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A representation of the exchange operator useful for large molecules

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Summary. A simple and efficient way of representing the kernel of an exchange operator that still maintains its non-local character, is presented here. Such an approach seems particularly effective in the case of large molecules constituted by separate, well-defined chemical fragments whose contributions to the kernel of the total exchange operator can be prepared through separate calculations on each fragment. The performance of the method is illustrated through calculations on a specific molecular example.

Key words: Exchange operator – Representation – Transferability

1. Introduction

It is well known that, in the case of large molecules, the main obstacle which hinders the use of the Hartree–Fock (HF) method for a preliminary quantitative estimate of the electronic molecular properties is constituted by the evaluation of the exchange energy contribution. In fact, even if a core-valence or $\sigma-\pi$ electronic partition is used together with a "frozen core" or simplified representation of the "inactive" electrons, the non-local character of the exchange operator introduces additional difficulties in obtaining an economic but still accurate representation of the operator.

In a series of papers [1–4] we have proposed a "valence-only" approach in which the contributions of the core electrons both to the wave function and to the energy expression are derived from separate atomic calculations and expressed in terms of a few constants or simple monoelectronic operators with matrix elements that are easy to evaluate. In our method the calculation of the core-valence exchange contributions is advantageous owing to the strictly atomic character of the orbitals representing the core electrons and to their localization inside finite spherical volumes.

These two characteristics, however, can no longer be exploited if one wants to represent exchange operators having kernels that are formed by molecular orbitals constructed for well-defined chemical fragments and localized inside volumes of complicated and irregular forms. The aim of this paper is to propose a simple and general way of representing such exchange operators making use of only constants and wave functions prepared through separate calculations on the isolated fragments.

The generality of our approach consists in the fact that it can be applied to any given type of molecular fragment and, therefore, as a particular case, also to exchange operators with kernels made up of atomic core orbitals. Its simplicity and economy derives from the fact that the evaluation of the matrix elements of the exchange operator is reduced to the sum of a few superposition integrals weighted by constant factors that can be calculated apart on the separate fragments.

Note that, although characterized by the presence of superposition integrals, our approach is basically different from those techniques [5–9] – based on the approximations proposed by Mulliken [10] and developed by Ruedenberg [11] – that simplify the polycentric electron repulsion integrals through a projection of the two-center charge distributions onto one-center distributions weighted by appropriate overlap factors. The advantage of our method with respect to these approaches is to approximate directly an exchange operator the kernel of which is made up by orbitals of a whole molecular fragment instead of approximating separate polycentric integrals. This fact, obviously, assures a large simplification in the computational procedures.

2. Matrix representation of the exchange operator

Let us consider first an exchange operator $\hat{K}_\varphi$ with a kernel $k_\varphi(\vec{r}, \vec{r}')$ made up of a L^2-function φ and defined through its application to any given function f as follows:

$$\hat{K}_\varphi f(\vec{r}) = \int k_\varphi(\vec{r}, \vec{r}')f(\vec{r}')\, d\vec{r}' = \varphi(\vec{r}) \int \varphi^*(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} f(\vec{r}')\, d\vec{r}'. \tag{1}$$

By introducing a complete set of orthonormal functions $\{\chi_j\}$ it can be easily proved that an equivalent representation of the kernel $k_\varphi(\vec{r}, \vec{r}')$ is the following:

$$k_\varphi(\vec{r}, \vec{r}') = \sum_{ij} \chi_i(\vec{r})\epsilon_{ij}\chi_j^*(\vec{r}') \tag{2}$$

where

$$\epsilon_{ij} = \langle \chi_i | \hat{K}_\varphi | \chi_j \rangle = \int \chi_i^*(\vec{r})k_\varphi(\vec{r}, \vec{r}')\chi_j(\vec{r}')\, d\vec{r}\, d\vec{r}' = (\chi_i\varphi \,|\, \varphi\chi_j) \tag{3}$$

are the elements of the matrix $\boldsymbol{E}_{\hat{K}_\varphi}$ representative of the exchange operator $\hat{K}_\varphi$ over the basis set $\{\chi_j\}$.

Note that Eq. (2) is general (i.e., not specific for the exchange operator) and based on the basis set completeness which allows one to use the following resolution of the identity operator:

$$\hat{I} = \sum_j |\chi_j\rangle\langle\chi_j|. \tag{4}$$

Furthermore, since $\hat{K}_\varphi$ is hermitian, its matrix $\boldsymbol{E}_{\hat{K}_\varphi}$ can be diagonalized and the kernel $k_\varphi(\vec{r}, \vec{r}')$ expressed in terms of the corresponding eigenvalues and eigenvectors as follows:

$$k_\varphi(\vec{r}, \vec{r}') = \sum_i \overline{\chi_j}(\vec{r})\lambda_j\overline{\chi_j^*}(\vec{r}') \tag{5}$$

where

$$\boldsymbol{E}_{\hat{K}_\varphi} = \boldsymbol{U}\boldsymbol{\Lambda}_{\hat{K}_\varphi}\mathbf{U}^+; \qquad \overline{\chi_j} = \sum_i \chi_i u_{ij}. \tag{6}$$

The usefulness of Eq. (2) or (5) rests on the fact that, if φ is strictly localized on a well defined chemical fragment, the basis set $\{\chi_j\}$ can also be chosen as it is made up only by functions centred on the same molecular fragment and the matrix elements $\{\epsilon_{ij}\}$ can be prepared through separate calculations on the fragment itself.

Moreover, if the molecule is obtained by assembling $\mathscr{M}$ distinct chemical fragments, each one having a given number $\{n_\mu\}$ of localized electrons, the total exchange operator $\hat{K}$ can be written as the sum of $\mathscr{M}$ contributions, each one with a kernel which depends on a density matrix (ϱ_μ) for the fragment itself:

$$\hat{K}f(\vec{r}) = \sum_\mu^{\mathscr{M}} \hat{K}_{\varrho_\mu} f(\vec{r}) = \sum_\mu^{\mathscr{M}} \int k[\varrho_\mu(\vec{r}, \vec{r}')] f(\vec{r}')\, d\vec{r}' = \sum_\mu^{\mathscr{M}} \int \frac{\varrho_\mu(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} f(\vec{r}')\, d\vec{r}' \tag{7}$$

where

$$\varrho_\mu(\vec{r}, \vec{r}') = \sum_j^{n_\mu} \varphi_j^{(\mu)}(\vec{r}) \varphi_j^{(\mu)*}(\vec{r}'). \tag{8}$$

This partition of the total exchange operator follows immediately when the total wave function is given as an antisymmetrized product of group functions [5, 6] – one for each localized group of electrons – that are mutually related by the strong orthogonality condition. Such a constrain mixes, obviously, the different group functions since the orbitals of each fragment have tails that are delocalized on the other fragments in order to satisfy the orthogonality request. However, if the various chemical fragments are clearly identified and the corresponding orbitals well localized, the mixing effects due to the orthogonalization are, in general, negligible and for many purposes they can be disregarded without introducing relevant errors.

It follows that, for this type of system, one can treat separately the various electronic groups and construct for each fragment μ an exchange operator with a kernel $k_\mu(\vec{r}, \vec{r}')$ given in terms of a matrix of constants $\boldsymbol{E}^{(\mu)}$ and a vector of functions $\boldsymbol{X}^{(\mu)}(\vec{r})$ obtained separately for the fragment itself:

$$k_\mu(\vec{r}, \vec{r}') = \sum_{ij} \chi_i^{(\mu)}(\vec{r}) \epsilon_{ij}^{(\mu)} \chi_j^{(\mu)*}(\vec{r}') \tag{9}$$

with

$$\epsilon_{ij}^{(\mu)} = \int \chi_i^{(\mu)*}(\vec{r}) \frac{\tilde{\varrho}_\mu(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \chi_j^\mu(\vec{r}')\, d\vec{r}\, d\vec{r}' \tag{10}$$

and $\tilde{\varrho}_\mu$ the density matrix calculated for the isolated fragment μ without introducing any orthogonality constraint to the orbitals of the other groups.

Moreover, as regards the total exchange operator, any given matrix element between two functions f and g can be simply expressed as the following sum of matrix products:

$$\langle g|\hat{K}|f\rangle = \sum_\mu^{\mathscr{M}} \langle g|\boldsymbol{X}^{(\mu)}\rangle \boldsymbol{E}^{(\mu)} \langle \boldsymbol{X}^{(\mu)}|f\rangle \tag{11}$$

where

$$\langle g|\boldsymbol{X}^{(\mu)}\rangle \boldsymbol{E}^{(\mu)} \langle \boldsymbol{X}^{(\mu)}|f\rangle = \sum_{ij} \langle g|\chi_i^{(\mu)}\rangle \epsilon_{ij}^{(\mu)} \langle \chi_j^{(\mu)}|f\rangle. \tag{12}$$

Note that the degree of accuracy that can be achieved using the two equivalent expansions (2) or (5) over a finite basis set depends on both the extension and the quality of this set – polycentric for a molecular fragment and made up by functions chosen according to various possible criteria (see also Refs. [5–9]) – and on the degree of trasferability of the kernel orbitals. The larger is this transferability the more localized are the electronic groups and chemically better defined the corresponding fragments: these two characteristics are prerequisites necessary for the application of our method.

3. A prototype calculation

In order to give an example of the performance of our method we have applied it to the following aromatic molecule obtained through the condensation of two pyrroles:

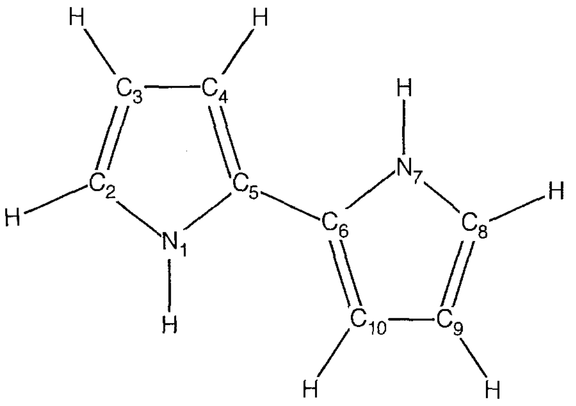

Fig. 1. Molecular structure of the 2,2′-bipyrrole with a progressive numbering of the heavy atoms

Because of the clear separation between σ and π electrons in the dimer the variational process for constructing its molecular orbitals can be reduced to the π-space while using, for the other electrons, orbitals obtained from a separate calculation on one pyrrole.

In our approach the preliminary problem is that of preparing functions properly localized on the atoms and along the bonds of each fragment. This step is necessary, in this case, to substitute the orbital corresponding to a C–H α-bond with that for a C–C bond connecting two pyrroles. Although there are several sophisticated methods proposed for localizing orbitals – see e.g. Refs. [7–9] – we have used a simple process that maximizes the overlaps among the HF orbitals and a given set of normalized reference functions having the required geometry and localization. This process – which is based on a repeated set of two by two unitary transformations of the HF core and σ orbitals of the pyrrole – guarantees an overlap of at least 95% between reference functions and final orbitals and therefore leads to a relevant localization of the latter.

The kernel of the exchange operator for the dimer is thus obtained by adding two kernels, each one made up by the core and σ orbitals of one pyrrole without a C–H α-bond, and a third kernel constructed with the orbital for the C–C bond between the two pyrroles that has been obtained from a HF calculation on the dimer.

The quality of our approach can be judged from the results reported in Tables 1 and 2 in which we compare the matrix elements of exchange operators with kernels constructed in two different ways but relative to the same set of electrons: the core and σ electrons of one pyrrole without a C–H α-bond. In Table 1 we show the matrix elements of the exchange operator with the exact kernel, i.e., that involving the localized HF orbitals of the dimer and calculated using the standard definition of Eq. (1). In Table 2, instead, we present the values of the exchange matrix elements when the kernel is approximated via Eq. (2) using a basis set of seven $2p$ Slater functions and starting from the localized orbitals obtained from a HF calculation for an isolated pyrrole. The basis functions for the kernel expansion have Slater exponents and are centred on the 1–5 positions of Fig. 1 with the two remaining functions centred one on C_6 and the other on a position $(C_{6'})$ symmetric to the previous one with respect to a reflection through a plane containing N_1 and perpendicular to the molecule.

Table 1. Exact exchange operator: the matrix elements are calculated among ten $2p$ functions on the two pyrrole rings. The functions are numbered as the positions in Fig. 1. All the elements are given in atomic units

	1	2	3	4	5	6	7	8	9	10
1	0.2031									
2	0.0447	0.1587								
3	0.0078	0.0497	0.1629							
4	0.0076	0.0091	0.0462	0.1622						
5	0.0421	0.0085	0.0090	0.0464	0.1088					
6	0.0025	0.0003	0.0003	0.0024	0.0058	0.0015				
7	0.	0.	0.	0.0003	0.0003	0.0001	0.0002			
8	0.	0.	0.	0.	0.	0.	0.	0.		
9	0.	0.	0.	0.	0.	0.	0.	0.	0.	
10	0.0005	0.	0.	0.0001	0.0004	0.0001	0.	0.	0.	0.0001

Table 2. Approximation of the exchange operator via Eq. (2): the matrix elements are calculated among ten $2p$ functions on the two pyrrole rings. The functions are numbered as the positions in Fig. 1. All the elements are given in atomic units

	1	2	3	4	5	6	7	8	9	10
1	0.2033									
2	0.0447	0.1587								
3	0.0078	0.0497	0.1629							
4	0.0076	0.0091	0.0463	0.1624						
5	0.0420	0.0085	0.0090	0.0463	0.1081					
6	0.0024	0.0003	0.0003	0.0024	0.0056	0.0023				
7	−.0003	0.	0.0001	0.0003	−.0016	0.0004	0.0001			
8	−.0001	0.	0.	−.0001	−.0007	0.0001	0.	0.		
9	−.0001	0.	0.	−.0001	−.0007	0.0001	0.	0.	0.	
10	0.0006	0.0001	0.	−.0004	−.0020	0.0004	0.0002	0.	0.	0.0002

The matrix elements of the two exchange operators have been calculated among ten $2p$ Slater functions, one for each heavy atom of the dimer. The orbital exponents have been obtained from the Slater rules ($\alpha_C = 1.625$; $\alpha_N = 1.95$) and the geometry of the dimer is that of Ref. [10].

By comparing the results of Tables 1 and 2 one can point out the following conclusions:

(1) As regards the matrix elements of the first ($5X5$) block, i.e., those among the functions centred on the first pyrrole where the density matrix of the kernel is also localized, one can observe that the very small differences between exact and approximate values are due to the fact that the kernel orbitals are respectively those of the dimer – Table 1 – and those of the pyrrole – Table 2. Since the largest error is of the order of 0.0007 a.u. one can conclude that the core and σ orbitals of the pyrrole are quite transferable if a proper localization process is used. This means also that the mixing effects due to the strong orthogonality relation between group functions of two separate pyrroles are negligible.

(2) As for the other matrix elements, we observe that the largest errors affect the (5, 7) and (5, 10) terms, i.e. those between the $2p$ on C_5 and the $2p$ on each of the two atoms closest to C_5 where no functions have been centred for describing the kernel of the exchange operator. These errors, however, are of a few millihartrees and can be further reduced by properly enlarging the basis set used for the kernel expansion.

In order to make a comparison of our results with those obtained using the well known X_α representation of the exchange operator [11, 12] we have reported in Table 3 a matrix, representative of the same exchange operator as in Tables 1 and 2, but with a kernel approximated as follows:

$$k(\vec{r}, \vec{r}\,') = \delta(\vec{r} - \vec{r}\,')\alpha\varrho^{1/3}(\vec{r}). \tag{13}$$

The value of the constant α has been obtained by minimizing the mean square deviation among exact and approximate matrix elements. The results of Table 3 show that the X_α representation provides less accurate values than our method, in particular for the elements between functions centred on the second pyrrole. These elements in fact differ from the exact ones by one or two orders of magnitude.

Table 3. X_α approximation of the exchange operator: the matrix elements are calculated among ten $2p$ functions on the two pyrrole rings. The functions are numbered as the positions in Fig. 1. All the elements are given in atomic units

	1	2	3	4	5	6	7	8	9	10
1	0.1868									
2	0.0303	0.1563								
3	0.0048	0.0344	0.1585							
4	0.0048	0.0058	0.0317	0.1581						
5	0.0293	0.0058	0.0058	0.0331	0.1333					
6	0.0016	0.0002	0.0002	0.0017	0.0109	0.0305				
7	0.	0.	0.	0.0002	0.0006	0.0067	0.0310			
8	0.	0.	0.	0.	0.0001	0.0015	0.0058	0.0209		
9	0.	0.	0.	0.	0.0001	0.0015	0.0011	0.0055	0.0208	
10	0.0003	0.	0.	0.0001	0.0007	0.0076	0.0013	0.0013	0.0062	0.0294

Table 4. Largest absolute errors ($\Delta_{\max}$) in the matrix representation of the exchange operator with a kernel approximated via Eq. (2) and using different sets of N basis functions centred on one pyrrole. In the last column the corresponding HF energies (E_π) for the π electrons of the dimer are reported. All the quantities are given in atomic units

N	$\Delta_{\max}$	E_{meth}
5	0.0173	−19.9695
15	0.0095	−19.9653
19	0.0094	−19.9545
7	0.0024	−19.9579
		$E_{\text{ex.}} = -19.9546$

Finally, for studying the degree of accuracy of our results when different sets of basis functions are used for representing the kernel of the exchange operator via Eq. (2), we compare in Table 4 the HF energies obtained for the π electrons of the dimer when the exchange operator – relative to the core and σ electrons of the dimer – has been assembled as previously explained and its kernel expanded via Eq. (2) using different basis sets. In this table we give also the largest absolute errors affecting the same exchange matrix as in Tables 1 and 2 but with the kernel expanded using different basis sets.

The results reported in the first row of Table 4 are relative to a minimal basis set of Slater functions on the first pyrrole, i.e., five $2p$ orbitals – one for each heavy atom – with Slater exponents. The set used for the second row calculations is the same as the previous one but enlarged with two expanded $2p$ functions on each heavy atom ($\alpha_C = 0.54, 0.18$; $\alpha_N = 0.6, 0.2$). Finally the basis set for the third row of Table 4 is increased with respect to the previous one by two $2p$ functions ($\alpha = 0.54, 0.18$) centred on the positions of the hydrogens bonded to C_2 and C_5 in the pyrrole.

We observe that by increasing the dimension of the basis set used for the representation of the exchange kernel via Eq. (2) the errors both in the matrix elements and in the energy are reduced appreciably. The energy value, in particular, converges quickly to the exact one, as expected from the small values of the absolute errors in the exchange matrix elements.

Furthermore, we point out that in all these calculations the largest error affects always the nondiagonal elements between the $2p$ function on C_5 and that on C_6 in the second pyrrole. A better local description of the kernel of the exchange operator should, therefore, reduce appreciably these errors, a fact that is confirmed by the results of the last row of Table 4 obtained using the basis set previously discussed for Tables 1 and 2, that is a minimal set enlarged by two $2p$ functions on C_6 and $C_{6'}$. We observe that with such a small increment of the number of basis functions one gets a decisive reduction of the largest error in the matrix elements and also a very good energy value.

Therefore, we conclude that, through a judicious choice of the type and localization of the basis functions, one can obtain an accurate and economic representation of the exchange operators via Eq. (2) or (5) at least in those cases in which their kernels are made up by orbitals clearly localized on well-defined molecular fragments.

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