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On Generalized Mulliken−Hush Approach of Electronic Transfer: Inclusion of Non-Zero Off-Diagonal Diabatic Dipole Moment

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A general formula for the adiabatic-to-diabatic mixing angle in terms of the electronic dipole moments is derived within a two-state model. It expresses the electronic coupling determining the rate of electronic transfer in terms of the off-diagonal diabatic dipole moment.

1. Introduction

The electronic coupling between the initial and final diabatic states is the major factor that determines the rate of electron transfer.[1,2] Within the Golden Rule approximation, the electronic transfer rate is proportional to the square of the electronic coupling.[2c] It is therefore expedient to develop such approaches which can provide reasonable estimations of the electronic coupling. One of these approaches was developed by Newton and co-workers[1] who named it the generalized Mulliken−Hush method.[3] This approach[1c,d] uses the expression for the mixing angle of the transformation from the adiabatic states diagonalizing the electronic Hamiltonian to the diabatic ones[4] in terms of the adiabatic dipole moment derived by Macías and Riera,[3a] and Werner and Meyer[5b] under the assumption that the diabatic states are so well localized that the corresponding off-diagonal diabatic dipole moment is equal to zero. These are in particular the charge-localized donor and acceptor states, which are widely used in modeling the electron coupling[1,2] and which can be viewed as a good approximation of "most" diabatic states.[4b] On the other hand, to calculate the electronic coupling, Cave and Newton[1c,d] used the block diagonalization procedure developed by Cederbaum et al.[6] for determining diabatic states. Such procedure is rather suitable for introducing chemically reasonable diabatic states and naturally defines an off-diagonal dipole moment whose magnitude can then be thoroughly examined.

Polarizable solvent may significantly influence the electronic coupling.[1,2,7a−e] This influence is controlled in particular by the off-diagonal dipole moment gained by the solute in terms of its vacuum diabatic states.[7d] In the case when such an off-diagonal diabatic dipole moment is small enough, the standard perturbation technique can be applied to estimate its effect on the electronic coupling. It has been recently pointed out by Matyushov and Ladanyi[7d] that, despite the smallness of this off-diagonal dipole moment compared to the diagonal ones, its contribution to the electronic transfer matrix elements can nevertheless reach the same order of the magnitude as that of diagonal moments. Also, in the case of weak donor−acceptor complexes, the off-diagonal dipole moment can be rather large so as to donate a considerable intensity to the charge-transfer band.[3b] The authors[7d] also emphasized the importance of the inverse problem in the study of the electronic transfer, namely, the problem of determining diabatic parameters from the known adiabatic ones. Such a problem cannot be solved with the aforementioned formula for the mixing angle.[7f]

The aim of the present work is to obtain a general formula for the mixing angle in terms of the adiabatic dipole moments which is derived without the assumption of neglecting the off-diagonal dipole moment and which therefore will be also useful for perturbation estimations when this dipole moment is small enough. This is done in section 2. In section 3, we derive the expression for the diabatic Hamiltonian in terms of the off-diagonal dipole moment and summarize our results.

2. Adiabatic-to-Diabatic Mixing Angle vs Dipole Moments

Consider electronic Hamiltonian $H(\mathbf{r};\mathbf{R})$ with corresponding eigenfunctions $\Psi_k(\mathbf{r};\mathbf{R})$ and eigenvalues $E_k(\mathbf{R})$. $\Psi_k(\mathbf{r};\mathbf{R})$'s form the adiabatic basis set. $\mathbf{r}$ denotes the electronic variables whereas $\mathbf{R} = (\mathbf{R}_1, ..., \mathbf{R}_\alpha, ...)$ nuclear ones. Projecting $H(\mathbf{r};\mathbf{R})$ onto two-dimensional subspace generated, say, by $\Psi_1 \equiv \Psi_\mathrm{i}$ and $\Psi_2 \equiv \Psi_\mathrm{f}$ results in a 2 × 2 diagonal Hamiltonian matrix with the diagonal matrix elements $H_{kk} = E_k$, $k = \mathrm{i,f}$ (i is used for the initial, f for final states, respectively). Such projection procedure gives rise to a so called two-state problem that appears to be a rather useful tool[1−3,7] in estimating the electronic coupling. The latter one is defined as an off-diagonal element of $H(\mathbf{r};\mathbf{R})$ in the diabatic basis set formed by $\tilde{\Psi}_\mathrm{i}$ and $\tilde{\Psi}_\mathrm{f}$: $\tilde{H}_\mathrm{if} \equiv \langle\tilde{\Psi}_\mathrm{i}|H|\tilde{\Psi}_\mathrm{f}\rangle_\mathrm{r}$. Here, the integration is carried out over $\mathbf{r}$ only. Within the two-state problem, the diabatic states are obtained by rotating the adiabatic ones via a certain orthogonal transformation,

$$\begin{pmatrix}\tilde{\Psi}_\mathrm{i}\\ \tilde{\Psi}_\mathrm{f}\end{pmatrix} = \begin{pmatrix}\cos\phi & -\sin\phi\\ \sin\phi & \cos\phi\end{pmatrix}\begin{pmatrix}\Psi_\mathrm{i}\\ \Psi_\mathrm{f}\end{pmatrix} \tag{1}$$

ϕ is the adiabatic-to-diabatic mixing angle. It is determined by the nonadiabatic derivative coupling $\mathbf{f}_\mathrm{if}^{(\alpha)} = \langle\Psi_\mathrm{i}|\nabla_{\mathbf{R}_\alpha}\Psi_\mathrm{f}\rangle_\mathbf{r}$ via the equation[4]

$$\nabla_{\mathbf{R}_\alpha}\phi = \mathbf{f}_\mathrm{if}^{(\alpha)} \tag{2}$$

Equation 2 implies that the nonadiabatic derivative coupling $\tilde{\mathbf{f}}_\mathrm{if}^{(\alpha)}$ in the diabatic basis completely vanishes. This is actually the definition of a diabatic or strictly diabatic basis.[4]

We now consider the adiabatic electronic dipole moment $\mathbf{m}_{kl} = \langle\Psi_k|\mathbf{r}|\Psi_l\rangle_\mathrm{r}$. Following Newton et al.,[1b−e] their components are dealt with in a common (mean) direction. Defining m_{kl} as the projection of $\mathbf{m}_{kl}$ on this chosen direction, one obtains that

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the two-state dipole matrix $\mathbf{m} \equiv (m_{kl})_{kl}$ obeys some sort of "equation of motion",

$$\nabla_{\mathrm{R}}\mathbf{m} = [\mathbf{m}, \mathbf{F}] \tag{3}$$

or in matrix form,

$$\begin{aligned}\nabla_{\mathbf{R}}\begin{pmatrix} m_{11} & m_{12} \\ m_{12} & m_{22}\end{pmatrix} &= \begin{pmatrix} m_{11} & m_{12} \\ m_{12} & m_{22}\end{pmatrix}\begin{pmatrix} 0 & \mathbf{f}_{12} \\ -\mathbf{f}_{12} & 0\end{pmatrix} - \begin{pmatrix} 0 & \mathbf{f}_{12} \\ -\mathbf{f}_{12} & 0\end{pmatrix}\begin{pmatrix} m_{11} & m_{12} \\ m_{12} & m_{22}\end{pmatrix} \\ &= \begin{pmatrix} -2\mathbf{f}_{12}m_{12} & \mathbf{f}_{12}(m_{11} - m_{22}) \\ \mathrm{f}_{12}(m_{11} - m_{22}) & 2\mathbf{f}_{12}m_{12}\end{pmatrix}\end{aligned} \tag{4}$$

In eq 3, $\mathbf{F}$ is a nonadiabatic derivative coupling matrix with matrix elements $\mathbf{f}_{ij}$ for any pair of states and [..., ...] are standard commutation brackets. Subscript α is hereafter suppressed.

Equation 3 is valid for an arbitrary finite basis set, not only for the two-state problem and for any electronic operator. In case of *n* states, the generalization of the nonadiabatic derivative coupling matrix is obvious. Defining the dipole moment matrix in this diabatic basis as $\tilde{\mathbf{m}}$ and taking into account that the nonadiabatic derivative coupling matrix vanishes in the diabatic basis set, one obtains from eq 3 that

$$\nabla_{\mathbf{R}}\tilde{\mathbf{m}} = 0 \tag{5}$$

Equation 5 expresses a "smoothness" of the dipole moments in the diabatic basis set.[8]

Introducing $m_{\pm} = m_{11} \pm m_{22}$, one then rewrites eq 4 as

$$\nabla_{\mathbf{R}}m_{12} = \mathbf{f}_{12}m_{-},\ \nabla_{\mathbf{R}}m_{+} = 0,\ \nabla_{\mathbf{R}}m_{-} = -4\mathbf{f}_{12}m_{12} \tag{6}$$

Applying further the orthogonal transformation (1) to the adiabatic dipole matrix $\mathbf{m}$, one converts it to the diabatic one,

$$\begin{aligned}\tilde{\mathbf{m}} \equiv \begin{pmatrix} \tilde{m}_{11} & \tilde{m}_{12} \\ \tilde{\mathrm{m}}_{12} & \tilde{\mathrm{m}}_{22}\end{pmatrix} &= \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi\end{pmatrix}\begin{pmatrix} m_{11} & m_{12} \\ \mathrm{m}_{12} & \mathrm{m}_{22}\end{pmatrix}\begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi\end{pmatrix} \\ &= \begin{bmatrix} \frac{1}{2}(m_{+} + m_{-}\cos 2\phi) + m_{12}\sin 2\phi & m_{12}\cos 2\phi - \frac{1}{2} - m_{-}\sin 2\phi \\ \mathrm{m}_{12}\cos 2\phi - \frac{1}{2}\mathrm{m}_{-}\sin 2\phi & \frac{1}{2}(m_{+} - m_{-}\cos 2\phi) - m_{12}\sin 2\phi\end{bmatrix}\end{aligned} \tag{7}$$

Equation 5 will be used now to determine the mixing angle ϕ. For this purpose, we substitute eq 7 into eq 5 and obtain

$$\begin{aligned}\nabla_{\mathbf{R}}\tilde{m}_{12} &= (\nabla_{\mathbf{R}}m_{12} - m_{-}\nabla_{\mathbf{R}}\phi)\cos 2\phi - \frac{1}{2}(\nabla_{\mathbf{R}}m_{-} + 4m_{12}\nabla_{\mathbf{R}}\phi)\sin 2\phi \\ \nabla_{\mathbf{R}}\tilde{m}_{11} = -\nabla_{\mathbf{R}}m_{22} &= (\nabla_{\mathbf{R}}m_{12} - m_{-}\nabla_{\mathbf{R}}\phi)\sin 2\phi + \frac{1}{2}(\nabla_{\mathbf{R}}m_{-} + 4m_{12}\nabla_{\mathbf{R}}\phi)\cos 2\phi\end{aligned} \tag{8}$$

These eqs 8 give us the general solution for the adiabatic-to-diabatic mixing angle

$$\tan 2\phi = \frac{m_{-} + 2\gamma m_{12}}{\gamma m_{-} - 2m_{12}} \tag{9}$$

Equation 9 can be easily verified. Here, γ is a numerical coefficient defined by the imposed boundary condition. This is equivalent to solving first-order differential eq 2 that requires imposing certain boundary condition. For instance, γ can be evaluated from some value of the off-diagonal dipole moment $\tilde{m}_{12}$. A choice of $\gamma = \infty$ in eq 9 yields the formula $\tan 2\phi_0 = 2m_{if}/m_{-}$ which was obtained by Macías and Riera[5a] and Werner and Meyer.[5b] The corresponding transformation (1) with the mixing angle ϕ_0 eliminates off-diagonal element $\tilde{m}_{if}$ of the diabatic dipole matrix. If $\gamma \neq \infty$, the mixing angle determined by eq 9 rewritten as $\tan 2\phi = \tan(2\phi_0 + \cot^{-1}\gamma)$ results in such expressions for the diabatic dipole matrix,

$$\tilde{m}_{11} = \frac{m_{+}}{2} \pm \frac{1}{2}\begin{cases} \gamma\sqrt{\dfrac{m^{2} + 4m_{12}^{\ 2}}{1 + \gamma^{2}}}, & |\gamma| \geq 2m_{12}/m_{-} \\ \dfrac{4m{-}m_{12} - \gamma(m_{-}^{\ 2} - 4m_{12}^{\ 2})}{\sqrt{(1 + \gamma^{2})(m_{-}^{\ 2} + 4m_{12}^{\ 2})}}, & \text{otherwise}\end{cases} \tag{10}$$

$$\tilde{m}_{22} = \frac{m_{+}}{2} \mp \frac{1}{2}\begin{cases} \gamma\sqrt{\dfrac{m_{-}^{\ 2} + 4m_{12}^{\ 2}}{1 + \gamma^{2}}}, & |\gamma| \geq 2m_{12}/m_{-} \\ \dfrac{4m{-}m_{12} - \gamma(m_{-}^{\ 2} - 4m_{12}^{\ 2})}{\sqrt{(1 + \gamma^{2})(m_{-}^{\ 2} + 4m_{12}^{\ 2})}}, & \text{otherwise}\end{cases} \tag{11}$$

$$\tilde{m}_{12} = \mp\frac{1}{2}\begin{cases} \sqrt{\dfrac{m_{-}^{\ 2} + 4m_{12}^{\ 2}}{1 + \gamma^{2}}}, & |\gamma| \geq 2m_{12}/m_{-} \\ \dfrac{4\gamma m{-}m_{12} - m_{-}^{\ 2} + 4m_{12}^{\ 2}}{\sqrt{(1 + \gamma^{2})(m_{-}^{\ 2} + 4m_{12}^{\ 2})}} & \text{otherwise}\end{cases} \tag{12}$$

Equations 10−12 include the value of γ equal to $2m_{12}/m_{-}$. It corresponds to the mixing angle $\phi = \pi/4$ that converts the adiabatic off-diagonal dipole moment m_{12} to the diabatic $\tilde{m}_{12} = -m_{-}/2$.

Equation 12 demonstrates that $\tilde{m}_{12}$ varies from a minimum of $(-m_{-}/2, -|m_{-}^{2} - 4m_{12}^{2}|/\sqrt{m_{-}^{\ 2} + 4m_{12}^{\ 2}})$ to a maximum of $(m_{-}/2, |m_{-}^{2} - 4m_{12}^{2}/\sqrt{m_{-}^{\ 2} + 4m_{12}^{\ 2}})$. It is worth noticing that the infinite value of γ is actually the singular point of m_{-} and $\tilde{m}_{12}$, that is, the point where all their derivatives with respect to γ vanish. It is interesting to notice that, as follows from the second equation in (6), one particular choice of $\tilde{m}_{12}$ that satisfies a "smoothness" (5) is that $\tilde{m}_{12} = \beta m_{+}$ where β is some numerical coefficient, $\beta = 1$ corresponds to the Mulliken approximation[9] (see also eq 40 in ref 7d). Such a choice of $\tilde{m}_{12}$ yields, for example, $\gamma = \sqrt{m_{-}^{\ 2} + 4m_{12}^{\ 2} - m_{+}^{\ 2}}/m_{+}$ if $m_{12}^{2} \geq m_{11}m_{22}$.

3. Diabatic Hamiltonian in Terms of Off-Diagonal Dipole Moment

Rotating the adiabatic Hamiltonian matrix by the mixing angle (9), one obtains its diabatic form,

$$\begin{aligned}\tilde{H}_{11} &= E_{0} \pm \frac{\Delta E}{2}\frac{\gamma m_{-} - 2m_{12}}{\sqrt{(1 + \gamma^{2})(m_{-}^{\ 2} + 4m_{12}^{\ 2})}} \\ \tilde{H}_{22} &= E_{0} \mp \frac{\Delta E}{2}\frac{\gamma m_{-} - 2m_{12}}{\sqrt{(1 + \gamma^{2})(m_{-}^{\ 2} + 4m_{12}^{\ 2})}} \\ \tilde{H}_{12} &= \mp\frac{\Delta E}{2}\frac{m_{-} + 2\gamma m_{12}}{\sqrt{(1 + \gamma^{2})(m_{-}^{\ 2} + 4m_{12}^{\ 2})}}\end{aligned} \tag{13}$$

In (13), $E_0 = (E_1 + E_2)/2$ and the energy offset $\Delta E = E_1 - E_2$.

Substituting $\gamma = \infty$, which corresponds to a vanishing off-diagonal diabatic dipole moment, into eq 13 results in the generalized Mulliken−Hush formula[1] for the diabatic electronic coupling

$$\tilde{H}_{12}^{(0)} = \frac{\Delta E m_{12}}{\sqrt{{m_-}^2 + 4{m_{12}}^2}} = \frac{\Delta E}{\sqrt{1 + \cot^2 \phi_0}} \tag{14}$$

Thus, in the general case when $\gamma \neq \infty$, eq 13 allows the electronic coupling to be expressed in terms of the off-diagonal diabatic dipole moment. Some consequences of this equation can be drawn. First, substituting $\gamma = 2m_{12}/m_-$ in the last equation (13) yields $|\tilde{H}_{12}| = \Delta E/2$. Second, within the Mulliken approximation[9] when $\tilde{m}_{12}$ is equal to m_+, one easily obtains that the electronic coupling becomes equal to

$$\tilde{H}_{12} = (\tilde{H}_{12}^{(0)})^2 \frac{m_+}{\Delta E m_-} \mp \frac{m_-}{m_+ m_{12}} \tilde{H}_{12}^{(0)} \sqrt{{m_-}^2 + 4{m_{12}}^2 - \left(\frac{m_+}{m_-}\right)^2 {m_{12}}^2} \tag{15}$$

Equation 15 implies that, with the fixed functions $\mu_{12}(\mathbf{R})$ and $\mu_\pm(\mathbf{R})$, the inclusion of off-diagonal diabatic dipole moments extends the domain of values of the electronic coupling $\tilde{H}_{12}$ that, in turn, may enhance or diminish the rate of electron transfer. Third, eq 13 can be applied for perturbative estimates of the electronic coupling if the off-diagonal diabatic dipole moment is small enough. Using eq 12 for $|\gamma| \geq 2m_{12}/m_-$, one derives that the zero-order electronic coupling $\tilde{H}_{12}^{|0|}$ exactly coincides with the generalized Mulliken−Hush coupling $\tilde{H}_{12}^{[0]}$ while its first- and second-order corrections take the following expressions:

$$\tilde{H}_{12}^{[1]} = \frac{\tilde{H}_{12}^{(0)}}{\sqrt{{m_-}^2 + 4{m_{12}}^2}} \tilde{m}_{12}$$

$$\tilde{H}_{12}^{[2]} = -\frac{2\tilde{H}_{12}^{(0)}}{{m_-}^2 + 4{m_{12}}^2} \tilde{m}_{12}^2 \tag{16}$$

One sees that to first order, inclusion of the off-diagonal diabatic dipole moment increases the electronic coupling. The second-perturbation term diminishes the sum of its two first terms. Furthermore, one may show that the mixing angle ϕ coincides with the angle $\tan^{-1}(2\tilde{H}_{12}/(\tilde{H}_{11} - \tilde{H}_{22}))$ diagonalizing the diabatic Hamiltonian matrix. Summarizing, based on a smoothness of the diabatic dipole moment, we obtain the formula for the electronic coupling that takes the off-diagonal diabatic dipole moment into account, and therefore, will be useful to estimate the electronic coupling in terms of quantities which are directly accessible through electronic spectroscopy.

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