap exchange (Eq. (11)) and dispersion [118] triplet dipole moment calculations have been performed for the quartet $H_3$ system in its right-triangle ($\theta=\pi/2$ rads) and linear ($\theta=\pi$ rads) spatial configurations, with 3 a.u. $\leqslant R \leqslant 10$ a.u. and 3 a.u. $\leqslant X_c \leqslant 10$ a.u. (right triangle) and 3 a.u. $\leqslant Q \leqslant 10$ a.u. (linear). The results for the triplet dipole moment in a.u. are plotted in Figs. 2-7.

The X-dispersion dipole moment points from the pair to the single atom in most of the region $X_c > R$ (Fig. 2) whereas the reverse trend is observed for the Z-component in most of the region $X_c < R$ (Fig. 3). The behaviour of the X-overlap-exchange dipole moment (Fig. 4) is similar to that of the X-dispersion dipole moment (Fig. 2), but the Z-overlap-exchange dipole moment (Fig. 5) is directed form the pair to the single atom in most of the region $R > X_c$. The overlap-exchange dipole moment (Fig. 6) for the linear configuration is directed from the single atom to the pair whilst the dispersion contribution (Fig. 7) points in the opposite direction, i.e., from the pair to the single atom. The order of magnitude of both contributions is comparable for all the configurations of Figs. 2-7. We do not present results for the isosceles-triangle configuration, but a similar trend is observed for its dispersion and overlap-exchange contributions. Therefore, the tiplet dipole moment is substantially affected by overlap-exchange effects in addition to the dispersion contribution. An analogous result holds for the corresponding contributions to the energy [174].

The controversy over the actual rôle that the overlap-exchange contribution plays in the many-body interactions has been noted in the introduction. We have found that short-range effects in a molecular property are very important when they are compared with the long-range contribution. This theoretical result may be checked against experimental data by computing the dipole moment of a unicomponent triplet, as in Section 4.2. The collision-induced absorption spectrum may thus be calculated [182] and the importance of dispersion and overlap-exchange contributions properly analysed. Further research along this line is likely to shed some light on the relative weight of short- and long-range contributions to the many-body effects on properties of systems for which the leading terms are due to triplet and higher-order associations. The behavior of the total dipole moment (taken as the sum of the different contributions) may permit inferences [249] about the form of the triplet dipole moment time-correlation function.

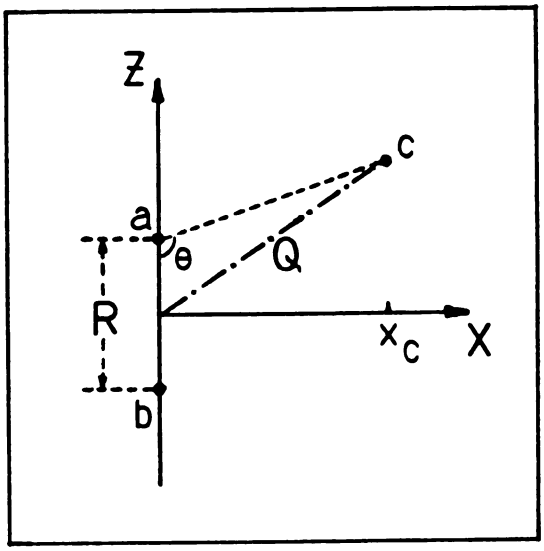

Figure 1. Spatial configuration of three identical nuclei (a, b, c). $\theta=\pi$, $\pi/2$, $\pi/3$ for the linear, right-triangle and isosceles-triangle configurations.

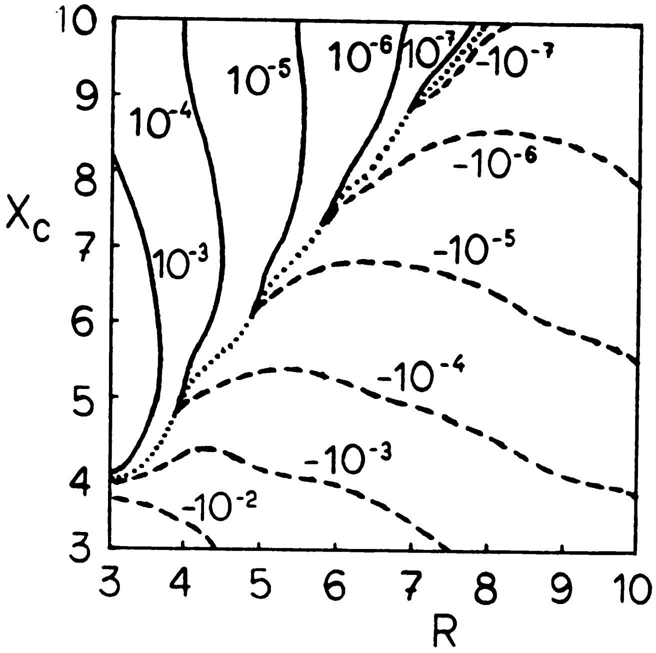

Figure 2. $H_3$ dispersion dipole moment.

X component. Right-triangle configuration.

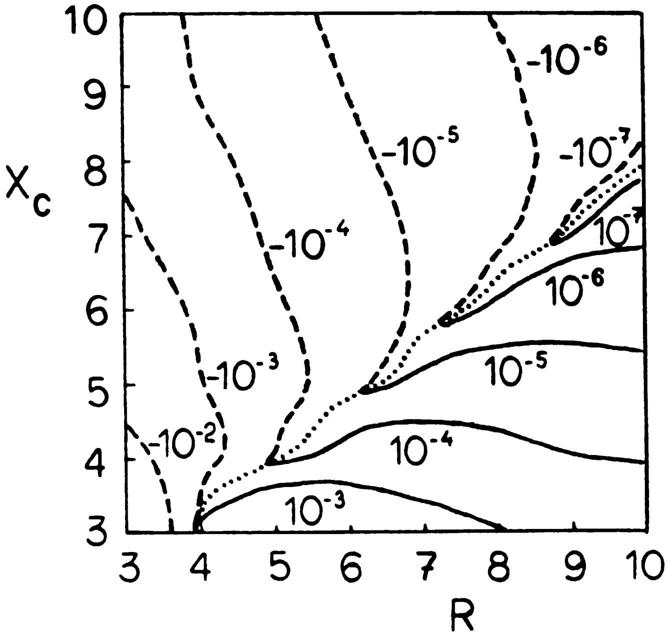

**Figure 3.** $H_3$ dispersion dipole moment.

Z component. Right-triangle configuration.

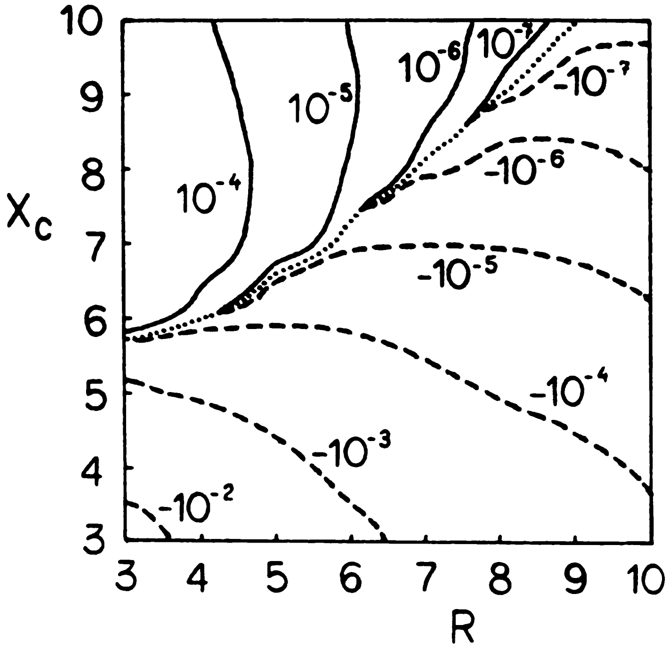

Figure 4. $H_3$ overlap-exchange dipole moment.

X component. Right-triangle configuration.

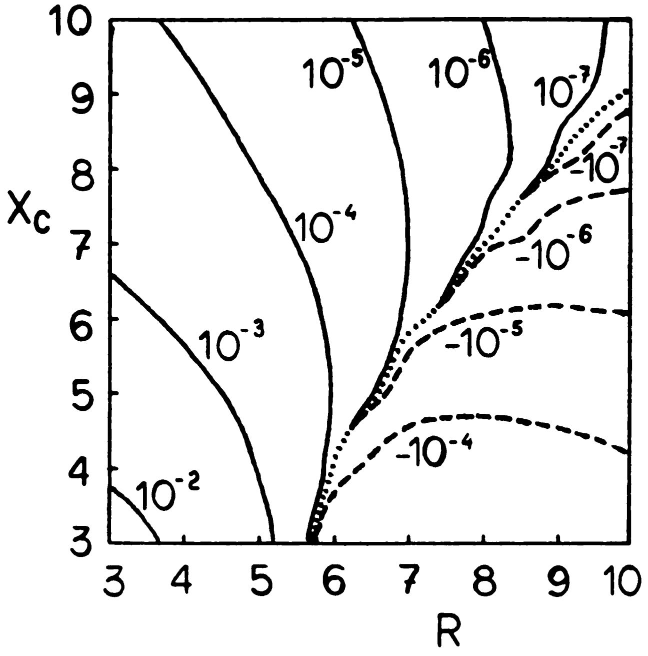

Figure 5. $H_3$ overlap-exchange dipole moment.

Z component. Right-triangle configuration.

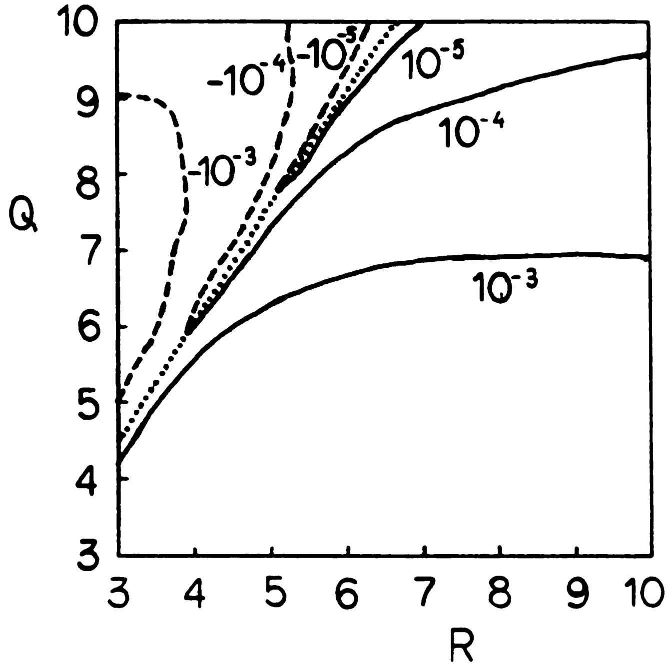

Figure 6. $H_3$ overlap-exchange dipole moment. Linear configuration.

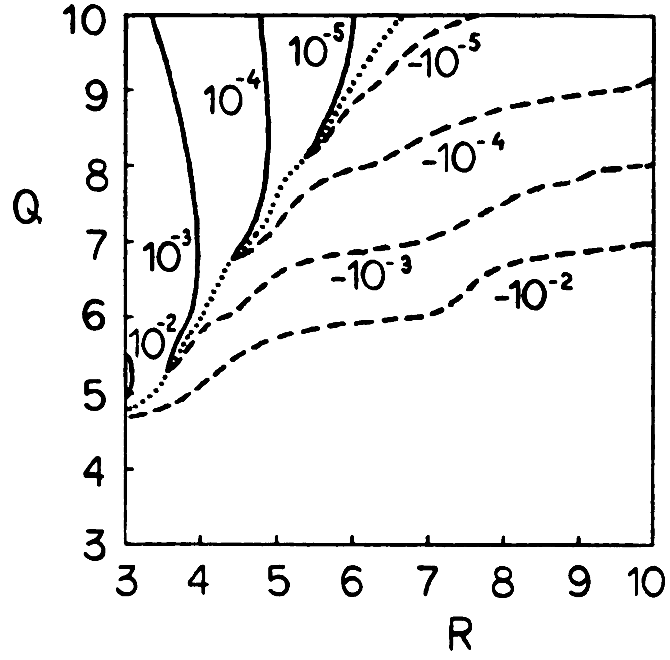

Figure 7. $H_3$ dispersion dipole moment. Linear configuration.

# CHAPTER 5.

## 5.1. - INTRODUCTION.

The interaction between two non-overlapping spherical neutral charge distributions is dominated by the London dispersion term [250-251]. When the charge distributions are so far away from each other that retardation effects must be taken into account, the interaction is still attractive, but its functional form in terms of the internuclear separation is slightly different. The use of the quantum theory of radiation [252] yields an attractive interaction inversely proportional to the seventh power of the separation. The retarded dispersion forces between macroscopic bodies may be calculated within the framework of classical electrodynamics [253], and the van der Waals forces between individual atoms and molecules are obtained as a special case [254-255]. Other treatments involving quatum electrodynamics have also been developed [256-257] to account for retardation effects. The study of retarded dispersion forces covers the interaction between molecules [258], effects in dielectrics at finite temperatures [259], three-body dispersion forces [130] and the interaction between an atom and a surface [260]. The results of such theoretical studies have in common that the retarded and unretarded dispersion forces between macroscopic and microscopic bodies are given in terms of properties of the individual interacting species, *viz.*, in terms of susceptibilities. Therefore, dispersion forces may be viewed from a unified standpoint *via* susceptibility theory [261]. The relationship among electromagnetic field fluctuations, susceptibilities, zero-point energy and long-range forces is discussed by Boyer [262]. Whether retarded (*i.e.*, proportional to $R^{-7}$) or not (*i.e.*, proportional to

$R^{-6}$), dispersion forces undergo a power-law divergence as the separation between the interacting systems goes to zero. Effects due to overlap and exchange should prevent this collapse by damping the power law which gives the dispersion energy. Second-order perturbation theory yields the dispersion contribution when the perturbation in the Hamiltonian is associated with the intersystem interaction. The matrix elements which involve the perturbation must be properly handled in order to include the overlap effects. The multipole series (which indeed is not intrinsic [88,263] to London's theory) cannot be used to expand the perturbation, for the series expansion require that the charge distributions do not overlap. Matrix elements of operators such as $|r_A - r_B|^{-1}$, where $r_\alpha$ is the position of a particle of system $\alpha$ = A, B have to be evaluated. Their evaluation without use of a multipole expansion is usually carried out by separating the coordinate $r_A$ and $r_B$ first.

Several techniques (all relying on use of the convolution theorem) allow for such a separation. The Fourier transform of the potential is used by Koide [264]. His method has been developed and used to calculate damping function for $He_2$, $Be_2$, HeH [265], and $(^3\Sigma_u^+)H_2$ [266], and to calculate interaction energy curves as well as dispersion damping interaction functions for $He_2$ [267], $Ar_2$ [268], $Xe_2$ [269], $(^3\Sigma_u^+)Li_2$[270] and He...$H_2$ and Ar...HCl [271]. An exchange correction term has been incorporated into the damped dispersion energy for $(^3\Sigma_u^+)Li_2$, $(^3\Sigma^+)$LiNa, $(^3\Sigma_u^+)Li_2^+$ and $(^2\Sigma^+)$NaAr [272]. Other _ab_ _initio_ computations of dispersion energies and damping functions have been performed [273] for $Ar_2$ and $Li_2$. A universal, empirical damping function has been proposed and applied [274] to the calculation of the van der Waals potentials of $(^3\Sigma)H_2$, $Ar_2$,

($^3\Sigma$)NaK and LiHg.

Nonlocal polarizability densities [275] and Coulomb interactions in $\underset{\sim}{k}$-space have also been used to derive expressions for damped dispersion energies [276].

In other work, the Fourier transform of the transition-density matrix in the dispersion energy has been used [277] to provide a dispersion force between closed-shell atoms finite at all distances. This method has been extended [278] to represent the transition amplitudes in terms of Slater-type ortitals. Damping effects for the first-order Coulomb molecule-molecule interactions have been calculated on the basis of a two-centre or bipolar expansion fo $|r_A - r_B|^{-1}$ [279], and the damped second-order Coulomb energy has been given in terms of response functions [280].

The full Coulomb interacting potential is also used in a reaction-field approach. A generalized form factor is related in this approach to the charge-density susceptibility with which we may calculate the second-order interaction energy. This method [281] is applied to the study of the $He_2$ [281-282] and $Ne_2$ [283] potentials.

Damping in the dispersion energy has been treated empirically in electron-gas calculations, applied to the potential energy of $H_2$...He, $H_2$...Ne, $H_2$...Ar [284] and $N_2$...$N_2$ [285]. Other procedures [286] are based on fitting expressions involving exponential damping to reliable results or experimental data.

The dispersion contribution to the dipole moment [53-54,287-290]; has a power-law divergence ($\propto R^{-7}$) at zero internuclear separation. Expressions for the damped dispersion dipole moment have been given [291-292] in terms of properties of the isolated systems. Nonlocal polarizability densities [275] and the full Coulomb interaction have been used to calculate damped molecular properties such as dipoles, quadrupoles and polarizabilities [293-294] within a reaction-field theory. The damped dispersion-pair dipole is given [293] in terms of the Fourier transforms of the nonlocal frequency-dependent polarizability density of one system and the first hyperpolarizability density of the other system. We present in Section 2 of this chapter a general method to transform the $n^{th}$-order charge-susceptibility density as obtained from generalized susceptibility theory [295] into a form which can easily be compared with the fully contracted $n^{th}$-order nonlocal hyperpolarizability. We derive an expression for the nonlocal polarizability and hyperpolarizability densities in Section 5.3 and we give in Section 5.4 the expression for the damped dispersion pair dipole moment in terms of reduced matrix elements.

## 5.2.-GENERALIZED FUNCTIONS AND CHARGE-SUSCEPTIBILITY DENSITIES

The expression

$$\lim_{\xi \to 0} \frac{1}{\omega \pm i\xi} = \mathrm{PV}\,\frac{1}{\omega} \mp i\pi\delta(\omega) \quad , \tag{1}$$

where PV stands for "principal value" and $\delta$ is Dirac's distribution, is used without proof in most work involving charge-susceptibility densities. Here we present a general method based on the theory of generalized functions [36,296] to carry out the limit involved in the charge-susceptibility density as obtained from perturbation theory. The method is equally applicable to susceptibility tensors, for the nature of the matrix elements in the numerators is irrelevant in this treatment. The method is general because it may be used with susceptibilities of any order - it is not restricted to the first order, to which Eq. (1) corresponds. This feature makes the method of potential use in the study of nonlinear phenomena, both in the nonresonant and resonant regions.

The third-order nonlocal charge susceptibility density is [292]

$$\chi^{(2)}(\underset{\sim}{r}'',\underset{\sim}{r}',\underset{\sim}{r};\omega',\omega) = [1 + P(\underset{\sim}{r}',\omega';\underset{\sim}{r},\omega)] \lim_{\substack{\xi\to 0\\ \eta\to 0}} \hbar^{-2} \cdot$$

$$\cdot \sum_k{}' \sum_n{}' \left\{ \frac{\rho_{0k}(\underset{\sim}{r}'')\cdot\rho_{kn}(\underset{\sim}{r}')\cdot\rho_{n0}(\underset{\sim}{r})}{(\omega_{0k}+\omega'+\omega-i\xi-i\eta)\cdot(\omega_{0n}+\omega-i\eta)} + \right.$$

$$+ \frac{\rho_{0k}(\underset{\sim}{r}')\cdot\rho_{kn}(\underset{\sim}{r}'')\cdot\rho_{n0}(\underset{\sim}{r})}{(\omega_{0k}-\omega'+i\xi)\cdot(\omega_{0n}+\omega-i\eta)} +$$

$$\left. + \frac{\rho_{0k}(\underset{\sim}{r}')\cdot\rho_{kn}(\underset{\sim}{r})\cdot\rho_{0n}(\underset{\sim}{r}'')}{(\omega_{0k}-\omega'+i\xi)\cdot(\omega_{0n}-\omega-\omega'+i\xi+i\eta)} \right\} , \tag{2}$$

where $\omega$ and $\omega'$ are the frequencies of the field due to an external source,

$\omega_{ok}$ is the difference of the energies (in units of $\hbar$) of the ground and excited (k) unperturbed states, $\rho(\underset{\sim}{r})$ is the charge-density operator and the primes in the sums stand for $k \neq 0$ and $n \neq 0$. The variables $\xi$ and $\eta$ are real and $P(\underset{\sim}{r}',\omega';\underset{\sim}{r},\omega)$ denotes the permutation of $\underset{\sim}{r}'$ with $\underset{\sim}{r}$ and of $(\omega' - i\xi)$ with $(\omega - i\eta)$ simultaneously.

The matrix elements in the numerators of Eq. (2) are not relevant in the analysis that we perform. Let us consider the representative term

$$\lim_{\substack{\xi\to0\\ \eta\to0}} \frac{1}{[((\omega_{0k} - \omega' + i\xi)\cdot(\omega_{0n} + \omega - i\eta)]}$$

Define $\omega_{0k} - \omega' \equiv x$, $\omega_{0n} + \omega \equiv y$ .

Let $1/(x.y)$ be a singular generalized function ( the terms distribution and generalized function are considered synonymous in this analysis).

Let $C_0^\infty(\mathbb{R}^2)$ be the space of test functions $\phi = \phi(x,y)$ required to be infinitely differentiable and to vanish identically outside some finite interval; <u>i.e.</u>, $\{\phi\}$ are a class of infinitely differentiable functions with bounded support.

The test functions $\phi = \phi(x,y)$ may also be elements of $\mathcal{S}(\mathbb{R}^2)$, the set of infinitely differentiable functions such that

$$\sup_{(\underset{\sim}{r})} ||\underset{\sim}{r}||^p \left|\frac{\partial^{k_1+k_2}}{\partial x^{k_1}\,\partial y^{k_2}}\phi(x,y)\right| < \infty \ , \quad \underset{\sim}{r} \equiv (x,y) \quad ,$$

<u>i.e.</u>, the set of functions which belong to $C^\infty$ and (together with their derivatives) vanish faster than any power when $|\underset{\sim}{r}| \to \pm\infty$, although they do not have bounded support. Also, there must be constants $K_{k_1,k_2,p}$ for all $\underset{\sim}{r}$ and every $k_1$, $k_2$, $p = 0, 1, \ldots,$ such that

$$||\underset{\sim}{r}||^{p} \cdot \left|\frac{\partial^{k_1+k_2}}{\partial x^{k_1}\,\partial y^{k_2}}\,\Phi(x,y)\right| < K_{k_1 k_2 p} \quad .$$

We have $C_0^\infty(\mathbb{R}^2) \subset \mathcal{S}(\mathbb{R}^2)$. In this case, 1/(x.y) is a tempered singular distribution [296]. We now find an equivalent expression for the singular distribution

$$S \equiv \frac{1}{xy} = \lim_{\substack{\xi\to 0^+\\ p\to 0}} \frac{1}{(x\pm i\xi)\cdot(y\pm i\eta)} \quad , \qquad (3)$$

where $\sigma = \pm 1$, $j = 1,2$. For every $\Phi \in C_0^\infty(\mathbb{R}^2)$, we have

$$\Phi(x,y) = 0 \ , \ \forall (x,y) \notin [a,-a] \times [b,-b] \subset \mathbb{R}^2 \quad .$$

$$\langle S|\Phi\rangle \equiv \lim_{\substack{\xi\to 0\\ \eta\to 0}} \int_{-a}^{a}\int_{-b}^{b} \frac{1}{(x+\sigma_1 i\xi)\cdot(y+\sigma_2 i\eta)}\,\Phi(x,y)\,dxdy =$$

$$=\lim_{\substack{\xi\to 0\\ \eta\to 0}} \int_{-a}^{a}\int_{-b}^{b} \frac{(x-\sigma_1 i\xi)\cdot(y-\sigma_2 i\eta)}{(x^2+\xi^2)\cdot(y^2+\eta^2)}\,[\Phi(x,0)-\Phi(x,0)+\Phi(0,y)-\Phi(0,y)\,+$$

$$+\Phi(0,0)+\Phi(x,y)-\Phi(0,0)]\,dxdy \quad . \qquad (4)$$

The integrations in Eq. (4) are performed as follows

$$\lim_{\substack{\xi\to 0\\ \eta\to 0}} \int_{-a}^{a}\int_{-b}^{b} \Phi(x,0)\frac{(x-\sigma_1 i\xi)\,.\,(y-\sigma_2 i\eta)}{(x^2+\xi^2)\cdot(y^2+\eta^2)}\,dxdy =$$

$$=\lim_{\substack{\xi\to 0\\ \eta\to 0}} \left[-\sigma_2\cdot 2i\cdot \operatorname{arctg}(b/\eta)\cdot\int_{-a}^{a}\frac{\Phi(x,0)}{(x+\sigma_1 i\xi)}\,dx\right] =$$

$$= -\sigma_2 i\pi\int_{-a}^{a}\frac{\Phi(x,0)}{x}\,dx = -\sigma_2 i\pi\int_{-b}^{b}\delta(y)dy\cdot PV\int_{-a}^{a}\frac{\Phi(x,0)}{x}\,dx\ -$$

$$-\sigma_1\sigma_2\pi^2\int_{-b}^{b}\int_{-a}^{a}dxdy\,\delta(x,y).\Phi(x,y) \quad . \qquad (5)$$

Analogously,

$$\lim_{\substack{\xi\to 0\\ \eta\to 0}} \int_{-a}^{a}\int_{-b}^{b} \Phi(0,y)\frac{(x-\sigma_1 i\xi)\cdot(y-\sigma_2 i\eta)}{(x^2+\xi^2)\cdot(y^2+\eta^2)}\,dx\,dy =$$

$$= -\sigma_1 i\pi\int_{-a}^{a}dx\;\delta(x)\;PV\int_{-b}^{b}\frac{\Phi(x,y)}{y}\,dy - \sigma_1\sigma_2\pi^2\int_{-a}^{a}\int_{-b}^{b}\Phi(x,y)\,\delta(x,y)dxdy \;.(6)$$

$$\lim_{\substack{\xi\to 0\\ \eta\to 0}} \Phi(0,0)\int_{-a}^{a}\int_{-b}^{b}\frac{(x-\sigma_1 i\xi)\cdot(y-\sigma_2 i\eta)}{(x^2+\xi^2)\cdot(y^2+\eta^2)}\,dxdy =$$

$$= \Phi(0,0)\lim_{\substack{\xi\to 0\\ \eta\to 0}}\left[(-\sigma_1 2i\ \mathrm{arctg}\ (a/\xi))\cdot(-\sigma_2 2i\ \mathrm{arctg}\ (b/\eta))\right] =$$

$$=-\sigma_1\sigma_2\pi^2\;\Phi(0,0) \quad . \qquad (7)$$

$$\lim_{\substack{\xi\to 0\\ \eta\to 0}} \int_{-a}^{a}\int_{-b}^{b}\frac{(x-\sigma_1 i\xi)\cdot(y-\sigma_2 i\eta)}{(x^2+\xi^2)\cdot(y^2+\eta^2)}[\;\Phi(x,y)\;+\Phi(0,0)-\Phi(x,0)-\Phi(0,y)]dxdy =$$

$$= PV\int_{-a}^{a}\int_{-b}^{b}\frac{\Phi(x,y)}{xy}\,dxdy + \Phi(0,0)\cdot PV\int_{-a}^{a}\frac{dx}{x}\cdot PV\int_{-b}^{b}\frac{dy}{y} - PV\int_{-a}^{a}\frac{\Phi(x,0)}{x}dx\cdot PV\int_{-b}^{b}\frac{dy}{y}$$

$$-PV\int_{-a}^{a}\frac{dx}{x}\cdot PV\int_{-b}^{b}\frac{\Phi(0,y)}{y}\,dy = PV\int_{-a}^{a}\int_{-b}^{b}\frac{\Phi(x,y)}{xy}\,dxdy \quad , \qquad (8)$$

For $PV\int_{-a}^{a}\frac{dx}{x} = 0$ in Eq. (8).

Equations (5), (6), (7) and (8) allow us to write Eq. (4) as

$$\langle S|\Phi\rangle = -\sigma_2 i\pi\int_{-b}^{b}dy\;\delta(y)\;PV\int_{-a}^{a}\frac{\Phi(x,y)}{x}dx - \sigma_1\pi\int_{-a}^{a}dx\,\delta(x)\;PV\int_{-b}^{b}\frac{\Phi(x,y)}{y}\,dy\; -$$

$$- 2\sigma_1\sigma_2\pi^2\int_{-a}^{a}\int_{-b}^{b}dxdy\,\delta(x,y)\ \Phi(x,y)\ +$$

$$+\sigma_1\sigma_2\pi^2\int_{-a}^{a}\int_{-b}^{b}\delta(x,y)\Phi(x,y)\ dxdy\ +\ PV\int_{-a}^{a}\int_{-b}^{b}\frac{\Phi(x,y)}{xy}\ dxdy\quad . \tag{9}$$

Therefore,

$$\lim_{\substack{\xi\to 0\\ \eta\to 0}}\frac{1}{(x+\sigma_1 i\xi)\cdot(y+\sigma_2 i\eta)} = PV\ \frac{1}{xy} - \sigma_1\sigma_2\pi^2\delta(x,y) - i\pi\Big[\sigma_1\delta(x)PV\frac{1}{y}\ +$$

$$+\sigma_2\delta(y)PV\frac{1}{x}\ \Big]\ , \tag{10}$$

where $\delta(x,y)$ is a two-dimensional Dirac distribution

The representative result given by Eq. (10) is used to perform the limits in Eq. (2) to obtain

$$\chi^{(2)}(\underset{\sim}{r}'',\underset{\sim}{r}',\underset{\sim}{r};\omega',\omega) = \Big[\ 1+P(\underset{\sim}{r}',\omega';\underset{\sim}{r},\omega\Big]\ \hbar^{-2}\ \cdot$$

$$\cdot\sum_k{}'\sum_n{}'\Big[PV\Big\{\frac{\rho_{0k}(\underset{\sim}{r}'').\rho_{kn}(\underset{\sim}{r}').\rho_{n0}(\underset{\sim}{r})}{(\omega_{0k}+\omega'+\omega)\cdot(\omega_{0n}+\omega)}$$

$$+\ \frac{\rho_{0k}(\underset{\sim}{r}').\rho_{kn}(\underset{\sim}{r}'').\rho_{n0}(\underset{\sim}{r})}{(\omega_{0k}-\omega')\cdot(\omega_{0n}+\omega)}\ +$$

$$+\ \frac{\rho_{0k}(\underset{\sim}{r}').\rho_{kn}(\underset{\sim}{r}).\rho_{0n}(\underset{\sim}{r}'')}{(\omega_{0k}-\omega')\cdot(\omega_{0n}-\omega-\omega')}\ \Big\}$$

$$-\pi^2\Big\{\ \sigma_{11}\sigma_{21}\rho_{0k}(\underset{\sim}{r}'')\cdot\rho_{kn}(\underset{\sim}{r}')\cdot\rho_{n0}(\underset{\sim}{r})\cdot\delta(\omega_{0k}+\omega'+\omega,\omega_{0n}+\omega)$$

$$+\sigma_{12}\sigma_{22}\rho_{0k}(\underset{\sim}{r}'')\cdot\rho_{kn}(\underset{\sim}{r}'')\cdot\rho_{n0}(\underset{\sim}{r})\cdot\delta(\omega_{0k}-\omega',\omega_{0n}+\omega)$$

$$+\sigma_{13}\sigma_{23}\rho_{0k}(\underset{\sim}{r}') \cdot \rho_{kn}(\underset{\sim}{r}) \cdot \rho_{0n}(\underset{\sim}{r}'') \cdot \delta(\omega_{0k}-\omega', \omega_{0n}-\omega-\omega')\Big\}$$

$$+ i\pi\Big\{\rho_{0k}(\underset{\sim}{r}'') \cdot \rho_{kn}(\underset{\sim}{r}') \cdot \rho_{n0}(\underset{\sim}{r})(-\sigma_{11}\delta(\omega_{0k}+\omega'+\omega) PV \frac{1}{\omega_{0n}+\omega} -$$

$$-\sigma_{21}\delta(\omega_{0n}+\omega) \; PV \; \frac{1}{\omega_{0k}+\omega'+\omega} \;)$$

$$-\rho_{0k}(\underset{\sim}{r}') \cdot \rho_{kn}(\underset{\sim}{r}'') \cdot \rho_{n0}(\underset{\sim}{r})(-\sigma_{12}\delta(\omega_{0k}-\omega') \; PV \; \frac{1}{\omega_{0n}+\omega} \quad -$$

$$-\sigma_{22}\delta(\omega_{0n}+\omega) \; PV \; \frac{1}{\omega_{0k}-\omega'})$$

$$-\rho_{0k}(\underset{\sim}{r}') \; \cdot \rho_{kn}(\underset{\sim}{r}) \cdot \rho_{0n}(\underset{\sim}{r}'')(-\sigma_{13}\delta(\omega_{0k}-\omega') \; PV \; \frac{1}{\omega_{0n}-\omega-\omega'}, \; -$$

$$-\sigma_{23}\delta(\omega_{0n}-\omega-\omega') \; PV \; \frac{1}{\omega_{0k}-\omega'} \;)\Big\}\Big] \quad , \qquad (11)$$

where $\sigma_{1\ell}$ and $\sigma_{2\ell}$ are equivalent to $\sigma_1$ and $\sigma_2$ in Eq. (10) and $\ell = 1, 2, 3$ refers to the $\ell^{th}$ term in the sum within brackets in Eq.(2).

The procedure that we have followed here may be applied to a term with n factors in the denominator, i.e., to the (n+1)-order nonlocal susceptibility density. The analogue of Eq. (10) in such a case would involve the principal value of the inverse of the product of n variables, plus a combination of n, (n-1), (n-2),..., 1-dimensional Dirac distributions each multiplied by the principal value of the inverse of the product of 0, 1, 2,..., (n-1) variables (respectively) that are not contained in the corresponding Dirac distribution.

We obtain the expression for the linear (or second order) charge susceptibility density given by Linder and Rabenold [295] when either Eq. (10) or Eq. (11) is particularized to the case n = 1. Furthermore, the limits in the $n^{th}$ -order charge susceptibility tensor [297] and the $n^{th}$ -order conductivity tensor [298] are easily obtained when we take $\zeta = \eta$ in Eq. (10), *i.e.*, when we carry out the transition to purely real frequencies by taking a common imaginary component of all frequencies [297-298] to zero.

## 5.3.-NONLOCAL POLARIZABILITY AND HYPERPOLARIZABILITY DENSITY CALCULATION

Response tensors may be given as sum-over-all-states [293,299-300] or as restricted sum-over-states expressions [293,300-303]. The expressions given as sums over all states have apparent divergences (secular divergences) which should be removable [300] because their origin is a number of redundant terms coming from a phase factor in the wave function. This phase factor is expanded in powers of the field. Here, we first derive and expression for the first hyperpolarizability by removing the secular divergences from a sum-over-all-states formula [300]. Secondly, we calculate the reduced hyperpolarizability and polarizability which we shall need in section 5.4 for the calculation fo the damped dispersion dipole. The derivation is restricted to systems whose ground-state dipole moment is zero.

The first nonlocal hyperpolarizability $\beta_{\alpha\beta\gamma}(\underset{\sim}{r},\underset{\sim}{r}',\underset{\sim}{r}'';i\omega,-i\omega,0)$ is [304]

$$\begin{aligned}\beta_{\alpha\beta\gamma}(\underset{\sim}{r},\underset{\sim}{r}',\underset{\sim}{r}'';i\omega,-i\omega,0)=\hbar^{-2}\sum_{m,n}[1+\text{ c.c.}]\Bigg\{&\frac{[P_\alpha(\underset{\sim}{r})]_{0m}[P_\gamma(\underset{\sim}{r}'')]_{mn}[P_\beta(\underset{\sim}{r}')]_{n0}}{(\omega_{m0}+i\omega)(\omega_{n0}+i\omega)}\\&+\frac{[P_\alpha(\underset{\sim}{r})]_{0m}[P_\beta(\underset{\sim}{r}')]_{mn}[P_\gamma(\underset{\sim}{r}'')]_{n0}}{(\omega_{m0}+i\omega)\omega_{n0}}\\&+\frac{[P_\beta(\underset{\sim}{r}')]_{0m}[P_\alpha(\underset{\sim}{r})]_{mn}[P_\gamma(\underset{\sim}{r}'')]_{n0}}{(\omega_{m0}-i\omega)\,\omega_{n0}}\Bigg\}\ ,\end{aligned}\qquad(12)$$

where $P_\alpha(\underset{\sim}{r})$ is the $\alpha$-component of the polarization and c.c. indicates that one must take the complex conjugate of the expression following it. We now split the unrestricted sum in Eq. (12) and perform the integration over the $\underset{\sim}{r}''$-variable to obtain the reduced hyperpolarizability $\hat{\beta}_{\alpha\beta\gamma}(\underset{\sim}{r},\underset{\sim}{r}';i\omega,-i\omega)$.

$$\hat{\beta}_{\alpha\beta\gamma}(\underset{\sim}{r},\underset{\sim}{r}';i\omega,-i\omega) = \hbar^{-2}[1+\mathrm{c.c.}]\Big\{ \sum_{m,n}{}' \frac{[P_\alpha(\underset{\sim}{r})]_{0m}[\mu_\gamma]_{mn}[P_\beta(\underset{\sim}{r}')]_{n0}}{(\omega_{m0}+i\omega)(\omega_{n0}+i\omega)} \tag{13.1}$$

$$+ \sum_{m,n}{}' \frac{[P_\alpha(\underset{\sim}{r})]_{0m}[P_\beta(\underset{\sim}{r}')]_{mn}[\mu_\gamma]_{n0}}{(\omega_{m0}+i\omega)\omega_{n0}} \tag{13.2}$$

$$+ \sum_{m,n}{}' \frac{[P_\beta(\underset{\sim}{r}')]_{0m}[P_\alpha(\underset{\sim}{r})]_{mn}[\mu_\gamma]_{n0}}{(\omega_{mn}-i\omega)\omega_{n0}} \tag{13.3}$$

$$+ \sum_{m} \frac{[P_\alpha(\underset{\sim}{r})]_{0m}[\mu_\gamma]_{m0}[P_\beta(\underset{\sim}{r}')]_{00}}{(\omega_{m0}+i\omega)i\omega} \tag{13.4}$$

$$+ \sum_{n}{}' \frac{[P_\alpha(\underset{\sim}{r})]_{00}[\mu_\gamma]_{0n}[P_\beta(\underset{\sim}{r}')]_{n0}}{i\omega(\omega_{n0}+i\omega)} \tag{13.5}$$

$$+ \sum_{n} \frac{[P_\alpha(\underset{\sim}{r})]_{00}[P_\beta(\underset{\sim}{r}')]_{0n}[\mu_\gamma]_{n0}}{i\omega\ \omega_{n0}} \tag{13.6}$$

$$+ \sum_{n} \frac{[P_\beta(\underset{\sim}{r}')]_{00}[P_\alpha(\underset{\sim}{r})]_{0n}[\mu_\gamma]_{n0}}{\omega_{n0}(-i\omega)} \Big\}, \tag{13.7}$$

Where $\sum'_{m,n}$ stands for the sum over m and n with the restriction $m \neq 0$ and $n \neq 0$. In the integration to obtain Eq. (13) we have used

$$\int d\underset{\sim}{r}''[P_\gamma(\underset{\sim}{r}'')]_{00} = [\mu_\gamma]_{00} = 0 \tag{14}$$

where $\mu_\gamma$ is the $\gamma$-component of the dipole moment [293], i.e., the reduced hyperpolarizability $\hat{\beta}_{\alpha\beta\gamma}(\underset{\sim}{r},\underset{\sim}{r}';i\omega,-i\omega)$ is specialized to a system without a ground-state dipole. After partial-fraction decomposition of the terms (13.4) and (13.5) above and some rearrangement in the sum [1+c.c.], cancellation occurs and we obtain the reduced hyperpolarizability as given in Eq. (15)

$$\hat{\beta}_{\alpha\beta\gamma}(\underset{\sim}{r},\underset{\sim}{r}';i\omega,-i\omega) = \hbar^{-2}[1+\text{c.c.}]\left\{\sum_{m,n}{}' \frac{[P_\alpha(\underset{\sim}{r})]_{0m}[\mu_\gamma]_{mn}[P_\beta(\underset{\sim}{r}')]_{n0}}{(\omega_{m0}+i\omega)(\omega_{n0}+i\omega)}\right.$$

$$+\sum_{m,n}{}' \frac{[P_\alpha(\underset{\sim}{r})]_{0m}[P_\beta(\underset{\sim}{r}')]_{mn}[\mu_\gamma]_{n0}}{(\omega_{m0}+i\omega)\;\omega_{n0}}$$

$$+\sum_{m,n}{}' \frac{[P_\beta(\underset{\sim}{r}')]_{0m}[P_\alpha(\underset{\sim}{r})]_{mn}[\mu_\gamma]_{n0}}{(\omega_{m0}-i\omega)\;\omega_{n0}}$$

$$-\sum_{m}{}' \frac{[P_\alpha(\underset{\sim}{r})]_{0m}[\mu_\gamma]_{m0}[P_\beta(\underset{\sim}{r}')]_{00}}{\omega_{m0}(\omega_{m0}+i\omega)}$$

$$\left.-\sum_{m}{}' \frac{[P_\alpha(\underset{\sim}{r})]_{00}[P_\beta(\underset{\sim}{r}')]_{0m}[\mu_\gamma]_{m0}}{\omega_{m0}(\omega_{m0}-i\omega)}\right\} . \quad (15)$$

Integration over the $\underset{\sim}{r}$- and $\underset{\sim}{r}'$-variables in Eq. (15) yields the (fully reduced) first hyperpolarizability in complete agreement with the expression given by Buckingham [303]. This first hyperpolarizability, $\beta_{\alpha\beta\gamma}(i\omega,-i\omega)$, gives the static nonlinear dipole in the presence of the electric fields $E_\alpha^{(\omega)}e^{-i\omega t}$ and $E_\beta^{(-\omega)}e^{i\omega t}$. The static nonlocal hyperpolarizability density obtained from Eq. (15) by taking $\omega = 0$ agrees in full with the expression given by Hunt [293] in formula (2.37).

Now the first-order correction to the wave function for a system perturbed by a uniform, static electric field in the $\alpha$-direction is given by

$$|\psi_\alpha^{(1)}\rangle = \sum_m{}' \frac{\langle m|\mu_\alpha|0\rangle}{\hbar\omega_{m0}} |\psi_m\rangle \equiv \sum_m{}' \frac{[\mu_\alpha]_{m0}}{\hbar\omega_{m0}} |m\rangle \; . \qquad (16)$$

Reshuffling of indices in Eq. (15), the use of Eq. (16) and Fourier transformation allow us to write the hyperpolarizability in $\underset{\sim}{k}$-space as

$$\begin{aligned}\hat{\beta}_{\beta\gamma\alpha}(\underset{\sim}{k},\underset{\sim}{k}';i\omega,-i\omega) = [1+\text{c.c.}']\Big\{ & \sum_n{}' \frac{\langle\psi_\alpha^{(1)}|P_\beta(\underset{\sim}{k})|n\rangle\langle n|P_\gamma(\underset{\sim}{k}')|0\rangle}{\hbar(\omega_{n0}+i\omega)} \\ & + \sum_m{}' \frac{\langle\psi_\alpha^{(1)}|P_\gamma(\underset{\sim}{k}')|m\rangle\langle m|P_\beta(\underset{\sim}{k})|0\rangle}{\hbar(\omega_{m0}-i\omega)} \\ & + \sum_{n,m}{}' \frac{[P_\beta(\underset{\sim}{k})]_{0m}[\mu_\alpha]_{mn}[P_\gamma(\underset{\sim}{k}')]_{n0}}{(\omega_{n0}+i\omega)(\omega_{m0}+i\omega)\hbar^2} \\ & -\hbar^{-2} \sum_n{}' \Big[ \frac{[P_\beta(\underset{\sim}{k})]_{00}[\mu_\alpha]_{0n}[P_\gamma(\underset{\sim}{k}')]_{n0}}{\omega_{n0}(\omega_{n0}+i\omega)} \\ & + \frac{[P_\gamma(\underset{\sim}{k}')]_{00}[\mu_\alpha]_{0n}[P_\beta(\underset{\sim}{k})]_{n0}}{\omega_{n0}(\omega_{n0}-i\omega)} \Big]\Big\} \; . \qquad (17)\end{aligned}$$

where c.c.' denotes the Fourier transform of the terms associated with c.c. in Eq. (15).

We shall need later the doubly contracted hyperpolarizability in $\underset{\sim}{k}$-space, viz., $k_\beta k'_\gamma \hat{\beta}_{\beta\gamma\alpha}(\underset{\sim}{k},\underset{\sim}{k}';i\omega,-i\omega)$, where the sum over repeated subscripts is implied. The divergence of the polarization is proportional to the charge density, and its Fourier transformation satisfies the condition

$$\underset{\sim}{k}\cdot\underset{\sim}{P}(\underset{\sim}{k}) = -i.\rho(\underset{\sim}{k}) . \qquad (18)$$

The use of Eq. (18) in Eq. (17) allows us to calculate the doubly contracted hyperpolarizability

$$\begin{aligned} k_\beta k'_\gamma \hat{B}_{\beta\gamma\alpha}(\underset{\sim}{k},\underset{\sim}{k}';i\omega,-i\omega) = [1+c.c] \Big\{ &- {\sum_m}' \frac{\langle\psi_\alpha^{(1)}|\rho(\underset{\sim}{k})|m\rangle\langle m|\rho(\underset{\sim}{k}')|0\rangle}{\hbar(\omega_{m0}+i\omega)} \\ &- {\sum_m}' \frac{\langle\psi_\alpha^{(1)}|\rho(\underset{\sim}{k}')|m\rangle\langle m|\rho(\underset{\sim}{k})|0\rangle}{\hbar\,(\omega_{m0}-i\omega)} \\ &- {\sum_{n,m}}' \frac{\langle 0|\rho(\underset{\sim}{k})|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\rho(\underset{\sim}{k}')|0\rangle}{\hbar^2(\omega_{m0}+i\omega)(\omega_{n0}+i\omega)} \\ &+ \hbar^{-2} {\sum_m}' \Big[ \frac{\langle 0|\rho(\underset{\sim}{k})|0\rangle\langle 0|\mu_\alpha|m\rangle\langle m|\rho(k')|0\rangle}{\omega_{m0}(\omega_{m0}+i\omega)} \\ &+ \frac{\langle 0|\rho(\underset{\sim}{k}')|0\rangle\langle 0|\mu_\alpha|m\rangle\langle m|\rho(\underset{\sim}{k})|0\rangle}{\omega_{m0}(\omega_{m0}-i\omega)} \Big]\Big\} \,. \qquad (19) \end{aligned}$$

The multipole moments $Q_\ell^m(k)$ are defined [264] by the equation

$$Q_\ell^m(k) = \sum_\alpha Z_\alpha \left(\frac{4\pi}{2\ell+1}\right)^{1/2} Y_\ell^m(\theta_\alpha,\phi_\alpha) \frac{(2\ell+1)!}{2^\ell\,\ell!}\, j_\ell(kr_\alpha) \qquad (20)$$

where $Z_\alpha$ is the electric charge of particle $\alpha$, $j_\ell$ is the $\ell^{th}$ spherical Bessel function, and $(r_\alpha,\theta_\alpha,\phi_\alpha)$ is the position vector of the particle $\alpha$. Then using the Rayleigh expansion of the plane wave $\exp(i\underset{\sim}{k}.\underset{\sim}{r}_\alpha)$in the Fourier transform of the charge density $\rho(\underset{\sim}{k})$, we may write

$$\rho(\underset{\sim}{k}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^\ell \frac{\ell!\, 2^\ell}{(2\ell)!} \frac{\sqrt{4\pi}}{\sqrt{2\ell+1}}\, Y_\ell^{\,m}(\theta,\phi)^*\, Q_\ell^m\,(k) \quad , \qquad (21)$$

with $\underset{\sim}{k} = (k,\ \theta,\ \phi)$.

Let the function $\Phi_\ell^m\,(k,\omega)$ be defined by

$$\Phi_\ell^m\,(k,\omega) \equiv \hbar^{-1} {\sum_n}' \frac{1}{\omega_{no}+\omega}\, |n\rangle\langle n|Q_\ell^m(k)|0\rangle \quad . \qquad (22)$$

We rewrite Eq. (19) with the aid of Eqns. (21) and (22) and we specialize it to spherically symmetric systems. Thus,

$$
\begin{aligned}
k_\beta k'_\gamma \hat{\beta}_{\beta\gamma\alpha}(\underset{\sim}{k},\underset{\sim}{k}';i\omega,-i\omega) = [1+c.c.] \Bigg\{ & \sum_{\ell,\ell'=0}^{\infty} \sum_{m=-\ell}^{\ell} \sum_{m'=-\ell'}^{\ell'} C(\ell,\ell') \cdot \\
\cdot \Big[ & -Y_{\ell'}^{m'}(\theta',\phi')^* Y_{\ell}^{m}(\theta,\phi)^* \langle \psi_{1m''} | Q_{\ell}^{m}(k) | \Phi_{\ell'}^{m'}(k',i\omega) \rangle \delta_{m'',m+m'} \, \delta_{\ell,\ell'\pm 1} \\
& -Y_{\ell}^{m}(\theta,\phi)^* Y_{\ell'}^{m'}(\theta',\phi')^* \langle \psi_{1m''} | Q_{\ell'}^{m'}(k') | \Phi_{\ell}^{m}(k,-i\omega) \rangle \delta_{m'',m'+m} \delta_{\ell,\ell'\pm 1} \\
& -Y_{\ell}^{m}(\theta,\phi) \; Y_{\ell'}^{m'}(\theta',\phi')^* \langle \Phi_{\ell}^{m}(k,-i\omega) | \mu_\alpha | \Phi_{\ell'}^{m'}(k',i\omega) \rangle \delta_{\ell,\ell'\pm 1} \delta_{m,m''+m'} \Big] \\
& + \frac{4\pi}{\sqrt{3}} \frac{1}{\hbar\omega} \Big[ (-1)^{m''+1} Y_0^0(\theta,\phi)^* Y_1^{m''}(\theta',\phi') \langle 0 | \mu_\alpha | \Phi_1^{\bar{m}''}(k',i\omega) \rangle \langle 0 | Q_0^0(k) | 0 \rangle \\
& + Y_1^{\bar{m}''}(\theta,\phi)^* Y_0^0(\theta',\phi')^* \langle 0 | \mu_\alpha | \Phi_1^{\bar{m}''}(k,-i\omega) \rangle \langle 0 | Q_0^0(k') | 0 \rangle \Big] \Bigg\}
\end{aligned}
\tag{23}
$$

where

$$
C(\ell,\ell') \equiv i^{\ell+\ell'} \frac{\ell!\ell'!2^{\ell+\ell'}}{(2\ell)!(2\ell')!} \; \frac{4\pi}{[(2\ell+1)(2\ell'+1)]^{1/2}} \; . \tag{24}
$$

In Eq. (23) $\delta_{i,j}$ is Kronecker's unit tensor, and the electric field has been taken in the direction $Y_1^{m''}$. We adopt the convention $\bar{m}'' \equiv -m''$ in Eq. (23) and within this context.

The doubly contracted hyperpolarizability given by Eq. (23) is in a suitable analytic form for computations, since the matrix elements can be calculated [266].

The doubly contracted Fourier transform of the nonlocal polarizability density is [276,293] the susceptibility $\chi(\underset{\sim}{k},-\underset{\sim}{k}';i\omega)$ ; with the same conventions and definitions as made for the hyperpolarizability

$$\chi(\underset{\sim}{k},-\underset{\sim}{k}';i\omega) = \sum_{L=0}^{\infty} \sum_{M=-L}^{L} C(L) Y_L^M(\theta,\phi) Y_L^M(\theta',\phi')^{*} \langle 0 | Q_L^M(k)^{*} | \Phi_L^M(k',i\omega) + $$

$$+ \Phi_L^M(k',-i\omega) \rangle \tag{25}$$

and

$$C(L) \equiv (-i)^{2L} \left[ \frac{L!2^L}{(2L)!} \right]^2 \frac{4\pi}{2L+1} \quad . \tag{26}$$

## 5.4.- DAMPED DISPERSION DIPOLE MOMENT CALCULATION

The α-component of the dispersion dipole on A in the A...B pair is given in terms of properties of molecules A and B by [293]

$$(\mu^{A}_{disp})_{\alpha}= \frac{\hbar}{(2\pi)^7} \int_{0}^{\infty}d\omega\int\beta^{A}_{\beta\gamma\alpha}(-\underset{\sim}{k},-\underset{\sim}{k}';i\omega,-i\omega).\alpha^{B}_{\delta\epsilon}(-\underset{\sim}{k},\underset{\sim}{k}';i\omega).T_{\beta\delta}(\underset{\sim}{k}).$$

$$.T_{\gamma\epsilon}(\underset{\sim}{k}')\; d\underset{\sim}{k}\; d\underset{\sim}{k}' \quad , \tag{27}$$

Where the dipole propagator in $\underset{\sim}{k}$-space is [293]

$$T_{\alpha\beta}(\underset{\sim}{k}) = - \frac{4\pi}{k^2}\, k_{\alpha}k_{\beta} \;. \tag{28}$$

Let $\underset{\sim}{R}$ be the vector from a center in A to a center in B and refer the position of all the particles in $\underset{\sim}{r}$-space to the origin of $\underset{\sim}{R}$. Then

$$(\mu^{A}_{disp})_{\alpha}= \hbar\,\frac{(4\pi)^2}{(2\pi)^7} \int_{0}^{\infty}d\omega\int\beta^{A}_{\beta\gamma\alpha}(\underset{\sim}{k},\underset{\sim}{k}';i\omega,-i\omega)\frac{k_{\beta}k'_{\gamma}}{k^2k'^2}\;(-1)\chi^{B}(\underset{\sim}{k},-\underset{\sim}{k}';i\omega)$$

$$.e^{-i(k+k')\cdot\underset{\sim}{R}}\; d\underset{\sim}{k}\; d\underset{\sim}{k}'. \tag{29}$$

To analyze Eq. (29), the plane-wave exp(-i$\underset{\sim}{k}$.$\underset{\sim}{R}$) is written again as a Rayleigh expansion

$$e^{-\underset{\sim}{k}\cdot\underset{\sim}{R}} = \sum_{\lambda=0}^{\infty}\;\sum_{\mu=-\lambda}^{\lambda}\; i^{\lambda}\; 4\pi Y^{\mu}_{\lambda}(\theta,\phi).Y^{\mu}_{\lambda}(\theta_R,\phi_R)^{*} j_{\lambda}(kR) \quad , \tag{30}$$

where $\underset{\sim}{R} = (R,\theta_R,\phi_R)$. Let us define

$$C(\ell,\ell',L) \equiv C(\ell,\ell').C(L) \tag{31}$$

with $C(\ell,\ell')$ and $C(L)$ defined by Eqns. (24) and (26), respectively.

The next step is to perform the angular integration in Eq. (29), where the B-susceptibility and the doubly-contracted A-hyperpolarizability have been written as in Eqns. (25) and (23), respectively. To do so, we make extensive use of the properties of spherical harmonics and Clebsch-Gordan coefficients, the Wigner-Eckart theorem, and the relationship

$$\sum_{\beta,\delta,\epsilon} \langle ab\alpha\beta|e\epsilon\rangle\langle ed\epsilon\,\delta|c\gamma\rangle\langle bd\beta\delta|f\phi\rangle =$$

$$= [(2e+1)(2f+1)]^{1/2}\, W(abcd;ef)\langle af\alpha\phi|c\gamma\rangle, \tag{32}$$

where $\langle ab\alpha\beta|e\epsilon\rangle$ denotes a Clebsch-Gordan coefficient and $W(abcd;ef)$ is the Racah coefficient, closely related to the 6-j symbol. We obtain [305] the damped dispersion dipole moment for a spherically symmetric system

$$(\mu^{A}_{\mathrm{disp}})_Z = \hbar\,\frac{2}{\pi^3}\int_0^\infty d\omega \int_0^\infty dk\; dk' \sum_{\lambda,\lambda'=0}^{\infty} i^{\lambda+\lambda'} j_\lambda(kR)\, j_{\lambda'}(k'R') \,\cdot$$

$$\cdot\,\frac{[(2\lambda+1)(2\lambda'+1)]^{1/2}}{4\pi}\,\langle\lambda\lambda'00|10\rangle\,\cdot$$

$$\cdot\sum_{L=0}^{\infty}\langle LL00|00\rangle\langle 0||Q_L(k)||\Phi_L(k',i\omega)+\Phi_L(k',-i\omega)\rangle[1+c.c'.]\,\cdot$$

$$\cdot \Big[ - \frac{(4\pi)^{1/2}}{3} \, \frac{1}{\hbar\omega} \, C(L) \; A(\lambda',1,\lambda) \cdot \Big[ \langle 0 || Q_0(k) || 0 \rangle \langle 0 || \mu || \Phi_1(k',i\omega) \rangle$$

$$+ \langle 0 || Q_0(k') || 0 \rangle \langle \Phi_1(k,i\omega) || \mu || 0 \rangle \Big] \delta_{L,\lambda}$$

$$+ \sum_{\ell,\ell'=0}^{\infty} C(\ell,\ell',L) . A(L,\ell',\lambda') [(2\ell+1)(2\lambda'+1)]^{1/2} \; W(1\ell'\lambda L;\ell\lambda')$$

$$\cdot \Big\{ A(\lambda,L,\ell) \Big[ \langle \psi_1 || Q_\ell(k) || \Phi_{\ell'}(k',i\omega) \rangle + \langle \psi_1 || Q_{\ell'}(k') || \Phi_\ell(k,-i\omega) \rangle \Big] \frac{1}{\sqrt{3}} +$$

$$+ \frac{A(\ell,L,\lambda)}{(2\ell+1)^{1/2}} \langle \Phi_\ell(k,-i\omega) || \mu || \Phi_{\ell'}(k',i\omega) \; \Big\} \Big], \quad (33)$$

where

$$A(a,b,c) \equiv (-1)^{a-b} \left[ \frac{(2a+1)(2b+1)}{4\pi} \right]^{1/2} \begin{bmatrix} a & b & c \\ o & o & o \end{bmatrix} \quad , \qquad (34)$$

the double-bar matrix elements are the reduced matrix elements generated by the use of the Wigner-Eckart theorem, and we have taken $\hat{R} = \hat{z}$.

Notice that the Clebsch-Gordan coefficients involved in Eq. (33) imply the existence of the factors $\delta_{\ell,\ell'\pm1}$ and $\delta_{\lambda,\lambda'\pm1}$ . Therefore, we may rewrite Eq. (33) as

$$(\mu^A_{disp})_Z = \sum_{\ell,L=0}^{\infty} \sum_{\substack{\lambda=|\ell-L| \\ (\ell+\lambda+L=\dot{2})}}^{\ell+L} \int_0^\infty dk \; j_\lambda(kR) \int_0^\infty dk' j_{\lambda\pm1}(k'R) \int_0^\infty d\omega \; G(k,k';i\omega;\ell,\lambda,L), \quad (35)$$

where $G(k,k';i\omega;\ell,\lambda,L)$ in Eq. (35) is defined by comparing this equation and Eq. (33).

An analysis analogous to Koide's for the damped dispersion energy [264] holds for Eq. (35) (or Eq. (33)). Consequently, we may say that $(\mu^A_{disp})_z$ vanishes as R goes to 0 and as R goes to infinity. Computations of $(\mu^A_{disp})_z$ and the dipole moment overlap-damping functions may be performed with the analytic expression given by Eq. (33).

# APPENDIX A.

A derivation of Eq. (21) is carried out in this Appendix. Let us rewrite Eq. (20)

$$A^{(n)} = (-1)^{n-1} \frac{1}{2\pi i} \oint_{\Gamma} R_0(\ell) H^{(1)} \overset{\cdot n \cdot}{\cdots} R_0(\ell) d\ell \tag{A.1}$$

$$R_0(\ell) = \frac{E_0}{\lambda_0 - \ell} + S + (\ell - \lambda_0) S^2 + (\ell - \lambda_0)^2 S^3 + \ldots \tag{A.2}$$

$$S_0(\ell) \equiv S + (\ell - \lambda_0)\, S^2 + (\ell - \lambda_0)^2 S^3 + \ldots \tag{A.3}$$

$$S \equiv S_0(\lambda_0) \tag{A.4}$$

From (A.1) and (A.2), taking into account definitions (A.3) and (A.4),

$$A^{(n)} = (-1)^{n-1} \frac{1}{2\pi i} \oint_{\Gamma} \left[ \frac{E_0}{\lambda_0 - \ell} + S_0(\ell) \right] H^{(1)} \overset{\cdot n \cdot}{\cdots} \left[ \frac{E_0}{\lambda_0 - \ell} + S_0(\ell) \right] d\ell \;. \tag{A.5}$$

In particular

$$A^{(1)} = \frac{1}{2\pi i} \oint_{\Gamma} R_0(\ell) H^{(1)} R_0(\ell) d\ell = \frac{1}{2\pi i} \oint_{\Gamma} \left[ \frac{E_0}{\lambda_0 - \ell} + S_0(\ell) \right] H^{(1)} \left[ \frac{E_0}{\lambda_0 - \ell} + S_0(\ell) \right] d\ell =$$

$$= \frac{1}{2\pi i} \oint_\Gamma \frac{E_0}{\lambda_0-\ell} H^{(1)} \frac{E_0}{\lambda_0-\ell} d\ell + \frac{1}{2\pi i} \oint_\Gamma S_0(\ell)H^{(1)} \frac{E_0}{\lambda_0-\ell} d\ell +$$

$$+ \frac{1}{2\pi i} \oint_\Gamma \frac{E_0}{\lambda_0-\ell} H^{(1)}S_0(\ell)d\ell + \frac{1}{2\pi i} \oint_\Gamma S_0 (\ell)H^{(1)}S_0(\ell)d\ell =$$

$$= -SH^{(1)}E_0 - E_0 H^{(1)}S \tag{A.6}$$

$$A^{(2)} = \frac{-1}{2\pi i} \oint_\Gamma R_0(\ell)H^{(1)}R_o(\ell)H^{(1)}R_0(\ell)d\ell = \frac{-1}{2\pi i} \oint_\Gamma \Big[ \frac{E_0}{\lambda_0-\ell} +$$

$$+ S_0(\ell) \Big] H^{(1)} \Big[ \frac{E_0}{\lambda_0-\ell} + S_0(\ell) \Big] H^{(1)} \Big[ \frac{E_0}{\lambda_0-\ell} + S_0(\ell) \Big] d\ell =$$

$$= \frac{-1}{2\pi i} \oint_\Gamma \frac{E_0}{\lambda_0-\ell} H^{(1)} \frac{E_0}{\lambda_0-\ell} H^{(1)} \frac{E_0}{\lambda_0-\ell} d\ell -$$

$$- \frac{1}{2\pi i} \oint_\Gamma \frac{E_0}{\lambda_0-\ell} H^{(1)}S_0(\ell)H^{(1)} \frac{E_0}{\lambda_0-\ell} d\ell -$$

$$- \frac{1}{2\pi i} \oint_\Gamma S_0(\ell)H^{(1)} \frac{E_0}{\lambda_0-\ell} H^{(1)} \frac{E_0}{\lambda_0-\ell} d\ell -$$

$$- \frac{1}{2\pi i} \oint_\Gamma S_0(\ell)H^{(1)}S_0(\ell)H^{(1)} \frac{E_0}{\lambda_0-\ell} d\ell -$$

$$- \frac{1}{2\pi i} \oint_\Gamma \frac{E_0}{\lambda_0-\ell} H^{(1)} \frac{E_0}{\lambda_0-\ell} H^{(1)}S_0(\ell)d\ell -$$

$$- \frac{1}{2\pi i} \oint_\Gamma \frac{E_0}{\lambda_0-\ell} H^{(1)} S_0(\ell)H^{(1)}S_0(\ell)d\ell -$$

$$- \frac{1}{2\pi i} \oint_{\Gamma} S_0(\ell)H^{(1)} \frac{E_0}{\lambda_0-\ell} H^{(1)}S_0(\ell)d\ell -$$

$$- \frac{1}{2\pi i} \oint_{\Gamma} S_0(\ell)H^{(1)}S_0(\ell)H^{(1)}S_0(\ell)d\ell =$$

$$= -E_0H^{(1)}S^2H^{(1)}E_0-S^2H^{(1)}E_0H^{(1)}E_0 +$$

$$+ SH^{(1)}SH^{(1)}E_0-E_0H^{(1)}E_0H^{(1)}S^2 +$$

$$+ E_0H^{(1)}SH^{(1)}S + SH^{(1)}E_0H^{(1)}S \qquad (A.7)$$

where Cauchy's integral theorem has been used in both (A.6) and (A.7). It should also be noted that $S_0(\ell)$ fulfills

$$\frac{d^q}{d\ell^q} S_0(\ell) = q! \; [S_0(\ell)]^{q+1}$$

The generalization to obtain (21) is now straightforward.

# APPENDIX B

## Expectation values of operators in label-free form

In this Appendix, a decomposition of the antisymmetrizer for an N-electron system is used to evaluate the expectation value of a permutation-invariant operator $\Omega$ in the state $\Psi$. The function $\Psi$ is assumed to be a normalized, fully antisymmetrized product of $N_A$ molecular orbitals on system A and $N_B$ on system B, with $N=N_A+N_B$.

The N-electron antisymmetrizer $\mathcal{A}$ is related to an idempotent projection operator $\mathcal{O}$ by

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_P \sigma_P P = \sqrt{N!}\, \mathcal{O} \qquad \text{(B.1)}$$

where the sum runs over the permutations in the symmetric group $S_N$, and $\sigma_P = \pm 1$, depending upon the parity of the permutation P. The operator $\mathcal{O}$ commutes with any operator $\Omega$ that is invariant with respect to each of the permutations. In particular

$$[\mathcal{O},H] = 0 \qquad \text{(B.2)}$$

where H is the full N-electron Hamiltonian for the "supermolecule" AB; and if the unperturbed Hamiltonian $H_0$ and the perturbation V due to A-B interaction are written in label-free form (Eqs. 2 and 3of chapter 3.2),

$$[\mathcal{O},H_0] = [\mathcal{O},V] = 0 \qquad \text{(B.3)}$$

The operator $\mathcal{O}$ may be decomposed into terms that perform the antisymmetrization within systems A and B and terms that perform the antisymmetrization between systems. Lagrange's theorem applied to the symmetric group $S_N$ and its subgroup $S_N \otimes S_N$ ensures that $\mathcal{O}$ may be split in this way [113,114]:

$$\mathcal{O} = \frac{1}{(N_A+N_B)!} \sum_P \sigma_P P = \frac{N_A!N_B!}{(N_A+N_B)!} \mathcal{O}_A \mathcal{O}_B \left(\mathbb{1} + \sum_{i=1}^{\ell} \sigma_i P_i^{AB}\right) \tag{B.4}$$

In Eq. B.4, $\mathcal{O}_A$ is the antisymmetrizing projection operator for molecule A with $N_A$ electrons, defined by analogy to $\mathcal{O}$ for the full N-electron system, and $\mathcal{O}_B$ is the corresponding operator for molecule B. $\mathbb{1}$ denotes the identity operator. $P_i^{AB}$ exchanges one or more particle labels assigned to A with labels assigned to B; it does not involve permutations within the set of electrons assigned to A or to B. The number $\ell$ of operators $P_i^{AB}$ is

$$\ell = \sum_{j=1}^{n} \binom{N_A}{j} \binom{N_B}{j} \ . \tag{B.5}$$

Since the upper limit n on the number of electrons exchanged is min $(N_A, N_B)$,

$$\ell = \frac{N!}{N_A!N_B!} - 1. \tag{B.6}$$

It is convenient to define P by

$$P = \sum_{i=1}^{\ell} \sigma_i P_i^{AB} \ . \tag{B.7}$$

Then the expectation value of $\Omega$ in the state $\Psi$ is

$$\langle\Psi|\Omega|\Psi\rangle = N! \ \langle \mathcal{O}\{\chi_1 \ldots \chi_N\} \ |\Omega| \ \mathcal{O}\{\chi_1 \ldots \chi_N\}\rangle \ / \ s \tag{B.8}$$

where the $\chi_i$'s are orbitals located on A or B and

$$s = N! \; \langle \mathcal{A}\{x_1 \ldots x_N\} \mid \mathcal{A}\{x_1 \ldots x_N\} \rangle$$

$$s = \frac{(N_A!)^2 \, (N_B!)^2}{N!} \quad \langle \mathcal{A}_A \mathcal{A}_B \, (1+P) \, \{x_1 \ldots x_N\} \mid \mathcal{A}_A \mathcal{A}_B \, (1+P) \, \{x_1 \ldots x_N\} \rangle$$

$$= N_A! \; N_B! \; \langle \mathcal{A}_A \mathcal{A}_B \, \{x_1 \ldots x_N\} \mid \mathcal{A}_A \, \mathcal{A}_B \, (1+P) \, \{x_1 \ldots x_N\} \rangle$$

$$= \langle \psi_A \psi_B \mid (1 + P) \, \psi_A \psi_B \rangle \, . \qquad \text{(B.9)}$$

In Eq. B.9 $\psi_A$ is the normalized antisymmetrized product wavefunction for system A (and $\psi_B$ for B). An analysis similar to that for s shows

$$\langle \Psi | \Omega | \Psi \rangle = \frac{1}{s} \, \langle \psi_A \psi_B | \Omega | \mathcal{A}_A \mathcal{A}_B \, (1+P) \, \{x_1 \ldots x_N\} \rangle \, . \qquad \text{(B.10)}$$

Substituting the form $\Sigma \, \Omega_i \Lambda_i$ for $\Omega$ yields

$$\langle \psi | \Omega | \psi \rangle = \frac{1}{s} \quad [\langle \psi_A \psi_B | \Omega_1 | \psi_A \psi_B \rangle \; +$$

$$+ \; \langle \psi_A \psi_B | \sum_{i=2}^{p} \Omega_i \Lambda_i | \mathcal{A}_A \mathcal{A}_B \sum_{j=1}^{\ell} \sigma_j P_j^{\;AB} \{x_1 \ldots x_N\} \rangle] , \qquad \text{(B.11)}$$

where $\Lambda_1$ is the projection operator that assigns the first $N_A$ electrons to molecule A and the remainder to B. Each of the operators $\Lambda_i$ in the second matrix element projects out a single $P_j^{AB}$ term from the ket. Eq. 22 in section 3.3.1 is obtained by identifying $\Omega$ with V.

# Appendix C

## Pair energy of He...H

The first-order pair energy E for the He...H system

$$E = E_H^{(0)} + E_{He}^{(0)} + V(F_z=0) + F_z \{T_1 + T_2 + T_3\} - \bar{\mu}_z F_z \tag{C.1}$$

from Eq. 11, with

$$\begin{aligned} V(F_z=0) = \frac{2}{R} + \frac{1}{s} \{ & -2\langle\chi_H|r_{He}^{-1}|\chi_H\rangle + 2\langle\chi_H|\chi_{He}\rangle\langle\chi_{He}|r_{He}^{-1}|\chi_H\rangle - 2\langle\chi_{He}|r_H^{-1}|\chi_{He}\rangle \\ & + \langle\chi_H|\chi_{He}\rangle[\langle\chi_{He}|r_H^{-1}|\chi_H\rangle + \langle\chi_H|\chi_{He}\rangle\langle\chi_{He}|r_H^{-1}|\chi_{He}\rangle] \\ & - \langle\chi_H\chi_{He}|r_{12}^{-1}|\chi_{He}\chi_H\rangle + 2\langle\chi_H\chi_{He}|r_{12}^{-1}|\chi_H\chi_{He}\rangle \\ & - \langle\chi_{He}\chi_{He}|r_{12}^{-1}|\chi_H\chi_{He}\rangle\langle\chi_H|\chi_{He}\rangle\} \;, \end{aligned} \tag{C.2}$$

$$T_1 = \frac{2}{s} \langle\chi_H|\chi_{He}\rangle(E_H^{(0)}\langle\chi_{He}|\chi_H^1\rangle - \langle\chi_{He}|h_H|\chi_H^1\rangle), \tag{C.3}$$

$$\begin{aligned} T_2 = \frac{2}{s} \Big[ & - \langle\chi_{He}|h_{He}|\chi_{He}\rangle\langle\chi_H|\chi_{He}\rangle[\langle\chi_H|\chi_{He}^1\rangle + \langle\chi_H^1|\chi_{He}\rangle] - \langle\chi_H|h_{He}|\chi_{He}\rangle\langle\chi_H^1|\chi_{He}\rangle \\ & - \langle\chi_H|h_{He}|\chi_{He}^1\rangle\langle\chi_H|\chi_{He}\rangle - \langle\chi_H\chi_{He}|r_{12}^{-1}|\chi_{He}\chi_{He}\rangle\langle\chi_H^1|\chi_{He}\rangle \\ & - \langle\chi_H\chi_{He}|r_{12}^{-1}|\chi_{He}^1\chi_{He}\rangle\langle\chi_H|\chi_{He}\rangle - \langle\chi_H\chi_{He}|r_{12}^{-1}|\chi_{He}\chi_{He}^1\rangle\langle\chi_H|\chi_{He}\rangle \\ & + E_{He}^{(0)}\langle\chi_H|\chi_{He}\rangle[\langle\chi_{He}|\chi_H^1\rangle + \langle\chi_H|\chi_{He}^1\rangle] \Big] \;, \end{aligned} \tag{C.4}$$

$$\begin{aligned} T_3 = \frac{2}{s} \Big[ & -2\langle\chi_H|r_{He}^{-1}|\chi_H^1\rangle - 2\langle\chi_{He}|r_H^{-1}|\chi_{He}^1\rangle + 2\langle\chi_H\chi_{He}|r_{12}^{-1}|\chi_H^1\chi_{He}\rangle \\ & + 2\langle\chi_H\chi_{He}|r_{12}^{-1}|\chi_H\chi_{He}^1\rangle - \frac{2}{R}\langle\chi_{He}|\chi_H\rangle(\langle\chi_{He}|\chi_H^1\rangle + \langle\chi_H|\chi_{He}^1\rangle) \end{aligned}$$

$$\begin{aligned}
&+ 2\langle \chi_{He} | r_{He}^{-1} | \chi_{H}^{1} \rangle \langle \chi_{H} | \chi_{He} \rangle + 2\langle \chi_{He} | r_{He}^{-1} | \chi_{H} \rangle \langle \chi_{H} | \chi_{He}^{1} \rangle \\
&+ \langle \chi_{H} | r_{H}^{-1} | \chi_{He} \rangle \langle \chi_{He} | \chi_{H}^{1} \rangle + \langle \chi_{H} | r_{H}^{-1} | \chi_{He}^{1} \rangle \langle \chi_{He} | \chi_{H} \rangle \\
&+ \langle \chi_{He} | r_{H}^{-1} | \chi_{He} \rangle \langle \chi_{H} | \chi_{He} \rangle (\langle \chi_{He} | \chi_{H}^{1} \rangle + \langle \chi_{H} | \chi_{He}^{1} \rangle) \\
&+ \langle \chi_{He} | r_{H}^{-1} | \chi_{He}^{1} \rangle \langle \chi_{H} | \chi_{He} \rangle^{2} - \langle \chi_{He}\chi_{H} | r_{12}^{-1} | \chi_{H}^{1}\chi_{He} \rangle - \langle \chi_{He}\chi_{H} | r_{12}^{-1} | \chi_{H}\chi_{He}^{1} \rangle \\
&- \langle \chi_{H} | \chi_{He} \rangle (\langle \chi_{He}\chi_{He} | r_{12}^{-1} | \chi_{H}^{1}\chi_{He} \rangle + \langle \chi_{He}\chi_{He} | r_{12}^{-1} | \chi_{H}\chi_{He}^{1} \rangle) \\
&- \langle \chi_{He}\chi_{He} | r_{12}^{-1} | \chi_{H}\chi_{He} \rangle \langle \chi_{H} | \chi_{He}^{1} \rangle + V(F_{z}=0)\ (\langle \chi_{He} | \chi_{H}^{1} \rangle + \langle \chi_{He}^{1} | \chi_{H} \rangle) \langle \chi_{He} | \chi_{H} \rangle \Big],
\end{aligned} \tag{C.5}$$

and

$$\bar{\mu}_{z} = \frac{\langle \chi_{H} | \chi_{He} \rangle}{s} \left[ 2\langle \chi_{H} | z | \chi_{He} \rangle - 2R\langle \chi_{H} | \chi_{He} \rangle \right] . \tag{C.6}$$

The notation

$$h_{q} = -\frac{\nabla^{2}}{2} - Z_{q} r_{q}^{-1} \tag{C.7}$$

$$s = 1 - \langle \chi_{H} | \chi_{He} \rangle^{2} \tag{C.8}$$

$$\langle \chi_{q} | g | \chi_{r} \rangle = \int d^{3}r_{1} \chi_{q}(1) g(1) \chi_{r}(1) \tag{C.9}$$

$$\langle \chi_{q}\chi_{v} | r_{12}^{-1} | \chi_{m}\chi_{u} \rangle = \int d^{3}r_{1} d^{3}r_{2} \chi_{q}(1) \chi_{v}(2)\ r_{12}^{-1}\ \chi_{m}(1) \chi_{u}(2) \tag{C.10}$$

$$\langle \chi_{q} | \chi_{v} \rangle = \int d^{3}r_{1} \chi_{q}(1) \chi_{v}(1) \tag{C.11}$$

is used in Eqs. C.1–C.6. Also, the internuclear distance is R, $r_{12}$ is the interelectronic distance, and $r_q$ is the distance from an electron to nucleus q; g is any one-particle operator and q, v, m, u = H or He. The functions $\chi_q^{(1)}$ and $\chi_q^{(0)}$ from the main text are abbreviated as $\chi_q^{1}$ and $\chi_q$, respectively. $Z_q$ is the atomic number of nucleus q.

# APPENDIX D

The hybrid integral $\langle 1s_{He} 1s_{He} | r_{12}^{-1} | 3p_Z^H 1s_{He} \rangle$ needed for the calculations in Chapter 3 is not one of the 79 hybrid integrals in terms of auxiliary functions compiled in Ref. 67. If we adopt the same conventions and symbology as in Ref. 67, the calculation proceeds in the following way. Define the charge distributions $\Omega_a \equiv 1s_{He} 1s_{He}$ and $\Omega_{ab} \equiv 1s_{He}\ 3p_z^H$ where a $\equiv$ He and b $\equiv$ H. $\Omega_{ab}$ is a $\Sigma$-type distribution according to the standard two-centre charge distributions given in Table III of Ref. 67. Furthermore,

$$\Omega = k\ \omega(\xi,\eta)\exp(-\alpha\xi)\exp(-\beta\eta) \tag{D.1}$$

$$\frac{\pi}{2}(\xi^2-\eta^2)\omega(\xi,\eta) = \sum_{n=0}^{4}\sum_{j=0}^{4}\omega_{nj}\xi^n\eta^j = \frac{1}{4\sqrt{30}}(\xi-\eta)(1-\xi\eta)(\xi^2-\eta^2) \tag{D.2}$$

$$\omega(\xi,\eta) = \frac{1}{2\pi\sqrt{30}}(\xi-\eta)(1-\xi\eta) \tag{D.3}$$

$$k = R^2(\zeta_{He}^{1s})^{3/2}(\zeta_H^{3p_z})^{7/2} \tag{D.4}$$

$$(\frac{R}{2})^2(\xi-\eta)\Omega = \frac{1}{8\pi\sqrt{30}}(\zeta_{He}^{1s})^{3/2}(\zeta_H^{3p_z})^{-1/2}\rho_H^4\exp(-\rho\xi-\rho\tau\eta)(\xi-\eta)^2(1-\xi\eta) \tag{D.5}$$

and $M = 0 = q$. The expression (D.5) expands by one the number of terms given in Table III of Ref. 67.

The one-centre distribution is $\Omega_{He} = [1S_{He}]$, and

$$1-\exp(-\bar{\rho}_a(\xi-\eta))[1+\frac{1}{2}\bar{\rho}_a(\xi-\eta)] = \frac{R}{2}(\xi+\eta)U\Omega_{He} \tag{D.6}$$

Therefore, $u_0 = 1$, $u_1 = 1/2$

$$[1S_{He}|1s_{He}3p_z^H] = (\zeta_{He}^{1s})^{3/2}(\zeta_H^{3p_z})^{-1/2}\rho_H^4 \int_0^\infty d\xi\int_{-1}^{1}d\eta[1-e^{-\bar{\rho}_{He}(\xi-\eta)}\sum_{k=0}^{1}$$

$$u_k\bar{\rho}_{He}^{k}(\xi+\eta)^k]e^{-\rho(\xi+\tau\eta)}\frac{1}{4\sqrt{30}}(\xi-\eta)^2(1-\xi\eta) =$$

$$= \frac{1}{4\sqrt{30}}(\zeta_{He}^{1s})^{3/2}(\zeta_H^{3pz})^{-1/2}\rho_H^4\int_1^\infty d\xi\int_{-1}^{1}d\eta\Big\{(\xi-\eta)^2(1-\xi\eta)$$

$$-e^{-\bar{\rho}_{He}(\xi-\eta)}[(\xi-\eta)^2(1-\xi\eta) -$$

$$-\frac{1}{2}\bar{\rho}_{He}(\xi+\eta)(\xi-\eta)^2(1-\xi\eta)]\Big\} e^{-\rho(\xi+\tau\eta)} =$$

$$= \frac{2^4}{4\sqrt{30}}(\zeta_{He}^{1s})^{3/2}(\zeta_H^{3p_z})^{-1/2}\Big[C_{02}^{010} - \sum_{\alpha=0}^{1}u_\alpha(2\mu)^\alpha C_{\alpha,2}^{010}(\rho_{He}^{*},\rho_H)] = \frac{4}{\sqrt{30}} I_{02}^{010} \quad (D.7)$$

$$[1S_{He}|1s_{He}3p_z^H] = \zeta_{He}^{3/2}\zeta_H^{-1/2}\Big\{H_0(\rho_{He},\rho_H) - H_0(\rho_{He}^{*},\rho_H)-\mu H_1(\rho_{He}^{*},\rho_H)\Big\} \quad (D.8)$$

From (D.7) and (D.8),

$$\frac{4}{\sqrt{30}} C_{\alpha 2}^{010} = H_\alpha \quad (D.9)$$

Thus, the number of monopole integrals given in Table VI of Ref. 67 may be increased by adding the term

| $[\Omega_a \mid \Omega_{ab}]$ | $H_0$ | $H_1$ | cf |
|---|---|---|---|
| $[1S_{He} \mid 1s_{He}3p_z^H]$ | $C_{02}^{010}$ | $C_{12}^{010}$ | $4/\sqrt{30}$ |

# APPENDIX E.

We outline here the proof that leads to Eq. (20) from Eq. (17) in chapter 4. We give first the expressions for the spherical-tensor dipole moment, the product of two spherical harmonics on one center, the product of a component of the dipole moment and a Slater-type orbital, and the transformation of spherical harmonics under rotations. We then write the α-component of the dipole moment from which Eq. (20) is derived. We refer to standard books [238-241] as the source of the mathematical relationships used in this appendix.

## E.1. Spherical-tensor dipole moment.

$$r_0 = z \tag{E1}$$

$$r_{\pm 1} = \mp (2)^{-1/2}(x \pm iy) \tag{E2}$$

or
$$r_m = \left(\frac{4\pi}{3}\right)^{1/2} r \, Y_{1m}(\theta,\phi) \quad , \text{ with } m = 0, \pm 1. \tag{E3}$$

## E.2. Product of two spherical harmonics on the same centre.

Let the spherical harmonics be $Y_{\ell_1 m_1}(\theta,\phi)$ and $Y_{\ell_2 m_2}(\theta,\phi)$. The product is given by the following expansion in terms of the Clebsch-Gordan coefficients $C(\ell,\ell',\ell'';m,m',m'')$

$$Y_{\ell_1 m_1}(\theta,\phi) \cdot Y_{\ell_2 m_2}(\theta,\phi) = \sum_{\ell,m} \left[ \frac{(2\ell_1+1)\,(2\ell_2+1)}{4\pi(2\ell+1)} \right]^{1/2} C(\ell_1 \ell_2 \ell;000) \,.$$
$$\cdot\, C(\ell_1 \ell_2 \ell; m_1 m_2 m)\, Y_{\ell m}(\theta,\phi). \tag{E4}$$

When we take $\ell_1 = 1$, the properties of the Clebsch-Gordan coefficients let us write

$$Y_{1m_1}(\theta,\phi).Y_{\ell_2 m_2}(\theta,\phi) = \sum_{\ell=|\ell_2\pm 1|} \left[\frac{3(2\ell_2+1)}{4\pi(2\ell+1)}\right]^{1/2} C(1\ell_2\ell;000).$$

$$. \; C\,(1\ell_2\ell;m_1,m_2,m_1+m_2)\; Y_{\ell,m_1+m_2}(\theta,\phi) \qquad \text{(E5)}$$

where $\sum_{\ell=|\ell_2\pm 1|}$ stands for the sum over at most two possible values for $\ell$, viz., $\ell_2+1$ and $|\ell_2-1|$.

### E.3. Product of a component of the dipole moment and a Slater-type orbital.

Let the normalized complex Slater-type orbital on centre a be

$$(n,\ell,m)_a = (2\zeta_a)^{n+\frac{1}{2}}[(2n)!]^{-1/2} r^{n-1} e^{-\zeta_a r}\, Y_{\ell m}(\theta_a,\phi_a)\ . \qquad \text{(E6)}$$

Then

$$r_{m_1}.(n,\ell_2,m_2)_a = \left(\frac{4\pi}{3}\right)^{1/2}(2\zeta_a)^{n+\frac{1}{2}}[(2n)!]^{-1/2} r^{n} e^{-\zeta_a r} Y_{1m_1}(\theta_a,\phi_a) Y_{\ell_2 m_2}(\theta_a,\phi_a) =$$

$$= \sum_{\ell=|\ell_2\pm 1|}\left[\frac{2\ell_2+1}{2\ell+1}\right]^{1/2} C(1\ell_2\ell;000).C(1\ell_2\ell;m_1,m_2,m_1+m_2)\ .$$

$$. \; \frac{[2n+2)(2n+1]^{1/2}}{2\zeta_a}\,(n+1,\ell,m_1+m_2)'_a \quad , \qquad \text{(E7)}$$

where Eqns. (E3, E5, E6) have been used and $(n+1,\ \ell,\ m_1+m_2)_a'$ is a modified Slater-type orbital on a defined by

$$(n+1,\ell,m_1+m_2)'_a = (2\zeta_a)^{n+\frac{3}{2}}[(2n+2)!]^{-1/2} r^{n} e^{-\zeta_a r} Y_{\ell,m_1+m_2}(\theta_a,\phi_a). \qquad \text{(E8)}$$

### D.4. Transformation of spherical harmonics under rotations.

Let (X', Y', Z') be the canonical reference frame. $\Omega$ denotes the rotation (passive interpretation) carrying the system (X, Y, Z) into coincidence with (X',Y',Z'). The transformation law is

$$Y_{\lambda\mu}(\theta',\Phi') = \sum_{m} D^{\lambda}_{m\mu}(\Omega) . Y_{\lambda m}(\theta,\Phi), \tag{E9}$$

where $D^{\lambda}_{m\mu}(\Omega)$ is the rotation matrix [241] defined by the convention given by Rose [238] and Messiah [239].

E.5. α-component of the electronic contribution to the dipole moment.

The use of E.1 through E.4 let us write Eq. (17) in chapter 4 as

$$\mu^{el}_{\alpha} = - \left[{\delta^i}_i + {T^i}_k {T^k}_i - {T^i}_k {\tau^k}_\ell {T^\ell}_i\right] {(r_\alpha)^i}_i - \tag{E.10.1.1}$$

$$- \left[-{T^i}_j + {T^i}_k {T^k}_j - {T^i}_k {\tau^k}_\ell {T^\ell}_j\right] {(r\ )^j}_i = \tag{E.10.1.2}$$

$$= \frac{N}{P} \sum_{\rho=1}^{P} (-R_{\alpha\rho}) - \sum_{\rho=1}^{P} R_{\alpha\rho} \sum_{i\in P_\rho} ({T^i}_k {T^k}_i - {T^i}_k {\tau^k}_\ell {T^\ell}_i) + \tag{E.10.2.1}$$

$$+ \sum_{\rho=1}^{P} \sum_{i\in P_\rho} \sum_{\substack{j\in P_\rho \\ (i\neq j)}} \left[{T^i}_j - {T^i}_k {T^k}_j - {T^i}_k {\tau^k}_\ell {T^\ell}_j\right] - \tag{E.10.2.2}$$

$$- \sum_{\rho=1}^{P} \sum_{i\in P_\rho} \sum_{\substack{j\in P_\rho \\ (i\neq j)}} \sum_{\ell=|\ell_i \pm 1|} \left[-{T^i}_j - {T^i}_k {T^k}_j - {T^i}_k {\tau^k}_\ell {T^\ell}_j\right] .$$

$$. \left[\frac{2\ell_i+1}{2\ell + 1}\right]^{1/2} . C(1\ \ell_i \ell;000) C(1\ell_i\ell;m_1,m_i,\ m_1+ m_i) .$$

$$. \frac{\left[(2n_i+2)(2n_i+1)\right]^{1/2}}{2\zeta_i} \langle(n^j \ell^j m^j) | (\bar{n}_i \ell \bar{m}_i)'\rangle + \tag{E.10.2.3}$$

$$+ \sum_{\rho=1}^{P} \sum_{i\in P_\rho} \sum_{j\notin P_\rho} \left[{T^i}_j - {T^i}_k {T^k}_j + {T^i}_k {\tau^k}_\ell {T^\ell}_j\right] R_{\alpha\rho} .$$

$$\times \sum_{m_i'} \sum_{m^{j'}} D^{\ell^j}_{m^{j'} m^j}(\Omega^{-1})\, D^{\ell_i}_{m_i' \ m_i}(\Omega^{-1}) .$$

$$. \langle(n^j \ell^j m^{j'}) | (n_i \ell_i m_i')\rangle - \tag{E.10.2.4}$$

$$- \sum_{\rho=1}^{P} \sum_{i \in P_\rho} \sum_{j \notin P_\rho} \left[ -T^{i}{}_{j} + T^{i}{}_{k} T^{k}{}_{j} - T^{i}{}_{k} \tau^{k}{}_{\ell} T^{\ell}{}_{j} \right] \cdot$$

$$\cdot \sum_{m_i'} \sum_{m^{j'}} \sum_{\ell = |\ell_i \pm 1|} \left[ \frac{2\ell_i + 1}{2\ell + 1} \right]^{1/2} C(1\ell_i\ell;000) \ .$$

$$. \ C(1\ell_i\ell;m_1,m_i,m_1+m_i) \ \frac{\left[(2n_i+2)(2n_i+1)\right]^{1/2}}{2\zeta_i} \ .$$

$$. \ \langle \ (n^j\ell^j m^{j'}) | (\bar{n}_i \ell \ \bar{m}_i)' \rangle \ . \ D^{\ell^j}_{m^{j'} m^j}(\Omega^{-1}) \cdot D^{\ell_i}_{m_i' m_i}(\Omega^{-1}), \quad \text{(E.10.2.5)}$$

where $\bar{n}_i \equiv n_i+1$ ; $\bar{m}_i \equiv m_1+m_i$ , and $\bar{m}_i' \equiv m_1+m_i'$ .

The terms in (E.10.2.1) come from the sum (E.10.1.1). The sums (E.10.2.2) and (E.10.2.3) include the terms in (E.10.1.2) with the orbitals i and j on the same nucleus. The sums (E.10.2.4) and (E.10.2.5) include the terms in (E.10.1.2) with orbitals i and j on different nuclei. Eq. (E7) has been used in (E.10.2.3) and (E.10.2.5). The inverse of Eq. (E9) has been used in (E.10.2.4) and (E.10.2.5).

Two spherical harmonics in the canonical reference frame on i and j satisfy

$$\langle Y_{\ell_i m_i} | Y_{\ell^j m^j} \rangle = \delta_{m_i m^j} \ . \quad \text{(E11)}$$

Furthermore,

$$\langle Y_{\ell_i m_i} | Y_{\ell^j m_i} \rangle + \langle Y_{\ell^j m_i} | Y_{\ell_i m_i} \rangle = 0 \ , \quad \text{(E12)}$$

when $\ell_i = |\ell^j \pm 1|$. The use of Eqns. (E11), (E12) and some orthogonality relationships in Eq. (E10) and its specialization to s-orbitals (i.e., $\ell_i = 0, \forall i$) yield

$$\mu_\alpha^{e\ell} = \frac{N}{p} \sum_{\rho=1}^{p} (-R_{\alpha\rho}) - \sum_{\rho=1}^{p} R_{\alpha\rho} \sum_{i\in P_\rho} \sum_{j\notin P_\rho} \left[T^i{}_j T^j{}_i - T^i{}_k \tau^k{}_j T^j{}_i\right] +$$

$$+ \sum_{\rho=1}^{p} \sum_{i\in P_\rho} \sum_{j\notin P_\rho} R_{\alpha\rho} \cdot \left[T^i{}_j T^j{}_i - T^i{}_k \tau^k{}_j T^j{}_i\right] =$$

$$= \frac{N}{p} \sum_{\rho=1}^{p} (-R_{\alpha\rho}) \qquad , \text{ q. e. d.} \tag{E13}$$

# APPENDIX F

The dipole moment for the $H_3$ system in its lowest quartet state is given by Eq. (24) in Section 4.2. The explicit expression for the transition element in Eq. (24) is

$$\begin{aligned}
\langle\Phi^{(0)}|\hat{V}'|\sum_{i=1}^{3}\Phi^{(1)}_{i\alpha}\rangle=6\Big\{&\langle\chi_a|r_b^{-1}|\chi^{1}_{\alpha a}\rangle(S^2_{bc}-S^2_{ac})+\langle\chi_a|r_c^{-1}|\chi^{1}_{\alpha a}\rangle(S^2_{bc}-S^2_{ab}) + \\
&+\langle\chi_c r_b^{-1}|\chi^{1}_{\alpha c}\rangle(S^2_{ab}-S^2_{ac}) + \\
&+ (S_{ab}-S_{ac}S_{bc})(\langle\chi_b|r_c^{-1}|\chi^{1}_{\alpha a}\rangle+\langle\chi_a|r_c^{-1}|\chi^{1}_{\alpha b}\rangle) + \\
&+ (S_{ac}-S_{ab}S_{bc})(\langle\chi_c|r_b^{-1}|\chi^{1}_{\alpha a}\rangle+\langle\chi_a|r_b^{-1}|\chi^{1}_{\alpha c}\rangle) + \\
&+ (S_{bc}-S_{ac}S_{ab})(\langle\chi_b|r_a^{-1}|\chi^{1}_{\alpha c}\rangle+\langle\chi_c|r_a^{-1}|\chi^{1}_{\alpha b}\rangle) + \\
&+S_{ab}(\langle\chi_c\chi_b|r_{12}^{-1}|\chi^{1}_{\alpha a}\chi_c\rangle-\langle\chi_b\chi_c|r_{12}^{-1}|\chi^{1}_{\alpha a}\chi_c\rangle+\langle\chi_a\chi_c|r_{12}^{-1}|\chi^{1}_{\alpha c}\chi_b\rangle - \\
&-2\langle\chi_c\chi_a|r_{12}^{-1}|\chi^{1}_{\alpha c}\chi_b\rangle-\langle\chi_c\chi_b|r_{12}^{-1}|\chi_a\chi^{1}_{\alpha c}\rangle) + \\
&+\langle\chi_a\chi_c|r_{12}^{-1}|\chi_c\chi^{1}_{\alpha b}\rangle-\langle\chi_c\chi_a|r_{12}^{-1}|\chi_c\chi^{1}_{\alpha b}\rangle) + \\
&+S_{cb}(\langle\chi_b\chi_a|r_{12}^{-1}|\chi_{\alpha a}\chi_c\rangle-2\langle\chi_a\chi_b|r_{12}^{-1}|\chi^{1}_{\alpha a}\chi_c\rangle+\langle\chi_c\chi_a|r_{12}^{-1}|\chi^{1}_{\alpha a}\chi_b\rangle+ \\
&+\langle\chi_b\chi_a|r_{12}^{-1}|\chi_a\chi^{1}_{\alpha c}\rangle-\langle\chi_a\chi_b|r_{12}^{-1}|\chi_a\chi^{1}_{\alpha c}\rangle+\langle\chi_c\chi_a|r_{12}^{-1}|\chi_a\chi^{1}_{\alpha b}\rangle-\langle\chi_a\chi_c|r_{12}^{-1}|\chi_a\chi^{1}_{\alpha b}\rangle) + \\
&+S_{ac}(\langle\chi_b\chi_c|r_{12}^{-1}|\chi^{1}_{\alpha a}\chi_b\rangle-\langle\chi_c\chi_b|r_{12}^{-1}|\chi^{1}_{\alpha a}\chi_b\rangle+\langle\chi_b\chi_a|r_{12}^{-1}|\chi^{1}_{\alpha c}\chi_b\rangle - \\
&-\langle\chi_a\chi_b|r_{12}^{-1}|\chi^{1}_{\alpha c}\chi_b\rangle+\langle\chi_b\chi_c|r_{12}^{-1}|\chi_a\chi^{1}_{\alpha b}\rangle-2\langle\chi_c\chi_b|r_{12}^{-1}|\chi_a\chi^{1}_{\alpha b}\rangle+ \\
&+\langle\chi_b\chi_a|r_{12}^{-1}|\chi_c\chi^{1}_{\alpha b}\rangle)\Big\}
\end{aligned} \tag{F1}$$

The notation

$$\langle \chi_q | g | \chi^1_{ur} \rangle = \int d^3 r_1 \chi_q(1) g(1) \chi^1_{ur}(1) \qquad \text{(F2)}$$

$$\langle \chi_q \chi_r | r^{-1}_{12} | \chi_m \chi_u \rangle = \int d^3 r_1 d^3 r_2 \chi_q(1) \chi_v(1) r^{-1}_{12} \chi_m(1) \chi_u(2) \qquad \text{(F3)}$$

is used in Eq. (F1). $r_{12}$ is the interelectronic distance; g is the electron-nucleus distance; q, r, v, m, and u label the different nuclei a, b, and c. $\chi^{(0)}_q$ and $\chi^{(1)}_q$ from the main text are abbreviated as $\chi_q$ and $\chi^1_q$. The remaining symbols retain the same meaning as in Section 4.2.

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[29]. At this point we briefly analyse the nature of long-range interactions between molecules. If the instantaneous motion of the electrons is intercorrelated, we may expect that the charge distributions of two interacting atoms far away from each other will relax in such a way that the electron-correlation effects will yield minimum energy. The relaxation of the electron charge distribution is sometimes referred to as an interaction between instantaneous virtual electric moments on each interacting system. Although the time average of such moments is zero, the average of their effect on the other system is not. The effect of the virtual electric moments is to yeild a charge distribution on each centre polarized towards the other. Hence, each nucleus undergoes an attraction towards the centroid of its own electron charge distribution, and a net attractive force, *i.e.*, van der Waals force, exists between the nuclei [30,31]. One way of incorporating the effect of the virtual electric moments in the expression for $\psi_k$ (Eq. (54)) is through a multipolar expansion of $H^{(1)}$, even though such an expansion is not intrinsically associated with the theory of long-range interactions. We shall refer to this point in chapter 5.

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[304] We focus our attention on the susceptibility at nonresonant frequencies. Therefore, we drop all the terms in Eq. (11) which involve Dirac distributions since we consider in this section the susceptibility and hyperpolarizability densities at purely imaginary frequencies.

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