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

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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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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 $\mathbf{M}^{+/-}$–**B**–**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 $\mathbf{M}^{+/-1/2}$–**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 H_2N–$(CH_2)_n$–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], Brèdas [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 antisymmetric (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].
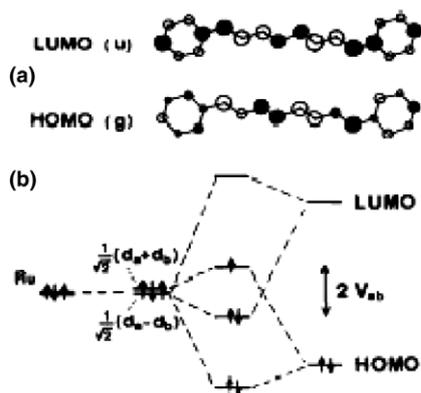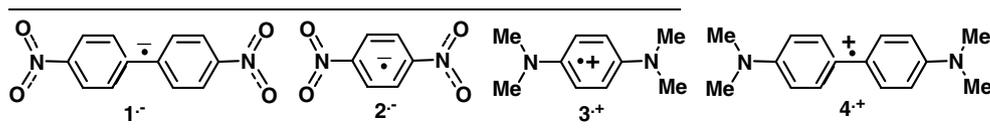

Fig. 2. (a) Shape of the HOMO and LUMO in py–(CH=CH)₄–py. (b) Interaction scheme showing the additivity of the HOMO and LUMO influences.

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**·⁺.

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

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
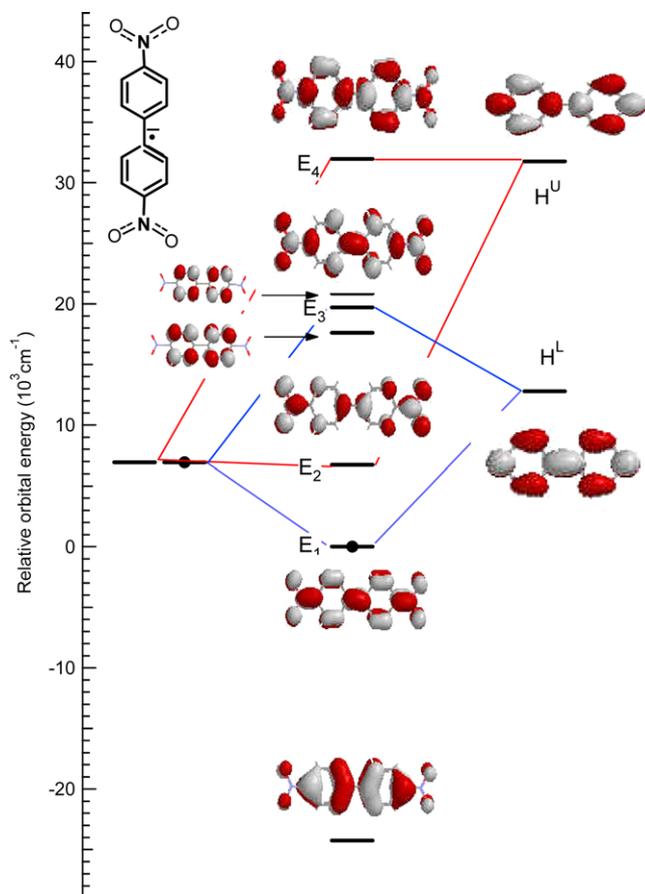
Fig. 1. Orbital drawings for $1^{\cdot-}$, a one-electron neighboring orbital system.

Fig. 2. Neighboring orbital drawings for $2^{\cdot-}$, a three-electron neighboring orbital system.

lowest unoccupied nitro group combination orbital, as indicated on the left of Figs. 1 and 2. These drawings show the adiabatic orbitals obtained using UB3LYP/6-31G* calculations in the center. The **M** diabatic combination orbital energies are indicated on the left, and the bridge diabatic orbitals that interact with them on the right (drawings of the corresponding orbitals for benzene and untwisted biphenyl are used for the pictures). The diabatic orbital energies were calculated by the method described in detail below. For $1^{\cdot-}$, the energies of two adiabatic orbitals that occur in the same general region as E_3 are given, with small drawings of these orbitals to the left of their energy position. They are not part of the neighboring orbital system because of the nodes passing through the C_4–N positions, so there is no overlap with the nitro group *lumo* combination that bears the odd electron. The lowest adiabatic energy orbital shown in Fig. 1 is also not part of the neighboring orbital system. It has strong C_4N overlap, but there is not a corresponding orbital having C_4N nodes using the same biphenylene orbital as this C_4N bonding orbital. The neighboring orbital system has bonding/antibonding pairs that use the same bridge orbital, indicated as E_1 and E_3 (shown connected in blue throughout this paper) and E_2 and E_4 (shown connected in red). Both the biphenylene orbitals used in the neighboring orbital system are virtual, so there is only one neighboring orbital electron in $1^{\cdot-}$.
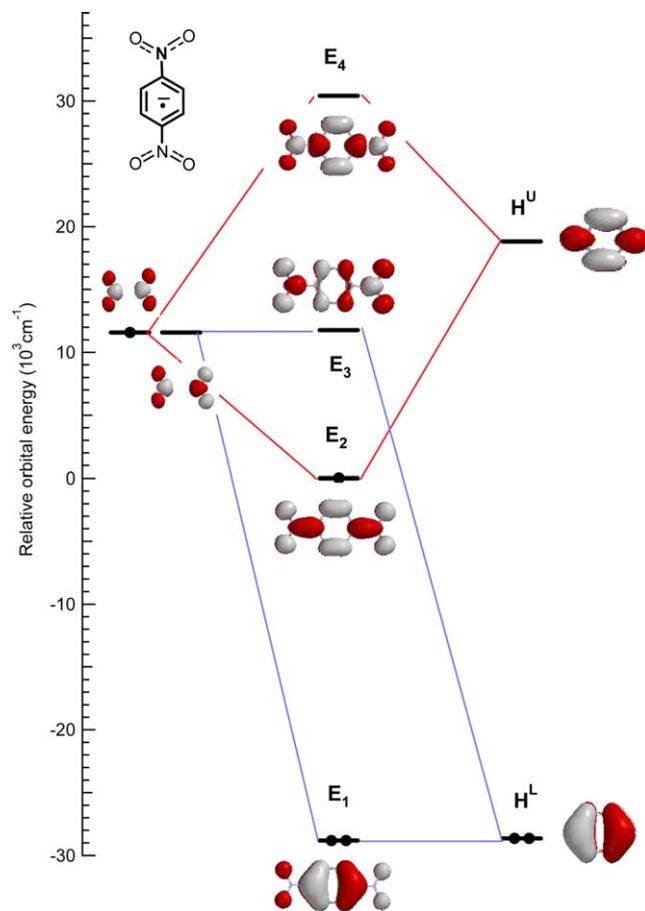
Fig. 2 shows the corresponding diagram for $2^{\cdot-}$. For it the antisymmetric virtual bridge orbital that can interact with the dinitro radical anion diabatic orbital lies so high in energy that the filled antisymmetric orbital shown has a larger interaction, although the energy difference between these orbitals is so great that the lower energy combination is very much concentrated on the bridge and the upper energy one is very much concentrated on the nitro groups. Because one filled bridge orbital has been used, the neighboring orbital system has three electrons for $2^{\cdot-}$.

Five and seven-electron neighboring orbital systems having the same bridges with **M** = NMe_2 and a +1 molecular charge are shown in Figs. 3 and 4. A resonance Raman study of a protected tetraalkyl *p*-phenylenediamine was discussed in terms of the two-state model [32], and the spectra of a protected version of $4^{\cdot+}$ and six compounds having ortho, ortho' bridging are considered using the neighboring orbital model elsewhere [36]. Two orbitals that have 1, 4-nodes and thus are not part of the neighboring orbital system are also shown for $3^{\cdot+}$ in Fig. 3. $3^{\cdot+}$ uses one filled *p*-phenylene orbital and one virtual one, which has a large energy gap from the three-quarters filled diabatic N-p orbital centered pair of orbitals, and hence very little electronic coupling. The only bridge π orbital that could interact with the N-centered orbitals is the very stabilized no node one.
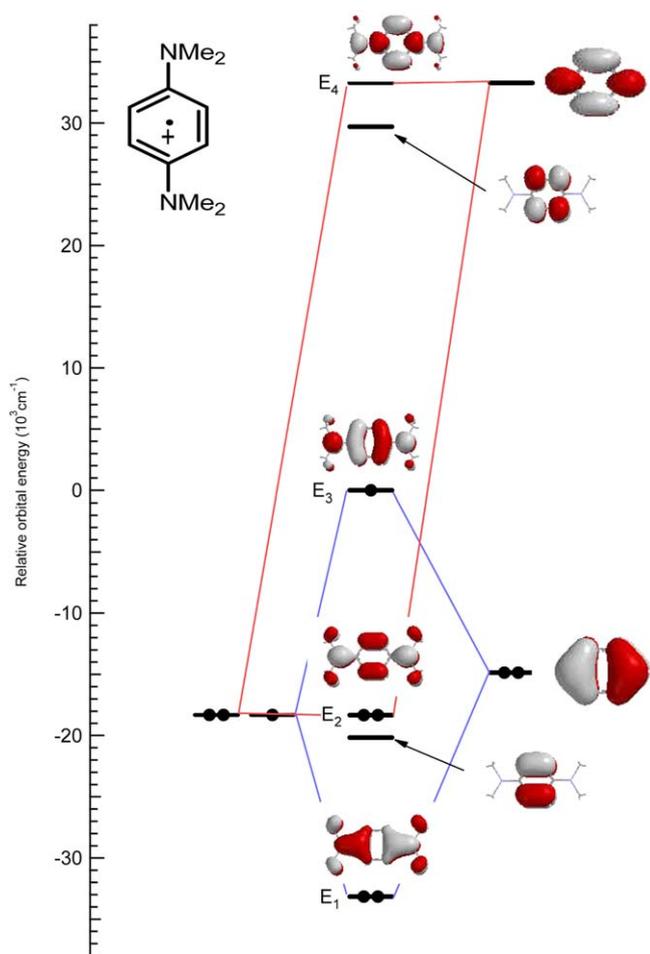
Fig. 3. Orbital drawings for $3^{·+}$, a five-electron neighboring orbital system.

Fig. 4. Neighboring orbital drawings for $4^{·+}$, a seven-electron neighboring orbital system.

Because there are three electrons in the diabatic NMe_2 p orbital pair (considering the charge-bearing units as bearing the charge), there are five neighboring orbital electrons for $3^{·+}$. Going to the 4,4′-biphenyl bridge of $4^{·+}$ provides a much less stabilized symmetric orbital for interaction with the diabatic NMe_2 p orbital pair, and this system has seven neighboring orbital electrons.

3. Results: obtaining diabatic orbital energies

The low energy transitions in radical ions are dominated by either Type A transitions, filled orbital to singly-occupied molecular orbital (*somo*) or Type B transitions, *somo* to virtual orbital transitions (using the two electron orbital nomenclature of this paper, which although not quite correct because there are no two electron orbitals in radical ions, is convenient), as pointed out long ago by Hoijtink [37,38]. Thus all three optical transitions that could determine the energies of the neighboring orbitals are Type B for 1-e systems, but they are both type A and type B for 3-e and 5-e systems, and all are type A for 7-e systems. However, there are seemingly insurmountable problems in determining the energies of the neighboring orbitals experimentally. In each case, one of the necessary transi-
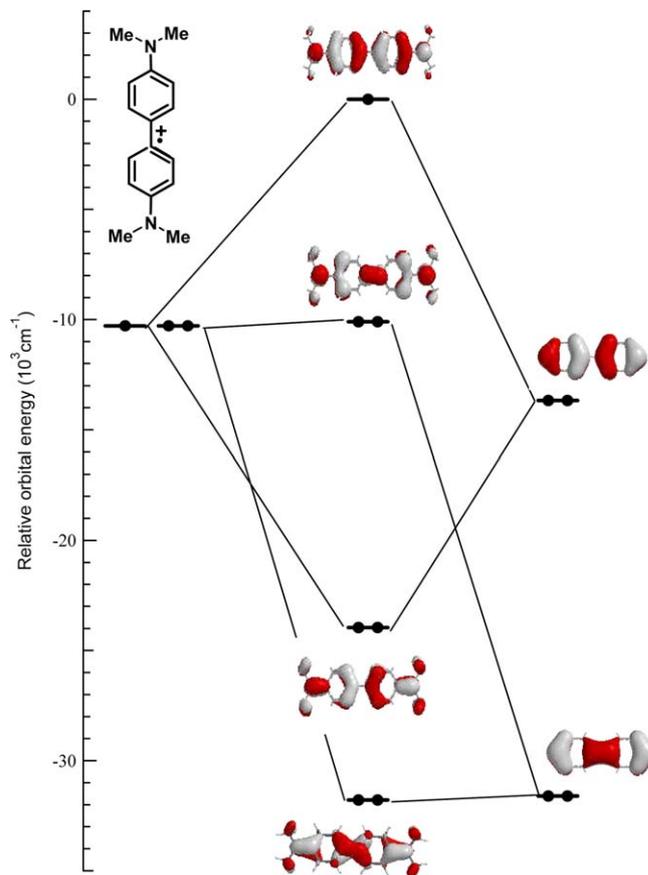
tions is between orbitals of the same symmetry and thus forbidden, so its intensity will be vanishingly small. Furthermore, configuration interaction is known to be significant for many optical transitions, so the experimental transition energies do not directly correspond to the orbital energy differences anyway. We therefore use Koopmans-based methods to determine the neighboring orbital energy gaps. We pointed out long ago that the orbital energy gap between the *homo*-1 and the *homo* orbitals for a hydrazine radical cation calculated with no charge (neutral in cation geometry) is an excellent approximation to the transition energy calculated by more sophisticated methods [39], and energy gaps calculated in this way correspond to Type A transitions. We only recently realized that calculating the dication at cation geometry for a radical cation produces the Type B transition energies, in the context of calculating the neutral in radical anion geometry for dinitroaromatic systems [40]. These calculations do not include configuration interaction effects, so they can be argued to actually be better for the purpose of obtaining the true diabatic energies than using real transition energies, which are unquestionably affected by configuration interaction. We are currently testing a variety of systems to see how well these Koopmans-based calculations do at predicting optical spectra, and shall not go into this aspect in detail here, because different systems will obviously be calculated with

different degrees of success. For the present paper, we will simply assume that Koopmans-based calculations give a good enough description of the adiabatic orbital positions to warrant analyzing them, which we believe we have established experimentally for both dinitro-substituted [35] and dialkylamino-substituted [36] Class III compounds. It will be noted that the adiabatic orbital separations are only obtained relative to the *somo*, so that comparison of neighboring orbital systems with different numbers of electrons is difficult, and we shall not attempt to do it here.

4. Neighboring orbital model

A simple physical representation that is relevant to **M**–**B**–**M** type molecules called the neighboring orbital model is shown in Fig. 5.

The coupling between the **M** units is mediated by neighboring orbitals from the intervening bridge unit. Because the though-bond coupling occurs via π interactions for the molecules addressed in this paper, this analysis focuses on the mixing of **M** unit π molecular orbitals with the appropriate π orbitals of the bridge. The most important of those orbitals are those closest in energy to the **M** unit orbitals because mixing will be greatest. The two **M** unit orbitals are degenerate because direct overlap between them is negligible, and in the absence of coupling they can be represented either by the π system of **M** on the left and that of **M** on the right, or by linear combinations of the left and right π systems. The linear combinations are in phase $\pi_M + \pi_M$ or out of phase $\pi_M - \pi_M$. The bridge orbitals of interest are the π bonding and the π antibonding orbitals with the same symmetries and similar energies as the **M** π systems. These bridge π orbitals must have nonzero overlap with the **M** π systems for mixing to occur. The bridge π bonding orbital has the appropriate symmetry to mix with the in-phase combination, $\pi_M + \pi_M$ and the bridge π antibonding orbital has the appropriate symmetry to mix with the out-of-phase combination, $\pi_M - \pi_M$. When the orbitals of the same symmetry mix, the degeneracy of the linear combinations, $\pi_M + \pi_M$ and $\pi_M - \pi_M$ is removed.

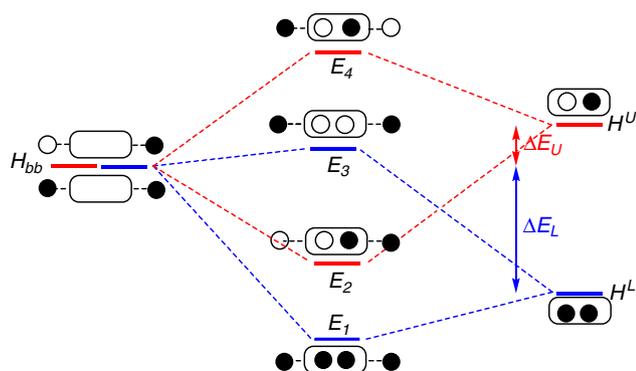The energies of the orbitals in Fig. 5 can be represented by the following energy matrix:

Fig. 5. Diagrammatic representation of neighboring orbital model.

$$H_{\text{unsym}} = \begin{pmatrix} H^L & \frac{1}{\sqrt{2}}V^L & \frac{1}{\sqrt{2}}V^L & 0 \\ \frac{1}{\sqrt{2}}V^L & H_{bb} & 0 & -\frac{1}{\sqrt{2}}V^U \\ \frac{1}{\sqrt{2}}V^L & 0 & H_{bb} & \frac{1}{\sqrt{2}}V^U \\ 0 & -\frac{1}{\sqrt{2}}V^U & \frac{1}{\sqrt{2}}V^U & H^U \end{pmatrix} \quad (1)$$

Diabatic energy H^L belongs to the π bonding bridge orbital and energy H^U is associated with the π antibonding orbital of the bridge. In this unsymmetrized basis, the energy H_{bb} in column 2 belongs to the π_M orbital on the left and the energy H_{bb} in column 3 belongs to the π_M orbital on the right. In the phase convention used here, both orbitals intrinsically have the same phase. In the diabatic basis, the phase of the π bonding bridge orbital is the same as that of the π_M orbitals. In other words, the all-positive linear combination of these orbitals results in the node-less bonding molecular orbital. Because orbital mixing involves the symmetric and asymmetric linear combinations of the π_M orbitals, it is more convenient to transform the diabatic energy matrix to the symmetrized form, $T^{-1}H_{\text{unsym}}T = H_{\text{sym}}$

$$H_{\text{sym}} = \begin{pmatrix} H^L & V^L & 0 & 0 \\ V^L & H_{bb} & 0 & 0 \\ 0 & 0 & H_{bb} & V^U \\ 0 & 0 & V^U & H^U \end{pmatrix} \quad (2)$$

using the transformation matrix

$$T^{-1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (3)$$

Now the energy H_{bb} in column 2 belongs to the symmetric combination of π_M orbitals with the same phase as π bonding bridge orbital and the energy H_{bb} in column 3 belongs to the asymmetric combination (see Fig. 5 for relative phase). The off diagonal V^L terms effectively mix H^L with H_{bb} and the V^U mixes H_{bb} with H^U. The transformation to the adiabatic basis $U^{-1}H_{\text{sym}}U = E$ uses the transformation matrix

$$U^{-1} = \begin{pmatrix} \cos\theta & \sin\theta & 0 & 0 \\ -\sin\theta & \cos\theta & 0 & 0 \\ 0 & 0 & \cos\phi & \sin\phi \\ 0 & 0 & -\sin\phi & \cos\phi \end{pmatrix} \quad (4)$$

where $\tan 2\theta = \frac{2V^L}{H_{bb}-H^L}$ and $\tan\phi = \frac{2V^U}{H^U-H_{bb}}$. The wavefunctions after transformation into the adiabatic basis are

$$\Psi_1 = \cos(\theta)\psi_a + \frac{1}{\sqrt{2}}\sin(\theta)(\psi_b^L + \psi_b^R) \quad (5)$$

$$\Psi_2 = \sin(\theta)\psi_c + \frac{1}{\sqrt{2}}\cos(\theta)(-\psi_b^L + \psi_b^R) \quad (6)$$

$$\Psi_3 = -\sin(\phi)\psi_a + \frac{1}{\sqrt{2}}\cos(\phi)(\psi_b^L + \psi_b^R) \quad (7)$$

$$\Psi_4 = \cos(\phi)\psi_c + \frac{1}{\sqrt{2}}\sin(\phi)(\psi_b^L - \psi_b^R) \quad (8)$$

where ψ_a and ψ_c represent the NN bonding and antibonding orbitals, respectively, and ψ_b^L and ψ_b^R represent the π system on the left and right, respectively. The eigenvalues or adiabatic energies associated with these wavefunctions are as follows:

$$E_1 = 1/2(H^L + H_{bb} - [(\Delta E^L)^2 + 4(V^L)^2]^{1/2}) \quad (9)$$

$$E_3 = 1/2(H^L + H_{bb} + [(\Delta E^L)^2 + 4(V^L)^2]^{1/2}) \quad (10)$$

$$E_2 = 1/2(H_{bb} + H^U - [(\Delta E^U)^2 + 4(V^U)^2]^{1/2}) \quad (11)$$

$$E_4 = 1/2(H_{bb} + H^U + [(\Delta E^U)^2 + 4(V^U)^2]^{1/2}) \quad (12)$$

where $\Delta E^U = H^U - H_{bb}$ and $\Delta E^L = H_{bb} - H^L$. It is important to note that energies E_1 and E_3 are associated with the top block diagonalized part of H_{sym} whereas energies E_2 and E_4 pertain to the bottom block.

The trace and determinant of a matrix are invariant when undergoing a similarity transform. Using these matrix properties, the diabatic orbital energies can be derived from Eqs. (9)–(12) giving

$$H^L = 1/2(E_1 + E_3 \pm [(E_1 + E_3)^2 - 4((V^L)^2 + E_1 E_3)]^{1/2}) \quad (13)$$

$$H_{bb} = E_1 + E_3 - H^L \quad (14)$$

$$H_{bb} = E_2 + E_4 - H^U \quad (15)$$

$$H^U = 1/2(E_2 + E_4 \pm [(E_2 + E_4)^2 - 4((V^U)^2 + E_2 E_4)]^{1/2}) \quad (16)$$

These can be solved if the relationship between V^L and V^U is known. The approximation made for this work is that the coupling is inversely proportional to the difference in energy between the two diabatic orbitals that are mixing, i.e.

$$\frac{V^L}{V^U} = \frac{\Delta E^U}{\Delta E^L} \quad (17)$$

The adiabatic state energies, $E_1 - E_4$ lie in the opposite order of the orbital energies. Relating the resulting adiabatic state energies derived using the neighboring orbital analysis to the two-state model, it is easy to see that "$2V_{ab}$" in the two-state model is equal to the difference between the E_3 and E_2, which in turn can be expressed in terms of the three diabatic orbital energies, H^L, H_{bb}, H^U, and the off-diagonal orbital mixing terms, V^U and V^L (see (18)).

$$\begin{aligned} H_{eff} &= E_3 - E_2 \\ &= 1/2(H^L - H^U + [(\Delta E^L)^2 + 4(V^L)^2]^{1/2} \\ &\quad + [(\Delta E^U)^2 + 4(V^U)^2]^{1/2}) \end{aligned} \quad (18)$$

This quantity should not be referred to simply as an electronic coupling.

5. Ground versus excited state mixed valence

Mixed valence can occur in either the ground state or the excited state. Tetramethyl *p*-phenylenediamine radical cation $3^{\cdot+}$ is the classical organic example of ground state

mixed valence (*GMV*). Amines are much easier to oxidize than aromatic rings, so the charge can be considered to mostly reside on the dimethylamino **M** groups, although some is also delocalized onto the bridge. $3^{\cdot+}$ is a Class III compound, so both of the **M**-centered resonance structures shown are necessary to properly represent the charge distribution. 2,3-diphenyl-2,3-diazabicyclo[2.2.2]octane radical cation, $5^{\cdot+}$, is an example of an excited state mixed valence (*EMV*) compound that uses similar building blocks in inverted order. The hydrazine bridge of $5^{\cdot+}$ is much more easily oxidized than its **M** group phenyl rings, so the single resonance structure shown provides a reasonable description of the radical cation, although there is obviously some charge delocalization onto the aryl groups. The phenyl group filled orbitals interacting with the NN π electrons are significantly lower in energy than the antibonding NN π bond orbital bearing the unpaired electron, so $5^{\cdot+}$ is a seven-electron neighboring orbital system. Electronic excitation of $5^{\cdot+}$ causes charge-transfer from the phenyl groups to the bridge, which results in a useful Marcus-Hush type displaced double well diabatic surface description for the excited state, resulting in a splitting of the excited state compared to a monophenyl analogue, as we have described in detail elsewhere [41]. The relative amounts of charge on the **M** groups and bridge for a class III compound will obviously vary with **M** and **B**, and intermediate cases would require quantitative knowledge of the diabatic energy levels to classify as *GMV*, *EMV*, or intermediate.

$3^{\cdot+}$ *GMV* $5^{\cdot+}$ *EMV*
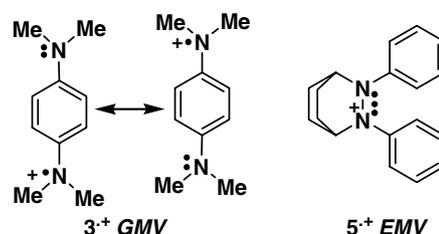
EMV can also occur for other electron counts in neighboring orbital systems. This is conceptually easy to imagine as involving photo-electron-transfer from either nitro group of a dinitro radical anion to the bridge. We have also shown that *EMV* occurs for the non-intervalence oxidation levels of aromatic-bridged bis(hydrazines), both in their neutral [42] and dication [43] oxidation levels.

6. Conclusions

The neighboring orbital model provides a simple and economical way of estimating the electronic couplings for delocalized intervalence compounds. Our numerical results for aromatic bridged dinitro radical anions [35] and compounds related to benzidine [36] are discussed in detail elsewhere. Applying the two-state model to such systems substantially underestimates the larger coupling of the two involved in the neighboring orbital model.

It is obviously important to be able to predict when intervalence systems will localize their charge. This is trivial using the two-state model – it is when $\lambda/2$ exceeds V_{ab}. Relating the V^U, V^L, ΔE^U and ΔE^U of the neighboring orbital model to the V_{ab} and λ of the two-state model is not simple, and we do not yet know how to do it. It presently appears that neither of the neighboring orbital couplings can be directly related to charge localization. We hope to approach this problem experimentally by using intervalence systems that are so delicately balanced at the Class II, Class III borderline that the Class II spectrum (for which Hush's familiar $E_{op} = \lambda$ and intensity successfully predict V_{ab}) is observed in high λ_s solvents, and the Class III spectrum (for which the neighboring orbital analysis may be used) is observed in low λ_s solvents. We recently reported the first system to show this behavior in collaboration with J. P. Telo, pseudo-para dinitro[2.2]paracyclophane radical anion [44]. This system clearly has direct overlap between the charge-bearing units, making a basic assumption of the neighboring orbital model presented here invalid. We hope to report studies on systems which allow quantitative comparisons in the future.

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