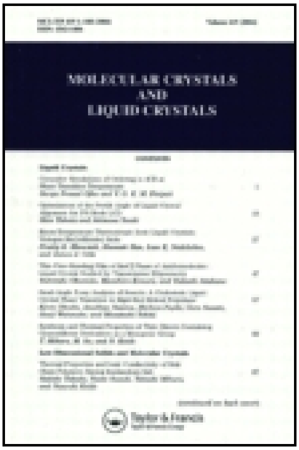

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TWO-ELECTRON TRANSFER THROUGH A LINEAR CHAIN

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Abstract Some aspects of the dynamics of two-electron transfer between metallic centers separated by a bridge of identical sites are briefly discussed by help of an effective Hamiltonian formalism.

Electron transfer processes have been widely studied for their exceptional interest in Biology as well as in Solid State and Solution Chemistry[1]. In the present theoretical contribution, however, we will focus on a subject which has received less attention in the scientific literature, the two-electron transfer problem. In order to fix ideas, let us consider a couple of redox pairs which in a certain chemical environment can exist in oxidation states differing by two electrons, say A(n)/A(n+2) and B(m)/B(m+2) and a more or less conducting chain of identical sites C, to which they can be bonded. In suitable conditions it should be possible to observe the following oxidation/reduction process via the chain bridge:

$$A(n)\ldots C\text{-}C\text{-}C\text{-}C\ldots B(m+2) \Rightarrow A(n+2)\ldots C\text{-}C\text{-}C\text{-}C\ldots B(m) \qquad (1)$$

The species A and B may be either a cation as in the case of metallic aquaions or an anion, if the metal ion is coordinated to negatively charged ligands.

While we do not know any experimental realization of such idea, we believe that it may reveal fruitful, mainly because it offers the possibility of studying in a controlled manner the role of electron-electron interactions in electron transfer processes. In fact the electron transfer has been only treated as an one-electron problem, with very few exceptions (to our knowledge: the many-electron computations by Newton[2] on transition metal redox pairs and some speculations of May on the role of electron correlation in the dynamics of electron transfer through finite chains[3]). We also notice that something similar in spirit to the process (1) could be realized by studying the time-resolved behaviour of suitable mixed-valence compounds after pulse excitation of the metal-metal charge transfer band[4].

Here we discuss some general features of two-electron transfer making use of the most naive picture. The process (1) is analyzed by help of a Hubbard Hamiltonian with one orbital per site for both metallic centers (A and B) and chain sites (C). For the latters we consider LUMO's. The Hubbard Hamiltonian can be written as:

$$H=\sum_{\sigma=\uparrow,\downarrow}[\epsilon_A a^{+}_{\sigma}a_{\sigma}+\epsilon_C\sum_j c^{+}_{j\sigma}c_{j\sigma}+\epsilon_B b^{+}_{\sigma}b^{+}_{\sigma}+t_A(a^{+}_{\sigma}c_{1\sigma}+h.c.)+t_C\sum_j(c^{+}_{j\sigma}c_{j+1\sigma}+h.c.)+$$

$$t_B(c^{+}_{N\sigma}b_{\sigma}+h.c.)]+U_A a^{+}_{\uparrow}a_{\uparrow}a^{+}_{\downarrow}a_{\downarrow}+U_C\sum_j c^{+}_{j\uparrow}c_{j\uparrow}c^{+}_{j\downarrow}c_{j\downarrow}+U_B b^{+}_{\uparrow}b_{\uparrow}b^{+}_{\downarrow}b_{\downarrow} \qquad (2)$$

where a ,b and c are electron annihilator operators for the orbitals on A, B and on the j-th site C, respectively (the orbitals are supposed to be orthogonal). The above Hamiltonian is quite general; for elucidating the main features of the process, we analyze in some detail the case in which the two ions form a redox pair (i.e. A=B) and assume that the only important electron-electron interaction involves the metallic orbitals (which means $U_A=U_B=U$, $\epsilon_A=\epsilon_B=\epsilon$ and $U_C=0$). For mimicking the instability of the intermediate oxidation state A(n+1) with respect to the disproportionation reaction:

$$2\ A(n+1) \Rightarrow A(n) + A(n+2) \qquad (3)$$

we assume that U is negative[5] in such a way that the above reaction gives rise to an energy gain $(2\ \epsilon_A+U)-2\ \epsilon_A = U$.

The Hamiltonian (1) can be numerically diagonalized to obtain the time evolution of the two-electron transfer process. In order to have a physical idea of what is happening it is however useful to translate first the Hamiltonian into a level and coupling scheme. Since we are interested in studying the time evolution of the initial singlet state containing two electrons in the orbital on A, we restrict to the singlet manifold. Furthermore, for the case $U_C=0$, we can easily diagonalize the chain Hamiltonian by introducing chain molecular orbitals:

$$c_{k\sigma} = \frac{2}{\sqrt{N+1}} \sum_j c_{j\sigma} \sin\frac{k\pi}{(N+1)} \quad ; \quad \epsilon_k = 2t_C \cos\frac{k\pi}{(N+1)} \tag{4}$$

In figure 1 it is shown the level and coupling scheme relevant for our case, with the notation exemplified below:

$$|1\rangle = a_\uparrow^+ a_\downarrow^+ |vac\rangle \; ; \; |2\rangle = b_\uparrow^+ b_\downarrow^+ |vac\rangle \; ; \; |3\rangle = \frac{1}{\sqrt{2}}(a_\uparrow^+ b_\downarrow^+ - a_\downarrow^+ b_\uparrow^+ |vac\rangle$$

$$|A,k\rangle = \frac{1}{\sqrt{2}}(a_{A\uparrow}^+ c_{k\downarrow}^+ - a_{A\downarrow}^+ c_{k\uparrow}^+)|vac\rangle \; ; \; |k,k'\rangle = \frac{1}{\sqrt{2}}(c_{k\uparrow}^+ c_{k'\downarrow}^+ - c_{k\downarrow}^+ c_{k'\uparrow}^+)|vac\rangle \quad etc.$$

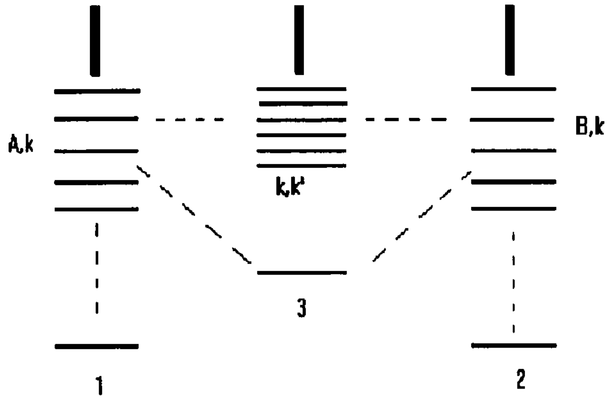

FIGURE 1 The level and coupling scheme for two-electron transfer between identical atoms.

The scheme in figure 1 contains three discrete levels corresponding to electrons on the metallic centers (notice that they are disposed here in a Λ-configuration, since U < 0) and three manifolds of states with one or two electrons on the chain. In actual cases the chain energies ϵ_k are well above atomic energies, so that one can project out the above manifolds corresponding to virtual charge-transfer excitations atom ⇒ chain. This is not an easy task, in general, since the manifolds are coupled. However, retaining only the lowest order contributions one has the following straightforward result for the matrix elements of the three by three effective Hamiltonian:

$$H_{13}^{eff} = \sum_k \frac{|<1|H|k>|^2}{(2\epsilon+U)-(\epsilon+\epsilon_k)} = \frac{2t_A^2\sqrt{2}}{N+1}\sum_k \frac{\sin(\frac{k\pi}{N+1})\sin(\frac{kN\pi}{N+1})}{\epsilon+U-\epsilon_k} \tag{5}$$

$$H_{12}^{eff} = \sum_{k,k'} \frac{<1|H|A,k><A,k|H|k,k'><k,k'|H|B,k><B,k|H|2>}{(\epsilon+U-\epsilon_k)^2(2\epsilon+U-\epsilon_k-\epsilon_{k'})} =$$

$$(\frac{4}{N+1})^2 t_A^2 \sum_{k,k'} \frac{\sin(\frac{k\pi}{N+1})\ \sin(\frac{k'\pi}{N+1})\ \sin(\frac{k'\pi}{N+1})\ \sin(\frac{k'N\pi}{N+1})}{(\epsilon+U-\epsilon_k)^2(2\epsilon+U-\epsilon_k-\epsilon_{k'})} \tag{6}$$

It is clear from figure 1 and from the above effective Hamiltonian that there are two interfering pathways for the pair transfer. In the first one only one electron at a time is virtually excited to chain orbitals, while in the second double excitations are involved. Which of the two routes is predominant depends on the parameters describing the system under study.

In the perturbative limit $(H^{eff}_{13})^2/\,|U|\,<<1$ the above effective three-level system can be further reduced to a two-level system in which the two degenerate states $|1>$ and $|2>$ (representing the pair on A and on B, respectively) are coupled by the effective matrix element:

$$V_{12} = H_{12}^{eff} + \frac{(H_{13}^{eff})^2}{U} \tag{7}$$

In such case, as is well known, quantum mechanics predicts that the pair goes back and forth between the two atoms with a period $T=\pi/V_{12}$ and $\tau=T/2$ can be used as an estimate of the pair transfer rate.

There are many interesting aspects of the above treatment that merit further discussion. For the lack of space we focus here on the dependence of matrix elements H_{12}^{eff} and H_{13}^{eff} on the number of sites in the chain, N. As far as H_{13}^{eff} is concerned we observe that, following Evenson and Karplus[6], the sum in eq. (5) can be performed to give:

$$H_{13}^{eff}=2(-1)^N\frac{t_A^2}{t_C}\,\frac{\sqrt{(\alpha^2-1)}}{[\alpha+\sqrt{(\alpha^2-1)}]^{N+1}-[\alpha-\sqrt{(\alpha^2-1)}]^{N+1}}\quad ;\quad \alpha=\frac{\epsilon_C-\epsilon}{2T_C} \qquad (8)$$

As discussed in ref 6, the adimensional parameter α determines if H_{13}^{eff} decays ($\alpha > 1$) or oscillates ($\alpha < 1$) as a function of N. We were not able to find a similar compact expression for H_{12}^{eff}, eq. (6). Some preliminary numerical calculations show that the two terms in V_{12}, eq. (7), may depend on N in a slightly different manner, with the interesting consequence that the relative weights of the two competing channel discussed before, i.e single versus double virtual charge transfer to the chain (the latter is indicated as path 2 in Table I), are functions of the number of sites. This behavior is illustrated in Table I for the set of parameters reported in the caption. For making easier the reading of transfer times we notice that the one-electron hopping between adjacent sites C occurs in a time $\pi/2$, in the same time units.

Table I Pair transfer times τ and percent of transfer following path 2 (see text) as a function of the number of sites N. The values of parameters are: $t_C=1.$, $t_A=t_B=0.5$, $U=-1.$, $\epsilon=-4.$, $\epsilon_C=0.$

N	% of path 2	τ
2	29	5134
3	38	$1.02\ 10^5$
4	47	$2.03\ 10^6$
5	55	$3.98\ 10^7$
6	62	$7.72\ 10^8$
7	68	$1.48\ 10^9$
10	82	$9.85\ 10^{13}$

In the example illustrated in Table 1, the importance of the path involving double virtual charge transfer to the chain increases with the chain dimensions. An examination of the behavior of the separate contributions coming from the two paths (which are not reported in Table I) shows that both decrease exponentially with N, but with a different rate and this originates the increasing yield of the path (2). It is also worthwhile to notice that such yield is independent on the values of the metal-chain hopping parameter t_A, as is clear from eqs. (5), (6) and (7).

No definite conclusions can be obviously derived from this very preliminary report. Our hope is that this paper may stimulate some experimental (as well as theoretical) work in this field.

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