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Exchange-induced dipole moments in atom pairs

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It is shown that an approach based on the use of label-free operators, which has been used to evaluate the interaction energies of pairs, can be adapted to evaluating the induced moments on each atom. Application of the method to H-H and H-He systems is given.

I. INTRODUCTION

The dipole moment induced on each atom of a pair when their distance of separation R is large arises from dispersion interaction,[1,2] and varies as R^{-7}. For smaller values of R at which overlap effects appear one would expect the exchange interaction between the atomic electrons to contribute to the induced moments. The effect of the antisymmetry of the combined wave function on the interaction energy of an atom pair is well known,[3] but the moments localized on the atoms and arising out of this wave function have not received as much attention. Only the lowest-order results for the dipole moment of atom pairs have been obtained[4] with some doubt expressed on whether the induced moment on each atom of a pair can be evaluated separately, as had been claimed earlier.[5]

The object of this paper is to present an evaluation of the induced moments on each of a pair of atoms through adaptation of techniques which have been used in studying interatomic forces by perturbation theoretic methods including exchange effects.[6–11]

II. USE OF "LABEL-FREE" OPERATORS

For two atoms A and B separated by the internuclear distance $\vec{R}$, with A having N_A and B having N_B electrons, the complete Hamiltonian

$$H=H_A+H_B+V\ , \tag{1}$$

where V is the Coulomb interaction of the charged particles of A and those of B, is symmetric with respect to exchange of electrons between the two atoms. The expectation values of the properties of the system are to be taken with wave functions which are antisymmetric with respect to N_A+N_B electrons. However, the operators associated with properties of the individual atoms of the pair are usually defined for a particular grouping of N_A electrons on A and N_B electrons on B. The use of label-free operators in the manner described below incorporates exchange symmetry into the operators associated with properties of individual atoms in a straightforward way.

In Eq. (1) the part

$$H_0=H_A+H_B \tag{2}$$

and V by itself are not invariant with respect to an exchange of electrons between the two atoms. For developing a perturbation theory including exchange effects the unperturbed Hamiltonian must be chosen to be invariant with respect to such an exchange, and this is achieved by writing the terms in the Hamiltonian in the "label-free" form,[6]

$$\mathscr{H}_0=\sum_{i=1}^{p}[H_{A(i)}+H_{B(i)}]\Lambda_i\ , \tag{3a}$$

$$\mathscr{V}=\sum_{i=1}^{p}V_{(i)}\Lambda_i\ , \tag{3b}$$

with each i corresponding to a particular grouping of N_A electrons on A and N_B electrons on B, and $V_{(i)}$ is the interaction between the two atoms for that particular grouping. And

$$p=(N_A+N_B)!/(N_A!N_B!)$$

is the number of ways N_A electrons can be exchanged with N_B electrons. Λ_i is a projection operator having the following property.

If we start with a product wave function

$\phi_{A(n_1)}\phi_{B(n_2)}$ which is an eigenfunction of H_0, an antisymmetric wave function can be constructed through the usual procedure,

$$\psi_n^{(0)}=f_n\sum_{\nu}(-1)^{\nu}P_{\nu}[\phi_{A(n_1)}\phi_{B(n_2)}] \\ =f_n\sum_{i=1}^{p}\phi_n^{(i)}\ , \tag{4}$$

where P_ν is ν consecutive permutations of electron pairs one from each atom, and f_n is the factor that normalizes $\psi_n^{(0)}$. Λ_i is defined through the equation

$$\Lambda_i\psi_n^{(0)}=f_n\phi_n^{(i)} \tag{5}$$

with i here referring to the ith grouping of N_A electrons on A and N_B on B, as before. Obviously from Eqs. (5) and (4),

$$\sum_{i=1}^{p}\Lambda_i\equiv 1\ . \tag{6}$$

$[H_{A(i)}+H_{B(i)}+V_{(i)}]$ is independent of the grouping of the electrons, and hence of the index i. Thus, adding Eqs. (3a) and (3b) and using (6) we get

$$\mathscr{H}_0+\mathscr{V}=H_A+H_B+V=H\ , \tag{7}$$

which, of course, is exchange symmetric. Also, by construction $\mathscr{H}_0$ and $\mathscr{V}$ are both exchange symmetric, and therefore can be the starting point for a perturbation theory incorporating exchange effects.[10]

A suitable definition of an operator associated with A (or B) separately can be written analogously as

$$\Omega_A=\sum_i\Omega_{A(i)}\Lambda_i \tag{8}$$

with a similar equation for Ω_B. If $\Omega_A=H_A$, for instance, it is easy to see that

$$\langle\psi_n^{(0)}\,|\,\sum_i H_{A(i)}\Lambda_i\,|\,\psi_n^{(0)}\rangle=E_A\ .$$

Thus the appropriate definitions of the dipole moment operators of the individual atoms are

$$\vec{\mu}_A=\sum_i\vec{\mu}_{A(i)}\Lambda_i\quad \vec{\mu}_B=\sum_i\vec{\mu}_{B(i)}\Lambda_i\ . \tag{9}$$

Here $\vec{\mu}_{A(i)}$ and $\vec{\mu}_{B(i)}$ are the dipole moments of A and B for the ith grouping of electrons, as in Eqs. (3a) and (3b).

III. SOME EXAMPLES

We shall give here the exchange-induced dipole moments for the hydrogen-hydrogen and hydrogen-helium systems as a function of the separation R. For large R when the overlap between the atomic orbitals is small, as already stated the dominant contribution to the induced moments is from the dispersion interaction and this leads to

$$\langle\vec{\mu}_{A,B}\rangle\propto\frac{1}{R^7}\ . \tag{10}$$

The explicit form of the constant of proportionality has been obtained ignoring exchange effects.[2]

For the H-H case,

$$H_{0(1)}=\left[-\frac{\hbar^2}{2m}\nabla_1^2-\frac{e^2}{r_1}\right]+\left[-\frac{\hbar^2}{2m}\nabla_2^2-\frac{e^2}{|\vec{r}_2-\vec{R}|}\right],$$

$$H_{0(2)}=\left[-\frac{\hbar^2}{2m}\nabla_2^2-\frac{e^2}{r_2}\right]+\left[-\frac{\hbar^2}{2m}\nabla_1^2-\frac{e^2}{|\vec{r}_1-\vec{R}|}\right];$$

$$V_1=\frac{e^2}{r^2}-\frac{e^2}{|\vec{r}_1-\vec{R}|}+\frac{e^2}{R}+\frac{e^2}{|\vec{r}_1-\vec{r}_2|},\ V_2=-\frac{e^2}{|\vec{r}_2-\vec{R}|}-\frac{e^2}{r_1}+\frac{e^2}{R}+\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\ ;$$

$$\vec{\mu}_{A(1)}=-e\vec{r}_1,\vec{\mu}_{A(2)}=-e\vec{r}_2\ ,$$

$$\vec{\mu}_{B(1)}=-e(\vec{r}_2-\vec{R}),\vec{\mu}_{B(2)}=-e(\vec{r}_1-\vec{R})\ ;$$

$$\psi_0=f_0[\alpha(1)\phi_0(r_1)\beta(2)\phi_0(|\vec{r}_2-\vec{R}|)-\alpha(2)\phi_0(r_2)\beta(1)\phi_0(|\vec{r}_1-\vec{R}|)]\ ;$$

and

$$\phi_0(r)=\frac{1}{(\pi a_0^3)^{1/2}}\exp(-r/a_0)\ .$$

Here α and β are the spin functions.

If $\alpha \neq \beta$, both $\langle \vec{\mu}_A \rangle$ and $\langle \vec{\mu}_B \rangle$ vanish in the leading order, indicating that hydrogen atoms in opposite spin states will not produce exchange-induced dipole moments. If $\alpha = \beta$, we get

$$f_0 = \{2[1 - S^2(R)]\}^{-1/2} ,$$

where the overlap integral $S(R)$ is

$$S(R) = \left[1 + \frac{R}{a_0} + \frac{1}{3}\left[\frac{R}{a_0}\right]^2\right] \exp(-R/a_0) . \tag{11}$$

The integrals for $\langle \vec{\mu}_A \rangle$ and $\langle \vec{\mu}_B \rangle$ are done trivially to give the result

$$\langle \vec{\mu}_A \rangle = e \frac{S(R)T(R)}{1 - S^2(R)} \tag{12}$$

with

$$T(R) \equiv \langle \phi_0(|\vec{r} - \vec{R}|) | \vec{r} | \phi_0(r) \rangle \tag{13}$$

and

$$\langle \vec{\mu}_B \rangle = -\langle \vec{\mu}_A \rangle . \tag{14}$$

In this case $T(R) \equiv (R/2)S(R)$, so that

$$\langle \vec{\mu}_A \rangle = \frac{eR}{2} \frac{S^2(R)}{1 - S^2(R)} . \tag{15}$$

Thus, although the total dipole moment of the two atoms vanishes, each atom develops a moment directed toward the other. Furthermore, for $R \rightarrow 0$, $\langle \vec{\mu}_A \rangle$ diverges as $1/R$ and for $R \rightarrow \infty$ it tends to zero.

For the H-He case with the hydrogen at the origin and the helium at R, we pick

$$\phi_1 = \phi_{\mathrm{H}}(1)\phi_{\mathrm{He}}(2,3) ,$$

$$\phi_{\mathrm{H}}(1) = \alpha(1) \frac{1}{(\pi a_0^3)^{1/2}} \exp(-r_1/a_0) ,$$

$$\phi_{\mathrm{He}}(2,3) = \frac{Z^3}{\pi a_0^3} \left[\frac{\alpha(2)\beta(3) - \beta(2)\alpha(3)}{\sqrt{2}}\right] \exp\left[-\frac{Z}{a_0}(|\vec{r}_2 - \vec{R}| + |\vec{r}_3 - \vec{R}|)\right], \quad \text{with } Z = \tfrac{27}{16} ;$$

$$\phi_2 = -\phi_{\mathrm{H}}(2)\phi_{\mathrm{He}}(1,3), \quad \phi_3 = -\phi_{\mathrm{H}}(3)\phi_{\mathrm{He}}(2,1) ;$$

$$\psi_0 = f_0(\phi_1 + \phi_2 + \phi_3), \quad f_0 = \{3[1 - S^2_{\mathrm{H-He}}(R)]\}^{-1/2} ;$$

with the overlap integral $S_{\mathrm{H-He}}(R)$ given by

$$\begin{aligned} S_{\mathrm{H-He}}(R) &= \frac{\sqrt{Z^3}}{\pi a_0^3} \int d^3r \exp\left[-\frac{r}{a_0}\right] \exp\left(-\frac{Z}{a_0}|\vec{r} - \vec{R}|\right) \\ &= 32 Z^{5/2} \left[\frac{a_0}{R}\right] \left\{ \left[\frac{1}{(Z^2-1)^3} + \left[\frac{RZ}{a_0}\right] \frac{1}{4Z^2(Z^2-1)^2}\right] \exp(-ZR/a_0) \right. \\ &\qquad \left. - \left[\frac{1}{(Z^2-1)^3} - \left[\frac{R}{a_0}\right] \frac{1}{4(Z^2-1)^2}\right] \exp(-R/a_0) \right\} . \end{aligned} \tag{16}$$

Here,

$$\vec{\mu}_{\mathrm{H}} = -e(\vec{r}_1\Lambda_1 + \vec{r}_2\Lambda_2 + \vec{r}_3\Lambda_3) ; \tag{17}$$

$$\vec{\mu}_{\mathrm{He}} = -e[(\vec{r}_2 + \vec{r}_3 - 2\vec{R})\Lambda_1 + (\vec{r}_1 + \vec{r}_3 - 2\vec{R})\Lambda_2 + (\vec{r}_1 + \vec{r}_2 - 2\vec{R})\Lambda_3] . \tag{18}$$

We then get

$$\langle \vec{\mu}_{\mathrm{H}} \rangle = \frac{e S_{\mathrm{H-He}}(R) T_{\mathrm{H-He}}(R)}{1 - S^2_{\mathrm{H-He}}(R)} , \tag{19}$$

where

$$\begin{aligned} T_{\mathrm{H-He}}(R) &= \frac{\sqrt{Z^3}}{\pi a_0^3} \int \vec{r}\, d^3r \exp\left[-\frac{Z}{a_0}|\vec{r} - \vec{R}|\right] \exp\left(-\frac{r}{a_0}\right) \\ &= 32 a_0 Z^{5/2} \left[\frac{\exp(-x)}{x} \left[\frac{24x + x^3(Z^2-1)^2 - 8x^2(Z^2-1) + 24}{4x(Z^2-1)^4}\right.\right. \\ &\qquad \left.\left. - \frac{\exp(-Zx)}{x} \left[\frac{6Zx + x^2(Z^2-1) + 6}{x(Z^2-1)^4}\right]\right]\right], \quad x \equiv R/a_0 \end{aligned} \tag{20}$$

and

$$\langle \vec{\mu}_{\mathrm{He}} \rangle = \langle \vec{\mu}_{\mathrm{H}} \rangle - \frac{e\vec{\mathrm{R}} S^2_{\mathrm{H-He}}(R)}{1 - S^2_{H-He}(R)} . \tag{21}$$

As can be seen in Fig. 1, $\langle \vec{\mu}_{\mathrm{H}} \rangle$ starts from zero, attains a sharp peak at $(R/a_0) \approx 0.5$, and then decays exponentially. The form of $\langle \vec{\mu}_{\mathrm{He}} \rangle$ is qualitatively similar, although the magnitude of the induced moment is smaller, as may be expected for a more tightly bound system. $\langle \vec{\mu}_{\mathrm{H}} \rangle$ and $\langle \vec{\mu}_{\mathrm{He}} \rangle$ are directed toward each other.

IV. CONCLUSION

The above examples illustrate the point that the use of label-free operators enables us to evaluate the exchange-induced dipole moments on the individual atoms of a pair in a simple unambiguous manner. It would be reasonable to expect a peaking of the induced moment when the atoms are unlike, as in the H-He system, at sufficiently small R.

For values of R when the overlap is small but not completely negligible, use of wave functions obtained by exchange-corrected perturbation theory[10] leads to a smooth transitition from the strong overlap region to the dispersion-induced region.

One of the limitations of the method given above is that from the manner of construction of $\psi_n^{(0)}$ in Eq. (4), it is obvious that it corresponds to a particular total spin projection which is the sum of the spin projections of A and B; however, total spin of the composite system is left undefined. The degeneracy associated with this lack of definition of the total spin can be handled by an adaptation of degenerate perturbation theory, and we shall not deal with the question here.

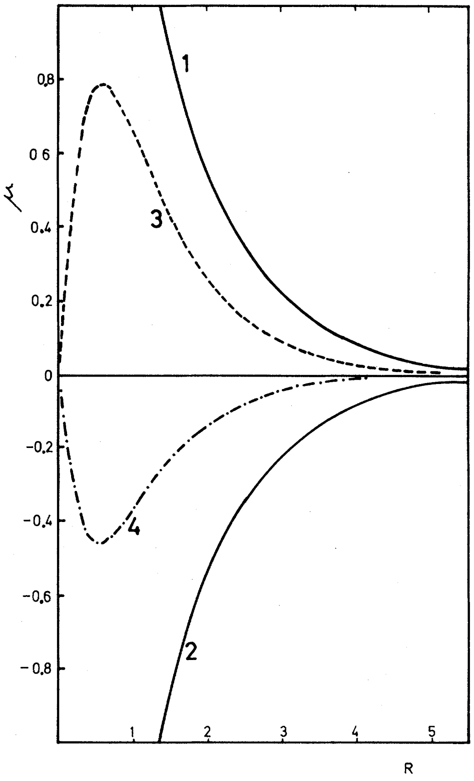

FIG. 1. Exchange-induced dipole moments in H-H (curves 1 and 2) and H-He (curves 3 for H and 4 for He) systems; R is in units of a_0 and the dipole moments are in units of (ea_0). For H-He system, $Z = \frac{27}{16}$.

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