## Label-free operator in calculations of individual properties of atoms in a pair

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The "label-free" operator has recently been used to calculate individual properties of each atom in a pair. Large values of individual induced-dipole moments have thus been obtained. We explain the origin of such artificial values. We also show why this approach is not consistent with quantum-mechanical principles and leads to logical inconsistencies. Such a formalism cannot be used to calculate individual properties of an atom in a pair. However, we specify the conditions for which this formalism could be extended to be useful in calculating global exchange properties of the total pair.

## I. INTRODUCTION

For atoms or molecules interacting at short-range distances, both polarization and exchange effects must be taken into account in order to calculate interactionenergy or interaction-induced changes of electric properties. Such calculations are of great interest for chemical and biological studies, and many different approaches have been proposed to account for them.<sup>1-8</sup> As presented, for example, in Ref. 9, each method has its own advantages and difficulties. However, in general terms, ab initio calculations are very long and expensive. The problem is, therefore, to find approximate treatments that account for intermolecular overlap. Many authors therefore use adapted perturbation theories. In some of them, the zero-order wave function is constructed either as a simple product of the wave functions of individual molecules or as an antisymmetrized product.

The "label-free' exchange perturbation method is based on a direct Rayleigh-Schrödinger perturbation theory with fully antisymmetrized zeroth-order wave functions. It was first introduced to calculate exchange interactions between two atoms in a pair. Such a calculation can be used at any distance and thus specifies both van der Waals and exchange effects.<sup>10,11</sup>

Recently the definition of label-free operators was used in order to describe individual properties of each atom in a pair: for instance, to calculate exchange-induced dipole moments of individual atoms of the pair,<sup>12,13</sup> quadrupole moments, or exchange-induced modification of individual polarizability.<sup>13</sup> The total dipole moment of a He-H pair was also calculated<sup>14</sup> and seemed to corroborate earlier *ab initio* calculations.

In this paper we show why such an attempt to study individual properties of each atom in a pair is inconsistent with quantum-mechanical principles. We explain why these above approaches lead, in the calculation of individual induced dipoles, to artificially large moments: when applied to study the electron density on one atom of the pair, the label-free operator leads to negative probabilities, which explains why very high values of the exchange-induced dipole moments are obtained within this theory.<sup>12</sup>

In Sec. III we show that, although the label-free operator cannot be used to study individual properties of atoms in a pair, it can however be used to calculate global exchange properties of the total pair.

## II. CRITICAL REVIEW OF THE USE OF THE "LABEL-FREE OPERATORS" IN STUDIES OF INDIVIDUAL PROPERTIES OF ATOMS IN A PAIR

We consider two interacting hydrogen atoms, A and B, and we limit ourselves to the simplest possible description of the diatom, as in Refs. 10–12. The Hilbert space of the two electrons is thus spanned by one-electron orbitals of each atom's linear combination of atomic orbitals (LCAO). In the label-free representation,<sup>10</sup> two configurations are possible: in the first one, electrons 1 and 2 are attached to A and B, respectively; in the other, they are attached to atoms B and A. For such a system the complete Hamiltonian (Coulombic approximation) can be written as

$$H = H_A + H_B + V , \qquad (1)$$

where  $H_A$  and  $H_B$  are atomic Hamiltonians of A and B, respectively, and where V represents the Coulombic interaction between the two atoms. The total Hamiltonian is symmetric with respect to the exchange of electrons between the two atoms; however, neither  $H_A + H_B$  nor V are themselves invariant with respect to such an exchange. The invariance can be achieved by writing the Hamiltonian in the label-free form as

$$H_0 = \sum_i (H_{A_i} + H_{B_i})\Lambda_i , \qquad (2)$$

$$V = \sum_{i} V_{i} \Lambda_{i} .$$
(3)

In these expressions the operator  $\Lambda_i$  (*i* = 1,2) projects the

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wave function of the total system onto the subspace corresponding to a particular grouping of the electrons on each atom A or B:  $\Lambda_1$  thus corresponds to the case when the first electron (noted 1) and the second one (noted 2) are attached to A and B, respectively;  $\Lambda_2$  corresponds to the case when they are attached to B and A, respectively.  $H_{A_i}(H_{B_i})$  is the Hamiltonian operator for the isolated atom A(B) in the *i*th configuration.  $V_i$  is the Coulomb interaction of the electron of A and of the electron of Bin this configuration.

Two hydrogen atoms are considered in Ref. 12. Taking the origin of the reference frame of atom A, with  $\mathbf{r}_1$ and  $\mathbf{r}_2$  the position of the first and second electrons, respectively, and with **R** the internuclear distance between A and B, the totally antisymmetric zeroth-order wave function  $|\Phi_0\rangle$  of the pair of electrons for the fundamental state is then built from the wave functions  $\phi(\mathbf{r}_1)$ ,  $\phi(\mathbf{r}_2 - \mathbf{R})$  (corresponding to the first configuration) and  $\phi(\mathbf{r}_2)$ ,  $\phi(\mathbf{r}_1 - \mathbf{R})$  (corresponding to the second configuration)

$$|\Phi_{0}\rangle = f_{0}[\sigma(1)\tau(2)\phi(\mathbf{r}_{1})\phi(\mathbf{r}_{2}-\mathbf{R}) -\sigma(2)\tau(1)\phi(\mathbf{r}_{2})\phi(\mathbf{r}_{1}-\mathbf{R})]$$
(4)

(in this expression, where  $f_0$  is a normalization constant, the functions of spin of the two electrons are denoted by  $\sigma$  and  $\tau$ , respectively). The use of  $\Lambda_i$  thus leads to

$$\begin{split} \Lambda_1 | \Phi_0 \rangle &= + f_0 \sigma(1) \tau(2) \phi(\mathbf{r}_1) \phi(\mathbf{r}_2 - \mathbf{R}) , \\ \Lambda_2 | \Phi_0 \rangle &= - f_0 \sigma(2) \tau(1) \phi(\mathbf{r}_2) \phi(\mathbf{r}_1 - \mathbf{R}) . \end{split}$$
(5)

Within this description, Mahanty and Majumdar<sup>12</sup> have then given the following definition of an operator associated with atoms A or B separately:

$$\Omega_A = \Omega_{A_1} \Lambda_1 + \Omega_{A_2} \Lambda_2 \tag{6}$$

with a similar equation for  $\Omega_B$ .

Following Ref. 12, Eq. (6) leads to the definition of the dipole moment operator of the individual atom A in the pair

$$\boldsymbol{\mu}_{A} = \boldsymbol{\mu}_{A_{1}} \boldsymbol{\Lambda}_{1} + \boldsymbol{\mu}_{A_{2}} \boldsymbol{\Lambda}_{2} . \tag{7}$$

By using Eqs. (4) and (5) and the hydrogen 1s orbital, we obtain in the case when the spin functions  $\sigma$  and  $\tau$  are identical,

$$\langle \mu_A \rangle = \frac{eR}{2} [S(R)]^2 / \{1 - [S(R)]^2\},$$
 (8)

where S(R) is the overlap integral.

This result was found by Mahanty and Majumdar.<sup>12</sup> They concluded that, although the total dipole moment of the pair is zero, each individual atom can be considered as having nonzero dipole moments with opposite signs. The variation of  $\mu_A$  according to the internuclear distance is then illustrated in Fig. 1. When the *R* axis is oriented from *A* toward *B*, the positive value of  $\mu_A$ shows that the two electrons have repulsive interactions.



FIG. 1. "Individual" exchange-induced dipole moment in a hydrogen pair. Curve a, case of two parallel spin states; curve b, case of two antiparallel spin states (vertical scales are different for curves a and b).

When applied to the case of two antiparallel spins, the above method (as claimed in Ref. 12) leads to the a priori surprising result  $\langle \mu_A \rangle = 0$ . Let us note, however, that in this case a result which could seem realistic could be obtained by taking some precautions as explained in Sec. III. Such a calculation would leads to a negative value of  $\langle \mu_{A} \rangle$  (Fig. 1) showing that, in this new case, the dipole moment of A is directed from B toward A (or, in other words, that electrons are attracted in the space lying between the two nuclei in a bonding orbital). These two results could seem to be physically satisfying: when the two atoms approach each other from infinity, each gets a permanent induced-dipole moment because of the van der Waals very-long-range interaction;<sup>15</sup> their electrons are thus attracted by the other atom. In the overlap region, spin effects become important via the Pauli principle and thus must be taken into account.

The label-free operator thus seems to give results that could agree with the usual representation of bonding and antibonding orbitals. However we are shocked to think that a fully quantum-mechanical treatment of undistinguishable particles (electrons 1 and 2) could be permitted to define individual properties of each atom in the pair.

With respect to the important problem of separability, the above results (Fig. 1) regarding individual dipole moments cannot hold true and our purpose is then to illustrate this and show an unacceptable consequence of the definition [Eq. (6)]: in the case of two parallel spins the

(12c)

individual label-free operator leads to a negative electron density of the atom.

To see this, let us study the electron density of "each" atom according to the above theory. Using the electron density operator, Eq. (6) leads in this case to

$$\rho_A(\mathbf{r}_e) = \delta(\mathbf{r}_e - \mathbf{r}_1)\Lambda_1 + \delta(\mathbf{r}_e - \mathbf{r}_2)\Lambda_2 , \qquad (9)$$

and we obtain for the electron density of atom A in the case of orientation of spins, as in Ref. 12 (two parallel spins):

$$\langle \rho_A(r_e) \rangle = \frac{[1 - S(R)^2]^{-1}}{\pi a_0^3} [\exp(-2r_e/a_0) - S(R) \exp(-2r_e/a_0) \exp(-2|\mathbf{r}_e - \mathbf{R}|/a_0)] .$$
(10)

(

We find that the electron density for the individual atom A is somewhere negative (in particular, around atom B). This explains the very large dipole moment observed in Fig. 1(a). It, of course, invalidates the use of the definition [Eq. (6)] of individual exchange-induced operators.

## III. USE OF THE LABEL-FREE OPERATOR IN CALCULATION OF GLOBAL EXCHANGE PROPERTIES OF THE COMPLETE SYSTEM

These results clearly show why the use of label-free operators cannot be extended to define individual properties of each atom in a pair. However, our aim is to go deeper into this problem and to show how this formalism can be used (as in Refs. 11 and 14) in order to evaluate the total contribution of exchange interactions between the two atoms. In order to perform such calculations it appears necessary to clarify the use of the wave function given in Eq.(4) and the projection operator.

In the paper of Mahanty and Majumdar,<sup>12</sup>  $\Lambda_i$  (i = 1 or 2) projects the totally antisymmetric function on the subspace constructed by the *i*th configuration where the electron *i* is associated with atom *A* and has the spin state  $\sigma$ originally associated with *A* [see Eqs. (4) and (5)]. In such an approach the antisymmetrized states which span the Hilbert space of the two atoms are (we use the simplified Slater notations and we neglect all ionic contributions)

$$A^{+}B^{+} = [a(1)b(2)\alpha(1)\alpha(2) - a(2)b(1)\alpha(1)\alpha(2)],$$
(11a)

$$A^{-}B^{-} = [a(1)b(2)\beta(1)\beta(2) - a(2)b(1)\beta(1)\beta(2)],$$
(11b)

$$A^{-}B^{+} = [a(1)b(2)\beta(1)\alpha(2) - a(2)b(1)\beta(2)\alpha(1)],$$
(11c)

$$A^{+}B^{-} = [a(1)b(2)\alpha(1)\beta(2) - a(2)b(1)\alpha(2)\beta(1)],$$
(11d)

where  $\alpha$  and  $\beta$  indicate up (+) and down (-) polarizations of electrons. These four equations correspond to Eq. (4) when spin functions are specified.

When applied to states  $A^+B^+$  and  $A^-B^-$ , the labelfree operator gives nonzero exchange contributions to the dispersive energy<sup>11</sup> as do other dynamic operator.<sup>12-14</sup> This comes from the fact that, when performing such calculations, the products of the spin functions factorized in Eqs. (11a) and (11b) can never be zero. On the contrary, the states  $A^{-}B^{+}$  and  $A^{+}B^{-}$  lead, in this same case, to identically null results for the exchange contributions. This comes from the fact that, in evaluating the different mean values, the spin functions  $\alpha(1)\beta(1)$  or  $\alpha(2)\beta(2)$  are orthogonal.

This shows the understructure of calculations presented in Ref. 12. When defining  $|\Phi_0\rangle$  [in Eq. (4)], the two atoms are first considered to be initially separate and then are brought together. Because of this, Eqs. (11) does not allow for the indistinguishability of the electrons.

In order to satisfy the general character of quantum mechanics in the calculation of exchange properties, we have to consider (instead of separated atoms) that the two atoms are originally not separated (and that they consequently will remain unseparated when their distance R increases). Because of this, we may not use the wave functions [Eqs. (4) and (11)] which do not correspond to a complete description of the pair;  $|\Phi_0\rangle$  is to be expanded through the total pair spin-orbital functions. In so doing the basis states are no longer the states of Eqs. (11) but are the following ones:

$$A^{+}B^{+} = [a(1)b(2) - a(2)b(1)]\alpha(1)\alpha(2) , \qquad (12a)$$

$$A^{-}B^{-} = [a(1)b(2) - a(2)b(1)]\beta(1)\beta(2) , \qquad (12b)$$

$$A^{+}B^{-} + A^{-}B^{+} = [a(1)b(2) - a(2)b(1)] \\ \times [\alpha(1)\beta(2) + \alpha(2)\beta(1)],$$

$$(A^{+}B^{-} - A^{-}B^{+}) = [a(1)b(2) + a(2)b(1)] \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)].$$
(12d)

Equation (12c) completes the description of the triplet (S=1) state and Eq. (12d) defines the singlet (S=0) state [which is missing in the above description (11)].

These wave functions [Eq. (12)] are the only possible wave functions to be considered. They can be used to calculate exchange properties and overlap mean values of dynamic operators for the total pair in all possible states. For example, an interesting calculation of the exchange dipole moment of a pair has been recently given by Timoneda and Hunt.<sup>14</sup>

In order to use these new states [Eq. (12)] with labelfree operators, it is necessary to clearly define the role of the projection operator  $\Lambda_i$  which only act on the spatial part of the wave function. For instance we have

$$\Lambda_{1}[a(1)b(2) + a(2)b(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)] = [a(1)b(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]. \quad (13)$$

All these modifications make it possible to use the label-free operator in order to calculate, for the state S = 0 as for the state S = 1, the exchange contributions to the dispersive energy or, in other words, the dispersive contribution to the exchange energy. The same holds true, of course, when using all other dynamic operators.

This, however, does not validate the use of the labelfree operator in order to calculate "individual" properties of atoms in a pair: it is always possible to decompose a dynamic operator  $\Omega$  defined in the pair *AB* into the sum of operators of the type [Eq. (6)]:

$$\Omega = \Omega_A + \Omega_B$$
  
=  $\Omega_{A_1} \Lambda_1 + \Omega_{A_2} \Lambda_2 + \Omega_{B_1} \Lambda_1 + \Omega_{B_2} \Lambda_2$ . (14)

We must, however, emphasize the dangerous application of  $\Omega_A$  or  $\Omega_B$  separately.

Let us note that in all these calculations, the expressions of the projection operators  $\Lambda_i$  are related to the basis set that has been chosen in the Hilbert space. A more precise representation of the diatom including ionic wave functions on A and B or a three-center expansion would require a new definition of these operators.

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