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Physical Factors Governing the Amplitude of the Electron Transfer Integral in Mixed-Valence Compounds

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This paper first reviews the various methods of calculation of the transfer integral in mixed valence compounds. The different physical effects affecting the electron transfer, namely overlap, through bond delocalization, relaxation and polarization of molecular orbitals, and correlation contributions are described and discussed. Illustrative model problems are proposed, and the ability of the various treatments to incorporate these physical effects is studied.

1. Introduction

Mixed-valence compounds are fascinating molecular architectures for both experimentalists and theoreticiens.[1,2] Their interest comes from the existence of an unpaired electron which can be located on two equivalent and remote sites A and B.

One may speak of a nearly degenerate problem, with two states of different symmetry, g and u, of close energies, if the electron is delocalized between these two sites and if the symmetry of the nuclear frame is maintained. One may also speak of versatile or highly polarizable systems since a small perturbation, such as an external electric field, may localize the unpaired electron. The reorganization of the nuclear conformation may also be a localizing perturbation, it may stabilize a localized form A+ ... B (i.e., trap the hole (or the electron) on one site). The electronic delocalization, which spreads the charge on the two centers, tends to maintain the symmetry, since its effect is maximum for symmetrical geometries, while the nuclear reorganization localizes the charge (see for instance, refs 3 and 4).

In principle the value of the transfer integral may be affected by the conformational relaxations of the partners, which break the symmetry. However, this effect is rather small (cf., for instance, ref 5) and it is usual[1,2,6] to concentrate on the symmetrical situations to study the electronic factors and the dependence on the intersystem distance.

The present paper is centered on the delocalization factor (i.e., the amplitude of the energy splitting between the two nearly degenerate states, g and u) in *symmetrical* situations. It tries to analyze the electronic factors governing the amplitude of this small energy difference and to discuss the relevance of the various ab initio methods of quantum chemistry to evaluate this interaction.

Section 2 presents the diverse levels of descriptions of the two relevant states, with increasing sophistication. Section 3 concentrates on the different physical effects, which are exemplified on model problems, and shows the required flexibility of the method to properly treat these physical effects.

2. Methods of Calculation of the Transfer Integral

2.1. The Two-State Model. The problem consists of the calculation of the energy difference between two eigenstates of different symmetry,[1,2] say ϕ_g and ϕ_u. At a zeroth-order level, two orbitals *g* and *u* play a dominant role. They define two equivalent orbitals *a* and *b*, which are localized essentially on two equivalent sites, A and B.

$$\text{delocalized:}\quad g = \frac{a+b}{\sqrt{2}},\quad u = \frac{a-b}{\sqrt{2}}$$

$$\text{localized:}\quad a = \frac{g+u}{\sqrt{2}},\quad b = \frac{g-u}{\sqrt{2}}$$

Depending on the nature of the systems, one may see the zeroth-order description of the problem as a one-electron in two-orbital problem,

$$\phi^0_{(1)g} = |\text{core } g|,\quad \phi^0_{(1)u} = |\text{core } u|$$

$$\phi^0_{(1)a} = |\text{core } a|,\quad \phi^0_{(1)b} = |\text{core } b|$$

or as a three-electron in two-orbital problem,

$$\phi^0_{(3)g} = |\text{core } u^2 g|,\quad \phi^0_{(3)u} = |\text{core } g^2 u|$$

$$\phi^0_{(3)a} = |\text{core } b^2 a|,\quad \phi^0_{(3)b} = |\text{core } a^2 b|$$

(In these determinants, the subscript between parentheses refers to the number of active electrons.) Hence, the zeroth-order active space may be reduced to two orbitals.

The zeroth-order energies of the two states are

$$E^0_g = \langle \phi^0_g | H | \phi^0_g \rangle$$

$$E^0_u = \langle \phi^0_u | H | \phi^0_u \rangle$$

and in symmetrical systems, $\phi_a{}^0$ and $\phi_b{}^0$ are degenerate,

$$E^0_g - E^0_u = 2\langle \phi^0_a | H | \phi^0_b \rangle = 2t^0_{ab}$$

The coupling integral t_{ab}, usually called H_{ab} in electron transfer

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theories,[2] is related to the kinetic constant of the electron transfer process that occurs between the centers A and B.

2.2. Single Determinantal Descriptions. For purely monoelectronic Hamiltonians, such as the extended Hückel Hamiltonian, $H = \sum_i h(i)$, the energy difference reduces to a difference between monoelectronic energies ϵ_g and ϵ_u:

$$E_g^0 - E_u^0 = (\epsilon_g - \epsilon_u)(2 - n_a) = 2(2 - n_a)\langle a|h|b\rangle$$

where n_a is the number of active electrons. Such a Hamiltonian, which frequently gives correct orders of magnitude, only incorporates the kinetic energy (scaled on the overlap) and exclusion effects, ruled through the orthogonalization.

When going to self-consistent single determinantal descriptions, one usually cannot rely on the monoelectronic energies of the neutral ground state, which would be of the type

$$\phi_{(2)}^0 = |\text{core } g^2|$$

since the energy of the virtual orbital u is calculated in the field of the $n_c + 2$ electrons, where n_c is the number of core electrons, while ϵ_g is calculated in the field of $n_c + 1$ electrons. This bias destroys the desired evenness between the two states, and can be avoided, for instance, using the orbital energies of the lowest triplet state:

$$\phi_{(2)}^3 = |\text{core } g\ u| = -|\text{core } a\ b|$$

Another possibility may consist of using the four-electron configuration

$$\phi_{(4)}^0 = |\text{core } g^2u^2| = |\text{core } a^2b^2|$$

and Koopmans' theorem. This procedure should be avoided when the four-active electron configuration introduces two excess electrons, in which case the orbitals in $\phi_{(4)}^0$ become exceedingly diffuse and meaningless, if nonminimal basis sets are used.

A better procedure is to perform variational restricted open-shell Hartree−Fock (ROHF) calculations for both ϕ_g^0 and ϕ_u^0, which imply the correct number of active electrons (i.e., the static electrostatic field). The resulting active MOs are less (respectively more) diffuse than those of the triplet state $\phi_{(2)}^3$ for the one (respectively three) electron problem, and the core orbitals are optimized in the specific field of the active electrons in the considered state.

Unrestricted Hartree−Fock (UHF) calculations are possible as well, introducing the spin polarization of the closed shells and lowering the energies by a small quantity, which in general is much weaker than the transfer integral. The disadvantage is the concomitant spin contamination.

The reader should be aware of another problem: the symmetry-breaking dilemma. In many cases, when the transfer integral is weak compared to the polarization energy,[3] one obtains a lower energy for a localized symmetry-broken solution:

$$\phi_{(1)a}^{\text{HF}} = |\text{core}'\ a'|$$

where $a' = a + \lambda b$, $\lambda \ll 1$. The polarization energy of the inactive electrons by the localized hole (or particle) may be greater than the polarization by the delocalized symmetry-adapted hole (or particle) g or u, and

$$E_{\phi_{(1)a}^{\text{HF}}} < E_{\phi_{(1)g,u}^{\text{HF}}}$$

Thus, one obtains two degenerate solutions, $\phi_{(1)a}^{\text{HF}}$ and

$$\phi_{(1)b}^{\text{HF}} = |\text{core}''\ b''|$$

where $b'' = b + \lambda a$, and where the core orbitals are polarized oppositely to those of $\phi_{(1)a}^{\text{HF}}$. The calculation of a first-order evaluation of the transfer integral is difficult

$$t_{ab} = \frac{\langle \phi_{(1)a}^{\text{HF}}|H|\phi_{(1)b}^{\text{HF}}\rangle - \langle \phi_{(1)a}^{\text{HF}}|\phi_{(1)b}^{\text{HF}}\rangle E_{\phi_{(1)a}^{\text{HF}}}}{1 - \langle \phi_{(1)a}^{\text{HF}}|\phi_{(1)b}^{\text{HF}}\rangle^2}$$

since it requires the calculation of the overlap and Hamiltonian interaction between two nonorthogonal determinants.[4] These matrix elements could be evaluated by using the corresponding orbital transformation proposed by King et al.[7] This transformation permits the orthogonalization of the two sets of eigenvectors and the evaluation of t_{ab}.[8]

If independent variational calculations for both states are performed, the core orbitals are different for the g and u states and the inclusion of the correlation must be performed on both states using two different MO sets. This means that one must calculate a large correlation energy, including all double excitations (at least), in a very large CI, with possible errors in the balance of the treatment of both states.

To avoid this problem, one may be tempted to use a common and balanced set of MOs by performing a state-average CASSCF calculation,[5,9,11] optimizing the sum of the energies of the two states g and u (i.e., imposing $E_g{}^0 + E_u{}^0$ to be minimum). The core orbitals are then optimized with the appropriate number of active electrons, but not for a specific hole. For one active electron, one uses a mean Fock operator,

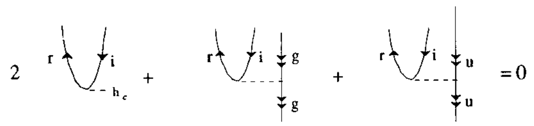
$$F = F_g + F_u$$

such as that for any pair of inactive occupied i and virtual r orbitals, the extradiagonal elements of the matrix **F** in the basis of this set of MOs are (cf. Chart 1):

CHART 1

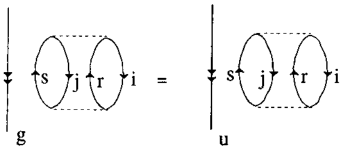
$$< i\ |F|\ r >=0$$

$$ie, \quad < i|\ 2h_c+J_g+J_u\ |\ r >=0$$



2.3. Correlated Descriptions. Starting from the corresponding determinants ϕ_g and ϕ_u one may calculate the second-order correction to the energy in a Møller−Plesset expansion. It is easy to see that the inactive double excitations ($ij \rightarrow rs$), where i, j are occupied molecular orbitals or holes and r, s are virtual orbitals or particles, give the same contributions in the two second order correction $E_g{}^{(2)}$ and $E_u{}^{(2)}$, (Chart 2):

CHART 2



Hence, one may conceive a difference dedicated CI which involves the two references (i.e., the CAS) and all semiactive simple and double excitations (i.e., excluding the purely inactive double excitations, which are the most numerous).[10] The size of that DDCI space scales such as $n_0\, n_v^2{+}n_0^2\, n_v$, where n_0 and n_v are the number of inactive occupied and virtual MOs, respectively. This has been proposed by Sanz and Malrieu[5] to treat electron transfer problems (see also ref 11). The DDCI strategy has been successfully used to study magnetic problems (i.e., the calculation of the weak energy differences between the lowest states of polyradicalar compounds) and for the calculation of the optical spectrum of closed-shell molecules.[12] It has been proposed recently to iterate the DDCI process, calculating mean quasinatural orbitals at each step, then performing a new DDCI calculation with these new orbitals.[13] The IDDCI results become independent of the starting MOs, the quality of which is questionable. This idea may be applied to mixed-valence problems as well. Another strategy consists of using dedicated MOs, which are designed for the calculation of the searched energy difference.[11]

As a further step one may consider a CAS-SDCI calculation for both states, incorporating now the inactive double excitations. This CI has to be made size consistent by an appropriate self-consistent size-consistent dressing (SC)^2 CAS-SDCI.[14] More sophisticated methods can be considered, such as coupled-cluster with singles and doubles (CCSD) for open-shell problems.[15] It is also possible to perform equation of motion (EOM) calculations[16] on the top of a CCSD of the closed-shell problem. The exact solution in the basis is of course the full CI (FCI).

3. Physical Factors

3.1. Overlap Effects. The integral t_{ab} between two localized orbitals a and b is frequently approximated[17] by

$$t_{ab} = kS_{ab}\frac{\epsilon_a + \epsilon_b}{2}$$

where S_{ab} is the overlap integral, $\langle a|b\rangle$, ϵ_a and ϵ_b being the localized orbital energies. This suggests an exponential decrease of the transfer integral with the distance[18] between the two active localized orbitals a and b,

$$t_{ab} \sim \lambda \exp^{-\beta R_{ab}}$$

provided that the orbitals have an appropriate exponential decrease. If Gaussian type orbitals are used, the decrease will be artificially more rapid ($\sim$exp($-\beta R_{ab}^2$). This exponential decrease appears on two model problems, Li_2^+ (1 active electron) (Figure 1) and Be_2^+ (three active electrons) (Figure 2), whatever the level of calculation. In both cases, extended Gaussian basis sets were used, and for quite large distances the Gaussian orbitals impose an exp($-\beta R_{ab}^2$) decrease.

The same logic explains orientational factors, for instance between two 2p atomic orbitals. One should notice here the possible role of the intramolecular overlap in the intermolecular transfer integral. Consider for example, the linear $(Li_2)_2^+$ and the $(Li_2)_2^-$ problems in minimal basis sets (Scheme 1).

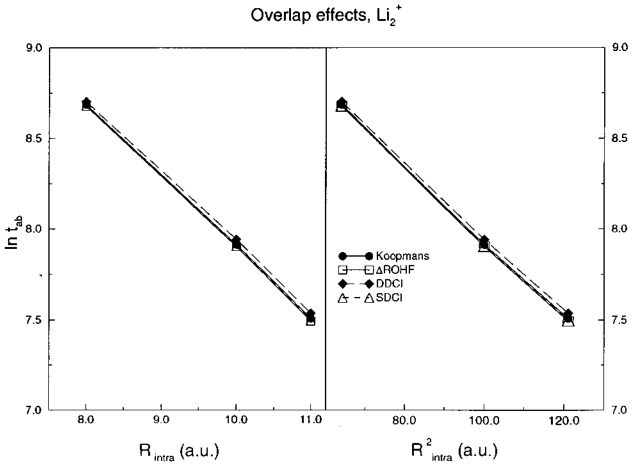


Figure 1. Overlap effects in a one-electron two-site model problem. Dependence of the transfer integral value on the distance between the lithium atoms, for the system Li_2^+. Left: ln t_{ab} vs R_{intra}. Right: ln t_{ab} vs R_{intra}^2. The behavior is independent of the sophistication level of the calculations. All of them were performed using triple-ζ quality basis plus polarization functions.

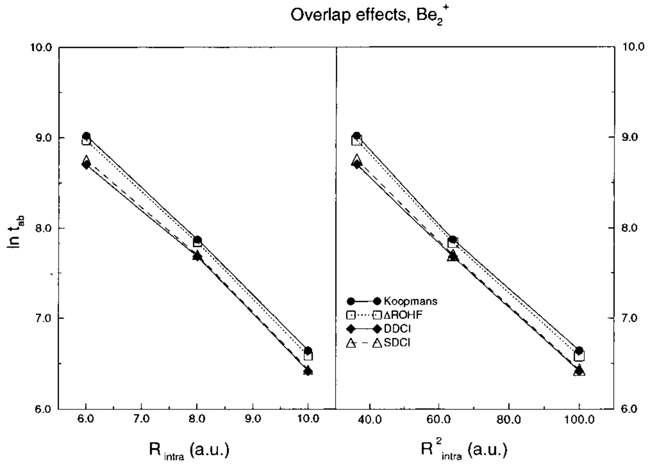
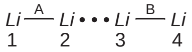


Figure 2. Overlap effects in a three-electron two-site model problem. Dependence of the transfer integral value on the distance between the beryllium atoms, for the system Be_2^+. Left: ln t_{ab} vs R_{intra}. Right: ln t_{ab} vs R_{intra}^2. The reduction of t_{ab} values observed at DDCI and SDCI levels with respect to ROHF results is due to the correlation of active electrons (see Section 3.5), effects that are not present in the case of the Li_2^+ system. All the calculations were performed using triple-ζ quality basis plus polarization functions.

SCHEME 1



The occupied orbital in Li_2 is

$$\sigma_a = \frac{2s_1 + 2s_2}{\sqrt{1 + S_{12}}}$$

for molecule A and

$$\sigma_b = \frac{2s_3 + 2s_4}{\sqrt{1 + S_{34}}}$$

for molecule B.

For an $(Li_2)_2^+$ problem the localized wave functions for both situations are

$$\phi_a^{0,+} = |\sigma_a\sigma_b\overline{\sigma_b}|; \quad \phi_b^{0,+} = |\sigma_a\overline{\sigma_a}\sigma_b|$$

and neglecting all interactions except those between s_2 and s_3, if $S = S_{12} = S_{34}$:

$$t_{ab}^{+} \sim \frac{t_{2s_2 2s_3}}{1 + S}$$

Considering now the $(Li_2)_2^-$ problem, one introduces the orbitals

$$\sigma_a^* = \frac{2s_1 - 2s_2}{\sqrt{1 - S_{12}}}; \quad \sigma_b^* = \frac{2s_3 - 2s_4}{\sqrt{1 - S_{34}}}$$

and the wave functions for the active electrons localize in A and B respectively, are:

$$\phi_a^{0,-} = |\sigma_a^2\, \sigma_b^2\, \sigma_a^*|; \quad \phi_b^{0,-} = |\sigma_a^2\, \sigma_b^2\, \sigma_b^*|$$

and the intermolecular transfer integral can be expressed as

$$t_{ab}^- \sim \frac{t_{2s_2 2s_3}}{1 - S}$$

Hence,

$$\frac{t_{ab}^-}{t_{ab}^+} \simeq \frac{1 + S}{1 - S}$$

(i.e., the transfer integral is larger for negative ions than for positive ones). For a fixed distance between atoms 2 and 3 in the above model, the absolute value of the transfer integral for the positive ion will increase when the intramolecular distance increases, while it will decrease for the negative ions. This rule is exemplified on the $(\mathrm{Li}_2)_2{}^{+/-}$ problem (Figure 3) and on the $(\mathrm{ethylene})_2{}^{+/-}$ problem (Figure 4). In both of them, R is the intramolecular distance, expressed in atomic units. An exponential behavior with this parameter is found and also the mentioned relationship between S and t_{ab}. The π nature of the intramolecular bond in the case of the $(\mathrm{ethylene})_2{}^{+/-}$ systems makes t_{ab} more sensitive to little variation of the intramolecular distance, than in the $(\mathrm{Li}_2)_2{}^{+/-}$ problem, for which the interatomic overlap is larger.

All these overlap effects are correctly included at the most elementary levels of calculations (EHT, Koopmans, ...).

3.2. Through Bond Delocalization. The coupling between two sites may proceed through the bonds connecting them, for instance organic ligands between two metallic centers. This is again a delocalization effect, which will be larger when the ligand is highly delocalized. The conjugated hydrocarbons deserve special attention, since molecular devices for molecular electronics have been proposed, in which two transition metal atoms of different degrees of oxidation are bridged by polyenic chains.[19]

It is known that the conjugated hydrocarbons, which do not involve odd-membered rings, are called alternant and present interesting features. One may divide the atoms into two sets (starred and unstarred), in such a way that each starred atom is surrounded by unstarred ones and vice versa. The so called pairing rule (Coulson, Longuet–Higgins perturbation theory)[20] establishes a one-to-one correspondence between each bonding MO φ_i and an antibonding MO φ_i* such that, in the Hückel Hamiltonian, the energies have opposite signs, $\epsilon_i + \epsilon_i{}^* = 0$, and that the coefficients of the starred atoms are identical in φ_i and φ_i*, while those of the unstarred atoms have opposite signs: $\mathbf{c}_{ir} = c_{i^*r}$, for r starred, and $\mathbf{c}_{ir} = -\, c_{i^*r}$, for r unstarred. If we now consider two sites bearing the orbitals a and b, connected respectively with atoms r and s of the ligand (Scheme 2) by equal matrix elements of the Fock operator $F_{\mathrm{ar}\,=\,F_{\mathrm{bs}}} = F$ the degenerate $g = (a + b)\sqrt{2}$ and $u = (a - b)\sqrt{2}$ MOs will be perturbed by their interaction with the delocalized MOs of the ligand φ_i and φ_i*, where

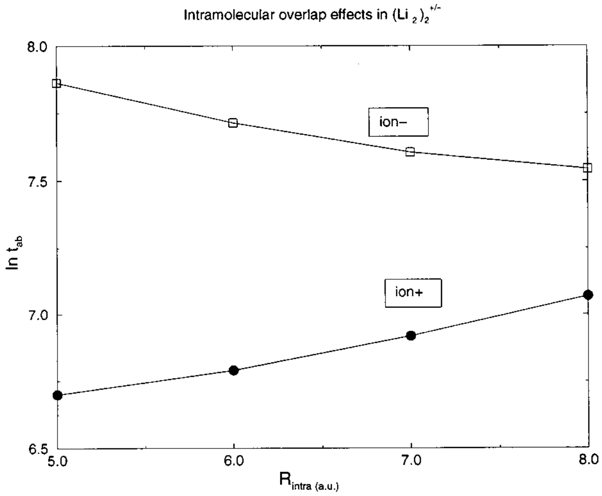


Figure 3. Intramolecular overlap effects over the transfer integral values in $(\mathrm{Li}_2)_2{}^{+/-}$ systems. Linear response of t_{ab} versus the intramolecular distance Li–Li. The t_{ab} values were obtained using Koopmans' theorem and minimal basis sets for lithium atoms.

$$\varphi_i = c_{ir}r + ... + c_{is}s$$

$$\varphi_i{}^* = c_{i^*r}r + ... + c_{i^*s}s$$

The perturbation will be

$$E_g^{(2)} = \sum_i \frac{\langle i|F|g\rangle^2}{\epsilon_i - \epsilon_g} - \sum_{i^*} \frac{\langle i^*|F|g\rangle^2}{\epsilon_g - \epsilon_{i^*}}$$

$$E_u^{(2)} = \sum_i \frac{\langle i|F|u\rangle^2}{\epsilon_i - \epsilon_u} - \sum_{i^*} \frac{\langle i^*|F|u\rangle^2}{\epsilon_u - \epsilon_{i^*}}$$

and it is easy to show that

$$\langle i|F|g\rangle \simeq \frac{F}{\sqrt{2}}(c_{ir} + c_{is}); \quad \langle i|F|u\rangle \simeq \frac{F}{\sqrt{2}}(c_{ir} - c_{is})$$

$$\langle i^*|F|g\rangle \simeq \frac{F}{\sqrt{2}}(c_{i^*r} + c_{i^*s}); \quad \langle i^*|F|u\rangle \simeq \frac{F}{\sqrt{2}}(c_{i^*r} - c_{i^*s})$$

and then

$$E_g^{(2)} = {}^1\!/_2 F^2 \left(\sum_i \frac{(c_{ir} + c_{is})^2}{\epsilon_i - \epsilon_g} - \sum_{i^*} \frac{(c_{i^*r} + c_{i^*s})^2}{\epsilon_g - \epsilon_{i^*}} \right)$$

$$E_u^{(2)} = {}^1\!/_2 F^2 \left(\sum_i \frac{(c_{ir} - c_{is})^2}{\epsilon_i - \epsilon_u} - \sum_{i^*} \frac{(c_{i^*r} - c_{i^*s})^2}{\epsilon_u - \epsilon_{i^*}} \right)$$

where ϵ_g, ϵ_u, ϵ_i, and ϵ_{i^*} are respectively the orbital energies of g, u, φ_i and φ_i*.

If $\epsilon_g = \epsilon_u = (\epsilon_i + \epsilon_{i^*})/2$ (i.e., if the substitute orbital energies ϵ_g and ϵ_u are in the middle of the band gap of the ligand) the two denominators are equal. If r and s are atoms of the same parity the numerators are equal and, $E_g{}^{(2)} = E_u{}^{(2)} = 0$, the two levels $(a + b)\sqrt{2}$ and $(a - b)\sqrt{2}$ remain degenerate, $t_{ab} \simeq 0$. On the contrary if the atoms r and s have opposite parities,

$$c_{ir} \pm c_{is} = c_{i^*r} \mp c_{i^*s}$$

the interactions with φ_i and φ_i* act in opposite directions on the $(a + b)/\sqrt{2}$ and $(a - b)/\sqrt{2}$ orbitals and increase $|t_{ab}|$. As

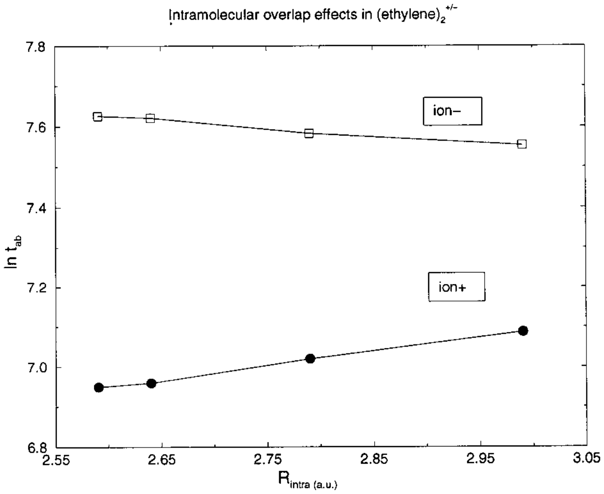


Figure 4. Intramolecular overlap effects over the transfer integral values in (ethylene)$_2^{+/-}$ systems. Linear response of t_{ab} versus the C−C distance in the ethylene molecule. The t_{ab} values were obtained using Koopmans' theorem and minimal basis sets for carbon and hydrogen atoms. The decay/increase of t_{ab} values are similar to that obtained in $(Li_2)_2^{+/-}$ systems, while the intramolecular distance variation here is one order lower than in the lithium systems. The π nature of the intramolecular bond in ethylene systems explains this behavior.

SCHEME 2

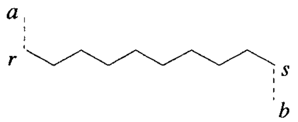


TABLE 1: Role of the Through Bond Delocalization[a]

molecule	Hückel	Koopmans	ΔROHF	DDCI-3
o-dimethylene-benzene + (1)	-0.295β	6682	8318	6688
m-dimethylene-benzene + (2)	0.	153	1469	1260
p-dimethylene-benzene + (3)	-0.311β	9821	13138	9586
1,5-dimethylene-naphthalene + (4)	0.	55	1875	1194
1,6-dimethylene-naphthalene + (5)	-0.188β	5574	9347	6810

[a] Values of the transfer integral for conjugated hydrocarbons. (Notation between parentheses corresponds with Scheme 3). The values of t_{ab} are expressed in cm^{-1}, except for these obtained through Hückel theory, which are in β units. DZV basis functions have been used for the benzene atoms and STO-3G for the naphthalene derivatives.

a consequence, t_{ab} will be small for meta substitutions in benzene or for mirror substitutions in naphthalene, as shown in Table 1.

The increase of t_{ab} value of system **3** with respect to **1** (Scheme 3) is due symmetry reasons. It is possible to see too that the polarization of inactive orbitals induces a systematic reduction of t_{ab} values (difference between ROHF and DDCI-3 results), effects that will be discussed below.

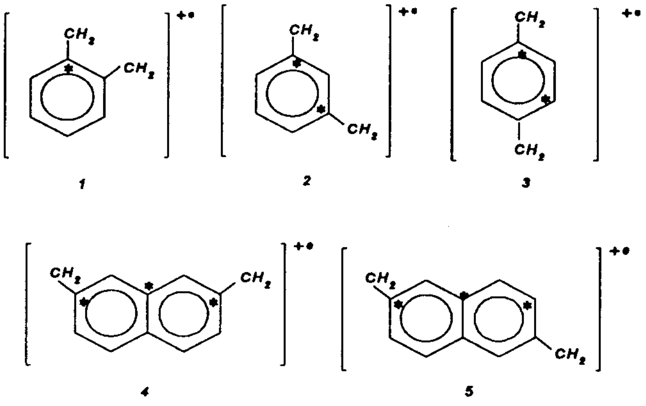
It is worth noticing here that the role of through bond delocalization has been established by Hoffmann et al.[21] 30 years ago. The rules proposed here may receive other rationalizations (see for example refs 1a, 1b, 22, 23).

3.3. Relaxation and Polarization of Active Orbitals. Starting from the g or u orbital of the neutral dimer, for instance in its triplet state $\varphi^3 = |gu|$, the orbitals of the positive ion, g or u, will be more concentrated, while they will become more diffuse in the negative ion. This phenomenon involves both relaxation and polarization of the orbitals.

Let us consider the Li_2 problem, where g and u are essentially built on the $2s_a$ and $2s_b$ orbitals of the neutral atoms. The relaxation, which is not directional, goes through a mixing with 3s type orbitals, which contracts the orbitals in the positive ion, dilates them in the negative ion. The polarization distorts the distribution around each atom and proceeds through excitations toward 2p$_z$ atomic orbitals. It is quite easy to demonstrate that this mixing of the 2s and 2p$_z$ atomic orbitals increases the density in the interatomic region for the positive ion, while it increases the density outside of the bond in the negative ion (Figure 5). These phenomena act on both the g and u states. In Table 2, the values for t_{ab} obtained at different levels are shown. The above mentioned effects can be isolated using basis sets of different quality. The polarization effects come from single excitations ($l \rightarrow l \pm 1$) and can be analyzed comparing the results obtained with the (33) and (33/3) basis sets. The relaxation effects are the result of single excitations ($n \rightarrow n + 1$), with l constant, and it is possible to see them analyzing the difference between the values found with (33/3) and (6111/11) basis sets. All results are obtained for an 8 a_0 interatomic distance. They confirm that (i) adding a polarization function increases the transfer integral for positive ions and diminishes it for negative ones, as expected from the distortion of the orbitals (Figure 5), and that (ii) going to multiple-ζ basis decreases the transfer integral for positive ions and increases it for negative ones, as expected from the contraction/dilatation of the active orbitals. However, the polarization appears to have a greater impact than the relaxation. It is worth noting the excellent accuracy of the DDCI calculations.

The contraction versus the dilatation of the orbitals will have a major effect on the $(Li_2)_2^{+/-}$ systems, since they will reduce the absolute value of the transfer integral in the positive ion of the dimer, increase it in the negative ion, working in the same direction as the previously discussed intramolecular overlap effect. The results are presented in Table 3. The polarization

SCHEME 3



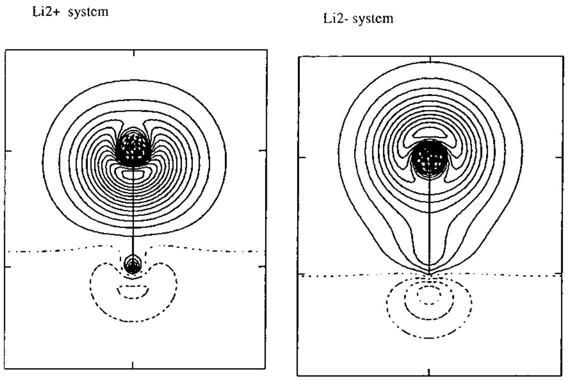


Figure 5. Electronic density maps of active orbitals for $Li_2^{+/-}$ systems. Effects of the polarization (see text). The maps were obtained using (6111/11) basis sets and FCI wave functions.

TABLE 2: Values of t_{ab} in the Negative and Positive Ions $Li_2^{+/-}$ [a]

	Li_2^+					Li_2^-				
basis	Koop	ROHF	DDCI	SD	FULL	Koop	ROHF	DDCI	SD	FULL
(33)	4850	4953	4955	4955	4955	4740	4741	4741	4741	4741
(33/3)	5059	6933	6927	6926	6927	4701	4703	2894	2896	2859
(6111/11)	4510	5928	5884	5866	5901	3987	3623	3433	3522	3410

[a] Relaxation and polarization effects on the value of the electron transfer integral (cm^{-1}).

TABLE 3: Effects of the Relaxation and Polarization of Active Orbitals on the Transfer Integral Value (in cm^{-1}) on $(Li_2)_2^{+/-}$ Systems

	basis	Koop	ROHF	DDCI
$(Li_2)_2^+$	(33)	809	784	734
	(33/3)	575	554	717
	(6111/11)	739	768	807
$(Li_2)_2^-$	(33)	2853	2612	2377
	(33/3)	1053	4308	3217
	(6111/11)	2875	3711	2780

2s → 2p ((33) vs (33/3) results) produces an increase of the intramolecular electron density in the case of a positive system, and intermolecular for the negative ion. This means in terms of the expression of section 3.1, bigger t_{ab}^- values and smaller t_{ab}^+ respect to the (33) results.

The relation between the (33/3) and (6111/11) results presents the same behavior than in the $Li_2^{+/-}$ problem. The relaxation 2s → 3s produces a contraction of the orbitals in the positive system. This contraction should in principle lead to a lower intermolecular overlap and a decrease of t_{ab}^+, but the corresponding reduction of the intramolecular overlap prevails, increasing t_{ab}^+. For negative system, the opposite effect is working.

3.4. Static and Dynamic Polarization of the Inactive Orbitals. Starting from the HF MOs of the neutral systems, the occupied *i* and virtual *r* inactive orbitals satisfy Brillouin's theorem,

$$\langle i|F^0|r\rangle = 0$$

where F^0 is the Fock operator for the neutral ground state ϕ_0. In the positive (or negative) ion, the static field created by the hole (or the additional electron) will lead to a mixing of the occupied and virtual inactive MOs.

For instance for

$$\hat{a}_g\phi_0 = \phi^0_{(1)g}$$

$$\langle i|F_g^{\ +}|r\rangle = \langle i|-J_g|r\rangle$$

where J_g is the Coulomb operator associated with the orbital *g*. The second order contribution to the static polarization energy for the g state is

$$E^{(2)s}_{ir,g} = \frac{(\langle i|J_g|r\rangle)^2}{\epsilon_i - \epsilon_r}$$

In the integral

$$\langle i|J_g|r\rangle = {}^1/_2(\langle i|J_a|r\rangle + \langle i|J_b|r\rangle) + (ir,ab)$$

the last term may be neglected since the *ab* distribution is small, *a* and *b* being far apart.

The *ir* distribution is at least dipolar, and is large only if *i* and *r* are located in the same region, for instance in the same bond of a ligand. One may consider two extreme situations:

SCHEME 4

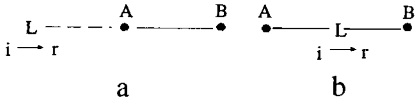


CHART 3

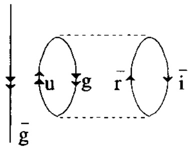
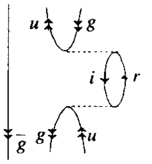


CHART 4



(i) The ligand is on the A···B axis, outside of the AB segment (Scheme 4a), then the two contributions $\langle i|J_a|r\rangle$ and $\langle i|J_b|r\rangle$ add and one has a significant static polarization energy. (ii) The ligand is on the A···B axis at equal distance of A and B (Scheme 4b), then the two contributions cancel in $\langle i|J_g|r\rangle$ and there is no static polarization. The same is true for the u state $\phi^0_{(1)u}$ since

$$\langle i|J_u|r\rangle = {}^1/_2\langle i|J_a + J_b|r\rangle - (ir,ab)$$

Hence the static polarization does not contribute much to the energy difference between the g and u states.

An important effect is the dynamical polarization which proceeds through a simultaneous change of the active orbital and the *i* → *r* inactive excitation (Chart 3).

$$E^{(2)d}_{ir,g} = \frac{\langle i\bar{\imath}g|H|i\bar{r}u\rangle\langle i\bar{r}u|H|i\bar{\imath}g\rangle}{\epsilon_i - \epsilon_r + \epsilon_g - \epsilon_u}$$

where it is possible to demonstrate that

$$\langle i\bar{r}u|H|i\bar{\imath}g\rangle = (gu,ir) = {}^1/_2((aa,ir) - (bb,ir)) = {}^1/_2\langle i|J_a - J_b|r\rangle$$

and then the second-order contribution to the dynamic polarization energy is

$$E^{(2)\mathrm{d}}_{ir,g} = {}^1/_4\,\frac{(\langle i|J_a - J_b|r\rangle)^2}{\epsilon_i - \epsilon_r + \epsilon_g - \epsilon_u}$$

This dynamic polarization energy expresses the dynamic response of the electrons of the ligand to the fluctuation of the hole position. It will be large when the ligand is between the two active sites A and B.

Such a phenomenon also exists in the u state (Chart 4),

$$E^{(2)\mathrm{d}}_{ir,u} = \frac{\langle i\bar{i}u|H|i\bar{r}g\rangle\langle i\bar{r}g|H|i\bar{i}u\rangle}{\epsilon_i - \epsilon_r + \epsilon_u - \epsilon_g} = {}^1/_4\,\frac{(\langle i|J_a - J_b|r\rangle)^2}{\epsilon_i - \epsilon_r + \epsilon_u - \epsilon_g}$$

which is slightly different from $E^{(2)\mathrm{d}}_{ir,g}$ since the denominators are different. Remember that

$$\epsilon_g - \epsilon_u = 2F_{ab}$$

hence,

$$E^{(2)\mathrm{d}}_{ir,u} - E^{(2)\mathrm{d}}_{ir,g} = F_{ab}\frac{(\langle i|J_a - J_b|r\rangle)^2}{(\epsilon_i - \epsilon_r)^2 + 4F_{ab}^2}$$

The dynamical polarization of a bridging ligand for which $\langle i|J_a|r\rangle = -\langle i|J_b|r\rangle$ will result in a decrease of the effective interaction (in absolute value).

$$F^{\mathrm{eff}}_{ab} = F_{ab}\left(1 - {}^1/_2\,\frac{\langle i|J_a - J_b|r\rangle^2}{(\epsilon_i - \epsilon_r)^2}\right)$$

In Scheme 5, two model systems $[\mathrm{Li_2(H_2)_2}]^{+/-}$ are represented. In A, the polarization induced over the H_2 orbitals when the hole (or particle) is in atom *a* is the same as when it is in atom *b*. In B, the polarization of inactive orbitals has opposite signs depending on where the hole (or particle) is. The polarization of inactive orbitals produces no change in t_{ab} value in model A, while in model B a reduction of t_{ab} value is expected. This effect involves only one occupied and one virtual inactive orbitals, and could be taken into account with a DDCI strategy over a space with two degrees of freedom restricted to a one hole-one particle (DDCI-2, 1h−1p), (see Table 4). Increasing the distance between the molecules of H_2 and the lithium atoms reduces the polarization of the orbitals of these molecules, and then the difference between the ROHF and DDCI-2 values is smaller than at a shorter distance.

It is worth noticing here that polarization is the origin of the Hartree−Fock symmetry breaking[3] mentioned in section 2. Actually, if the charge is localized in site A, the polarization energy is

$$E^{(2)\mathrm{s}}_{ir,a} = \frac{(\langle i|J_a|r\rangle)^2}{\epsilon_i - \epsilon_r}$$

whatever the position of the MO *i* with respect to A and B.

If it is close to A, the polarization is large, but there is no counterpart of the polarization of the symmetrical MO *i′* which lies close to B, $E^{(2)\mathrm{s}}_{i'r',a} = 0$. Hence, the static polarization of the external ligands is twice as larger when the charge is localized on one site than in the symmetry-adapted description,

$$E^{(2)\mathrm{s}}_{ir,a} + E^{(2)\mathrm{s}}_{i'r',a} \simeq 2(E^{(2)\mathrm{s}}_{ir,g} + E^{(2)\mathrm{s}}_{i'r',g})$$

For the internal ligands, which are at equal distance of A and B, the static polarization by the localized charge will be large, while the polarization by the symmetrical charge is zero. One has, therefore, the following inequality between the static polarization energies in the symmetry-broken and symmetry-adapted descriptions,

$$|E^{(2)\mathrm{s}}_{\mathrm{pol},a}| \geq 2|E^{(2)\mathrm{s}}_{\mathrm{pol},g}|$$

The static polarization, being brought by single excitations, can be obtained through a variational single determinant description.

SCHEME 5

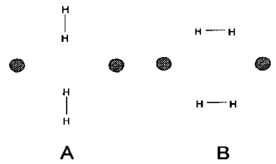
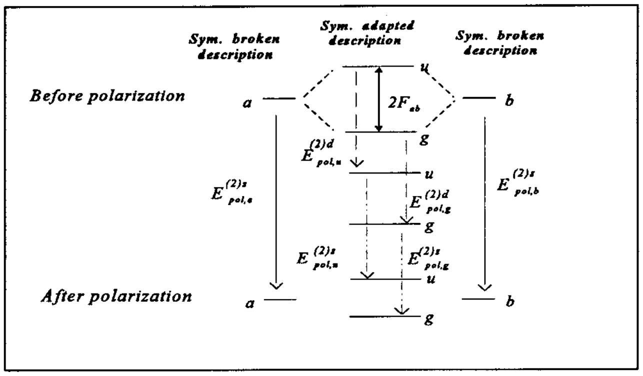


TABLE 4: Effect of the Polarization of the Inactive Orbitals over the Value of t_{ab} ($\mathrm{cm^{-1}}$)[a]

		ion⁺		ion⁻	
Li···H₂ (Å)		model A	model B	model A	model B
4.23	ΔROHF	1399	1126	1166	728
	1h−1p	1398	1104	1167	715
4.01	ΔROHF	1163	710	911	364
	1h−1p	1164	676	919	356

[a] Models A and B refer to Scheme 5. The distance Li···H₂ corresponds to the separation between the H−H bound middle point and Li atom. See text for details.

SCHEME 6



One must notice that the symmetry-broken description looses the benefit of the resonance between the left and right degenerate solution. Hence the condition for the occurrence of a symmetry breaking of the HF description is

$$|E^{(2)\mathrm{s}}_{\mathrm{pol},a}| \geq |E^{(2)\mathrm{s}}_{\mathrm{pol},g}| + |F_{ab}|$$

$$\text{i.e.,}\quad |E^{(2)\mathrm{s}}_{\mathrm{pol},a}| \geq 2|F_{ab}|$$

However, it should be pointed out that adding the dynamical polarization effect, (which is a correlation effect), the lacking part of the polarization effect is obtained, since neglecting $|F_{ab}|$ in front of $|\epsilon_i - \epsilon_r|$, one can see that the static polarization energy in the localized description is the sum of the (static + dynamic) polarization energies in the symmetry-adapted description.

$$E^{(2)\mathrm{s}}_{\mathrm{pol},a} \simeq E^{(2)\mathrm{s}}_{\mathrm{pol},g} + E^{(2)\mathrm{d}}_{\mathrm{pol},g}$$

The whole discussion can be pictured in the Scheme 6.

As already mentioned in section 2, it is simpler to stay in the symmetry-adapted description since the calculation of the interaction between the two localized HF determinants is quite difficult (and may be shown to be size inconsistent).

3.5. Correlation of Active Orbitals. Correlation of the electrons occupying the active orbitals only takes place for the three electrons in two MO problems (for instance, $\mathrm{Li_2}^-$ or $\mathrm{Be_2}^+$). Since this problem can be seen as the resonance between $|a\bar{a}b|$ and $|ab\bar{b}|$, it is clear that the dynamical radial and angular correlation will act on the electronic pair occupying instantaneously the same atom. If a is of 2s character, the radial

TABLE 5: Be_2^+ Problem. Correlation of Active Electrons. Effect of the Interatomic Distance[a]

d(au)	Koop	HF	DDCI	SD	(SC)^2	FULL
8	2622	2535	2165	2206	2136	2079
10	768	722	612	622	610	603
12	208	186	155	158	155	152

[a] Values in cm^{-1}.

CHART 5

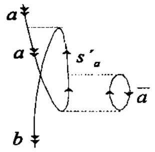
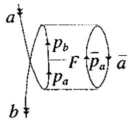


CHART 6



correlation is brought by excitations of the type $(a\bar{a} \rightarrow 3s_a 3\bar{s}_a)$, the angular correlation being obtained through excitations of the type $(a\bar{a} \rightarrow 2p_a 2\bar{p}_a)$ or to higher-*l* orbitals. Moreover, it is well known that the dynamical correlation in the atom reduces spatial extension of the electronic distribution, and therefore it is expected that this type of correlation reduces the absolute value of the transfer integral. This is illustrated on the Be_2^+ system, comparing the column relative to HF (uncorrelated) with the column concerning the DDCI results or higher levels in Table 5.

From a perturbative point of view the effect on the transfer integral is of third order, and may be visualized as a contribution to the extradiagonal matrix element of an effective Hamiltonian spanned by $|a\bar{a}b|$ and $|ab\bar{b}|$ respectively, $|a\bar{a}b\bar{b}|$ being the vacuum reference (Chart 5). Another contribution of the correlation involves a dispersive intermolecular interaction and an intramolecular double excitation, with a hopping integral between the virtual orbitals (Chart 6).

3.6. Semiactive Excitations. The correlation between the active electron(s) on an atom and the other valence electrons or the core electrons of the same atom essentially results in a contraction of the active orbital and therefore in a reduction of the absolute value of the transfer integral.

The correlation between the active electrons and the electrons of the ligands will be essentially of dispersive character (i.e., it goes through an interaction between the transition dipole of the active electrons), for instance, $(a \rightarrow p_a)$ and a transition dipole $(l \rightarrow l^*)$ of the ligand electrons.

The corresponding quantity will, in general, be positive

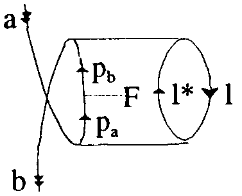
$$F_{p_a p_b} \frac{(bp_b, ll^*)(ll^*, ap_a)}{\Delta E^2}$$

since $Fp_a p_b$ will be positive. Hence this correlation effect will diminish the effective transfer integral (in absolute value) (Chart 7).

4. Conclusion

The purpose of this paper is essentially pedagogical. It tries to show that quantum chemistry is not simply a tool to obtain numerical values, comparing (hopefully well) with experiment, but that it provides a way to analyze the leading physical properties which govern the amplitude of an observable, here the electron transfer integral in mixed valence architectures. It is possible to judge the ability of a given method to take into account these physical effects. While mean field calculations are able to treat static effects (overlap, polarization, relaxation, through bond delocalization effects, etc.), the inclusion of dynamical responses requires the introduction of the fluctuations brought by the electronic correlation. However, the examples presented here confirm that reliable results may be obtained by considering only the semiactive double excitations, and neglecting the (most numerous) inactive double excitations (DDCI method).

CHART 7



An open question concerns the ability of DFT methods to reproduce the correlation effects. One may expect that such methods are able to reproduce the difference between t_{ab}^+ (one electron on two sites) and t_{ab}^- (three electrons on two sites). It is not clear whether they will reproduce the dynamical polarization effects, which involves the fluctuation of the electric field on the ligands. This analysis, analogous to the one recently performed for the magnetic coupling constants in diradicals,[24] should be the subject of further work.

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