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A novel approach to relax extremely localized molecular orbitals: the extremely localized molecular orbital–valence bond method

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Abstract. Orbitals rigorously defined on molecular fragments, like the extremely localized molecular orbitals, represent a possible way to build up the electronic structure of large molecules, using molecular fragments assembled on small molecules. Of course a rigorous localization is strictly connected to a reduction in the number of variational parameters, which reflects itself in an increased value of the associated energy. In order to get a more accurate description of the target molecule, we have developed a method which allows a relaxation of the electronic structure based on transferred localized orbitals. The relaxation is realized by means of a valence bond technique, which in turn uses the localized nature of the orbitals to reduce the number of excitations. Applications to the transferability of extremely localized molecular orbitals are presented.

Keywords: Extremely localized molecular orbitals – Transferability – Valence bond approaches

Introduction

The theoretical development of methods allowing us to study large molecules is still a challenging target for the computational chemist. The problems scientists have to deal with in the field of drug design or in the modelling related to the discovery of new materials require the application of traditional methods of computational chemistry to molecules of increasing complexity.

Molecular orbital (MO) methods have always had a prominent role in the framework of theoretical chemistry, and owing to their orthogonality have permitted the development of many well-known packages to determine the electronic structure of molecules with increasing accuracy. For small molecules theoretical results have reached an accuracy which is comparable, and sometimes superior, to experimental values.

The application of theoretical chemistry to large molecules requires methods which scale favourably with the increasing dimension of the system, and a lot of work has been done by different groups in order to build up the so called N-linear methods [1, 2, 3, 4].

A possible approach to set up algorithms for the study of large molecules derives from two ideas that are well recognized by every chemist: the concepts of locality and transferability. When looking at a new molecule, our first step to rationalize its structure and properties is to look up the different functional groups which constitute it: we are looking for local entities. Once we have determined them, we start to do previsions on the molecule, as we already know those of its different functional groups: we are applying the transferability property.

Hence it is quite natural that theoreticians have tried to insert these ideas in the framework of different models. Traditional MO methods do not seem adequate for this purpose, owing to the delocalization of the canonical MOs on the whole system. Also a slight modification of the structure of the molecule, for example, the addition of a methyl group, requires a complete redetermination of all the MOs of the molecule. In order to overcome these problems, different well-known localization schemes have been proposed [5, 6, 7]. The MOs can be in fact transformed in different sets characterized by different spatial extension, but with the same energy value.

In this way it is possible to define local MOs (LMOs) which allow us to recover the local concepts. However, owing to the orthogonal nature of the LMOs, they are characterized by the presence of tails which extend beyond the local region, preventing a rigorous application of the transferability.

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Extremely localized MOs (ELMOs) or strictly localized MOs [8, 9] or nonorthogonal localized MOs [10] are MOs which are developed on only the atomic centres of preselected molecular fragments and, in this way, they have no tails on the atomic centres of the other fragments. This is easily obtained by defining for each ELMO a proper linear combination of atomic orbitals on only the atoms which belong to its molecular fragment.

The ELMOs are, of course, closely connected to the group function method introduced by McWeeny [11], which can be considered as one of the first theoretical attempts to describe a wavefunction through functions associated with subsets of electrons. The ELMOs are not orthogonal and, even though their definition and the theory to determine them was set up many years ago [12], recently there has been renewed interest in their determination and use [13, 14, 15, 16]. The algorithms to obtain ELMOs are not trivial, as it is well known that serious convergence difficulties arise. Couty et al. [16] have explicitly treated the nonorthogonality using the Löwdin formula for the computation of the nonorthogonal matrix elements. To reduce the computational cost associated with the evaluation of the Hessian matrix, they computed its diagonal blocks using an approximate formula, while for the other blocks they used an updated scheme based on the Davidon–Fletcher–Powell or Broyden–Fletcher–Goldfarb–Shanno methods. Very recently, Szekeres and Surjan [15] proposed a method based on the use of appropriate projection operators to determine ELMOs.

In our laboratory we have developed a method [13] based on the generalization of the equations proposed by Gianinetti et al. [17] for the self-consistent field (SCF) for molecular interactions. Very recently, we proposed another approach [14] based on the equations by Stoll [12] and we are now extending it to the density functional theory [18]. After much work on the convergence routines, we think we have realized a robust algorithm, which up to now has always converged also when using some well-known delicate localization schemes, such as an extremely localized description of the π system of benzene. We have tested the transferability of the ELMOs [19], showing that electronic properties of some ortho-substituted biphenyl molecules determined at the Hartree–Fock (HF) level are quite well reproduced by optimizing only the ELMOs defined on the substituent group, while keeping all the other ELMOs identical to the corresponding ELMOs determined for the unsubstituted biphenyl molecule. We have also compared the different transferability of ELMOs with respect to tails-deleted LMOs in reproducing electrostatic properties of acetone [14] determined at the HF level.

From these works it was evident that the ELMOs provide results of superior quality with respect to the LMOs, as one could easily guess owing to the non-negligible perturbation introduced by the deletion of the tails. It was also evidenced that a very close agreement between the results obtained with transferred ELMOs and the HF ones can be obtained with just a simple relaxation, such as that provided by a single SCF iteration using the transferred ELMOs as starting orbitals.

The ELMOs could also be a valuable tool to define frontier region in the mixed quantum mechanics/molecular mechanics methods based on the use of localized MOs to describe the covalent bonds which connect quantum and classical regions, according to the local SCF proposed by Assfeld and coworkers [20, 21].

It is evident that the price to pay in order to have rigorously defined ELMOs is a loss in the number of variational parameters that we use to describe them. This has a quite evident effect on the energy values associated with the ELMO wavefunction, which are significantly higher with respect to the restricted HF (RHF) values, but also significantly lower with respect to those obtained using LMOs after the deletion of tails. Therefore, it appears quite important to develop methods which, starting from the ELMOs approach, try to improve the wavefunction using cheap methods. One could guess that the extremely localized nature of the orbitals could help in this effort, similarly to the good efficiency provided by the local MP n methods [22] which use the local nature of the orbitals to efficiently determine correlation energies.

In this paper, we propose a novel approach where occupied and virtual ELMOs are used to build up a valence bond (VB) expansion of the wavefunction. In this approach the extremely localized nature of the ELMOs is particularly relevant, as it permits us to significantly reduce the VB expansion on the basis of a "distance" between the ELMOs involved in the excitations. The proposed method is then particularly suitable to assemble the wavefunction of large molecules using the ELMOs determined on smaller fragments, as a favourable scaling in the length of the VB expansion with respect to the molecular dimensions should be expected. It is shown that the relaxation of the ELMOs introduced by the VB expansion allows us to recover a good percentage of energy with respect to the HF wavefunction, without the need to perform a traditional RHF calculation on the target molecule.

Test calculations were performed on the butane molecule in order to assess the potential of the ELMO–VB wavefunction. The transferability properties of the present approach were then tested on the 3-pentanone molecule using ELMOs built up on smaller fragments.

The proposed method can be considered as a natural development of the perturbative configuration interaction using localized orbitals [23, 24] and of the studies carried out to reduce the configuration interaction expansion using LMOs [25].

Theory

Let us consider a closed-shell molecule. ELMOs are defined by partitioning the N MOs (where $2N$ is the total number of the electrons) into n_{f} molecular fragments, where each of them is defined by its own basis set,

$\left(\chi_{\mu}^{i}\right)_{\mu=1}^{m_i}$, m_i being the number of the atomic orbitals belonging to the ith fragment. The αth ELMO of the ith fragment can thus be written as

$$\varphi_{\alpha}^{i} = \sum_{\mu}^{m_i} c_{\mu\alpha}^{i} \chi_{\mu}^{i}.$$

The coefficients $c_{\mu\alpha}^{i}$ are determined through a minimization of the expectation value of the energy associated with the ELMO wavefunction:

$$\psi_{\text{ELMO}} = A(\Phi), \text{ with } \Phi = \prod_{i}^{n_{\text{f}}} \prod_{\alpha}^{N_i^0} \varphi_{\alpha}^{i} \overline{\varphi_{\alpha}^{i}},$$

where A is the antisymmetrizer operator and N_i^0 is the number of doubly occupied ELMOs belonging to the ith fragment.

It should be noted that fragments can share atomic orbitals; then a natural nonorthogonality between ELMOs of different fragments arises. Different algorithms to determine ELMOs have been proposed [12, 13, 14, 15, 16]. It should be observed that the nonorthogonality of the orbitals determines nontrivial convergence difficulties.

The limitations introduced in the expansion definition of the ELMOs causes an obvious increment of the energy associated with the ELMO wavefunction with respect to the HF one. It is expected that this penalty should be larger when ELMOs are determined on smaller molecules and then transferred on a larger one without optimization. Hence the development of strategies to relax the ELMO wavefunction to get an energy-lowering with respect to the value obtained by a simple transfer of the ELMOs is of relevant interest.

To overcome the limitations connected with the expansion definition of the ELMOs, they should be combined, once the convergence is reached, with the virtual orbitals of the other fragments. Linear combinations of occupied orbitals of a fragment with their own virtual orbitals cannot give a lowering in energy owing to the Brillouin theorem, and the same remains true if one tries to combine between them doubly occupied orbitals of different fragments.

Hence, a relaxation of the ELMO wavefunction can be obtained by only allowing the occupied ELMOs of a fragment to delocalize using the virtual ELMOs of the other fragments. In other words, we permit an interaction between the ELMO wavefunction and a number of structures derived from it by exciting the electrons from the occupied ELMOs to the virtual ones. Owing to the nonorthogonal nature of the ELMOs, their configuration interaction can be thought of as a VB expansion:

$$\Psi_{\text{ELMO-VB}} = c_0 \Psi_{\text{ELMO}} + \sum_{ir}^{n_{\text{f}}} \sum_{\alpha}^{N_i^0} \sum_{\mu}^{N_r^v} c_{\alpha\mu}^{ir} \Psi_{\alpha\mu}^{ir} + \ldots, \tag{1}$$

where N_r^v is the number of virtual ELMOs of the rth fragment, $c_{\alpha\mu}^{ir}$ is the weight of the structure $\Psi_{\alpha\mu}^{ir}$ which is a single excitation from the αth ELMO of the ith fragment to the μth virtual orbital of the rth fragment, and is expressed by

$$\Psi_{\alpha\mu}^{ir} = A\left[\Phi\begin{pmatrix} i \\ \alpha \end{pmatrix} \varphi_{\alpha}^{i} \varphi_{\mu}^{r} \Theta_{0,0}^{2}\right],$$

where $\Phi\begin{pmatrix} i \\ \alpha \end{pmatrix}$ is the product of all the occupied ELMOs with the exception of the pair $\varphi_{\alpha}^{i}\overline{\varphi_{\alpha}^{i}}$, i.e., $\Phi = \Phi\begin{pmatrix} i \\ \alpha \end{pmatrix} \varphi_{\alpha}^{i}\overline{\varphi_{\alpha}^{i}}$ [in a similar way $\Phi\begin{pmatrix} ij \\ \alpha\beta \end{pmatrix}$ is defined by $\Phi = \Phi\begin{pmatrix} ij \\ \alpha\beta \end{pmatrix} \varphi_{\alpha}^{i}\overline{\varphi_{\alpha}^{i}}\varphi_{\beta}^{j}\overline{\varphi_{\beta}^{j}}$] and $\Theta_{0,0}^{2}$ is the singlet spin eigenfunction for the electrons belonging to the orbitals $\varphi_{\alpha}^{i}\varphi_{\mu}^{r}$ which are singly occupied.

Of course the expansion of Eq. (1) could be extended to higher orders of excitations, but here we are just looking for a relaxation of the occupied ELMOs and higher excitations would bring us to a very demanding algorithm, removing the advantages to use an approach based on localized orbitals.

For this reason we limit Eq. (1) to single excitations. It should be recalled that in this approach, in contrast to a traditional MO configuration interaction, single excitations give a contribution to the energy as each ELMO was obtained using only its own basis set.

Owing to the nonorthogonal nature of the orbitals, the computation of the Hamiltonian matrix elements $\left\langle \Psi_{\alpha\mu}^{ir} | H | \Psi_{\beta\nu}^{js} \right\rangle$ should require the use of the Löwdin formula [26] for a system of $2N$ electrons, so the calculation would soon become prohibitive.

In order to reduce the computational effort, the orbitals are subjected to the following transformations:

1. The occupied ELMOs are subjected to a Löwdin orthogonalization giving rise to a new set of occupied ELMOs $\left(\overline{\overline{\varphi_{\alpha}^{i}}}\right)_{i=1;\alpha=1}^{n_{\text{f}};N_i^0}$.

2. Each virtual orbital φ_{μ}^{r} is subjected to a Gram–Schmidt orthogonalization with respect to the Löwdin-orthogonalized occupied ELMOs, and the orbitals $\left(\overline{\overline{\varphi_{\beta}^{r}}}\right)_{r=1;\beta=1}^{n_{\text{f}};N_r^v}$ are obtained.

The orthogonalization procedure just described was chosen in order to have a new set of occupied orbitals describing the same functional space of the original occupied ELMOs. The Löwdin method was chosen to reduce the deformation of the orbitals during the orthogonalization step in order to maintain as much as possible the localized nature of the orbitals. It should be noted that when Eq. (1) involves all the single excitations to the selected virtual orbitals, the results obtained with the orthogonalized orbitals are identical to those obtained with the starting nonorthogonal ELMOs.

A VB calculation is then performed using the ELMO wavefunction $\overline{\overline{\Psi}}_{\text{ELMO}}$ built up using the occupied $\overline{\overline{\varphi_{\alpha}^{i}}}$ orbitals and the single excitations $\overline{\overline{\Psi_{\alpha\mu}^{ir}}}$ in the set of the Gram–Schmidt orthogonalized virtual orbitals:

$$\Psi_{\text{ELMO-VB}} = \overline{\overline{c_0}}\,\overline{\overline{\Psi_{\text{ELMO}}}} + \sum_{ir}^{n_f} \sum_{\alpha}^{N_i^0} \sum_{\mu}^{N_r^v} \overline{\overline{c_{\alpha\mu}^{ir}}}\,\overline{\overline{\Psi_{\alpha\mu}^{ir}}}. \qquad (2)$$

It should be observed that step 2 does not introduce an orthogonalization between the virtual orbitals, which remain nonorthogonal. In this way a partial localization nature of the virtual orbitals is preserved.

In order to perform the VB calculation, it is necessary to compute the matrix elements of the Hamiltonian operator between the structures appearing in the VB expansion (Eq. 2). Owing to the orthogonality between the virtual orbitals and the occupied ones, the calculation of these matrix elements can be greatly simplified [27] through a straightforward manipulation of the Löwdin formula. For example, the matrix elements between a couple of single excitations, i.e., $\left\langle \overline{\overline{\Psi_{\alpha\mu}^{ir}}} | H | \overline{\overline{\Psi_{\beta\nu}^{js}}} \right\rangle$, can be expressed in the following way:

$$\left\langle \overline{\overline{\Psi_{\alpha\mu}^{ir}}} | H | \overline{\overline{\Psi_{\beta\nu}^{js}}} \right\rangle = \left\langle A \left[\overline{\overline{\Phi\begin{pmatrix} ij \\ \alpha\beta \end{pmatrix}}}\, \overline{\overline{\varphi_\beta^j \varphi_\beta^j}}\, \overline{\overline{\varphi_\alpha^i \varphi_\mu^r}} \Theta_{0,0}^4 \right] \right\rangle |H| \left\langle A \left[\overline{\overline{\Phi\begin{pmatrix} ij \\ \alpha\beta \end{pmatrix}}}\, \overline{\overline{\varphi_\alpha^i \varphi_\alpha^i}}\, \overline{\overline{\varphi_\beta^j \varphi_\nu^s}} \Theta_{0,0}^4 \right] \right\rangle, \qquad (3)$$

where $\overline{\overline{\Phi\begin{pmatrix} ij \\ \alpha\beta \end{pmatrix}}}$ has already been defined and is applied here to the $\overline{\overline{\varphi_\alpha^i}}$ orbitals, and $\Theta_{0,0}^4 = \alpha\beta\Theta_{0,0}^2$ is the spin function.

The structures contained in the bra and ket parts of the previous equation are characterized by a common set of $N' = N-2$ doubly occupied orbitals described by $\overline{\overline{\Phi\begin{pmatrix} ij \\ \alpha\beta \end{pmatrix}}}$, which we here briefly indicate as $\phi_1\phi_2\ldots\phi_{N'}$, and by four orbitals singlet paired and orthogonal to the $\overline{\overline{\Phi\begin{pmatrix} ij \\ \alpha\beta \end{pmatrix}}}$ alignment.

We indicate with $\left(\varsigma_r^a\right)_{r=1}^4$ and $\left(\varsigma_s^b\right)_{s=1}^4$ the orbitals $\overline{\overline{\varphi_\beta^j \varphi_\beta^j \varphi_\alpha^i \varphi_\mu^r}}$ and $\overline{\overline{\varphi_\alpha^i \varphi_\alpha^i \varphi_\beta^j \varphi_\nu^s}}$ and with ψ_a and ψ_b the single excitations $\overline{\overline{\Psi_{\alpha\mu}^{ir}}}$ and $\overline{\overline{\Psi_{\beta\nu}^{js}}}$, respectively.

The Hamiltonian matrix element of Eq. (3) is given by

$$\begin{aligned} \langle \Psi_a | H | \Psi_b \rangle = {} & 2D_{ab} \sum_{k=1}^{N'} \langle \phi_k | h | \phi_k \rangle + D_{ab} \sum_{k,h=1}^{N'} \langle \phi_k\phi_k || \phi_h\phi_h \rangle \\ & - \langle \phi_k\phi_h || \phi_h\phi_k \rangle + \sum_{r,s=1}^{4} \left\langle \varsigma_r^a \middle| h^{eff} \middle| \varsigma_s^b \right\rangle D_{ab}[r|s] \\ & + \sum_{r<s}^{4} \sum_{t<u}^{4} \left\langle \varsigma_r^a \varsigma_t^b || \varsigma_s^a \varsigma_u^b \right\rangle D_{ab}[rs|tu] \\ & - \sum_{r<s}^{4} \sum_{t<u}^{4} \left\langle \varsigma_r^a \varsigma_u^b || \varsigma_s^a \varsigma_t^b \right\rangle D_{ab}[rs|ut], \end{aligned} \qquad (4)$$

where $\langle ab||cd \rangle = \iint \mathrm{d}r_1 \mathrm{d}r_2 a(r_1) b(r_1) \frac{1}{|r_1 - r_2|} c(r_2) d(r_2)$, and D_{ab}, $D_{ab}[r|s]$ and $D_{ab}[rs|tu]$ are the elements of the transition density matrices with respect to zero, one and two particles [11], respectively, and the h^{eff} operator gives the effect of the electrons described by $\overline{\overline{\Phi\begin{pmatrix} ij \\ \alpha\beta \end{pmatrix}}}$ on the other electrons.

Equation (4) can be efficiently programmed, considering that the terms which explicitly take into account the nonorthogonality of the orbitals are characterized by summations with indexes ranging from 1 to 4. The remaining terms contain expressions with indexes ranging from 1 to N', but as they do not vary significantly when changing the excitations, it is possible to compute them by appropriate differences with respect to the value obtained with $N' = N$. For example, the first term of Eq. (4), apart from the trivial multiplicative factor D_{ab}, can be computed through

$$\sum_{k=1}^{N} \langle \phi_k | h | \phi_k \rangle - \langle \varphi_\alpha^i | h | \varphi_\alpha^i \rangle - \left\langle \varphi_\beta^j | h | \varphi_\beta^j \right\rangle,$$

where the first term is independent of the pairs of excitations considered.

Using the present approach it is possible to obtain an algorithm which allows us to save more than 1 order of CPU time with respect to a direct application of the Löwdin formula.

Particular care has to be dedicated to the selection of the virtual orbitals that have to be introduced in the VB expansion. We have to recall that in the ELMO approach we obtain m_i orbitals for each fragment; as the fragments can share the same atomic basis functions, it results that $\sum_i^{n_f} m_i > M$, where M is the total number of basis functions. This fact does not cause any problem in the determination of the ELMOs, but requires particular attention in the VB expansion, as linear-dependence problems can easily arise if no criteria are introduced in the selection of the virtual orbitals.

As a matter of fact we noted that it is quite common to find virtual ELMOs of a fragment which are linear combinations of the occupied ELMOs of the other fragments. In this case these orbitals are automatically removed by our procedure during step 2 where they are Gram–Schmidt orthogonalized with respect to the occupied orbitals.

Of course this procedure does not guarantee that the surviving virtual orbitals are not linearly dependent on each other. In order to be sure to select a proper linearly independent set of virtual orbitals, it is possible to submit the set of the virtual orbitals from step 2, $\left(\overline{\overline{\varphi_\beta^r}}\right)_{r=1;\beta=1}^{n_f;N_r^v}$, to a Gram–Schmidt procedure, and we obtain a new set of orbitals which we denote $\left({}^{\text{GS}}\varphi_\beta^r\right)_{r=1;\beta=1}^{n_f;N_r^v}$. If the norm of the orbital ${}^{\text{GS}}\varphi_\beta^r$ immediately after the Gram–Schmit orthogonalization step is greater than a given threshold, the original $\overline{\overline{\varphi_\beta^r}}$ orbital is added to the set of virtual orbitals that have to be included in the VB expansion.

The use of the set $\left(\overline{\overline{\overline{\varphi_\beta^r}}}\right)_{r=1;\beta=1}^{n_\mathrm{f};N_r^v}$ instead of $\left(\mathrm{GS}_{\varphi_\beta^r}\right)_{r=1;\beta=1}^{n_\mathrm{f};N_r^v}$ is due to the localized nature of the first one, that allows us, as we will see in the examples reported in this work, to favourably truncate the VB expansion.

Test calculations

Some test calculations were performed to evaluate the proposed approach.

First of all, we wanted to check both the capability of the VB expansion in relaxing the ELMOs and the possibility to introduce criteria to reduce the length of the expansion. After this step, we focused our attention on the possibility to use the present approach to assemble the wavefunction of a molecule using the ELMOs determined on smaller fragments.

The first point was analysed using the butane molecule, for which we used the geometry optimized at the RHF level with the standard 6-31G basis set. To perform the ELMO calculation, we defined the molecular fragments following the scheme depicted in Fig. 1.

Fragments 1–4 correspond to the cores of the carbon atoms and are defined using only the atomic functions of their respective centres; fragments 5, 6, 7, 9, 10, 12, 13, 15, 16 and 17 describe the C–H bonds and each of them is defined using the corresponding atomic functions of the carbon and hydrogen atoms describing that bond; finally fragments 8, 11 and 14 describe the C–C bonds and each of them is defined according to the atomic functions of the two carbon atoms involved.

The RHF calculation was performed using the PC-GAMESS package [28, 29], which was also used to obtain the monoelectronic and bielectronic integrals necessary to perform the ELMO–VB calculations; the ELMO calculations were carried out using a modified version of the PC-GAMESS package [14], and for the ELMO–VB calculations we used a program written in our laboratory to test the proposed method. It was checked using a general purpose VB program [30].

The energy values are reported in Table 1. We can observe that owing to the extremely localized nature of the orbitals, the energy corresponding to the ELMO wavefunction differs by 27.9 kcal/mol with respect to the RHF value. This difference is largely increased, up to 80.9 kcal/mol, if we use a wavefunction built up using LMOs obtained through the Pipek–Mezey procedure [7], subjected to deletion of the tails outside the molecular fragments defined in Fig. 1.

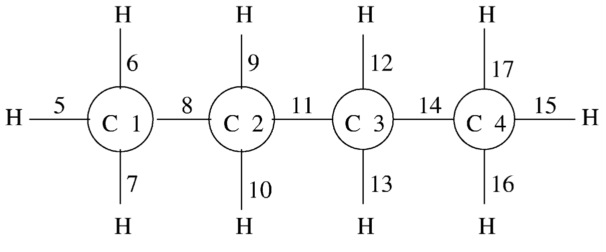

Fig. 1. Definition of the molecular fragments for the butane molecule

We then performed two ELMO–VB calculations, denoted with ELMO–VB(1) and ELMO–VB(2), where one or two virtual ELMOs for each fragment were selected, respectively. The selected virtual orbitals were the orbitals with the lowest orbital energies which survive after the orthogonalization step and the check on the linear independence described in the Theory section.

Owing to the orthogonalization with respect to the occupied ELMOs, the virtual orbitals acquire a partial delocalization with respect to the original ones, but anyway they conserve a quite stringent localized nature, as can be seen in the examples reported in Fig. 2.

The ELMO–VB(1) wavefunction, based on the use of only one virtual orbital for each fragment, is constituted by 289 excitations and it recovers 24% of the difference energy between the RHF and the ELMO wavefunctions. The use of two virtual orbitals for each fragment allows the ELMO–VB(2) wavefunction to recover 84% of the difference energy, still remaining a compact wavefunction, as it is constituted by 578 excitations.

In order to see the contributions of the excitations to the ELMO–VB(1) and ELMO–VB(2) expansions, we ordered the excitations according to their decreasing absolute weights and we performed a series of ELMO–VB calculations introducing an increasing number of excitations according to their weights. In this way we can have an idea of the relative importance of the different excitations.

The energy values of the different ELMO–VB wavefunctions are plotted against the number of excitations included into the VB expansion in Fig. 3. The corresponding percentages of energy recovered with respect to the RHF value are reported in Fig. 4.

From Figs. 3 and 4 it is evident that not all the structures have the same importance in the ELMO–VB expansion. Roughly the same results of the complete ELMO–VB wavefunction can be obtained with just half the number of total excitations. This result can be ascribed to the localized nature of all the orbitals involved in the VB expansion. The occupied orbitals, despite the Löwdin orthogonalization, remain well localized, and

Table 1. Energy values for the butane molecule. The acronyms are described in the text

Method	Energy (au)	ΔE (kcal/mol)
RHF	−157.23468353	0.00
LMO	−157.10578937	80.88
ELMO	−157.19015516	27.94
ELMO–VB(1)	−157.20084621	21.23
ELMO–VB(2)	−157.22766442	4.40
ELMO–VB(Top_1)	−157.19903195	22.37
ELMO–VB(Top_2)	−157.22499207	6.08

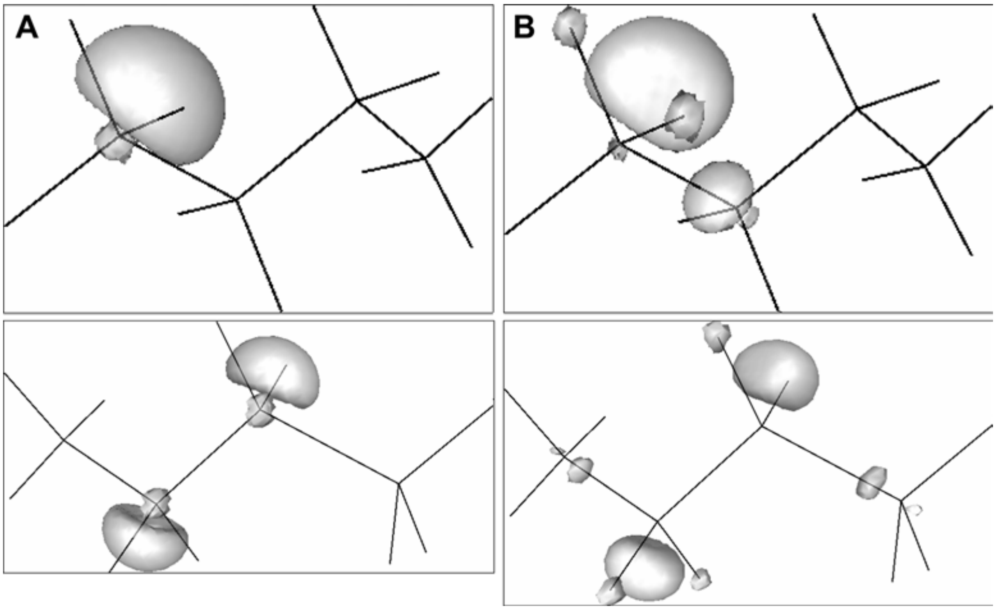

Fig. 2. Plots of two virtual extremely localized molecular orbitals (ELMOs) **a** before and **b** after the Gram–Schmidt orthogonalization described in the text, corresponding to an isosurface value of 0.04

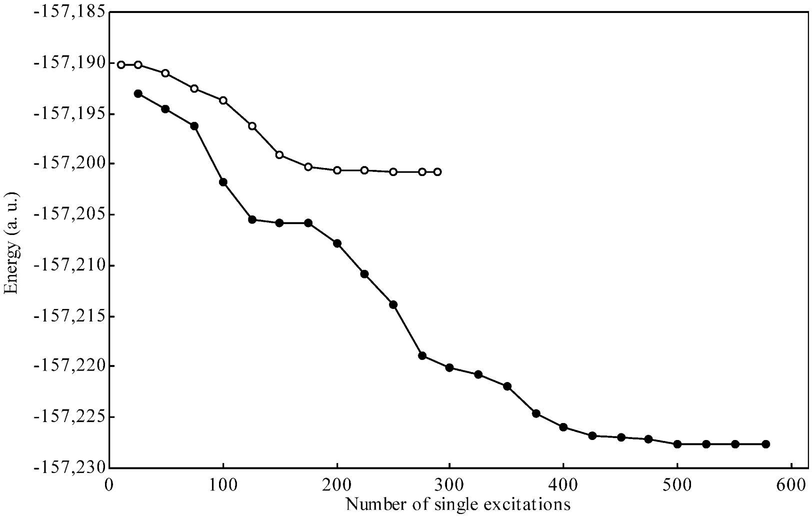

Fig. 3. Energy values of different ELMO–valence bond (*VB*) calculations with respect to the increasing number of single excitations. The *empty* (*full*) *circles* refer to the use of one (two) virtual orbitals for each fragment

the virtual ones acquire a partial but very limited delocalization after the Gram–Schmidt orthogonalization. These considerations suggest that the VB expansion can be compacted by taking into account the local nature of the orbitals [23, 24, 25].

In order to investigate this point further we performed two additional ELMO–VB calculations, where we selected only the following excitations:

1. From an occupied ELMO describing a bond (i.e., a C–C or a C–H fragment) to virtual ELMOs localized on the first-neighbour fragments (e.g., from fragment 5 to fragment 6 or from fragment 5 to fragment 1) and on the second-neighbour fragments (e.g., from fragment 5 to fragment 9 or from fragment 5 to fragment 2).
2. From an occupied ELMO describing a bond (C–C or C–H) to virtual ELMOs localized on the third-neighbour core fragments (e.g., from fragment 5 to fragment 3 or from fragment 9 to fragment 4).

These are a sort of criteria based on what we could call "a topological selection" aimed at inserting in the VB expansion only the more interacting excitations.

The energy values obtained with these calculations are reported in Table 1. The ELMO–VB(Top_1) calculation, using just a single virtual orbital for each fragment, is constituted by 161 excitations (i.e., 56% of the VB expansion with no topological selection), but it recovers 19.9% of the energy with respect to the HF value compared with 24% if all the structures are included.

The favourable comparison is more evident with the ELMO–VB(Top_2) wavefunction, using two virtual ELMOs for each fragment and topological selection. In this case the wavefunction is constituted by 322 excitations (i.e., 56% with respect to the VB expansion with no

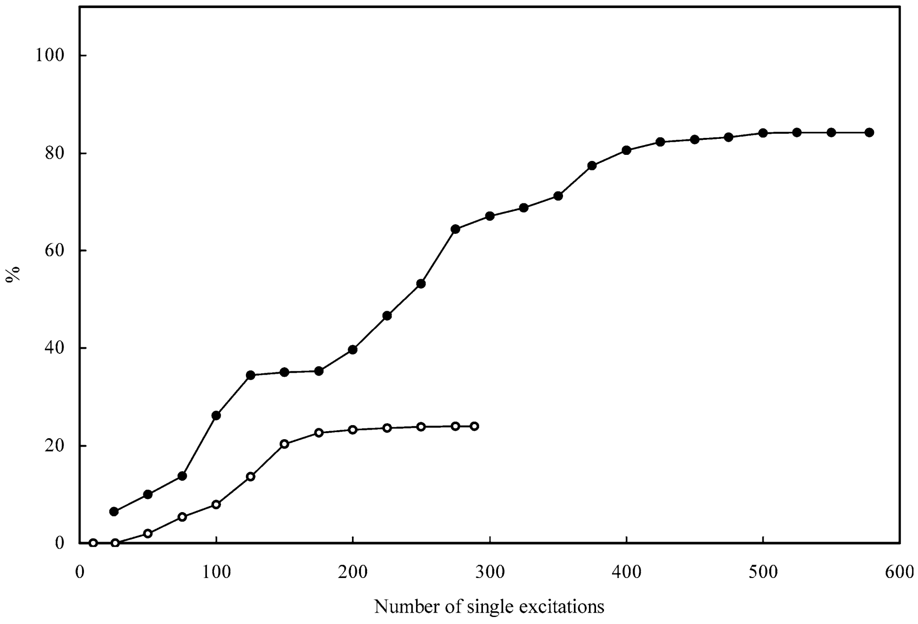

Fig. 4. Percentage of energy recovered with respect to the restricted Hartree–Fock value from different ELMO–VB calculations against the number of single excitations. The *empty* (*full*) *circles* refer to the use of one (two) virtual orbitals for each fragment

topological selection), but it recovers 78.2% of the energy compared with 84.2% without restrictions on the excitations included.

We then analysed the applicability of the present approach to the transferability problem. We considered the possibility to build up a proper wavefunction for the 3-pentanone molecule under severe conditions, i.e., using very simple starting molecular fragments. Using the optimized geometry at the RHF level with the 6-31G basis set, we first carried out an ELMO calculation using the molecular fragments depicted in Fig. 5.

The definition of the fragments is similar to that adopted for the butane molecule. In this case we observe that the fragment 4, defined using the atomic orbitals of the oxygen atom, is constituted by three occupied MOs, describing the core and the lone-pairs electrons; fragment 14 is built up using the atomic functions of the oxygen atom and of the bonded carbon atom, and it is constituted by two occupied MOs which describe the $C=O$ double bond.

The energy values are reported in Table 2. Once again we observe that the energy associated with the ELMO wavefunction is higher than the RHF value by 54.3 kcal/mol. Anyway we note that the use of LMOs subjected to the deletion of tails in order to reproduce the same definition of the molecular fragments of the ELMOs increases this difference up to 124.7 kcal/mol.

In order to investigate the transferability properties of the ELMOs, we then performed ELMO calculations on the ethane, formaldehyde and acetaldehyde molecules, using the same definition of the molecular fragments adopted so far (i.e., bond and core/lone pair fragments). In this way we defined ELMOs for all the molecular fragments which are present in the 3-pentanone molecule. The complete absence of tails permits the direct transfer of the ELMOs from the three smaller molecules to the 3-pentanone one (Fig. 6).

We observe that the molecular fragments used are very simple, and, despite the different acidity of the hydrogen atoms in the 3-pentanone molecule, we decided to use the same C–H fragment, determined on the ethane molecule, for all the C–H bonds. This reflects our intention to use severe conditions in order to test if the ELMO–VB method can efficiently relax the transferred orbitals. Of course, one expects that the results could be further improved by the proper choice of the molecular fragments to be determined, in a fashion similar to what is done in the use of different atom types in the force field approaches.

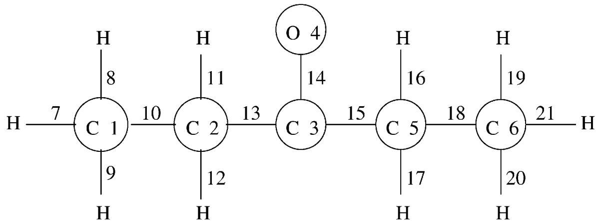

Fig. 5. Definition of the molecular fragments for the 3-pentanone molecule

Table 2. Energy values for the 3-pentanone molecule.The acronyms are described in the text

Method	Energy (au)	ΔE (kcal/mol)
RHF	−269.91403081	0.00
LMO	−269.71535498	124.67
ELMO	−269.82754481	54.27
ELMO-Transf	−269.82315703	57.02
ELMO–VB(1)	−269.86551984	30.44
ELMO–VB(2)	−269.89686563	10.77
ELMO–VB(Top_1)	−269.85384479	37.77
ELMO–VB(Top_2)	−269.89106528	14.41

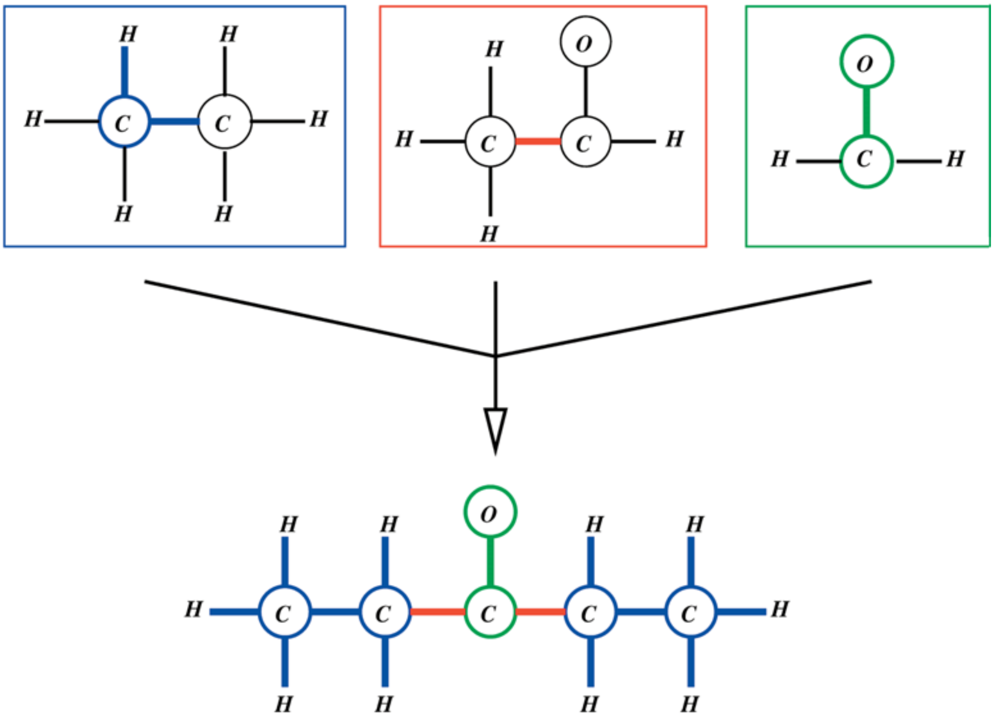

Fig. 6. Transfer of the ELMOs for the 3-pentanone molecule

Using the transferred ELMOs we determined the energy, ELMO-Transf, of the 3-pentanone molecule, which is only 2.7 kcal/mol higher with respect to that achieved through optimized ELMOs. So the resulting difference with respect to the HF value is 57.0 kcal/mol.

We then performed ELMO–VB calculations using one/two, ELMO–VB(1)/(2), virtual orbitals for each fragment, selected with the same criteria described for the butane molecule. The ELMO–VB(1)/(2) expansion is constituted by 504 (1,008) excitations and allows us to recover 44.0% (80.3%) of the energy difference between the RHF and the ELMOs values. It is quite satisfying that the use of transferred ELMOs and the ELMO–VB approach permits us to obtain a wavefunction quite close to the RHF calculation on the 3-pentanone molecule. It should be observed that there are 1,776 variational coefficients defining the 3-pentanone RHF wavefunction, and only 290 coefficients which define the ELMO wavefunction.

In order to see if it is possible to reduce the VB expansion while retaining good accuracy, we performed two additional ELMO–VB calculations using the topological selection individuated for the butane molecule, the occupied orbitals of the oxygen lone pairs being treated as the occupied orbitals describing the bonds. The energy values are reported in Table 2. The two VB expansions, denoted as ELMO–VB(Top_1)/(Top_2), are now reduced to 224/448 excitations and they recover 30.4%/73.5% of the energy difference between the RHF and ELMO calculations. Hence it can be concluded that the topological selection allows us to halve the lengths of the VB expansion, while the accuracy of the results is only slightly affected.

Conclusions

The ELMOs provide a description of a molecule using variationally determined orbitals. Owing to the large reduction of the variational coefficients, the ELMO wavefunction is characterized by a nonnegligible increase of the energy. Anyway this is the price to pay in order to have localized MOs which are really transferable without perturbation. Of course a different approach could be to perform a posteriori localization of the canonical MOs, and to delete their tails before transferring them; however this procedure is characterized by a greater increase in the energy, and we have recently evidenced [14] that the electronic properties also suffer from such an approach.

It is therefore of relevant importance to develop methods which are based on the ELMOs, and allow us, at the same time, to increase the accuracy of the electronic description of the system.

In this paper we proposed a method based on a VB expansion of the ELMO wavefunction. The localized nature of the orbitals has permitted us to define a topological selection of the excitations to be included in the VB expansion, allowing us to reduce the computational requests without substantial reduction in the accuracy of the results. The calculations also evidenced that just two virtual orbitals for each fragment allow us to obtain results close to the HF wavefunction.

These results prompted us to use the ELMO–VB approach to build up the wavefunction for the 3-pentanone molecule using ELMOs determined on smaller fragments. The results have shown that, owing to the extremely localized nature of the orbitals, it is possible to build up a good wavefunction for target molecules using transferred ELMOs, and to increase its energetic accuracy by means of a compact VB expansion. This approach permits us to obtain accuracies similar to those obtained by means of a traditional RHF calculation on the target molecule.

In the present method we strongly limited the VB expansion, having truncated it to single excitations. Even if this could be considered a severe approximation, we must recall that the aim of the present work is not to introduce correlation using localized orbitals, but to relax ELMOs in order to get results closer to the HF ones with respect to those obtained by the ELMO wavefunction. In addition, it should be observed that the last objective of all the methods that try to assemble the electronic structure using molecular fragments should be the application to large molecules, so the number of higher excitations for these systems would become prohibitively expensive.

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References

1. Goedecker S (1999) Rev Mod Phys 71:1085
2. Lee TS, York DM, Yang W (1996) J Chem Phys 105:2744
3. Van der Vaart A, Gogonea V, Dixon SL, Merz KM Jr (2000) J Comput Chem 21:1494
4. Dixon SL, Merz KM Jr (1996) J Chem Phys 104:6643
5. Boys SF (1960) Rev Mod Phys 32:296
6. Edmiston C, Ruedenberg K (1965) J Chem Phys 43:S97
7. Pipek J, Mezey PG (1989) J Chem Phys 90:4916
8. Naray-Szabo G (2000) Comput Chem 24:287
9. Angyan JG, Naray-Szabo G (1991) In: Maksic ZB (ed) Theoretical models of chemical bonding, part 4. Springer, Berlin Heidelberg New York, p 1
10. Smits GF, Altona C (1985) Theor Chim Acta 67:461
11. McWeeny R (1992) Methods of molecular quantum mechanics. Academic, New York
12. Stoll H, Wagenblast G, Preuss H (1980) Theor Chim Acta 57:169
13. Sironi M, Famulari A (1999) Theor Chem Acc 103:417
14. Fornili A, Sironi M, Raimondi M (2003) J Mol Struct (THEOCHEM) 632:157
15. Szekeres Z, Surjan PR (2003) Chem Phys Lett 369:125
16. Couty M, Bayse CA, Hall MB (1997) Theor Chem Acc 97:96
17. Gianinetti E, Raimondi M, Tornaghi E (1996) Int J Quantum Chem 60:157
18. Burresi E, Sironi M Theor Chem Acc, in press
19. Sironi M, Famulari A, Raimondi M, Chiesa S (2000) J Mol Struct (THEOCHEM) 47:529
20. Assfeld X, Rivail JL (1996) Chem Phys Lett 263:100
21. Ferré N, Assfeld X, Rivail JL (2002) J Comput Chem 23:610
22. Pulay P (1983) Chem Phys Lett 100:151
23. Diner S, Malrieu JP, Claverie P (1969) Theor Chim Acta 13:1
24. Daudey JP, Diner S (1972) Int J Quantum Chem 6:575
25. Bonaccorsi R, Petrongolo C, Scrocco E, Tomasi J (1969) Theor Chim Acta 15:332
26. Löwdin PO (1955) Phys Rev 97:1474
27. McWeeny R, Ohno KA (1960) Proc R Soc Lond Ser A 255:367
28. Granovsky AA http://classic.chem.msu.su/gran/gamess/index.html
29. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JJ, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14:1347
30. Raimondi M A general purpose valence bond program. Universita' di Milano, Milan