

# Multistate Effects in Calculations of the Electronic Coupling Element for Electron Transfer Using the Generalized Mulliken–Hush Method

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A simple diagnostic is developed for the purpose of determining when a third state must be considered to calculate the electronic coupling element for a given pair of diabatic states within the context of the generalized Mulliken–Hush approach (*Chem. Phys. Lett.* **1996**, 275, 15–19). The diagnostic is formulated on the basis of Löwdin partitioning theory. In addition, an effective 2-state GMH expression is derived for the coupling as it is modified by the presence of the third state. Results are presented for (i) a model system involving charge transfer from ethylene to methaniminium cation, (ii) a pair of donor–acceptor-substituted acridinium ions, and (iii) (dimethylamino)benzotrile, and the diagnostic is shown to be a useful indicator of the importance of multistate effects. The effective 2-state GMH expression is also shown to yield excellent agreement with the exact 3-state GMH results in most cases. For cases involving more than three interacting states a similar diagnostic is presented and several approximations to the full  $n$ -state GMH result are explored.

## Introduction

The need for a detailed understanding of electron-transfer (et) processes arises in a wide variety of fields, ranging from studies of photosynthesis and oxidative phosphorylation to the development and refinement of molecular electronics devices.<sup>1,2</sup> The major initial theoretical advances in this area occurred via the work of Marcus,<sup>3</sup> Hush,<sup>4</sup> and Levich and Dogonadze<sup>5</sup> and provided a framework for understanding how the medium (e.g. solvent in solution phase et) and the structure/energetics of the reacting species affect the overall rate of electron transfer. More recent studies have produced increasingly detailed models for describing the nuclear rearrangements associated with the electron-transfer process. Examples of this work include the studies of Friedman and Newton for nondipolar solvents,<sup>6</sup> the work of Matyushov examining molecular models of the solvation and activation process,<sup>7</sup> and attempts at using modern electronic structure theory to calculate outer- and inner-sphere reorganization energies.<sup>8–10</sup>

In concert with this increased sophistication concerning the nuclear part of the electron-transfer problem has come the ability to describe the electronic portion of the problem in ever greater detail. The early work of McConnell<sup>11</sup> and Halpern and Orgel<sup>12</sup> highlighted the effects that intervening medium and/or ligands could have on the “electronic coupling element” ( $H_{DA}$ ) for electron transfer. In cases where the donor and acceptor are weakly interacting, the rate of electron transfer is predicted to be proportional to  $|H_{DA}|^2$ .<sup>1,2</sup> Since  $H_{DA}$  is expected to decay approximately exponentially with distance between the donor and acceptor, it is critical to have a molecular description of how this coupling is mediated by intervening medium to understand the behavior of long-distance electron transfers. In fact, McConnell’s work, which gave rise to the concept of “superexchange”, has been an extremely fruitful model for the

treatment of long-range electron transfers. Beratan and co-workers<sup>13</sup> employed superexchange at a variety of levels of detail to understand long-distance electron transfer in synthetic and natural systems,<sup>14</sup> introducing the “pathways” concept to help explain the structure-dependence of the electronic coupling element. Liang and Newton,<sup>15</sup> Curtis and Miller,<sup>16</sup> and Jordan, Paddon-Row, and co-workers<sup>17</sup> have all used this idea to interpret the distance dependence of the electronic coupling in model systems.

To perform quantitative investigations of the electronic coupling element one needs a means of relating experimental data or results from quantum chemical calculations (at whatever level of sophistication one chooses to employ) to the electronic coupling element, and a variety of theoretical methods have been proposed to calculate  $H_{DA}$ .<sup>13,18–24</sup> In symmetrical systems  $H_{DA}$  can be obtained from the splitting of pairs of symmetric and antisymmetric states, but in asymmetrical systems extracting  $H_{DA}$  from electronic structure theory calculations has been more of a challenge. Recently, one of us, in collaboration with M. Newton, has introduced the generalized Mulliken–Hush method<sup>25</sup> which allows accurate calculation of  $H_{DA}$  in a wide variety of systems, independent of symmetry, geometrical constraints, or the number of interacting states. As its name suggests, the method is rooted in the pioneering work of Mulliken<sup>26</sup> and Hush.<sup>27–29</sup>

Mulliken<sup>26</sup> and Hush<sup>27–29</sup> proposed using spectroscopic information to extract the electronic coupling element from charge-transfer (CT) transition spectra. The Mulliken–Hush method postulated that CT intensity arose from mixing between the diabatic initial and CT states and that this mixing was governed by the size of  $H_{DA}$ . The Mulliken–Hush expression for the splitting is

$$H_{DA} = \frac{\mu_{12}\Delta E_{12}^D}{\Delta\mu_{12}^D} \quad (1)$$

where  $\mu_{12}$  is the transition dipole moment connecting the two

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adiabatic states in the CT transition,  $\Delta E_{12}^D$  is the difference in energy between the initial and final diabatic states, and  $\Delta\mu_{12}^D$  is the difference in diabatic state dipole moments. Within the Mulliken–Hush perturbative treatment the energy splitting between the pair of diabatic states was approximated as equal to the adiabatic splitting ( $\Delta E_{12}$ ), and the difference in dipole moments between the diabatic states was approximated as  $eR_{DA}$ , where  $R_{DA}$  is the center-to-center distance between donor and acceptor. Later work by Creutz, Sutin, and Newton<sup>30</sup> showed that in a nonperturbative formulation within a 2-state approximation the electronic coupling element is actually proportional to the adiabatic, and not the diabatic, energy splitting.

In the introduction of the GMH method<sup>25</sup> it was shown that the need to separately approximate the diabatic dipole moment difference as in these earlier variants was unnecessary, once one had accepted the Mulliken–Hush definition for diabatic states (zero transition dipole moment for states localized at different centers). One thus arrived at the 2-state generalized Mulliken–Hush result:

$$H_{DA} = \frac{\mu_{12}\Delta E_{12}}{\Delta\mu_{12}^D} = \frac{\mu_{12}\Delta E_{12}}{(\Delta\mu_{12}^2 + 4\mu_{12}^2)^{1/2}} \quad (2)$$

The denominator in the second equality yields a definition of the diabatic dipole moment difference, entirely in terms of adiabatic quantities.

As noted above, one advantage of the GMH method is that it is able to deal with situations where more than two adiabatic states enter into the description of the diabatic states of interests (i.e. multistate situations). For ground-state electron transfers it is often a good assumption that the pair of diabatic states of interest are well-described by a pair of adiabatic states, but for excited-state electron transfers there are certainly examples where such is not the case. The question of the effects of a third state has been discussed by Murrell,<sup>31</sup> Mulliken and Person,<sup>32</sup> Bixon, Jortner, and Verhoeven,<sup>33</sup> Gould et al.,<sup>34</sup> and Herbich and Kapturkiewicz.<sup>35</sup> In all of these treatments a Mulliken–Hush-like perturbative treatment is used to estimate the electronic coupling element between the three states of interest, either using specific solvent effects to shift the CT state's energy or by examining cases where excited-state mixing can be estimated on the basis of changes in intensity of a locally excited transition. In combination with experimental results these formalisms have helped explain the variation in fluorescence intensity from a CT state in terms of mixing with an LE state (i.e. CT fluorescence intensity borrowing when the two diabatic states are near in energy). In the context of these studies, it is in fact the variation in mixing of the LE, CT, and GS that allows one to extract independent estimates of the electronic coupling elements in the system.

By contrast, using the 3-state (or  $n$ -state in the general case) GMH method one is able to extract all of the coupling elements of interest from a single calculation at a fixed geometry (environment), provided one has information about the energies of the states and the various adiabatic dipole moments (diagonal and off-diagonal) in the system. However, the question arises as to how one might easily recognize the need for a multistate treatment in the context of the GMH method. That is, it may be that one is focusing on the interaction of a pair of diabatic states, and near degeneracy effects with a third state will be present but not immediately apparent. The aim of the present contribution is to (i) understand the origin of such multistate effects in the GMH method, (ii) propose a simple diagnostic for the detection of when one needs to expand the GMH

approach from a 2-state to a 3-state treatment, and (iii) present a simple effective 2-state expression for the electronic coupling which is useful when a third (or  $n$ ) state(s) alters the calculated electronic coupling.

The remainder of the article is organized as follows. In the next section we present a brief review of the 2-state and locally adiabatic 3-state GMH approach. We then develop the diagnostic on the basis of an application of Löwdin partitioning theory<sup>36</sup> and derive the effective 2-state expression for the electronic coupling element in a perturbative treatment. In the third section we present numerical results for several model systems where we test both the diagnostic and the approximate 2-state expression. In the final section we offer concluding remarks.

## Method

For concreteness in discussing the 3-state result we will consider a model having a pair of diabatic states with the “transferring electron” localized on the donor (e.g. the ground state (GS) of the system and a locally excited (LE) state of the donor) and a single charge-transfer state (CT), having the “transferring electron” localized on the acceptor. The adiabatic states are assumed to be composed of these three diabatic states, and at large donor–acceptor distances the adiabatic states become equivalent to the diabatic states. Thus, at large separations the adiabatic state dipole moments will be able to be grouped into two categories, except in cases of exact degeneracy. The first category will have a pair of states with similar values for the dipole moment (correlating with the GS and LE state), while the second category will consist of a single state, with dipole moment value that is significantly different from either of the other two (correlating with the CT state). The difference between the two classes of dipole moments is expected to be on the order of  $eR_{DA}$ , where  $R_{DA}$  is the distance between the donor and acceptor sites in the et process. At shorter donor–acceptor separations it may not be simple (or even possible) to assign the adiabatic states to these categories, due to potentially strong mixing of the diabatic states. Nevertheless, we assume that the diabatic basis states continue to exhibit distinct classes of dipole moments, corresponding to the local or charge-transfer character appropriate to the given states.

Given the above diabatic basis states, there are three limiting cases that can be used to characterize the adiabatic states which arise from their mixing:

Case 1: Each of the three adiabatic states is a strong admixture of the three diabatic states. In this case there is no simple approximation that yields accurate diabatic coupling elements short of the full 3-state GMH treatment. However, since all three states yield similar dipole moments due to the strong mixing, it is relatively easy to determine that a three-state treatment is required in this limit. As a result, we do not consider this case further here, and one would merely apply the 3-state GMH method to the system to obtain electronic coupling elements.

Case 2: Two diabatic states are strongly mixed in forming the adiabatic states, while a third state only weakly interacts with these two. A simple example of this type of behavior would arise when the diabatic LE and CT states are near one another in energy but well-separated from the GS. In this limit there will be two classes of dipole moments, but due to the strong mixing for the pair of excited states it will be observed that the difference in dipole moments between the two classes is significantly smaller than  $eR_{DA}$ . The diagnostic proposed here will be effective in determining whether a 3-state treatment is required, but the effective 2-state approximation to  $H_{DA}$  will

generally work only for the weak effects of the GS on the 2-state coupling element between the LE and CT states.

Case 3: All three states are relatively weakly interacting. In this limit the adiabatic dipole moments can be separated into two classes, and the difference in dipole moments between states in separate classes will approximate  $eR_{DA}$ . In this limit one cannot use the diagonal dipole matrix elements to determine whether a multistate treatment is necessary (as was possible in cases 1 and 2), since the dipole moments fall in the same classes that they would at infinite donor–acceptor separation. However, in this limit (a) the diagnostic formulated below easily determines whether a 3-state treatment is required and (b) the effective 2-state GMH treatment is found to be quite accurate.

**A. Summary of GMH Results.** To facilitate the development of the diagnostic and the approximate 2-state result it is useful to summarize the exact 2- and 3-state GMH procedures. The three diabatic basis states will be denoted  $\phi_{GS}$ ,  $\phi_{LE}$ , and  $\phi_{CT}$ , and they are assumed to fulfill the locally adiabatic GMH conditions ( $\mu_{ij} = 0$  if  $i$  and  $j$  are states with the transferring electron localized on different sites, and  $H_{ij} = 0$  if  $i$  and  $j$  are states having the transferring electron localized on the same site). In terms of these basis states the adiabatic states of the system will be represented as

$$\begin{aligned}\varphi_1 &= c_{GS,1}\phi_{GS} + c_{LE,1}\phi_{LE} + c_{CT,1}\phi_{CT} \\ \varphi_2 &= c_{GS,2}\phi_{GS} + c_{LE,2}\phi_{LE} + c_{CT,2}\phi_{CT} \\ \varphi_3 &= c_{GS,3}\phi_{GS} + c_{LE,3}\phi_{LE} + c_{CT,3}\phi_{CT}\end{aligned}\quad (3)$$

In case 1 as discussed above, all three coefficients representing a given adiabatic state in terms of the diabatic basis states are expected to be of comparable size. In case 2 one would expect  $c_{GS,i} \gg c_{LE,i}$  and  $c_{GS,i} \ll c_{LE,i}$ ,  $c_{CT,i}$  for  $i=2$  or 3. Finally, for case 3 one would expect  $c_{GS,1} \gg c_{CT,1} > c_{LE,1}$ ,  $c_{CT,2} \gg c_{LE,2}$ ,  $c_{GS,2}$  and  $c_{LE,3} \gg c_{CT,3} > c_{GS,3}$  for the case where adiabatic state 2 correlates with the CT state. The second inequality in the first and third relations for case 3 stems from the lack of direct coupling between the diabatic states localized on a given site. On the basis of these adiabatic states the energy and (parallel)<sup>25</sup> dipole moment matrix have the form

$$\begin{aligned}\mu_{ad} &= \begin{pmatrix} \mu_{11} & \mu_{12} & \mu_{13} \\ \mu_{21} & \mu_{22} & \mu_{23} \\ \mu_{31} & \mu_{32} & \mu_{33} \end{pmatrix} \\ E_{ad} &= \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}\end{aligned}\quad (4)$$

The transformation to the locally adiabatic GMH diabatic states involves (a) diagonalization of  $\mu_{ad}$  and transformation of  $E_{ad}$  with the eigenvectors of the dipole moment matrix, (b) diagonalization of the transformed  $E$  matrix within blocks corresponding to same-site states, and (c) transformation of the dipole matrix over the same blocks. The resulting structure of the diabatic dipole and energy matrixes is

$$\mu_{diab} = \begin{pmatrix} \mu_{GS}^{diab} & 0 & \mu_{GS,LE}^{diab} \\ 0 & \mu_{CT}^{diab} & 0 \\ \mu_{LE,GS}^{diab} & 0 & \mu_{LE}^{diab} \end{pmatrix}$$

$$E_{diab} = \begin{pmatrix} H_{GS} & H_{GS,CT} & 0 \\ H_{CT,GS} & H_{CT} & H_{CT,LE} \\ 0 & H_{LE,CT} & H_{LE} \end{pmatrix}\quad (5)$$

It is seen that the defining relation for the diabatic state corresponding to the CT state (within the present 3-state model) is that it is completely decoupled from the other two diabatic states in the diabatic dipole moment matrix (i.e. the CT diabatic state is an eigenfunction of the dipole moment matrix).

The 2-state GMH result is obtained by merely diagonalizing the 2-state dipole moment matrix, followed by transformation of the energy matrix using the dipole eigenstates, yielding eq 2.

**B. Diagnostic.** To develop a simple diagnostic, we consider whether the relative contribution of a pair of adiabatic states to a given diabatic state is altered significantly upon including additional adiabatic states in the GMH treatment. As a concrete example, we will examine if the coefficients of adiabatic states 1 and 2 in the final diabatic GS and CT diabatic states are significantly altered on moving from a 2-state to a 3-state treatment (i.e. upon addition of the LE state). If the ratio is altered significantly one also would expect a significant change in the electronic coupling elements obtained using the 2- and 3-state treatments.<sup>37</sup>

As noted above, the diabatic CT state is an eigenvector of the dipole moment matrix and is determined by

$$\begin{pmatrix} \mu_{11} & \mu_{12} & \mu_{13} \\ \mu_{21} & \mu_{22} & \mu_{23} \\ \mu_{31} & \mu_{32} & \mu_{33} \end{pmatrix} \begin{pmatrix} C_{1,CT} \\ C_{2,CT} \\ C_{3,CT} \end{pmatrix} = \mu_{CT}^{diab} \begin{pmatrix} C_{1,CT} \\ C_{2,CT} \\ C_{3,CT} \end{pmatrix}\quad (6)$$

Using Löwdin partitioning theory<sup>36</sup> we can convert the 3-state problem to an effective 2-state problem:

$$C_{3,CT} = (\mu_{CT}^{diab} - \mu_{33})^{-1}(\mu_{31}C_{1,CT} + \mu_{32}C_{2,CT})\quad (7a)$$

$$\begin{pmatrix} \mu_{11} + \frac{\mu_{13}\mu_{31}}{\mu_{CT}^{diab} - \mu_{33}} & \mu_{12} + \frac{\mu_{13}\mu_{32}}{\mu_{CT}^{diab} - \mu_{33}} \\ \mu_{21} + \frac{\mu_{23}\mu_{31}}{\mu_{CT}^{diab} - \mu_{33}} & \mu_{22} + \frac{\mu_{23}\mu_{32}}{\mu_{CT}^{diab} - \mu_{33}} \end{pmatrix} \begin{pmatrix} C_{1,CT} \\ C_{2,CT} \end{pmatrix} = \mu_{CT}^{diab} \begin{pmatrix} C_{1,CT} \\ C_{2,CT} \end{pmatrix}\quad (7b)$$

Equations 7 are equivalent to eq 6 but represent the effects of the third state in a 2-state framework via eq 7b. Thus, in this dressed, 2-state approach, the relative size of  $C_{1,CT}$  and  $C_{2,CT}$  is determined by the relation

$$\frac{C_{1,CT}}{C_{2,CT}} = - \frac{\mu_{12} + \frac{\mu_{13}\mu_{32}}{\mu_{CT}^{diab} - \mu_{33}}}{\mu_{11} + \frac{\mu_{13}\mu_{31}}{\mu_{CT}^{diab} - \mu_{33}} - \mu_{CT}^{diab}}\quad (8)$$

In the limit of weak interactions (case 3 and potentially case 2), we can approximate  $\mu_{CT}^{diab} \approx \mu_{22}$  and eq 8 becomes

$$\frac{C_{1,CT}}{C_{2,CT}} \cong - \frac{\mu_{12} + \frac{\mu_{13}\mu_{32}}{\mu_{22} - \mu_{33}}}{\mu_{11} + \frac{\mu_{13}\mu_{31}}{\mu_{22} - \mu_{33}} - \mu_{22}}\quad (9)$$

Finally, since we are dealing with charge-transfer transitions (where one expects  $\mu_{13} \ll eR_{DA}$ , except for short-range interactions), it is expected that

$$\mu_{11} - \mu_{22} \gg \frac{\mu_{13}\mu_{31}}{\mu_{22} - \mu_{33}} \quad (10)$$

leading to

$$\frac{C_{1,CT}}{C_{2,CT}} \cong - \frac{\mu_{12} + \frac{\mu_{13}\mu_{32}}{\mu_{22} - \mu_{33}}}{\mu_{11} - \mu_{22}} \quad (11)$$

for the effective 2-state approximation. On the other hand, the actual 2-state GMH based on adiabatic states 1 and 2 (again assuming that  $\mu_{CT}^{diab} \approx \mu_{22}$ ) yields

$$\frac{C_{1,CT}}{C_{2,CT}} \cong - \frac{\mu_{12}}{\mu_{11} - \mu_{22}} \quad (12)$$

By comparison of eqs 11 and 12 it is apparent that the 2-state treatment is adequate (i.e.  $C_{1,CT}/C_{2,CT}$  is unchanged by addition of a third state) whenever

$$\left| \frac{\left( \frac{\mu_{13}\mu_{32}}{\mu_{22} - \mu_{33}} \right)}{\mu_{12}} \right| = |\lambda_D| \ll 1 \quad (13)$$

$\lambda_D$  thus becomes a diagnostic for the onset of multistate effects, which are expected to be negligible when  $|\lambda_D|$  is much less than unity. One sees that inclusion of a third state will be important either when  $\mu_{13}$  is large (large transition dipole connecting the GS-like and LE-like adiabatic states) or when states 2 and 3 are strong mixtures of the CT and LE states (leading to large  $\mu_{32}$  and/or small diagonal dipole moment difference between states 2 and 3). In the case 3 limit the mixing between diabatic states is modest, thus eq 13 will tend to be violated only when there is a large transition dipole moment between adiabatic states localized on the same site. Obviously, cases 1 and 2 are situations where one can violate eq 13 due to large mixing, but whatever the case, eq 13 functions to indicate the presence of multistate effects.<sup>38</sup>

On the basis of the discussion above, it is relatively easy to generalize the above diagnostic to the  $n$ -state result. In this case, the dressed off-diagonal element between sites  $i$  and  $j$  ( $j$  being the CT-like adiabatic state) takes the form

$$\mu_{ij}^{2\text{-state}} = \mu_{ij} + \mu_{i,n-2}(\mu_j I - \mu_{n-2,n-2})^{-1} \mu_{n-2,j} \quad (14)$$

In complete analogy with the 3-state case, one expects substantial effects due to the additional  $n - 2$  states if  $\mu_{ij}^{2\text{-state}}$  differs significantly from  $\mu_{ij}$ . (Note that  $I$  is the unit matrix,  $\mu_{i,n-2}$  is a row vector, and  $\mu_{n-2,n-2}$  is the  $n - 2 \times n - 2$  square dipole moment matrix for the additional states.)

**C. Effective 2-State Result.** The above diagnostic can be applied in cases 1–3, and where eq 13 (or the analogue based on eq 14) is not satisfied it signals the need to use a 3 ( $n$ )-state GMH treatment. In cases 1 and 2 there is, in general, no further approximation that can be made to obtain the electronic coupling element between a given pair of diabatic states, other than the full 3 ( $n$ )-state GMH treatment. In case 3, however, one can develop a simple perturbative approximation to the coupling

element, for example between the GS and CT states, based on adiabatic states 1 and 2, dressed by their interaction with a third state.

In the case 3 limit the interaction is relatively weak between all three diabatic states, and we expect the adiabatic energies and diabatic diagonal  $H$  matrix elements to be similar. Thus, we

(a) use eq 7 to define the mixing coefficients of adiabatic states 1 and 2 in forming the diabatic CT state, dressed by their interaction with state 3,

(b) realize that with modest mixing the contribution of the LE state to adiabatic state 1 is quite small (see the steps to reach eq 5) and to a good approximation the coefficients of the adiabatic states contributing to the diabatic GS are determined by orthogonality to the CT state, and

(c) assume that if the mixing is small between the LE and CT diabatic states in adiabatic state 2, the normalized coefficients of adiabatic states 1 and 2 in the expression for the CT state in terms of the three adiabatic states are not significantly different from those that would be obtained by just considering  $C_{1,CT}$  and  $C_{2,CT}$  obtained from eq 7. We then normalize the 2-state diabatic CT state on the basis of this approximation (i.e. in case 3  $C_{2,CT}$  is close to 1).

The above assumptions are equivalent to performing a dressed 2-state GMH treatment using the adiabatic matrixes

$$\mu_{ad} = \begin{pmatrix} \mu_{11} + \frac{\mu_{13}\mu_{31}}{\mu_{22} - \mu_{33}} & \mu_{12} + \frac{\mu_{13}\mu_{32}}{\mu_{22} - \mu_{33}} \\ \mu_{21} + \frac{\mu_{23}\mu_{31}}{\mu_{22} - \mu_{33}} & \mu_{22} + \frac{\mu_{23}\mu_{32}}{\mu_{22} - \mu_{33}} \end{pmatrix}$$

and

$$E_{ad} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \quad (15)$$

Using these expressions for the adiabatic dipole and energy matrixes, along with eq 2 above yields

$$H_{GS,CT} = \frac{\mu_{12}^{dressed} \Delta E_{12}}{\Delta \mu_{12}^{D,dressed}} = \frac{\mu_{12}^{dressed} \Delta E_{12}}{((\Delta \mu_{12}^{dressed})^2 + 4(\mu_{12}^{dressed})^2)^{1/2}} \quad (16)$$

where the superscript “dressed” indicates use of the dipole moment matrix elements of eq 15 in evaluating the GMH expression rather than the “bare” dipole matrix elements. In terms of the adiabatic quantities one obtains

$$H_{GS,CT} = \frac{\left( \mu_{12} + \frac{\mu_{13}\mu_{32}}{\mu_{22} - \mu_{33}} \right) \Delta E_{12}}{\left( \left( \mu_{11} - \mu_{22} + \frac{\mu_{13}^2 - \mu_{23}^2}{\mu_{22} - \mu_{33}} \right)^2 + 4 \left( \mu_{12} + \frac{\mu_{13}\mu_{32}}{\mu_{22} - \mu_{33}} \right)^2 \right)^{1/2}} \quad (17)$$

While eq 17 can be used as written, it is simpler (and within the spirit of the approximations made in arriving at eq 17) to expand about the point

$$\frac{\mu_{13}\mu_{32}}{\mu_{22} - \mu_{33}} \cong \epsilon = 0 \quad \frac{\mu_{13}^2 - \mu_{23}^2}{\mu_{22} - \mu_{33}} \cong \delta = 0 \quad (18)$$

to first order (i.e., expanding about the bare, 2-state GMH result), yielding

$$H_{\text{GS,CT}}^{\text{dressed}} = H_{\text{GS,CT}}^{\text{bare}} + \Delta E_{12} \left( \frac{\epsilon}{\alpha} - \frac{4\mu_{12}^2 \epsilon}{\alpha^3} - \frac{\mu_{12}(\mu_{11} - \mu_{22})\delta}{\alpha^3} \right) \quad (19)$$

where  $H_{\text{GS,CT}}^{\text{bare}}$  is the 2-state GMH result and  $\alpha = (\Delta\mu_{12}^2 + 4\mu_{12}^2)^{1/2}$ . In the case 3 limit we expect  $\mu_{12} < \alpha$ ; thus, the dominant term in parentheses in eq 19, and the principal correction to the undressed electronic coupling element, should be  $\Delta E_{12}(\epsilon/\alpha)$ . When this term grows large relative to  $H_{\text{GS,CT}}^{\text{bare}}$  (consistent with eq 13 no longer being satisfied, given the definitions of  $H_{\text{GS,CT}}^{\text{bare}}$  and  $\epsilon$ ), a significant correction to the electronic coupling element is expected by inclusion of the third adiabatic state, and in the case 3 limit the corrected coupling element is given to a good approximation by eq 19. Generalizations of the effective 2-state result to treat more than three interacting adiabatic states are presented and tested in the following section.

## Results

In this section we apply the above diagnostic and effective 2-state approximation to (a) a model system involving electron transfer between ethylene and methaniminium (MI) cation, (b) charge-shift reactions (CSH) in a pair of substituted acridiniums that have been studied by Jones et al.,<sup>39,40</sup> and (c) calculation of the electronic coupling element in twisted (dimethylamino)-benzotrile (DMABN). Due to the simplicity of the ethylene + methaniminium system we examine various features of the diagnostic and 2-state approximation in detail.

**(a) Ethylene and Methaniminium Cation.** This system represents a simple, computationally tractable model for the study of charge shift transitions.<sup>39,40</sup> Our main interest in this study was not to obtain chemical accuracy for excitation energies and properties; rather, our purpose was to generate a manifold of states in which to apply the above diagnostic and effective 2-state approach. Thus, the small basis and simplified method for excited states do not represent a limitation, given their intended use.

In the calculations presented below the following geometry was adopted: (a) Ethylene and MI were coplanar, with the N-end of MI nearest ethylene and the N–C and C–C bonds collinear (we take this line to be the  $z$  axis in the system). (b) The ethylene geometry was the experimental ground-state geometry of Allen et al.<sup>41</sup> (c) The MI geometry<sup>42</sup> was obtained from an optimization of MI in the 6-31G\*\* basis<sup>43</sup> at the MP2 level of theory.<sup>44</sup> All calculations were performed using the Gaussian 98 program.<sup>45</sup> The nearest ethylene-C to MI-N distance was chosen to be 5 Å. The 6-31+G basis<sup>46</sup> was used for the excited-state calculations, which allows for some diffuse character in the excited states.

Excited states were obtained using the CIS method.<sup>47</sup> Excited-state dipole moments were calculated using the 1-particle density for the CIS wave function of interest.<sup>48</sup> In the results presented below, we consider at most four states (all singlet states), comprising the ground state and three  $\pi \rightarrow \pi^*$  states. The lowest excited state is the charge-transfer state ( $\pi(\text{eth}) \rightarrow \pi^*(\text{MI})$ ), with the next two states being locally excited states on ethylene (the second excited state being more valencelike, while the third excited state is more diffuse in character). We label the four states, in order of increasing energy, as GS, CT, LE1, and LE2 (locally excited states 1 and 2, respectively).

**TABLE 1: Excitation Energies and Dipole Moment Matrix for the Four States of Interest in Ethylene + Methaniminium<sup>a</sup>**

property	GS	CT	LE1	LE2
$\Delta E$ (eV) <sup>b</sup>		6.142	7.805	9.049
$\mu$ (D) <sup>c</sup>	13.922	0.213	-4.443	-1.408
		-18.238	-1.554	0.973
			12.206	5.135
				8.109

<sup>a</sup> Details concerning basis sets and wave functions are presented in the Results section. <sup>b</sup> Excitation energies relative to the GS, at the geometry discussed in the Results section. <sup>c</sup> The upper right triangle of the  $4 \times 4$  matrix of the  $z$  component of the dipole moment operator. The origin for property evaluation was between ethylene and methaniminium, along the line containing the C–C and N–C bond, 2.562 Å from the central ethylene C and 2.438 Å from the N of MI. While the choice of origin has no effect on dipole moment differences, it does affect the diagonal elements of the dipole moment matrix in a charged system.

**TABLE 2: Electronic Coupling Elements within the 3-State Space of GS, CT, and LE1 at Various Levels of Approximation<sup>a</sup>**

states	2-state GMH <sup>b</sup>	state/ $\lambda_D$ <sup>c</sup>	effective 2-state GMH <sup>d</sup>	3-state GMH <sup>e</sup>
GS, CT	0.0407	LE1/-1.065	-0.0019	-0.0026
LE1, CT	0.0844	GS/0.019	0.0845	0.0845

<sup>a</sup> All values of  $H_{\text{DA}}$  are in eV. <sup>b</sup> Equation 2. <sup>c</sup> Equation 13. <sup>d</sup> Equation 19. <sup>e</sup> Equation 5.

In Table 1 we present the matrix of the  $z$  component of the dipole moment operator (the only nonzero component, given the above geometry) over these four states and the excitation energies to the three excited states. The diagonal elements of the dipole moment matrix can be classified easily according to whether they are CT-like in character or LE-like: only the first excited state (labeled CT) exhibits a dipole moment markedly different from that of the ground state. This set of states falls within case 3, as discussed above. If one imagined that charge transfer corresponded to a single electron transferring from the bond midpoint of ethylene to the bond midpoint of MI, the dipole moment difference would be approximately 30 D ( $e\Delta R_{\text{DA}} = 4.803 \times 6.2\text{Å}$ ), so it is clear that the mixing is weak between the CT state and the GS or LE states. In terms of energetics, while the ground state is well-separated from the excited states, the three excited states fall within in a 3 eV range. Thus, neither on the basis of energy nor dipole moment differences can one easily determine whether significant mixing between diabatic states has occurred that might alter, for example, the GS–CT electronic coupling element. However, the above diagnostic and effective 2-state model allow one to answer this question.

We first consider the 3-state manifold of the GS, CT state, and the LE1 state, the GMH results for which are shown in Table 2. It is seen that the 2-state GMH results (based on eq 2) yield results in good agreement with the three-state result for the LE, CT pair but in poor agreement for the GS, CT pair. The diagnostic (eq 13) indicates that one should expect this, yielding a value of slightly less than 0.02 for the effects of the GS on the LE, CT coupling element, whereas the effect of the LE1 state on the GS, CT pair yields a diagnostic value near -1. The size and sign of the diagnostic for the effects of the LE1 state on the GS, CT coupling element suggest that inclusion of the effects of the LE1 state on the GS, CT pair will significantly reduce the GS, CT coupling element, and that is observed in the full 3-state GMH calculation. On the other hand the small value of the diagnostic for the GS effects on the LE1,

**TABLE 3: Electronic Coupling Elements within the 3-State Space of CT, LE1, and LE2 at Various Levels of Approximation<sup>a</sup>**

states	2-state GMH <sup>b</sup>	state/ $\lambda_D$ <sup>c</sup>	effective 2-state GMH <sup>d</sup>	3-state GMH <sup>e</sup>
LE1, CT	0.0844	LE2/0.122	0.0972	0.0980
LE2, CT	-0.1070	LE1/0.269	-0.1389	-0.1388

<sup>a</sup> All values of  $H_{DA}$  are in eV. <sup>b</sup> Equation 2. <sup>c</sup> Equation 13. <sup>d</sup> Equation 19. <sup>e</sup> Equation 5.

CT coupling element suggests that the 2-state and 3-state GMH results should be quite similar, as they are. It is also seen that the use of the effective 2-state model (eq 19) yields quite good agreement with the full 3-state values.

The physical reasons for this behavior are reasonably easy to understand. Because of the nearness in energy of the LE1 and CT diabatic states, one expects a nonzero contribution of each to the adiabatic CT state. Since there is a large transition dipole moment connecting the diabatic LE1 state and GS, mixing of LE1 into the CT adiabatic state will tend to artificially raise the transition dipole moment connecting the CT-like and GS-like adiabatic states, relative to that arising from mixing of the GS and CT diabatic states (which arises from Mulliken–Hush charge-transfer effects). This mixing of the LE1 state into the CT-like adiabatic state is the same behavior that gives rise to intensity borrowing in fluorescence spectra and has been discussed and utilized by Gould et al. in their treatment of contact ion pairs.<sup>34</sup> In terms of the dipole matrix elements in Table 1, the large dressing arises from the product of  $\mu_{GS,LE1}\mu_{LE1,CT}$  in the numerator of the dressing term, and this turns out to be sufficiently large to yield a correction comparable in magnitude to the direct GS, CT adiabatic transition dipole moment. On the other hand, the GS effects on the LE1, CT coupling element are much smaller, due to the greater energy difference between the GS and CT diabatic states and the somewhat smaller spatial extent of the GS relative to the LE state, leading to the MH-like contribution being the dominant term in this case. In terms of the dipole moment matrix elements, in this case the numerator of the dressing term is  $\mu_{LE1,GS}\mu_{GS,CT}$  and this product is significantly smaller than the comparable term for LE1 effects on the GS, CT pair.

A similar analysis can be done on the CT, LE1, and LE2 states, and the results are shown in Table 3. The pairwise 2-state GMH results are in reasonable agreement with the full 3-state results, as one would expect on the basis of the diagnostic values, suggesting not much more than a 25% change in the CT, LE2 coupling upon dressing by the interaction with LE1. Again, the dressed 2-state coupling elements (eq 19) are in excellent agreement with the results from the full 3-state treatment.

Equation 19 contains three first-order correction terms to the “bare”  $H_{DA}$ . In practice we have found that, for systems satisfying the criteria sufficient to demand utilization of eq 19, it is usually the first correction term that makes a significant contribution. This is illustrated in Table 4, using the GS, CT, and LE1 states, as in Table 2. Thus, in Table 4 we present the “bare”  $H_{DA}$  and the values of the three successive terms, followed by the complete effective 2-state value of the coupling

element. In the case of the GS, CT coupling element, it is seen that only the first correction term in eq 19 ( $\Delta E_{12}(\epsilon/\alpha)$ ) makes any significant contribution to the overall coupling element. The first term arises from the effects of dressing on the transition dipole moment, rather than on the diagonal dipole matrix elements (third correction term), and for modest mixing of the diabatic states should be significantly larger than the second correction term. In the LE1, CT case, it is seen that the first correction term is itself quite small and thus of comparable size to the third term (the third term is only of this size due to the relatively large transition dipole moment connecting the LE1 and CT states, thus ensuring that the correction is small relative to the bare coupling element for well-separated donor and acceptor centers).

As an example that considers multistate interactions beyond the 3-state case, we consider the full 4-state manifold of Table 1. In Table 5 we present the analogous diagnostic for the effects of the two extra states on the  $ij$  coupling element (i.e. the ratio of  $\mu_{i,n-2}(\mu_{jI} - \mu_{n-2,n-2})^{-1}\mu_{n-2,j}$  to  $\mu_{ij}$ , where  $j = CT$  in each case). By comparison with the diagnostic results of Tables 2 and 3, where the effects of only one additional state were considered, it is seen that the addition of the fourth state yields only a modest change relative to the *larger* of the diagnostics for the given pair of states from Tables 2 and 3. To confirm this, in Table 6 we present the results for the electronic coupling elements on the basis of the full 4-state manifold of Table 1 using the locally adiabatic GMH in the 4-state space (denoted full 4-state GMH) and a variety of approximate treatments (see below). The full 4-state results are not markedly different from the full 3-state results of Tables 2 and 3, except perhaps for the GS, CT coupling element, which is of the same magnitude as obtained in Table 2 but has changed sign. (While the relative signs of the coupling elements are not observables for this system, the present analysis shows there are destructive interference effects contributing to this coupling element, hence the indication of a sign change in this case.)

In the spirit of eq 19, for the 3-state case, we tested several approximate 4-state treatments. In all of the equations below the subscripts  $i$  and  $j$  refer to adiabatic quantities. In order of complexity they are the following:

(i) The “effective 2-state GMH/diagonal” result is first. In this case we calculate  $\mu_{ij}^{\text{dressed}}$  using only the inverse of the matrix formed from the diagonal elements of the matrix  $(\mu_{jI} - \mu_{n-2,n-2})$ . That is we take  $\mu_{ij}^{\text{dressed}} = \mu_{ij} + \mu_{i,n-2}(\mu_{jI} - \mu_{n-2,n-2})_{\text{diag}}^{-1}\mu_{n-2,j}$ . Furthermore, we neglect any effects of the additional states on the denominator of the 2-state GMH result, leading to an estimate of the 2-state element as

$$(H_{ij}^{\text{dressed}})_{\text{diag}} = \frac{\mu_{ij}^{\text{dressed}} \Delta E_{ij}}{(\Delta \mu_{ij}^2 + 4\mu_{ij}^2)^{1/2}}$$

(ii) The “cumulative 2-state GMH result” is next, where one performs two separate effective 2-state calculations on the basis of 3-state spaces (using eq 19) and adds the corrections for two distinct additional states, yielding an overall estimate of the dressed coupling element. This approach includes the effects

**TABLE 4: Comparison of Contributions to the Effective 2-State Coupling Elements<sup>a</sup>**

states ( $i, j$ )	$H_{ij}^{\text{bare}}$	$\Delta E_{ij}(\epsilon/\alpha)$	$-\Delta E_{ij}(4\mu_{ij}^2\epsilon/\alpha^3)$	$-\Delta E_{ij}(\mu_{ij}(\mu_{II} - \mu_{jj})\delta/\alpha^3)$	$H_{ij}^{\text{dressed}}$
GS, CT	0.040 68	-0.043 31	0.000 007 6	0.000 720	0.0019
LE1, CT	0.084 40	0.001 60	0.000 016 5	0.001 680	0.0845

<sup>a</sup> Results for the same data used in Table 2. All values in eV. In this table, the subscripts  $i$  and  $j$  correspond to the diabatic states of interest, while the subscripts  $I$  and  $J$  denote the adiabatic states that correlate with the pair of diabatic states.

**TABLE 5: Diagnostic for Multistate Effects on the Electronic Coupling Element in the 4-State Manifold of Table 1**

interacting states	additional states/ $\lambda_D^a$
GS, CT	LE1, LE2/ $-0.919$
LE1, CT	GS, LE2/ $0.109$
LE2, CT	GS, LE1/ $0.269$

<sup>a</sup> Diagnostic based on eq 4.

of the effective 2-state GMH/diagonal approach and also approximately includes effects due to modification of the denominator terms.

(iii) The “effective 2-state GMH” approach is the most complex. In this case we calculate  $\mu_{ij}^{\text{dressed}}$  using the inverse of the full matrix  $(\mu_j I - \mu_{n-2,n-2})$ . That is, we take  $\mu_{ij}^{\text{dressed}} = \mu_{ij} + \mu_{i,n-2}(\mu_j I - \mu_{n-2,n-2})^{-1}\mu_{n-2,j}$ . As in the diagonal approach, we neglect any effects of the additional states on the denominator of the 2-state GMH result, leading to an estimate of the 2-state element as

$$(H_{ij}^{\text{dressed}})_{\text{diag}} = \frac{\mu_{ij}^{\text{dressed}} \Delta E_{ij}}{(\Delta \mu_{ij}^2 + 4\mu_{ij}^2)^{1/2}}$$

On the basis of the results presented in Table 6, it is seen that all three methods are of similar accuracy in reproducing the full 4-state GMH results. The effective 2-state GMH method is slightly better at approximating the GS, CT coupling element, because the use of the full inverse matrix allows for more complete treatment of interference effects between the contributions of the two external states. However, any one of the three approximations yields quite adequate estimates of the full 4-state GMH results, and any one would be a reasonable indicator of the size of the electronic coupling element. Once one proceeds beyond the 4-state case, it is likely that only the effective 2-state GMH/diagonal or the cumulative 2-state GMH approaches are easily applied, but in the event that more than 2 external states are considered important, it is probably better to apply the  $n$ -state locally adiabatic GMH treatment, which will properly treat any interference effects that might arise.

Equation 19 above is similar to results obtained in work of Gould et al.,<sup>34</sup> Bixon et al.,<sup>33</sup> and Herbich and Kapturkiewicz.<sup>35</sup> In these studies the authors were interested in understanding the solvent and substituent dependence of the radiative rates of a CT transition in terms of intensity borrowing by the CT state from a nearby LE state. Thus the fundamental quantity of interest is the adiabatic GS–CT transition dipole moment in their studies. Using Mulliken–Hush-like arguments they express this transition dipole moment in terms of contributions from the LE and CT states. Their results for the relation between the adiabatic GS–CT transition dipole moment and a given electronic coupling element can be related to eq 19 above.<sup>49</sup> By fits of the radiative rates vs emission wavelength (with input concerning the LE intensity) these studies were able to extract one or more of the relevant electronic coupling elements for the systems of interest, as well as provide a quantitative explanation for the variation in radiative rates with solvent or substitution.

**TABLE 6: Electronic Coupling Elements within the 4-State Space of GS, CT, LE1, and LE2 at Various Levels of Approximation<sup>a</sup>**

states	2-state GMH <sup>b</sup>	effective 2-state GMH/diagonal <sup>c</sup>	effective 2-state GMH <sup>c</sup>	cumulative 2-state GMH <sup>c</sup>	4-state GMH <sup>d</sup>
GS, CT	0.0407	0.0073	0.0033	0.0081	0.0037
LE1, CT	0.0844	0.0931	0.0936	0.0974	0.0978
LE2, CT	$-0.1070$	$-0.1369$	$-0.1359$	$-0.1402$	$-0.1388$

<sup>a</sup> Results based on data of Table 1; all values in eV. <sup>b</sup> Equation 2. <sup>c</sup> See Results for definitions. <sup>d</sup> Equation 5.

A difference between these approaches and our treatment arises because in all of these previous studies specific variation of system parameters was required to extract the couplings, and the presence of multistate effects was already apparent, based on the radiative rate behavior. On the other hand, using the GMH one can compute the electronic coupling for the states of interest at a fixed set of nuclear coordinates and determine, at that point, whether additional states are important in determining the coupling (i.e. using eq 13). The ability to do so without variation of system energy parameters is provided, within the context of the GMH, by the CT–LE state transition dipoles (see above). Thus, while our perturbative expression relating the adiabatic transition dipole moment to the 2-state electronic coupling element is formally similar to these previous studies (as it must be, given the fact that the observed effects are all rooted in an intensity borrowing mechanism), our method of obtaining the relation from energetic quantities is distinct from that of previous results and allows us to develop the diagnostic for the importance of multistate effects. The two methods are in fact, quite complementary, since from an experimental point of view it may be significantly easier to study the variation of intensity with solvent than to extract transition dipole moments involving excited states, as is required in the GMH method outlined above. Computationally, however, such transition dipole information is readily available, and the present results not only provide a means for detecting the need for a multistate treatment but also yield an accurate method for the correction of a 2-state result when such effects are important.

However, one can use the ideas developed in the work of Gould et al.<sup>34</sup> and Bixon et al.<sup>33</sup> to consider ways to minimize the multistate effects in the present system or related systems. If the multistate effects arise from weak mixing of the LE1 and CT states, due to near-degeneracy, a perturbation that shifts the states further out of resonance should decrease these effects. In fact, if they are moved sufficiently out of resonance, one should move to a situation where only a 2-state treatment is required. We have performed a test of this hypothesis by adding external charges, with values  $+2e$  at  $10 \text{ \AA}$  from the C of MI and  $-2e$  at  $10 \text{ \AA}$  from the outer C on ethylene. By so doing, we can stabilize the CT state relative to the ground state and expect that the excitation energies from the GS to the LE states should be minimally affected. In these calculations we also modified the basis set to be the 6-31G\* basis, since in the 6-31+G basis the LE1 state polarizes dramatically with charges present. The relative energies and dipole moments, with and without charges present, are shown in Table 7. The addition of the external charges has a large effect on the energy of the CT state, dropping it relative to the GS by almost 1.7 eV. The values of the dipole and transition dipole moments with and without charges present are quite similar, with the exception of the CT–LE transition dipole moment, which, by eq 13, suggests a diminution of the effects of the LE state on the GS–CT coupling element. The results of Table 8 support this idea, showing that while the GS–CT 3-state coupling elements are the same with and without charges, it is only in the charged case, where the CT and LE states are relatively far apart in energy, that the 2-state result is

**TABLE 7: Energies and Dipole Moments for Ethylene and Methaniminium at 5 Å, in the 6-31G\* Basis, with and without External Charges<sup>a</sup>**

charges	property	GS	CT	LE1
no	$\Delta E$ (eV) <sup>b</sup>		6.454	8.540
	$\mu$ (D) <sup>c</sup>	13.9241	0.015	-4.574
			-17.9159	-0.042
yes				14.2200
	$\Delta E$ (eV) <sup>b</sup>		4.4581	8.556
	$\mu$ (D) <sup>c</sup>	12.9798	0.016	-4.575
			-18.625	-0.022
				13.552

<sup>a</sup> Details concerning basis sets, wave functions, and charges are presented in the Results. <sup>b</sup> Excitation energies relative to the GS, at the geometry discussed in the Results. <sup>c</sup> See Table 1 for details.

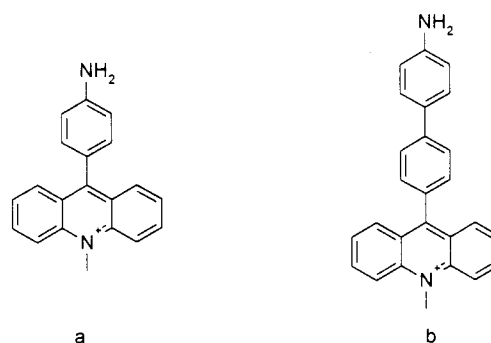
**TABLE 8: Comparison of 2-State and 3-State Results for Ethylene and Methaniminium Cation with and without External Charges<sup>a</sup>**

charges <sup>b</sup>	states	2-state GMH <sup>c</sup>	state/ $\lambda_D$ <sup>d</sup>	effective 2-state GMH <sup>e</sup>	3-state GMH <sup>f</sup>
no	GS, CT	0.0030	LE1/-0.40	0.0019	0.0019
no	LE1, CT	0.0027	GS/-0.05	0.0026	0.0026
yes	GS, CT	0.0023	LE1/-0.2	0.0019	0.0019
yes	LE1, CT	0.0028	GS/-0.1	0.0026	0.0026

<sup>a</sup> Results obtained in 6-31G\* basis set. Geometry identical to that used in results of Table 1. <sup>b</sup> Indicates whether external charges were included. <sup>c</sup> Equation 2. <sup>d</sup> Equation 13. <sup>e</sup> Equation 19. <sup>f</sup> Equation 5.

a good approximation to the full 3-state result. It is also important to note that the 3-state GS-CT coupling element is in reasonable agreement with that obtained from the 4-state results in the 6-31+G basis at this geometry (Table 6). This might be expected, given that the GS and CT state are valencelike and, thus, their descriptions will be only slightly modified by the presence or absence of diffuse functions. However, the 2-state GS-CT coupling elements are quite different in the two basis sets, and the similarity of the 3-state results points to the ability of the GMH approach to properly account for (and remove) multistate effects when properly applied. In the event that one wishes to avoid treatments using greater than two states, the results of Table 8 show that external perturbations can be used to separate the pair of states of interest from the remaining states and then perform a 2-state GMH treatment. Of course, the need to achieve exact resonance (or minimization of the energy splitting) is not required, since the external perturbation is only applied to remove *other* states from consideration, while the electronic coupling is calculated using the GMH method.

**(b) Substituted Acridiniums.** Two donor-acceptor 9-aryl-acridinium ions are considered here, Apac (9-(aminophenyl)-10-methylacridinium) and Abpac (9-(aminobiphenyl)-10-methylacridinium) (see Figure 1; each carries a charge of +1). Compounds of this type have been studied because, upon photexcitation, they exhibit a very fast transition from a locally excited acridinium to a charge-shift species (CSH) and solvent-dependent rates for charge recombination.<sup>39,40</sup> Equilibrium geometries were obtained using RHF wave functions in the 3-21G basis (see Supporting Information for geometries). In the equilibrium geometries for Apac the angle between the acridinium and phenyl rings is nearly 90°, leading to quite small electronic coupling elements. We have thus performed a rigid rotation about this bond (to an angle of approximately 55°) for the calculations in Tables 9 and 10. For Abpac the optimized acridinium-phenyl dihedral angle is approximately 76°, and we have thus used the equilibrium geometry in our calculations.

**Figure 1.** Apac (a) and Abpac (b).**TABLE 9: Energies and Dipole Moments for Apac, Based on INDO/S SCI Calculations<sup>a</sup>**

property	GS	CT	LE1
$\Delta E$ (eV) <sup>b</sup>		2.654	3.447
$\mu$ (D) <sup>c</sup>	0.00	5.547	2.495
		14.936	-5.300
			-0.553

<sup>a</sup> Details concerning geometry and method are presented in the Results. <sup>b</sup> Excitation energies relative to the GS, at the geometry discussed in the Results. <sup>c</sup> The upper right triangle of the  $3 \times 3$  matrix of the dipole moment matrix, projected on the average charge-transfer direction.<sup>25</sup> Diagonal elements are all relative to the ground-state dipole moment.

**TABLE 10: Electronic Coupling Elements for Apac within the 3-State Space of GS, CT, and LE1, Based on INDO/S SCI Calculations at Various Levels of Approximation<sup>a</sup>**

states	2-state GMH <sup>b</sup>	state/ $\lambda_D$ <sup>c</sup>	effective 2-state GMH <sup>d</sup>	3-state GMH <sup>e</sup>
GS, CT	0.791	LE1/-0.154	0.664	0.673
LE1, CT	0.224	GS/-0.175	0.181	0.191

<sup>a</sup> All values of  $H_{DA}$  are in eV. <sup>b</sup> Equation 2. <sup>c</sup> Equation 13. <sup>d</sup> Equation 19. <sup>e</sup> Equation 5.

**TABLE 11: Energies and Dipole Moments for Abpac, Based on INDO/S SCI Calculations<sup>a</sup>**

property	GS	CT	LE1
$\Delta E$ (eV) <sup>b</sup>		2.572	3.415
$\mu$ (D) <sup>c</sup>	0.00	-2.885	-3.993
		26.703	-5.346
			0.391

<sup>a</sup> Details concerning geometry and method are presented in the Results. <sup>b</sup> Excitation energies relative to the GS, at the geometry discussed in the Results. <sup>c</sup> The upper right triangle of the  $3 \times 3$  matrix of the dipole moment matrix, projected on the average charge-transfer direction.<sup>25</sup> Diagonal elements are all relative to the ground-state dipole moment.

Excited-state energies and dipole moments were obtained using the INDO/S SCI method of Zerner et al.<sup>50</sup> For Apac we included single excitations from the highest 31 occupied MOs into the lowest 31 virtual MOs, and for Abpac we included single excitations from the highest 35 occupied MOs into the lowest 28 virtual MOs. The three lowest singlet states of the system, in order of increasing energy, are GS, CSH, and LE1 (the state characters are easily deduced from the respective adiabatic dipole moments).

In Tables 9 and 11 we present excitation energies and the projected dipole moment matrix for Apac and Abpac, respectively, for the three states of interest. The electronic coupling elements based on these data are presented in Tables 10 and 12 (Apac and Abpac, respectively), and in each system the diagnostic predicts a modest change in either coupling element



**TABLE 12: Electronic Coupling Elements for Abpac within the 3-State Space of GS, CT, and LE1, Based on INDO/S SCI Calculations at Various Levels of Approximation<sup>a</sup>**

states	2-state GMH <sup>b</sup>	state/ $\lambda_D$ <sup>c</sup>	effective 2-state GMH <sup>d</sup>	3-state GMH <sup>e</sup>
GS, CT	0.269	LE1/−0.284	0.191	0.193
LE1, CT	0.159	GS/−0.080	0.149	0.150

<sup>a</sup> All values of  $H_{DA}$  are in eV. <sup>b</sup> Equation 2. <sup>c</sup> Equation 13. <sup>d</sup> Equation 19. <sup>e</sup> Equation 5.

due to the addition of the third state. This is shown to be the case in comparing the 2- and 3-state GMH results. It is also seen that the effective 2-state GMH result is in fairly good agreement with the full 3-state results.

(c) **(Dimethylamino)benzotrile.** (Dimethylamino)benzotrile has been extensively studied as a molecule that exhibits twisted intramolecular charge-transfer behavior.<sup>51–53</sup> In polar solvent dual fluorescence is observed,<sup>51,52</sup> and a variety of theoretical studies have appeared seeking to characterize the low-lying excited states of the system.<sup>52,53</sup> The states that have generally been considered in previous studies are the GS, a locally excited state (designated 1B), and the charge-transfer state (designated 2A, having the same symmetry as the GS). The geometry we consider possesses no symmetry, but we still retain the symmetry labels from  $C_2$  symmetry, to indicate the parentage of the state. In the calculations below we treat these states and a fourth state (designated 3A). An interesting feature of this model, compared to the other models considered above, is that the CT distance is relatively small, while the transition dipole moments are sizable. As a result, we find that the effective 2-state GMH results are somewhat less accurate, and the diagnostic tends to overestimate the size of the effects of mixing. However, this is a somewhat extreme case (CT distances on the order of only 2.5 Å), and it will be seen that the results are still semiquantitative.

An equilibrium geometry for the molecule was obtained from an AM1 calculation<sup>54</sup> (the dimethylamino group shows modest nonplanarity with the ring, as has been observed previously<sup>53</sup>). A rigid rotation of 75° was performed about the phenyl–amino group bond, and it is this geometry (see Supporting Information) for which results are presented below. Only close to a twist angle of 90° can the CT diabatic state be considered weakly interacting with the other diabatic states considered here. We have chosen the 75° twist geometry as an intermediate point, where sizable coupling elements are observed along with significant state mixing. Since our interest in the present case is to use DMABN as a model for testing the above diagnostic and effective 2-state model in a strongly interacting system, we have not performed exhaustive calculations as a function of geometry. However, some smaller angles have been treated (i.e. closer to the ground-state equilibrium geometry) and aside from points where two states nearly cross (where adiabatic dipole moment differences become small) results similar to those discussed below were obtained.

Excitation energies and dipole moment matrix elements were obtained from INDO/S SCI calculations using all virtual orbitals and the 11 highest occupied MOs. The results of these calculations are shown in Table 13. The diagonal dipole moment differences are seen to be at most about 10 D and, thus, of magnitude similar to the largest of the transition dipole moments. Our results for dipole moment differences and excitation energies are similar to those obtained in other studies of gas-phase DMABN,<sup>52,53</sup> except that our 2A state is approximately 0.3 eV higher in energy. Exploratory studies using 2-state models for DMABN suggest that the coupling elements are not

**TABLE 13: Energies and Dipole Moments for DMABN, Based on INDO/S SCI Calculations<sup>a</sup>**

property	GS	2A	1B	3A
$\Delta E$ (eV) <sup>b</sup>		4.250	4.397	5.016
$\mu$ (D) <sup>c</sup>	5.372	−2.276	−0.342	4.023
		15.213	1.130	2.263
			6.008	0.1185
				7.321

<sup>a</sup> Details concerning geometry and method are presented in the Results. <sup>b</sup> Excitation energies relative to the GS, at the geometry discussed in the Results. <sup>c</sup> The upper right triangle of the  $4 \times 4$  matrix of the z component of the dipole moment operator, projected on the average charge-transfer direction.<sup>25</sup>

**TABLE 14: Electronic Coupling Elements for DMABN within 3-State Spaces Selected from the Manifold of GS, 2A, 1B, and 3A, Based on INDO/S SCI Calculations<sup>a</sup>**

pair of states	2-state GMH <sup>b</sup>	state/ $\lambda_D$ <sup>c</sup>	effective 2-state GMH <sup>d</sup>	3-state GMH <sup>e</sup>
GS, 2A, 1B	GS, 2A 0.892	1B/0.018	0.896	0.890
	2A, 1B 0.0176	GS/0.070	0.0178	0.0182
GS, 2A, 3A	GS, 2A 0.892	3A/−0.507	0.624	0.577
	2A, 3A 0.191	GS/−0.411	0.152	0.146
2A, 1B, 3A	2A, 1B 0.0176	3A/0.030	0.0169	0.0179
	2A, 3A 0.191	1B/0.006	0.189	0.187

<sup>a</sup> All values of  $H_{DA}$  are in eV. <sup>b</sup> Equation 2. <sup>c</sup> Equation 13. <sup>d</sup> Equation 19. <sup>e</sup> Equation 5.

**TABLE 15: Electronic Coupling Elements within the 4-State Space of GS, 2A, 1B, and 3A for DMABN at Various Levels of Approximation<sup>a</sup>**

states	2-state GMH <sup>b</sup>	cumulative 2-state GMH <sup>c</sup>	4-state GMH <sup>d</sup>
GS, 2A	0.892	0.629	0.530
2A, 1B	0.0176	0.0171	0.0179
2A, 3A	0.191	0.150	0.142

<sup>a</sup> Results based on data of Table 13; all values in eV. <sup>b</sup> Equation 2. <sup>c</sup> See Results for definitions. <sup>d</sup> Equation 5.

strongly sensitive (within a factor of 2 or better) to theoretical methods near this geometry.<sup>55</sup>

The results of 2-state, effective 2-state, and 3-state GMH calculations picking the CT state and any pair of non-CT states are presented in Table 14. Using the diagnostic developed above, the 1B state is predicted to have little effect on the electronic coupling elements involving the 2A and GS/3A states, and this is indeed the case. The diagnostic does predict a significant effect of the GS on the 2A–3A coupling and the 3A state on the 2A–GS coupling, and this is observed in the full 3-state calculations. The effective 2-state results compare reasonably well with the 3-state results, but the agreement is not as good as in the results presented above for the other model systems. Using these effective 2-state results we have also calculated cumulative 2-state results to approximate the full 4-state GMH results (Table 15). The cumulative 2-state results, while not in exact agreement with the full 4-state results, nevertheless capture the essence of the effects of the additional states.

DMABN represents a relatively extreme test case for the diagnostic and the effective 2-state result due to the proximity of the donor and acceptor sites, coupled with their strong interaction. As a result, there are several factors responsible for the somewhat greater inaccuracy of the effective 2-state results for DMABN than the other model systems studied here. First, with the relatively small adiabatic dipole moment differences and large transition dipole moments in DMABN, somewhat larger errors are made by assuming  $\mu_{CT} = \mu_{22}$ . This error manifests itself in the definition of  $\epsilon$  and  $\delta$  in eq 19 and will tend to exaggerate their contributions. In addition, in DMABN

at this geometry the corrections due to  $\epsilon$  and  $\delta$  are of opposite sign. This leads to the diagnostic tending to overestimate the effects of an additional state and larger errors in the effective 2-state GMH method when the errors in the  $\epsilon$  and  $\delta$  are not equal.<sup>56</sup> Our experience has been that, for greater CT distances, the contribution from the  $\delta$  term decreases significantly, and thus, there is only a single dominant correction coming from the first  $\epsilon$  term. Generally one will deal with somewhat larger CT distances than in the DMABN case (donor and acceptor separated by at least a single atom), and under these conditions the diagnostic and the effective 2-state method are expected to perform quite well.

## Conclusions

The results above show that significant multistate effects can arise in estimating the electronic coupling element using the GMH approach. These effects are in fact similar to those discussed by a number of other workers in their studies of 3-state systems, where they varied the relative energies of the diabatic states (using solvent) to extract individual coupling elements. The physical basis for these effects is similar to that which gives rise to intensity borrowing in fluorescence spectra. The diagnostic developed above allows one to assess when these multistate effects will be important, even for cases where the states are well-localized. Furthermore, in the limit of localized initial and final states, we have developed an effective 2-state approximation to the full  $n$ -state GMH result that is quite accurate and simple to apply. The diagnostic and effective 2-state results were applied to several model system and generally yielded excellent results both for the determination of when multistate effects are important and for the estimation of the full  $n$ -state coupling element.

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**Supporting Information Available:** Equilibrium geometries obtained using RHF wavefunctions in the 3-21 G basis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The simple diagnostic (eq 13) is based on two approximations, the first being that  $\mu_{CT}^{diab} \approx \mu_{22}$ . Making this approximation will tend to overestimate the multistate effects (see the results for DMABN), but where there is a significant error caused by making the assumption, it is already a sign of strong mixing between diabatic states in the adiabatic states. If this strong mixing involves state 3, the overestimation nevertheless points to the need to consider state 3 in the accurate calculation of the electronic coupling, and the diagnostic has worked properly. On the other hand, if state 3 is not involved in the strong mixing, then the denominator in eq 13 will still be relatively large for long-range et (since we have assumed that 3 being unmixed, will have a dipole moment comparable to that of the LE diabatic state). Our second approximation was to assume  $\mu_{11} - \mu_{22} \gg \mu_{13\mu 31}/(\mu_{22} - \mu_{33})$ , leading to eq 11. This approximation is made to obtain a more compact expression for the diagnostic. It could be relaxed but generally need not be. Except where the mixing between the GS and CT state is large, or the CT distance is quite short, this approximation will be valid.
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(48) From the point of view of application of the GMH approach this is the appropriate dipole moment to use, since it is the field-free mixing of the diabatic states that one transforms away in the diagonalization of the dipole moment matrix.

(49) Modest differences arise due to our (a) use of the GMH rather than MH result for the dipole difference, (b) allowance for differences in dipole moments between the GS and LE state, and (c) use of energetic quantities obtained from a single nuclear configuration.

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(56) In an extreme example, at a twist angle of  $60^\circ$  considering the GS, 2A, and 1B states, the following results are obtained (adiabatic):  $E(2A) = 4.28$  eV;  $E(1B) = 4.32$  eV;  $\mu(\text{GS}) = 5.48$  D;  $\mu(2A) = 12.30$  D;  $\mu(1B) = 8.16$  D. We obtain  $(H_{\text{GS},2A})^{3\text{-state}} = 1.49$  eV,  $(H_{\text{GS},2A})^{2\text{-state}} = 1.55$  eV,  $(H_{\text{GS},2A})^{\text{effective } 2\text{-state}} = 1.67$  eV,  $\lambda_{\text{D}}(1B) = 0.32$ ,  $(H_{2A,1B})^{3\text{-state}} = 0.0162$  eV,  $(H_{2A,1B})^{2\text{-state}} = 0.0151$  eV,  $(H_{2A,1B})^{\text{effective } 2\text{-state}} = 0.0150$  eV, and  $\lambda_{\text{D}}(2A) = 0.33$ . Note that  $\lambda_{\text{D}}$  in each case predicts a 30% change (indicative of a large correction to the numerator in eq 19, while the second  $\epsilon$  term and the  $\delta$  term in eq 19 are indicative of significant changes in diagonal dipole moments upon addition of a third state); nevertheless, the 2-state and 3-state coupling elements are quite similar. However, this equivalence arises from a cancellation of the contributions from the  $\epsilon$  and  $\delta$  terms in the actual 3-state results, which only partially cancel in the first-order treatment (eq 19). Thus, while there is significant state mixing, the net result is a small change in the coupling.