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Dedicated Molecular Orbitals for the Variational Determination of the Electron-Transfer Matrix Element. Method and Application to a Cu(I)−Cu(II) Mixed Valence Compound

Carmen Jiménez Calzado and Javier Fernández Sanz*

Departamento de Química Física, Facultad de Química, Universidad de Sevilla, E-41012 Sevilla, Spain

Oscar Castell and Rosa Caballol

Departament de Química, Universitat Rovira i Virgili, E-43005 Tarragona, Spain

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A method to obtain molecular orbitals specially suited for the variational calculation of the electron-transfer matrix element V_{ab} is reported. These electron-transfer dedicated molecular orbitals (ET-DMOs) are determined from the diagrammatic second-order expansion of the transfer integral H_{ab} and are associated to a participation index which allows for a truncation of the molecular orbital basis set and, therefore, for a reduction of the variational space in a difference-dedicated configuration interaction (DDCI) calculation. The suitability of these ET-DMOs is first tested with some simple organic models for which a reduction of the second-order space of 40−60% is possible without significant loss of precision. The calculation of the transfer integral for a Cu(I)−Cu(II) mixed-valence system is also reported. Using as model a cluster of formula $Cu_2Cl_6^{3-}$, H_{ab} is estimated to be 2000 cm^{-1} from a perturbational-variational calculation. The stability of the ET-DMOs for this system is found to be excellent allowing for a reduction of the variational space of 76% with a relative error of only 0.15%.

1. Introduction

The electron-transfer matrix element V_{ab} plays a pivotal role in the theory of ubiquitous electron-transfer (ET) reactions.[1] The most widely theoretical approach used for these reactions is[2] the so called "two-states model" according to which V_{ab} is conventionally defined as half the splitting between the adiabatic potential energy surfaces at the crossing seam (Figure 1):

$$2V_{ab} = E^{+} - E^{-} \tag{1}$$

Within the two-states framework, E^+ and E^- are the solutions for the secular equation

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - E \end{vmatrix} = 0 \tag{2}$$

In this equation, $H_{aa} = \langle\psi_a|\mathbf{H}|\psi_a\rangle$, $H_{bb} = \langle\psi_b|\mathbf{H}|\psi_b\rangle$, $H_{ab} = \langle\psi_a|\mathbf{H}|\psi_b\rangle$, and $S_{ab} = \langle\psi_a|\psi_b\rangle$, **H** being the electronic Hamiltonian. At the crossing point $H_{aa} = H_{bb}$, and if S_{ab} is small, V_{ab} almost equals the transfer integral coupling states ψ_a and ψ_b: $V_{ab} \approx H_{ab}$.

In the ab initio determination of V_{ab}, two different strategies can in principle be employed.[1a] The first is to compute the adiabatic energies and to obtain V_{ab} making use of eq 1. This procedure can be easily set up from a multiconfigurational calculation, for instance, or even approximated by using Koopmans' theorem.[3] The second possibility, or diabatic method, involves explicit determination of the matrix elements of eq 2 which is usually accomplished by exploiting the properties of symmetry-broken SCF solutions for weakly coupled systems.[1a,4]

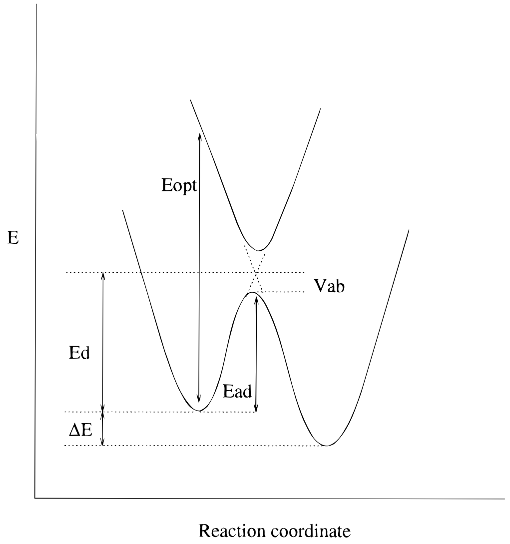

Figure 1. Schematic potential energy for an electron-transfer reaction. E_{opt}, E_d, and E_{ad} refer to the optical transition, diabatic, and adiabatic activation energies, respectively.

The central problem in the calculation of the transfer integral H_{ab} arises from the smallness of the electronic coupling. Typically H_{ab} values range between 100 and 1000 cm^{-1}, and if the coupling is very weak H_{ab} becomes $\approx$10 cm^{-1}. Although electron correlation effects have been proposed to be small, it seems convenient that in a proper and accurate determination of H_{ab} correlation corrections should be taken into account. However, up to the present most of the calculations have been limited to the Hartree−Fock level. The reason for this limitation is basically due to the technical requirements which would be involved in such a calculation. Effectively, in an adiabatic approach, the calculation of E^+ and E^- (from a MRCI expansion for instance) should ensure that the same degree of electron correlation is incorporated into the two adiabatic states. On the other hand, the diabatic procedure would involve the computation of the Hamiltonian matrix elements on the basis of the correlated diabatic wave functions.

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* Author to whom correspondence should be addressed. E-mail: sanz@quimix.us.es.

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In a recent paper Sanz and Malrieu[5] reported an alternative method to compute V_{ab} at the correlated level in which the determination of adiabatic energies or diabatic wave functions was not compulsory. In this procedure, only electron correlation contributions to the off-diagonal term H_{ab} were explicitly computed. The method, based on the quasi degenerate perturbation theory (QDPT),[6] was developed along two directions: (i) direct determination of H_{ab} through a second-order perturbative development in which only the determinants contributing to H_{ab} are explicitly considered and (ii) variational calculation by means of the CI matrix built up from the minimal set of determinants contributing to the energy *difference* between the adiabatic states a and b (difference-dedicated CI, DDCI). The use of such a variational procedure introduces higher order effects and improves the reliability of the method since instabilities due to the smallness of denominators are avoided. Notice that the list of determinants contributing to the energy difference (the second-order differential space) is the same as that contributing to the off-diagonal element H_{ab}.

The usefulness of differential spaces has been shown to be a powerful tool also in the calculation of small quantities such as singlet−triplet splitting, electronic transitions, and magnetic couplings.[7] However, although such differential spaces are noticeably smaller than the spaces involved in a second-order expansion of states a and b, it turns out that they grow rapidly for medium- and large-sized systems, and therefore, some kind of truncation is necessary if a variational answer is desired. The truncation procedure, either on the molecular orbital basis set or on the list of determinants, always introduces some degree of arbitrariness; however, in 1991 Miralles, Caballol, and Malrieu[8] generalized the natural orbital suggestions of Löwdin[9] and proposed a method to obtain dedicated molecular orbitals (DMOs) which would be specially suited for the calculation of a given observable. Such DMOs are the eigenvectors of a participation matrix whose eigenvalues represent a participation index in the determination of a specific observable, allowing then for a rational truncation. The method was proposed to be general and applied to the calculation of bond dissociation energies and singlet−triplet gaps and was later extended to the computation of exchange coupling constants in polyradical systems.[8,10]

In the present work we report on the applicability of this method for the variational calculation of the electron transfer integral H_{ab}. With this aim, a procedure to obtain electron-transfer dedicated molecular orbitals (ET-DMOs) is developed first. The suitability of these ET-DMOs is then tested by analyzing the stability of the differential spaces arising from truncation of the ET-DMO basis set according to their participation index. In this analysis two different kind of compounds are examined. In the first, some simple organic models constituted by two ethylene subunits separated by a bridge are considered. In the second, the calculation of the transfer integral in a much more realistic system, a Cu(I)−Cu(II) mixed-valence compound, is performed.

2. Theoretical Method

The procedure to obtain the ET-DMO basis will make use of the diagrammatic expansion of the second-order correction to H_{ab}. This methodology has been reported in ref 5, and only a brief summary is given here. Let us consider a system $(\mathrm{A{-}L{-}B})^+$, where A is a donor center, B is an acceptor center, and L is a bridge ligand. The Hartree−Fock wave function for the ground and first excited states at the crossing point can be written:

$$\phi_1^0 = |1\bar{1}2\bar{2}...g\bar{g}u|; \quad \phi_2^0 = |1\bar{1}2\bar{2}...gu\bar{u}| \tag{3}$$

where 1, 2, ... indicate inner molecular orbitals, and g and u are symmetric and antisymmetric linear combination of atomic orbitals centered on the donor and acceptor units. By an appropriate rotation or another localization method (Boys method, for instance) it is possible to define two localized molecular orbitals, a and b (the active MOs), which can be used to build up two localized determinants, ϕ_a^0 and ϕ_b^0, which are degenerate at the seam.

$$\phi_a^0 = |1\bar{1}2\bar{2}...a\bar{a}b|; \quad \phi_b^0 = |1\bar{1}2\bar{2}...ab\bar{b}| \tag{4}$$

According to the QDPT,[6] these diabatic states can be used to define a model space, S_0, where the effective hamiltonian can be expressed as a 2 × 2 matrix

$$\begin{pmatrix} H_{aa}^{eff} & H_{ab}^{eff} \\ H_{ab}^{eff} & H_{bb}^{eff} \end{pmatrix} \tag{5}$$

and since the model wave functions are orthogonal, the off-diagonal element of this matrix is identified with the electron-transfer matrix element, V_{ab}.

H_{ab}^{eff} can thus be obtained from a perturbational development, which to the second-order is (Möller−Plesset partition)

$$H_{ab}^{eff(2)} = \langle\phi_a^0|\mathbf{H}|\phi_b^0\rangle + \sum_{\alpha} \frac{\langle\phi_a^0|\mathbf{H}|\phi_\alpha^0\rangle\langle\phi_\alpha^0|\mathbf{H}|\phi_b^0\rangle}{(\epsilon_0 - \epsilon_\alpha)} \tag{6}$$

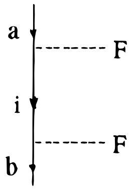
where $\{\phi_\alpha^0\}$ are all determinants interacting with *both* ϕ_a^0 and ϕ_b^0. These determinants constitute the second-order differential space and are generated by single and double excitations from the zeroth-order determinants ϕ_a^0 and ϕ_b^0. Alternatively, the variational calculation of H_{ab}^{eff} involves a diagonalization of the CI matrix restricted to the space $[\phi_a^0 + \phi_b^0 + \{\phi_\alpha^0\}]$. As stated in the introduction, the size reduction of such a space is the main goal of the present work.

In order to obtain the ET-DMOs, the so-called participation matrix $\mathbf{R}$ has now to be determined. According to Miralles et al.,[8] the $\mathbf{R}$ matrix arises from a low perturbation of the density matrix in which occupied and virtual MOs are treated in two separated blocks

$$R_{ij} = \langle\psi|a_j^+ a_i|\psi\rangle; \quad R_{pq} = \langle\psi|a_q^+ a_p|\psi\rangle \tag{7}$$

where *i*, *j* labels run over occupied MOs and *p*, *q* over virtual ones.

The diagrams for the density matrix are then obtained from the second-order energy diagrams by introducing an interaction line (···**X**) with the $a_j^+ a_i$ operator on either the hole or particle propagation lines. For instance, the simplest diagram involved in eq 6 corresponds to the first-order correction and is given by



The diagram for the participation matrix is then

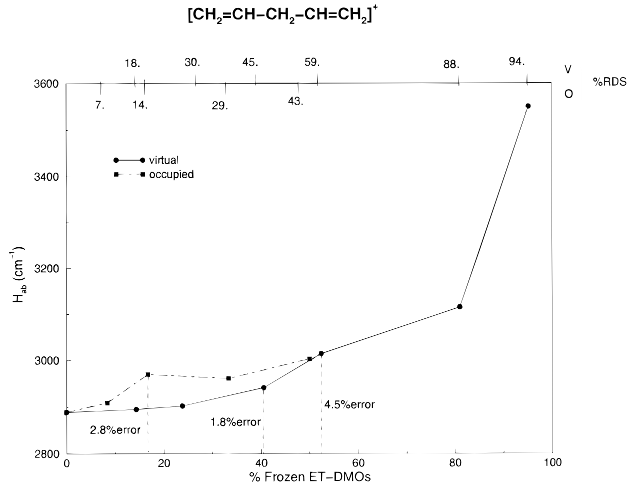
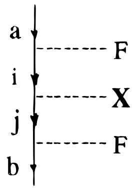


Figure 2. Stability of H_{ab} against the percentage of the frozen ET-DMOs for compound **1**. The reduction in the differential spaces is given separately for virtual and occupied blocks at the top.



and the contribution to the R_{ij} element is:

$$-\frac{\langle \mathrm{a}|\mathbf{F}|i\rangle\langle j|\mathbf{F}|\mathrm{b}\rangle}{(\epsilon_j-\epsilon_\mathrm{b})(\epsilon_i-\epsilon_\mathrm{b})} \qquad (8)$$

Following this principle, the different contributions to R_{ij} and R_{pq} have been systematically determined from the diagrams of ref 5. The corresponding expressions are reported in the Supporting Information. Once the occupied and virtual blocks of the **R** matrix are known, the ET-DMOs are simply their eigenvectors, the eigenvalues representing their participation number.

In summary, the computational steps are

(1) Determination of delocalized MOs from either a Hartree–Fock SCF or a state-averaged MCSCF calculation and further localization of the active orbitals a and b.

(2) Molecular integral transformation from the AO basis set to the MO one.

(3) Determination of **R** matrix from the expressions given in the Supporting Information.

(4) Obtention of ET-DMOs through diagonalization of the **R** matrix.

(5) Truncation of the new ET-DMO basis set according to their participation number and determination of the differential space.

(6) Molecular integral transformation to the truncated ET-DMO basis set.

(7) Computation of the CI matrix and further diagonalization.

(8) Determination of H_{ab} following the procedure given in ref 5. When the system is at the crossing seam, H_{ab} is simply half the difference between the two lowest roots of the CI matrix.

3. Testing the ET-DMOs

The procedure developed above has been set up to compute the transfer integral H_{ab} between two ethylenes connected through a bridge: $[CH_2{=}CH{-}L{-}CH{=}CH_2]^+$, with L being CH_2, O, and S. These compounds, labeled as **1**, **2**, and **3**, were already treated in ref 5, and the computational details concerning the basis set can be found there.

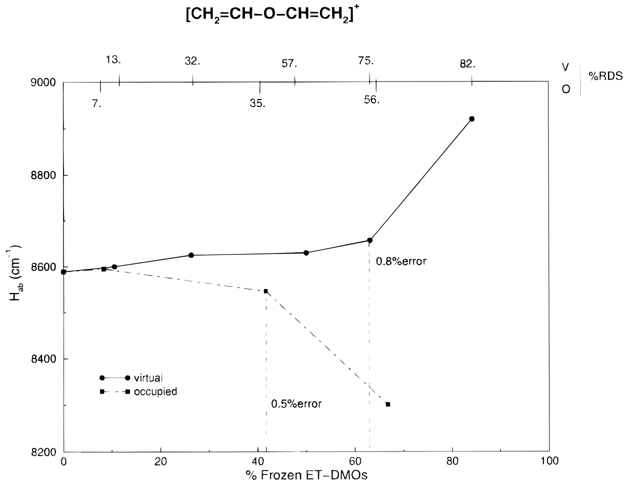
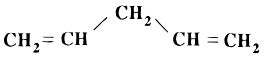


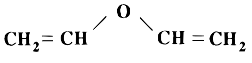
Figure 3. Stability of H_{ab} against the percentage of the frozen ET-DMOs for compound **2**.

The first step of the procedure is the obtention of the canonical MOs. As stressed in our previous work, one of our main concerns was that such MOs should be "democratic"; i.e., they would not be right- or left-polarized at the seam. Such MOs can easily be obtained from a state-averaged MCSCF calculation or from a closed shell SCF calculation on the *neutral* species. These MOs, labeled as SAMOs and CSMOs, respectively, were shown to give variational H_{ab} values close to each other. In the present work we have also considered both type of orbitals, and as far as the properties of ET-DMOs are concerned, we have also found similar behavior; that is why only results using SAMOs as starting point will be reported.



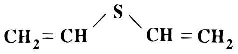
$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

1



$CH_2{=}CH{-}O{-}CH{=}CH_2$

2



$CH_2{=}CH{-}S{-}CH{=}CH_2$

3

Once the ET-DMOs have been obtained, the simplest way to analyze their properties is through a progressive truncation of the virtual or occupied spaces according to their participation number, ρ, and further diagonalization of the differential spaces which arise.[11] The results are reported in Figures 2–4.

Starting the analysis with compound **1**, it can be seen in Figure 2 how H_{ab} remains almost unchanged upon truncation of 40% of the virtual ET-DMOs. This corresponds to a threshold of $\rho = 0.05$ and allows for a reduction of the differential space of 45% with an error in H_{ab} of only 1.8%. Increasing the threshold to $\rho = 0.1$ reduces the number of determinants to be diagonalized by 60% with an error of 4.5%. Truncation of the occupied block is also possible, although as can be seen, there is a small oscillation in the curve. Freezing 8.5% of the occupied ET-DMOs introduces an error of 0.7%, but it increases to 2.8% when the orbitals have been frozen in 17%. These preliminary results show the excellent behavior of the ET-DMOs, suggesting that one can reduce the differential space to almost 50% without loss of precision.

Results for compounds **2** and **3** show similar trends to those of compound **1**. However, since the electronic coupling is now stronger, the relative deviations are even smaller. The curves of Figures 3 and 4 make it evident that a truncation of about 45–60% of the virtual ET-DMOs is possible with errors of only

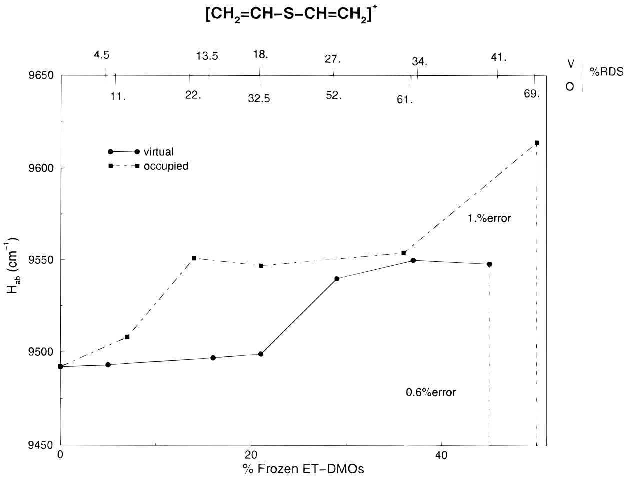


Figure 4. Stability of H_{ab} against the percentage of the frozen ET-DMOs for compound **3**.

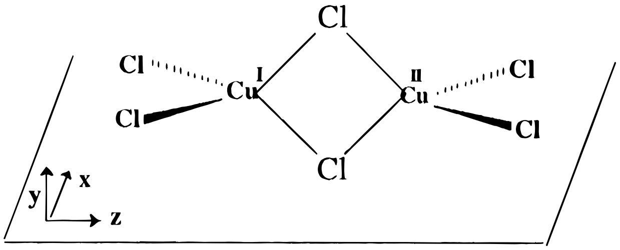
0.6−0.8%. The range of truncation in the occupied block for a given degree of deviation appears to be somewhat lower, but it should be noted that it is preferable to truncate the virtual orbitals since they are by far the most numerous, and therefore, the reduction of the differential space is larger.

One can wonder now what the benefit of the truncation of the ET-DMOs is against truncation of the canonical MOs. In order to clarify this point we have performed a set of calculations in which the same number of virtual or occupied canonical MOs have been deleted from the Fock space, according to their energies (i.e., either the highest virtual or the lowest occupied MOs). The results for compound **3**, reported in Figure 5, make clear that such a truncation leads to an oscillatory behavior which is clearly undesirable.

4. The Cu(I)−Cu(II) Mixed-Valence System

The Cu(I)−Cu(II) system falls among the most important mixed-valence compounds in both biochemistry (proteins) and inorganic chemistry. Recently, Cu(I)−Cu(II) halides have been shown to form linear chains[12] with semiconductive behavior and characterized as belonging to the Robin and Day class II.[13] The conductive properties of this system prompted us to attempt the calculation of the electron transfer integral between the two Cu centers using the methodology based on the effective Hamiltonian. Our main goals are firstly to give an estimate of H_{ab} at the correlated level and secondly, to test the suitability of the ET-DMOs for compounds in which transition metals are involved.

To model the Cu(I)−Cu(II), system we have selected a cluster of formula $Cu_2Cl_6^{3-}$ which is the same unit used by Sherwood and Hoffmann[14] in their extended Huckel MO band calculations. Basically it consists of two $CuCl_2$ subunits bridged by two chloride ligands for which an idealized geometry formally corresponding to the crossing seam has been adopted.



The metal centers are equivalent with D_{2d} local symmetry, and the bridge plane is assumed to be perpendicular to the ending $CuCl_2$ units. All Cu−Cl distances are assumed to be the same (2.3 Å), and the Cu−Cu distance is fixed to 3.1 Å. The calculations have been performed under C_{2v} symmetry constraint, and the computational details are given in ref 15. Notice that the full symmetry D_{2h} may not be employed since after the localization step, the active orbitals a and b are not longer symmetric or antisymmetric with respect to the center of inversion.

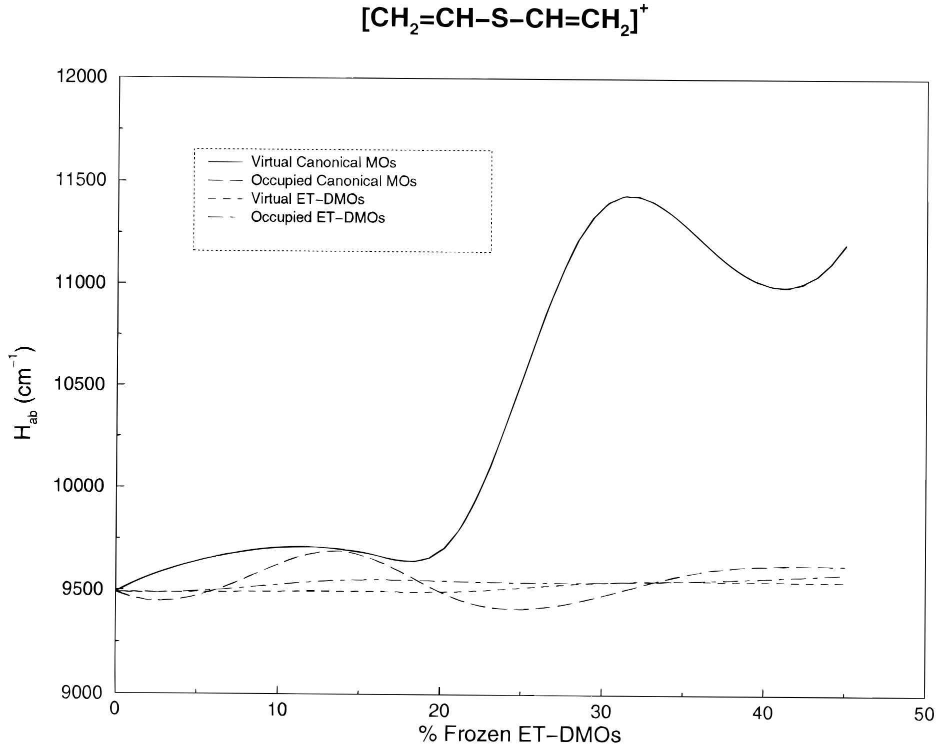


Figure 5. Comparison of the stability of H_{ab} for compound *3* against truncation of the canonical MOs or the ET-DMOs. Here the original MOs are those arising from a closed shell calculation (CSMOs).

TABLE 1: Zeroth-, First-, and Second-Order Perturbational Contributions (in cm^{-1}) to H_{ab} for the Cu(I)−Cu(II) System[a]

nature	determinants	contrib.
reference	$\|a\bar{a}b\|$; $\|ab\bar{b}\|$	2337.[b]
L → Cu	$\|..b\bar{i}...a\overline{ab}\|$	0[c]
L → Cu + L → L′	$\|..b\bar{i}j\bar{p}..a\overline{ab}\|$; $\|..b\bar{i}p\bar{j}..a\overline{ab}\|$; $\|..p\bar{i}b\bar{j}..a\overline{ab}\|$	−85.[d]
L → L′ + Cu → Cu	$\|..j\bar{p}..b\overline{ab}\|$; $\|..p\bar{j}..b\overline{ab}\|$	
L → L′	$\|..j\bar{p}..a\overline{ab}\|$; $\|..p\bar{j}..a\overline{ab}\|$	36.[d]
Cu → L + L → Cu	$\|..b\bar{j}..p\overline{ab}\|$	
Cu → L′	$\|...p\overline{ab}\|$	170.[d]
Cu → L′ + L → L′	$\|..p\bar{i}..q\overline{ab}\|$; $\|..i\bar{p}..q\overline{ab}\|$	−58.[e]

[a] The nature of the excitations is done in the first column. L stands for copper and ligand occupied MOs, L′ for virtual MOs, and Cu for active a and b orbitals. Indices *i*, *j* run over occupied (hole) MOs, and *p*,*q* over virtual (particle) MOs. [b] Zeroth-order. [c] First-order, vanishing because of the generalized Brillouin's theorem. [d] 2h-1p space. [e] 2p-1h space.

The first problem to solve in dealing with the calculation of the electronic coupling in this system is the size of the second-order differential space. Effectively, the number of the determinants in this space amounts to more than 500 000. Since our present computational capabilities prevent us from performing such a calculation, the truncation of such a space is in order. The largest number of determinants arises by far from the two particles-one hole (2p-1h) excitations which are represented at the end of the Supporting Information. The contribution of these determinants is expected to be small since they involve higher energy excitations, and therefore the CI could be in principle restricted to the two hole-one particle (2h-1p) subspace as done in ref 5. In order to check this hypothesis, a perturbational calculation of the transfer integral was performed using eq 6. The second-order estimate of H_{ab} is 2400 cm^{-1}. The contributions to this value arising from the different classes of determinants are summarized in Table 1. As can be seen, the contribution of the 2p-1h determinants is only −58 cm^{-1}. This analysis confirms our assumption, and, even more, it suggests a computational strategy according to which the full differential space would be divided into two subspaces denoted as 2h-1p and 2p-1h (of course, the 2h-1p subspace includes the determinants corresponding to the first-order correction as well as the zero-order model functions ϕ_a^0 and ϕ_b^0). Then, the 2h-1p subspace contribution would be variationally computed, whereas the corrections due to the 2p-1h determinants would be estimated from perturbation

$$H_{ab} = H_{ab}^{var}(2h\text{-}1p) + H_{ab}^{per}(2p\text{-}1h) \qquad (9)$$

This procedure would lead to the best estimate of the electron-transfer element provided the perturbation contribution would be small as in the present case.

For the system at hand, the diagonalization of the 2h-1p space (47 400 determinants) gives a value for H_{ab}^{var} of 2058 cm^{-1}. Therefore, according to eq 9, the best estimate for the electron transfer element is H_{ab} = 2000 cm^{-1}, i.e., 400 cm^{-1} less than the perturbational value. There is no experimental values for this system, but our estimate is of the same order than those reported for instance by Westmoreland et al.[18] for half-met-L derivatives of hemocyanin. These authors found from spectroscopic analysis and using the Hush formalism[19] values of H_{ab} ranging between 790 and 1200 cm^{-1} depending on the nature of the bridge.

Let us now analyze the performance of the ET-DMOs for this system. In principle, all the contributions to the R_{ij} elements could be taken into account; however, since the CI space is limited to the 2h-1p determinants, it seems more coherent not to include the 2p-1h diagrams in the calculation of the **R** matrix. The results are reported in Figure 6. The virtual space can be truncated by 70% (ρ = 0.05) with a relative error of only 1%. This truncation leads to a diagonalization of only 14 439 determinants. Truncation of the occupied ET-DMO space for the same threshold allows a reduction of the 2h-1p space by 61% with an error of 1.4%. Finally, as shown also in Figure 6, the possibility to truncate both virtual and occupied ET-DMOs has also been considered. Thus, freezing all ET-DMOs with a participation index lower than 0.02, disregarding if they belong to the virtual or occupied blocks,[20] allows for a reduction of the differential space by 76% with an error of 0.15%. For ρ = 0.05, the 2h-1p space reduces by 88% with an error of 2.2%. In these cases only the diagonalization of 11 546 and 5590 determinants, respectively, is necessary.

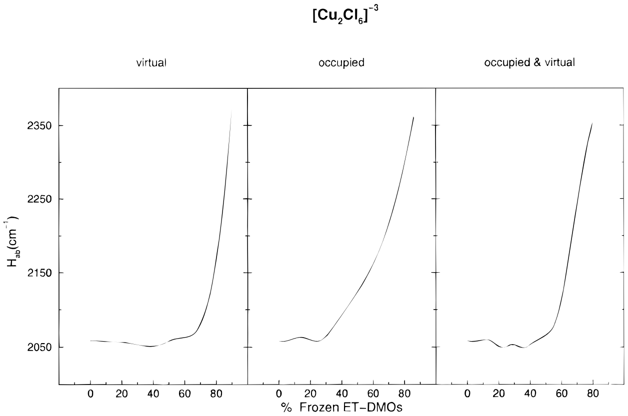


Figure 6. Effect of the truncation of the ET-DMO basis set on H_{ab} for the $Cu_2Cl_6^{3-}$ cluster: left; virtual block; middle; occupied block; right; both virtual and occupied blocks.

5. Conclusions

The accurate ab initio calculation of small quantities such as the electron transfer matrix element V_{ab} requires computational techniques able to introduce the effects of the electron correlation. With this aim, the use of second-order differential spaces under the QDPT formalism appears to be a suitable choice since the largest contributions are thus included. However, even using these second-order differential spaces, a variational calculation (DDCI) still involves a high computational effort, and some kind of truncation is necessary. In this paper we have reported a computational strategy to obtain electron-transfer dedicated molecular orbitals (ET-DMOs) which allow us to truncate the molecular orbital basis set with a noticeable reduction of the CI matrix. The stability of these ET-DMOs has been tested with some simple organic models for which a full comparison is possible. The results have shown that it is possible to reduce the CI space by 40−60% without loss of precision.

The electron-transfer integral for a Cu(I)−Cu(II) mixed-valence compound has also been considered. Because of the size of this system, a complete DDCI calculation has not been possible, and we have proposed a partition of the differential space and a perturbational-variational theoretical scheme which gives rise to an estimate for H_{ab} of 2000 cm^{-1}. The stability of the ET-DMOs for this system has also been found to be excellent allowing for a dramatic reduction of the CI space (76%) with an error of only 0.15%. We hope that the use of such ET-DMOs will permit systematic variational calculations of the electron-transfer matrix element in more involved systems.

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Supporting Information Available: Appendix of expressions describing the determination of the **R** matrix elements R_{ij} and R_{pq} (6 pages). Ordering information is given on any current masthead page.

References and Notes

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(20) Notice that because of the formal character of the discusion, both in this section and in the preceding one, truncation of the ET-DMOs has been discussed in terms of their participation number ρ. However, the ρ values are largely dependent on the system, and therefore, from a practical point of view, it is preferable to use ρ just as a guide for the truncation. Our results show that a truncation of the virtual ET-DMOs of about 40–60% is quite safe.