

Use of the neighboring orbital model for analysis of electronic coupling in Class III intervalence compounds

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Received 24 June 2005; accepted 10 January 2006

Available online 24 February 2006

Dedicated to Professor Noel Hush on the occasion of his 80th birthday.

Abstract

Symmetrical charge-delocalized intervalence radical ions should not be described by the traditional two-state model that has been so successful for their localized counterparts. If they lack direct overlap between their charge-bearing units (**M**), their diabatic orbitals have an equal energy pair of symmetrized **M**-centered combination orbitals that are symmetric (*S*) or antisymmetric (*A*) with respect to a symmetry element at the center of the molecule. The **M** combination orbitals will mix separately with bridge orbitals of the same symmetry. We call the simplest useful model for this situation the neighboring orbital model, which uses the *S* and *A* bridge orbitals of high overlap that lie closest in energy to the **M** orbital pair, resulting in two two-state models that have a common energy for one pair. This model is developed quantitatively, and examples having 1, 3, 5, and 7 electrons in the neighboring orbitals are illustrated.

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Keywords: Marcus-Hush; Electronic coupling; Koopmans' theorem; Radical ions; Intervalence compounds; Neighboring orbital model

1. Introduction

Two-state theory was first applied by Hush to localized symmetrical intervalence compounds [1], which may be characterized as having two charge-bearing units **M** attached symmetrically to a bridge **B**, and being at an oxidation level for which the **M** units might have different charges, that is +1 or –1 for neutral **M** and **B** groups. Robin-Day Class II [2] compounds may be usefully described as $\mathbf{M}^{+/-}-\mathbf{B}-\mathbf{M}$ systems, with one oxidized or reduced **M** group, and two-state theory is extremely successful for interpreting their optical spectra. Two-state theory predicts that the transition energy for the intervalence band of a delocalized (Class III) intervalence compound, a compound usefully described as $\mathbf{M}^{+/-1/2}-\mathbf{B}-\mathbf{M}^{+/-1/2}$, will be equal to twice the electronic coupling (off-diagonal

matrix coupling element), called V_{ab} here. We believe that this was first explicitly pointed out in the 1983 review of intervalence compounds by Creutz [3]. Ratner stated in 1990 that “half the splitting between the lowest empty and highest occupied molecular orbitals” is what is implied for V_{ab} by the “simple two-site Hückel-type model”, and that it would only apply if V_{ab} were large [4]. The use of Koopmans' theorem to evaluate the V_{ab} of electron-transfer theory was independently employed for $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NH}_2^+$ by Broo and Larsson [5] and for bond-linked alkenes by Paddon-Row and Wong in 1990 [6]. It has been used extensively to calculate electronic couplings, for example by the groups of Larsson [7–12], Paddon-Row and Jordan [13–17], Newton [18–20], Curtiss [21–23], Li [24–27], Brédas [28], and Nelsen [29–33].

We recently became aware of a problem with equating the transition energy for a Class III intervalence compound with V_{ab} . It is not numerically correct because the simple two-state model does not apply unaltered to any delocalized

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intervalence compound. A symmetric delocalized intervalence compound has all its orbitals either symmetric or anti-symmetric (*S* or *A*) with respect to a symmetry element at the center of the molecule. The charge-bearing unit (**M**) *S* and *A* symmetrized diabatic orbitals will be isoenergetic when they do not overlap significantly with each other, which is typically the case. The bridge diabatic *S* and *A* orbitals that are closest in energy to the **M** orbitals (so that their interactions with them will be the largest) will lie at quite different energies, and the *S* and *A* **M** and **B** diabatic orbitals will interact separately with each other to produce four adiabatic orbitals. Thus the simplest realistic model for a Class III intervalence compound has two interpenetrating two-state models that may contain one, three, five, or seven electrons (using a ROHF model that employs two electron orbitals). This situation is clearly shown, for instance, in Fig. 2 of Joachim, Launay, and Woitellier's paper on bridged ruthenium pentamine intervalence compounds [34]. They label the energy separation between the highest doubly filled and the singly-occupied adiabatic orbitals as $2V_{ab}$, although some qualifying phrases that both the effects of interaction with the bridge highest occupied and lowest unoccupied molecular orbitals (*homo* and *lumo*) are present are also given in the text. The equation of the intervalence transition energy with $2V_{ab}$ has also been accepted by the authors of Refs. [3–34].

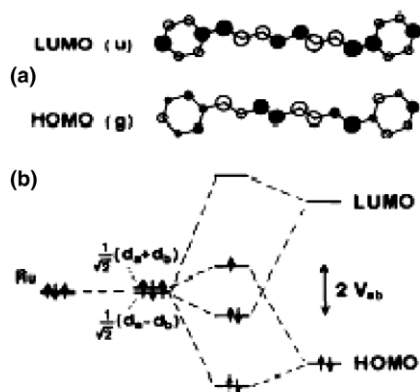
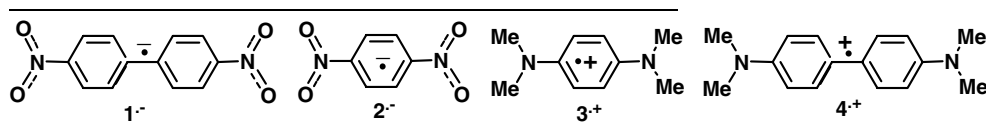


Fig. 2. (a) Shape of the HOMO and LUMO in py-(CH-CH)₂-py. (b) Interaction scheme showing the additivity of the HOMO and LUMO influences.



In this paper we emphasize that because the intervalence transition is between orbitals of different symmetry, both diabatic energy differences and electronic couplings contribute to the “intervalence” transition energy of delocalized compounds, which should not be considered as

being “ $2V_{ab}$ ” in any quantitative sense. We also illustrate the 1–7 electron neighboring orbital cases with examples, show a method for extracting V values from calculated diabatic energies of the neighboring orbitals, and briefly discuss systems for which two-state diabatic displaced parabola models are useful for excited states instead of ground states.

2. Results: one- to seven-electron neighboring orbital systems

As noted above, the *S* and *A* bridge combination orbitals will mix separately with various *S* and *A* bridge orbitals. The mixing will be largest for the diabatic bridge orbitals that are closest in energy to the diabatic **M** combination orbitals, which will be at the same energy if there is negligible direct overlap between the **M** orbitals, as is often the case. We will call these four diabatic orbitals the neighboring orbital system. The simplest reasonable analysis to extract electronic coupling will therefore involve two separate two-state systems, each having its own electronic coupling, that are related by the diabatic **M** combination orbitals having the same energy. It seems easiest to consider that the charge and hence the unshared electron is on the **M** groups, although the charge is shared by the **M** groups and the bridge in all delocalized cases. The two bridge neighboring orbitals can therefore have zero, two or four electrons, depending upon whether its orbitals that are closest in energy to the **M** pair are both virtual, one virtual and one occupied, or both occupied. Similarly, the pair of diabatic **M** orbitals has an odd number of electrons, either one or three. The four diabatic neighboring orbitals will mix to produce four adiabatic neighboring orbitals, that we label E_1 to E_4 in order of increasing energy. These neighboring orbitals can hold one, three, five, or seven electrons for the Class III intervalence compounds under discussion. We will first illustrate examples of these four possibilities, which can be done using benzene-1,4-diyl and biphenyl-4,4'-diyl bridges, and **M** = NO₂ radical anions and NMe₂ radical cations, compounds 1^{·-} to 4^{·+}.

The optical spectra of several dinitroaromatic compounds have been recently discussed in detail, first in terms of a two-state analysis [33], and later using a neighboring orbital analysis [35]. Since nitro groups are far more easily reduced than aromatic rings, the odd electron goes into the

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