A unified diabatic description for electron transfer reactions, isomerization reactions, proton transfer reactions, and aromaticity.

Jeffrey R. Reimers[ab]*, **Laura K. McKemmish,**[cd] **Ross H. McKenzie,**[e] **and Noel S. Hush**[df]

a: International Centre for Quantum and Molecular Structure, College of Sciences, Shanghai University, Shanghai 200444 China; Tel: 61 293514468; E-mail: Jeffrey.Reimers@uts.edu.au
b: School of Mathematical and Physical Sciences, University of Technology Sydney, NSW 2007 Australia
c: Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT UK
d: School of Chemistry, The University of Sydney, Sydney, NSW 2006 Australia
e: School of Mathematics and Physics, The University of Queensland, QLD 4072 Australia
f: School of Molecular Biosciences, The University of Sydney, NSW, 2006 Australia

Inclusion of additional terms in the 3-state 1-mode vibronic-coupling model for non-degenerate closed-shell reactions.

a. Inclusion of inequivalent interactions between the single excitation and the ground state and doubly excited state.

It is naïve expectation that the coupling between the singly excited state and the doubly excited state should parallel that with the ground state, but this is based on neglect of contributions that are present even in simple electronic structure descriptions such as Hartree-Fock theory. For example, a configuration-interaction calculation restricted to just the two key orbitals (o, occupied in the Hartree-Fock wavefunction, and v, unoccupied therein) expresses the relative energies of the three adiabatic states at the high-symmetry geometry as

$$E_s - E_g = 2J_G = \varepsilon_v - \varepsilon_o - J_{ov}$$
$$E_d - E_s = 2J_D = \varepsilon_v - \varepsilon_o - 3J_{ov} + J_{oo} + J_{vv} \tag{S1}$$

where ε_o and ε_v are the energies of molecular orbitals ψ_o and ψ_v, and the two-electron Coulomb integrals are given by

$$J_{ij} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \, \psi_i(1)\psi_i^*(1)\frac{1}{r_{12}}\psi_j(2)\psi_j^*(2) \ , \tag{S2}$$

so that the one parameter J in Eqn. (19) needs to be replaced in quantitative studies of the excited states by two independent parameters J_G and J_D. Similarly, α needs to be replaced by α_G and α_D, giving a more accurate 5-parameter 3-state model

$$\mathbf{H^{3D}} = \begin{bmatrix} T + \dfrac{k}{2}Q^2 & \alpha_G Q & 0 \\[2ex] \alpha_G Q & T + \dfrac{k}{2}Q^2 + 2|J_G| & \alpha_D Q \\[2ex] 0 & \alpha_D Q & T + \dfrac{k}{2}Q^2 + 2|J_G| + 2|J_D| \end{bmatrix}. \qquad (S3)$$

At the high-symmetry geometry, the curvatures of these states are

$$\omega_i = \omega \left[1 - \frac{\lambda_G}{2|J_G|}\right]^{1/2}, \quad \omega_s = \omega \left[1 + \frac{\lambda_G}{2|J_G|} - \frac{\lambda_D}{2|J_D|}\right]^{1/2}, \quad \omega_d = \omega \left[1 + \frac{\lambda_D}{2|J_D|}\right]^{1/2} \qquad (S4)$$

where $\lambda_G = 2\alpha_G^2 / k$ and $\lambda_D = 2\alpha_D^2 / k$ so that the ground state and doubly excited state are no longer paired as "twin states". Also, the curvature of the singly excited state becomes modulated, allowing for the possibility that this state even adopts a double-minimum structure if it couples much more strongly to the doubly excited state than to the ground state. Hence the general expectation appropriate for electron-transfer phenomena that the singly excited state will have a vibration frequency in excess of the ground state could be thought of as an expected result for reactions involving closed-shell species but is by no means an assured or characteristic result.

b. Inclusion of higher-order terms in the vibronic coupling model

By their nature, interacting diabatic surfaces are useful over large nuclear displacements, displacements so large that the assumptions concerning harmonic diabatic potentials, linear vibronic coupling, and a coordinate-independent resonance interaction no longer remain valid. This would therefore inhibit the fitting of diabatic surfaces to adiabatic potential-energy functions evaluated computationally, for example. Including these effects, the basic 3-state model expands to include 11 free parameters and can be expressed in delocalized form as

$$\mathbf{H^{3D}} = \begin{bmatrix} T + \dfrac{k}{2}Q^2 + \dfrac{k_4}{24}Q^4 & \alpha_G Q + \dfrac{\gamma_G}{6}Q^3 & \dfrac{\beta}{2}Q^2 \\[2ex] \alpha_G Q + \dfrac{\gamma_G}{6}Q^3 & T + \left(\dfrac{k}{2} + \beta_G\right)Q^2 + 2|J_G| + \dfrac{k_4}{24}Q^4 & \alpha_D Q + \dfrac{\gamma_D}{6}Q^3 \\[2ex] \dfrac{\beta}{2}Q^2 & \alpha_D Q + \dfrac{\gamma_D}{6}Q^3 & T + \left(\dfrac{k}{2} + \beta_G + \beta_D\right)Q^2 + 2|J_G| + 2|J_D| + \dfrac{k_4}{24}Q^4 \end{bmatrix} \qquad (S5)$$

and in localized form as

$$H_{LL}^L = T - \frac{\lambda'}{4} + \frac{3J_G + J_D}{2} + \frac{k}{2}(Q + Q_m')^2 + \frac{\beta + 3\beta_G + \beta_D}{2}Q^2 + \frac{(\gamma_G + \gamma_D)}{6\sqrt{2}}Q^3 + \frac{k_4}{24}Q^4$$

$$H_{CC}^L = T + J_G + J_D + \frac{k - \beta + \beta_G + \beta_D}{2}Q^2 + \frac{k_4}{24}Q^4$$

$$H_{RR}^L = -\frac{\lambda'}{4} + \frac{3J_G + J_D}{2} + \frac{k}{2}(Q - Q_m')^2 + \frac{\beta + 3\beta_G + \beta_D}{2}Q^2 - \frac{(\gamma_G + \gamma_D)}{6\sqrt{2}}Q^3 + \frac{k_4}{24}Q^4$$

$$H_{LC}^L = -\frac{(J_G + J_D)}{\sqrt{2}} + \frac{\alpha_G - \alpha_D}{2}Q - \frac{\beta_G + \beta_D}{2\sqrt{2}}Q^2 + \frac{\gamma_G - \gamma_D}{12}Q^3 \qquad \text{(S6)}$$

$$H_{LR}^L = \frac{J_G - J_D}{2} - \frac{\beta - \beta_G + \beta_D}{4}Q^2$$

$$H_{CR}^L = \frac{(J_G + J_D)}{\sqrt{2}} + \frac{\alpha_G - \alpha_D}{2}Q + \frac{\beta_G + \beta_D}{2\sqrt{2}}Q^2 + \frac{\gamma_G - \gamma_D}{12}Q^3$$

where

$$\alpha' = \frac{\alpha_G + \alpha_D}{\sqrt{2}}, \quad Q_m' = \frac{\alpha'}{k} \quad \text{and} \quad \lambda' = 2k(\delta')^2 .$$

The six new parameters are: a general anharmonicity k_4, cubic vibronic coupling constants γ_G and γ_D, a second-order interaction between the ground and doubly excited states β, and non-Condon dependencies of the resonance couplings on the nuclear coordinate β_G and β_D. In terms of this expanded model, the adiabatic vibration frequencies at the high-symmetry geometry are:

$$\omega_i = \omega\left[1 - \frac{\lambda_G}{2|J_G|}\right]^{1/2},$$

$$\omega_s = \omega\left[1 + \frac{2\beta_G}{k} + \frac{\lambda_G}{2|J_G|} - \frac{\lambda_D}{2|J_D|}\right]^{1/2}, \quad \text{and} \qquad (27)$$

$$\omega_d = \omega\left[1 + \frac{2\beta_G + 2\beta_D}{k} + \frac{\lambda_D}{2|J_D|}\right]^{1/2},$$

Also the associated fourth derivatives that provide a basic depiction of the anharmonicity of single-welled adiabatic surfaces and of the location of the minima in double-welled surfaces are

$$\frac{\partial^4 E_g}{\partial Q^4} = k_4 + \frac{3\alpha_G^4}{|J_G|^3} - \frac{3\alpha_G^2\alpha_D^2}{J_G^2(|J_G| + |J_D|)} - \frac{4\alpha_G\gamma_G}{|J_G|},$$

$$\frac{\partial^4 E_s}{\partial Q^4} = k_4 - \frac{3\alpha_G^4}{|J_G|^3} + \frac{3\alpha_D^4}{|J_D|^3} + \frac{3\alpha_G^2\alpha_D^2}{J_G^2 J_D^2}(|J_D| - |J_G|) + \frac{4\alpha_G\gamma_G}{|J_G|} - \frac{4\alpha_D\gamma_D}{|J_D|} - \frac{6\alpha_G^2\beta_G}{J_G^2} + \frac{6\alpha_D^2\beta_D}{J_D^2} - \frac{6\alpha_G\alpha_D\beta}{|J_G J_D|} \quad .\text{(S7)}$$

$$\frac{\partial^4 E_s}{\partial Q^4} = k_4 - \frac{3\alpha_D^4}{|J_D|^3} + \frac{3\alpha_G^2\alpha_D^2}{J_D^2(|J_G| + |J_D|)} + \frac{4\alpha_D\gamma_D}{|J_d|} - \frac{6\alpha_D^2\beta_D}{J_D^2} + \frac{3\beta^2}{|J_G| + |J_D|} + \frac{6\beta\alpha_D\alpha_G}{|J_G|(|J_G| + |J_D|)} .$$

All 11 parameters can be determined uniquely from calculated energies, second, fourth, and sixth derivatives of the 3 adiabatic potential-energy surfaces at $Q = 0$, but if β, β_G, and β_D can be

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ignored than the remaining 8 diabatic-model parameters are easily determined from just adaibatic energies, second, and fourth derivatives:

$$\left|J_G\right| = (\varepsilon_s - \varepsilon_g)/2, \quad \left|J_D\right| = (\varepsilon_d - \varepsilon_s)/2,$$

$$k = \frac{1}{3}\left(\frac{\partial^2 \varepsilon_g}{\partial Q^2} + \frac{\partial^2 \varepsilon_s}{\partial Q^2} + \frac{\partial^2 \varepsilon_d}{\partial Q^2}\right),$$

$$\alpha_G^2 = J_G\left(k - \frac{\partial^2 \varepsilon_g}{\partial Q^2}\right), \quad \alpha_D^2 = J_D\left(-k + \frac{\partial^2 \varepsilon_d}{\partial Q^2}\right)$$

$$k_4 = \frac{1}{3}\left(\frac{\partial^4 \varepsilon_g}{\partial Q^4} + \frac{\partial^4 \varepsilon_s}{\partial Q^4} + \frac{\partial^4 \varepsilon_d}{\partial Q^4}\right), \tag{S8}$$

$$\gamma_G \alpha_G = \frac{J_G}{4}\left(k_4 - \frac{\partial^4 \varepsilon_g}{\partial Q^4}\right) - \frac{3\alpha_G^2 \alpha_D^2}{4J_G(J_G + J_D)} + \frac{3\alpha_G^4}{4J_G^2},$$

$$\gamma_D \alpha_D = \frac{\left|J_D\right|}{4}\left(-k_4 + \frac{\partial^4 \varepsilon_g}{\partial Q^4}\right) - \frac{3\alpha_G^2 \alpha_D^2}{4J_D(J_G + J_D)} + \frac{3\alpha_D^4}{4J_D^2}.$$

Our findings are that, in general, that while Taylor expansions to order 4 of the three potential-energy surfaces (evaluated say using high-level electronic-structure calculations) about the symmetric structure can qualitatively reproduce the ground state over the chemically significant region, they fail dramatically to describe the excited states; expansions of order 6 are adequate for all states, however. In contrast, the basic 3-parameter diabatic description qualitatively describes all effects, becomes semi-quantitative when expanded to five parameters, and accurately reproduces all surfaces when 8 parameters are included. Nevertheless, explicit evaluation of the higher derivatives indicates that all six higher parameters k_4, γ_G, γ_D, β, β_G, and β_D should be, in principle, equally as important as each other in determining the shapes of the adiabatic surfaces. Hence extraction of accurate individual higher parameters from observed or calculated data is likely to be difficult as including more that 8 parameters in fits does not significantly improve their quality.