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An orbital approach of electron transfer in multisite systems. Implications for carbon-rich spacers

Jean-Pierre Launay [*]

CEMES-CNRS, 29 rue Jeanne Marvig, BP 94347, F-31055 Toulouse cedex 4, France
Université de Toulouse, UPS, 118 route de Narbonne, F-31062 Toulouse cedex 9, France

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ABSTRACT

A simple orbital approach is presented to treat electron transfer in mixed valence compounds with either organometallic ($M(dppe)_2Cl$, $M(dppe)Cp^*$) or organic sites (triarylamine) and various bridges or spacers in particular carbon-rich ones. The orbital approach is based on the inspection of the HOMO of fragments constituting the complete system. The link is also made with solid-state concepts such as Holstein and Holstein-Peierls polarons. The HOMOs of different fragments are examined, in particular their decay along a conjugated chain starting from a donor group grafted at one extremity. Overlap considerations allow the qualitative prediction of the existence (or not) of an electronic interaction along a bridge. This approach is applied to a large variety of bridging systems with either an even or odd number of atoms: conjugated bridges, cross-conjugated systems, platinum bridges, aromatic bridges such as azulene or pyridine.

The orbital approach allows also a discussion of the effect of oxidation on geometry changes (polaron formation), showing that the larger the fragment, the smaller the polaron energy. This is qualitatively applied to a series of mixed valence systems bridged by benzene, naphthalene or anthracene in the frame of a three-center model.

(**) in honor of Claude Lapinte, recognizing and appreciating a major actor of the chemistry developed in Rennes

1. Introduction

Intramolecular Electron transfer in multisite systems, in particular mixed-valence ones is still an area of considerable interest [1]. There is indeed a huge variety of molecules containing several redox sites, either inorganic or organic, for which experimentalists can "play" with the different oxidation states. In the recent years have appeared many intriguing systems in which redox sites are linked by carbon-rich spacers such as conjugated triple bonds or allenylidene moieties. Many groups have been involved worldwide in this last area [2] and major contributions are due to the Rennes chemists. The study of such systems is now performed by an association of several structural (X-ray) and spectroscopic (UV–Vis–NIR, Mossbauer, IR) or magnetic techniques, in close interaction with state-of-the-art computational methods. This gives now a nice and complete description of the subtle phenomena occurring during intramolecular electron transfer, in particular the interplay of electronic and structural changes.

The spirit of the present paper is however more pedagogical. The aim is to help to the emergence of simple rules allowing in a qualitative way the prediction of electron transfer abilities of complex structures. These rules must be compatible with the "modular chemistry" approach [3] which is more and more used by synthetic chemists. In other words, we try to identify parameters specific of a given subunit and of the interaction between subunits. For this, we use an orbital approach, and more specifically the properties of the HOMO of fragments, because most investigated systems are obtained by partial oxidation of parent molecules with several redox centers. The orbital approach is simple and robust, allows a visual interpretation (accepting the risk of too naïve pictures in a first step), but can be perfected by more recent developments such as DFT. A last advantage is its relation to the tight-binding model used in solid state physics.

Thus we shall try to model the system with the least number of parameters, in particular: (i) an electronic parameter describing the electronic communication between subunits, which will depend on overlap considerations; (ii) an electron–phonon parameter describing the consequences of a change in electronic structure on the geometrical structure, which will depend on the nodal properties (bonding/antibonding) of the relevant orbitals.

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[*] Address: CEMES-CNRS, 29 rue Jeanne Marvig, BP 94347, F-31055 Toulouse cedex 4, France. Tel.: +33 5 62 25 78 32; fax: +33 5 62 25 79 99.
E-mail address: launay@cemes.fr

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By the way and looking at the abundant literature, we once more can highlight the profound unity of electron transfer processes, as it manifests in inorganic, organic and organometallic systems. They will be treated in parallel as much as possible.

Note also that the present paper is devoted mainly to electron transfer, and we treat only occasionally magnetic coupling. But we use a common formalism based on fragment orbitals.

The paper is thus organized as follows: In Section 2 we stress the link between molecular mixed valence concepts and solid-state concepts such as electron–phonon couplings, because chemists synthesize now larger and more complex molecules, more and more related to solid state systems. Section 3 is devoted to the qualitative interpretation of electronic interaction through a bridging ligand, using the concept of overlap between magnetic orbitals, borrowed from magnetic exchange studies. We begin with the definition of magnetic orbitals and the role of their overlap, then we mention the delocalization effects across an aromatic cycle and recall the isolobal analogy between d^6 metal sites and organic nitrogen donors. The heart of the section is the discussion of the decay of electronic influences across a long bridge, and the comparison the case of even-atom and odd-atom ones. We also consider the case of some aromatic spacers like azulene or pyridine under their different substitution schemes. In Section 4, we come back to the properties of molecular polarons, their dependence on the molecule size and their influence on the electronic coupling. Finally in Section 5, we show the utility to treat complex systems by a three-center model.

2. Link with solid-state concepts: Holstein and Peierls electron–phonon couplings

It is well known that the presence or absence of an electron modifies the geometrical structure. This effect is central in the description of molecular mixed valence compounds because the distortion induced by the change in electronic occupation of a site restrains the electron transfer. But this is also known in solid-state physics through the polaron concept, i.e. the pseudo particle made of an electron (or hole) associated with the corresponding distortion. The concept was initially developed for predominantly ionic solids by Landau in 1933 and thoroughly discussed later by Mott in 1969 [4]. But in the recent years, it has been extended to molecular solids.

In mixed valence systems, the standard paradigm is the two-state system with one extra electron (Fig. 1a and b). Using the Marcus–Hush potential energy curves [5,6], one can show the competition between an electronic coupling parameter (denoted V_{ab}) which favors the electron delocalization between the two sites, and a parameter (denoted λ) describing the energetic consequences of the change in geometry upon oxidation or reduction, which restrains the delocalization. These parameters appear on Fig. 1a, together with a simplified representation of the structural changes. λ designates the vertical energy difference (intervalence transition energy) between the two possible electronic states (see Section 3.1.2. in [7]). According to the relative values of V_{ab} and λ, the lowest potential energy curve can exhibit either two or one minimum, and the corresponding systems are denoted as class II or class III [1] (Fig. 1b). The critical condition is $V_{ab} < \lambda/2$ (class II) or $V_{ab} > \lambda/2$ (class III). For a class II compound, the extra electron is essentially localized on one site, because the geometry is not symmetric (this is a consequence of the non-equal occupation of the two sites!). In other words there is a self-trapping (self-consistent process) of the extra electron by its own distortion of a particular site.

In solid state systems, the overall process is similar. We show on Fig. 1c a linear array of chemically identical sites, one of which being distorted and accommodating the extra electron. The dotted lines suggest a process in which there is a concerted change in site geometry allowing the electron transfer between the initial site and a neighboring one (here the right site). The molecular motion is the same as in Fig. 1a. A polaron energy can be defined as the energy change when the system relaxes after addition of a charge [4]. This corresponds to $\lambda/2$ in the Marcus–Hush formalism.

Note that in the two above examples, the geometrical distortions modify only the site individual energies but not the electronic coupling.

The advent of molecular materials with conducting properties (molecular metals, semi-conductors, etc...) led to a modification of the above formalism, as shown on Fig. 2. Let us take the example of polyacetylene, which is known to exist in a "dimerized" or "Peierls-distorted" state ([7], Section 3.3.3), i.e. with an alternation of long (essentially single) and short (essentially double) bonds. A simple electronic description uses two parameters: the electron energy on a site (α) and the electronic coupling between different sites (β). This corresponds to the simple Hückel model, familiar to chemists, but also used by physicists under the name of "tight-binding" model. The β parameter is the equivalent of the V_{ab} parameter above. If now the geometry is changed, for instance by a change in bond lengths, the main effect will bear on β, the inter-site coupling.

We thus have to distinguish two types of modifications of the electronic structure induced by structural distortions. These modifications are called "electron–phonon couplings" (a term borrowed from solid-state studies). Assuming that the molecule can be divided in sites, each one being able to receive or lose an electron, the current trend is to distinguish two types of polarons: pure Holstein polarons and Holstein–Peierls polarons.

In the Holstein case, the distortion is local and limited to the concerned site, i.e. it bears only on α, the site energy. The Holstein polaron concept was established in 1959 ([8,9] and references inside), almost at the same time than the Marcus–Hush model of electron transfer in solution [5,6], which is based on the same principle: the addition (or removal) of an electron on a redox site changes its geometry. (The main difference between the two treatments is that solution studies involve in addition a solvent relaxation term). At this time, a "site" was typically an atomic site, for instance a transition metal ion, but now it can be a molecule, part of a molecular material. The Holstein polaron energy is now amenable to accurate quantum chemical calculations at the DFT level, providing invaluable information on the geometrical and energetic changes associated with charge transport [10].

In the Holstein–Peierls case, by contrast the distortion is non-local and concerns also the interaction between sites, i.e. the resonance or transfer integral β parameter (see Fig. 2) [8,9]. Note that the terminology "Peierls" has been borrowed from the famous Peierls theorem established in the 1930s, which is now used to explain the distortion in 1D half-filled systems such as polyacetylene [7]. But the Peierls terminology has shifted from simple 1D arrays of atoms or CH sites to the case of 1D arrays of *molecules* (Fig. 2c). A more detailed picture will be given in Section 4.

3. Electronic interaction through overlap of "magnetic-like" orbitals

3.1. "Magnetic-like orbitals" and overlap of tails

In systems with several sites, the concept of "magnetic orbitals" has revealed very fruitful and heuristic to predict and explain magnetic properties. Magnetic orbitals are orbitals containing an unpaired electron and localized mainly on a given atom or more generally a given site, with partial delocalization on the neighboring entities (either bridging ligand or ancillary non-bridging ones) [11]. Here, we are not concerned with magnetic properties, but we