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Testing the Condon Approximation for Electron Transfer via the Mulliken−Hush Model

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For nonadiabatic electron-transfer reactions, it is common to make a Condon approximation assumption that the mixing matrix element is independent of nuclear geometry. We test the validity of the Condon approximation using Mulliken-Hush analysis applied to the biphenyl alcohol molecule at various geometries. Calculations of the energy splitting and electronic coupling matrix element as functions of geometry using semiempirical and ab initio methods are presented. Breakdown of the Condon approximation is observed, quantified, and analyzed.

Introduction

Electronic transfer (ET) plays a central role in chemistry and biology. There is a substantial current interest in the details of the electronic coupling of the localized donor (D) and acceptor (A) sites. This interest ranges from photosynthesis[1−3] to molecular electronics design.[4−9] In many systems of interest, the donor and acceptor are spatially well separated (typically 10−20 Å).[10,11] Due to this separation there is no direct coupling between the donor and the acceptor, and the coupling is mediated by intervening bridge states. This kind of ET reaction is exemplified in biological systems where the bridge can be a protein, a protein and cofactors,[12−16] or DNA.[17,18] In long-range ET systems the diabatic electronic coupling matrix element, H_{ab}, primarily governs the geometry dependence of the ET rate, where a and b refer generically to the initial and final diabatic states. The ET rate constant k is normally given by the Fermi golden rule:[2]

$$k = \frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2\ \mathrm{DWFC} \qquad (1)$$

where DWFC signifies Franck−Condon factors weighted by the density of states and is related to the nuclear motion spectrum of the DA system and its surroundings, and H_{DA} is the effective electronic coupling matrix element in a two-state ET description (often, the two-state description is oversimplified).[19] Equation 1 already assumes the Condon approximation. We will denote adiabatic states (eigenfunctions of the adiabatic electronic Hamiltonian) by numerical subscripts.

Adiabatic electronic wave functions obtained from either semiempirical or ab initio methods have been previously utilized to calculate H_{ab} through various techniques:[20−30] such as perturbative and nonperturbative approaches, partitioning technique[21] or Green's functions.[30] All these studies have been carried out in the context of the two-state model. Most have used Hartree−Fock wavefuctions and thus have been limited to reactions involving the lowest state of a certain symmetry; other studies have used correlated wave functions.[29] The H_{ab} values can be computed as one-half the adiabatic energy splitting for symmetric localized donor and acceptor groups.[26−29] The matrix element between the two unsymmetrical nonorthogonal initial and final diabatic states,[23,24] or the minimum splitting between the two adiabatic states tuned suitably by applying external perturbation or varying judiciously the coordinates.[27] (See ref 31 for lucid discussion of the difficulties encountered with aforementioned methods for evaluating H_{ab}, especially when treating excited states.) Cave and Newton[32] have developed two independent methods for the nonperturbative calculation of H_{ab} for ET reactions. The first is based on the generalized Mulliken−Hush (GMH) model,[33] a multisystem generalization of the Mulliken−Hush (MH) model[33] that will be used in this article for evaluating H_{ab}. The second is based on the block diagonalization (BD)[32] approach of Cederbaum, Domcke, and co-workers.[34] Both methods can be applied to both ground and excited state systems and can be used in cases where several electronic states interact strongly. Either method can be applied to an arbitrary nuclear geometry and, therefore, can be used to test the validity of the Condon approximation. Both methods are exact within a chosen set of electronic states, and can be implemented in terms of entirely adiabatic state information. Since adiabatic state quantities (such as state energies, dipole moments, and transition moments) are the only input to GMH, it can be used with experimental data to estimate the electronic coupling matrix element.[35] BD and GMH are employed to circumvent the difficulties and limitations of the simpler methods for evaluating the electronic coupling matrix element.

The GMH model is based on diagonalizing the adiabatic dipole moment matrix, whereas the BD approach is based on block diagonalization of the Hamiltonian using CI coefficients. In the limiting case of a two-state ET system the GMH, exactly, becomes the MH model. One of the crucial GMH assumptions is that the diabatic states localized at different sites have zero off-diagonal transition dipole moment matrix elements, namely $\mu_{\mathrm{ab}} = 0$; this assumption is used to define uniquely diabatic states in n-state systems. This provides a general method for defining diabatic states for charge-transfer processes in terms of adiabatic quantities. Essentially, a unitary transformation that diagonalizes the adiabatic dipole moment operator is identified as the transformation to the MH diabatic states. Applying this same transformation to the adiabatic Hamiltonian (diagonal by definition) yields the diabatic Hamiltonian. Applying the same procedure to n-state systems generalizes the MH to GMH model.

In this article we exploit the MH scheme to compute the electronic coupling matrix element as a function of geometry at different levels of theory, thereby testing the validity of the Condon approximation.

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Computational Details

The biphenyl alcohol radical anion is a good candidate to test the Condon approximation using the GMH model for calculating the nonadiabatic electronic coupling matrix element for the ET rate. We are considering a two-state ET system in which the GMH model becomes the MH model. Since the MH can be applied to an arbitrary geometry, one can calculate H_{ab} as a function of geometry by rotating one ring with respect to another, thus varying the torsion angle (θ). The variation of energy gap with reaction coordinate yields a corresponding variation in the electronic coupling matrix element, thus allowing a measure of the breakdown of the Condon approximation. These calculations were completed using different electronic structure models.

Extended Huckel (EH) calculations were carried out over a range of torsion angles, from $\theta = 0°$ to $\theta = 180°$ in increments of 10° for calculating H_{ab}. Biphenyl is a symmetric molecule (center of inversion is present), and therefore the GMH H_{ab} becomes $\Delta E_{12}/2$. We utilize the MH formula:[31-33]

$$H_{ab} = |\vec{\mu}_{12}|\Delta E_{12}/|\Delta\vec{\mu}_{ab}| \tag{2}$$

$$|\Delta\vec{\mu}_{ab}| = [|\vec{\mu}_{11} - \vec{\mu}_{22}|^2 + 4|\vec{\mu}_{12}|^2]^{1/2}, \text{(2a)} \tag{2a}$$

where ΔE_{12}, $\vec{\mu}_{11}$, $\vec{\mu}_{22}$, and $\vec{\mu}_{12}$ are respectively the vertical excitation energy, ground and excited states dipole moments, and transition dipole moment. (Another standard assumption of MH is that $\Delta\mu_{ab}$ can be approximated by eR_{DA}, where R_{DA} is the assumed separation distance between the centroids of the D and A orbitals and e is the electronic charge. R_{DA} is normally inferred from structural data (crystal structural data).)

To break the symmetry equivalence of the two phenyl rings a *p*-hydroxyl group was added. EH calculations were then performed to evaluate ΔE_{12}. Since the system of interest is a charged molecule, the dipole moment is origin dependent, a MATHEMATICA program was written to evaluate the EH dipole moments, where the Pariser approximation[36] was used (the origin dependence drops out in eq 29). The fact that the EH density matrix is diagonal (occupation numbers) simplifies the calculations.

The Q-Chem package was used for performing ab initio calculations, which were completed at the single-excitation configuration interaction (CIS)[37-40] and random phase approximation (RPA) levels of theory.[37,39,41,42] CIS is the least computationally demanding excited state method implemented in Q-Chem, and while it is an uncorrelated method whose accuracy for computing vertical excitation energies is poor for higher excited states, it is useful for the first excited state. RPA extends CIS by including other excitations and is simply described using propagator decouplings.[43] RPA calculations are nonvariational and require a two-electron integral transformation, which impedes their application to very large systems.[44] UCIS and URPA were performed with two basis sets: 3-21G and 6-31G*. The use of UHF theory introduces spin contamination (the states emerging from this computation are not eigenstates of the spin-squared operator). This can lead to inadequate evaluation of properties such as geometry optimization and dipole moments. Our biphenyl UHF results have been checked against ROHF; they were virtually the same, and the spin contamination was minimal. Ab initio UHF calculations have been performed before on the biphenyl radical anion at the level of UHF in the investigation of the ET reaction between anionic and neutral biphenyl.[44-46]

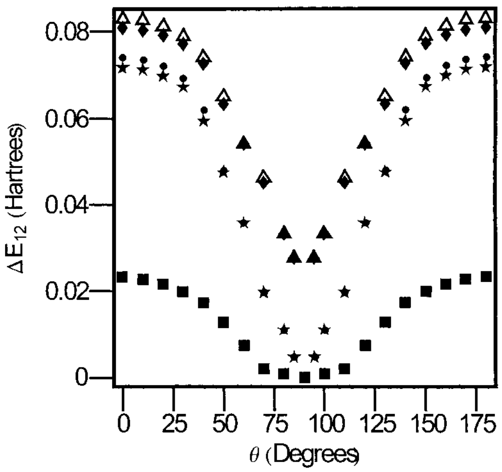

Figure 1. Energy splittings (ΔE_{12}) calculated for biphenylyl alcohol using different levels of theory: EH (boxes), UCIS/3-21G (triangles), UCIS/6-31G* (diamonds), URPA/3-21G (circles), and URPA/6-31G* (stars). The variation of ΔE_{12} upon changing the optimized geometry is a clear breakdown of the Condon approximation. The value of ΔE_{12} at $\theta = 90°$ is missing in ab initio calculations due to URPA instability with this geometry. ΔE_{12} is minimum at $\theta = 90°/85°$ and maximum at $\theta = 0°$.

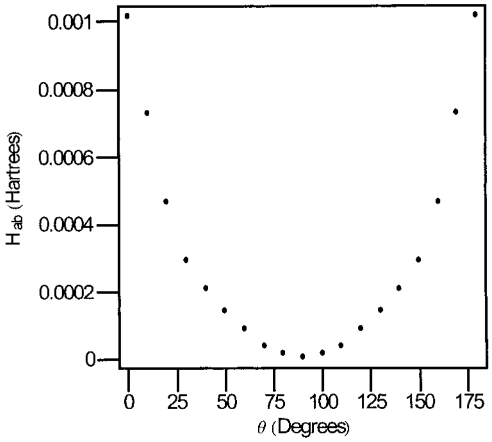

Figure 2. Diabatic electronic coupling matrix element calculated using eqs 2, where ΔE_{12}, dipole moments, and transition moments were evaluated using EH level of theory. Clearly, H_{ab} is not independent of geometry; the Condon approximation is invalid here.

Results

The symmetric biphenyl EH calculations (results not shown here) demonstrate that H_{ab} peaks at $\theta = 0°$ and 180° and minimizes at $\theta = 90°$, as expected, and considerable changes of H_{ab}, and ΔE_{12}, values occur upon varying θ. This change is a clear indication of the Condon approximation breakdown, caused by reduction of molecular orbital overlap as the molecule twists from $\theta = 0°$ to $\theta = 90°$.

The variation of ΔE_{12} in biphenyl alcohol radical anion resulting from EH, UCIS, and URPA (using both 3-21G and 6-31G* basis sets) calculations upon twisting is shown[47] in Figure 1. ΔE_{12} resulting from EH is obtained by taking the difference between the HOMO and the LUMO and excited and the ground-state energies, respectively. Evaluating H_{ab} using EH (Figure 2) and UCIS (Figure 3) levels of theory illustrates the Condon breakdown. The graph for H_{ab} in Figure 3 resulting from UCIS/3-21G calculation exhibits an anomaly, which does not show up with the 6-31G* basis, in the region between $\theta = 0°$ and $\theta = 10°$; one would expect the H_{ab} value at $\theta = 0°$ to be larger than it is at $\theta = 10°$. This behavior may be attributed

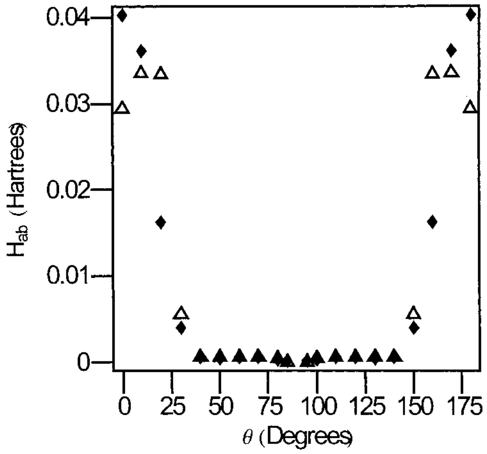

Figure 3. Same as in Figure 2 but done with UCIS using 3-21G (open triangles) and 6 31G* (diamonds).

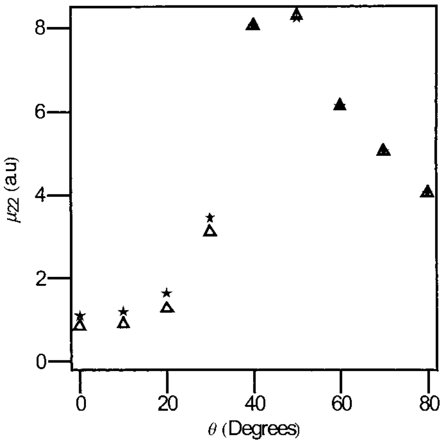

Figure 4. Excited-state dipole moment calculated with UCIS using 3-21G (open triangles) and 6-31G* (stars) basis sets.

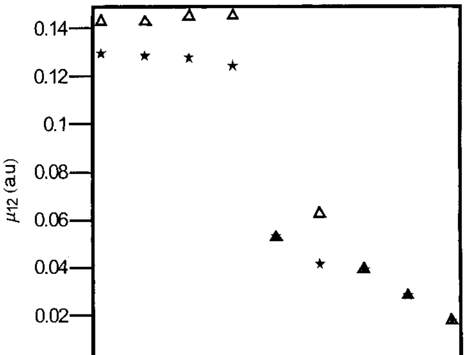

Figure 5. Transition dipole moment calculated with UCIS using 3-21G (open triangles) and 6-31G* (stars) basis sets. Note the irregular behavior of the transition dipole moment calculated with UCIS/3-21G.

to the fact that the transition dipole moment magnitude is not behaving monotonically in this region (see Figure 5) (this may have to do with the fact that basis 3-21G does not have a polarization function).

The ground state dipole moment monotonically increases as one twists the molecule from $\theta = 0°$ to $\theta = 90°$. Figure 4 shows that the UCIS/3-21G excited state dipole moment starts off with a value less than 1.0 a.u., and it increases slowly at the torsion angles 10° and 20°. It rises drastically at $\theta = 30°$ to a value of $\sim$3.0 a.u., creating a noticeable gap in the H_{ab} graph. Although the excited-state dipole moment is about 3.0 a.u. by both UCIS basis sets calculations, this gap is not as pronounced in the UCIS/6-31G* H_{ab} curve as it is in the UCIS/3-21G H_{ab} curve because the excited state dipole moment gradually increases as one twists the molecule from 0° to 30°. In both UCIS calculations, however, the excited state dipole moment rises sharply, taking on the values of $\sim$3.0 and 8.0 a.u. upon twisting at 30° and 40°, respectively. Excited-state dipole moments become comparable in value at the torsion angles 40° and 50° and start back down when the torsion angle is 60° and thereafter, whereas the ground-state dipole moment keeps on increasing, and the splitting keeps on decreasing, as UCIS calculations dictate.

The UCIS transition dipole moment adopts the same behavior, except that it starts roughly flat between the 0° and 30°. It drastically drops down at 40° and decreases monotonically when the torsion angle is 50° and thereafter (see Figure 5). As one twists the molecule the symmetry changes and the correct calculation of the transition dipole moment requires multiple configurations, and not a single configuration. This behavior of the transition dipole moment gives rise to a roughly flat H_{ab} curve, as shown in Figure 3.

Our ab initio UCIS calculations of the biphenyl alcohol radical anion show that the CI coefficients of the electronic configurations change upon twisting the molecule. This reflects the presence of multiple configurations, and it would be wrong to treat the twisting behavior of the biphenyl alcohol as single configuration. Therefore, using the UCIS wave function for this problem will yield incorrect quantities such as the dipole/transition moments. The MH/GMH model depends crucially on dipole/transition moments, and using the inaccurate quantities (such as the UCIS produces) yields wrong electronic coupling magnitudes. This should explain the roughly flat structure at the bottom of the of H_{ab} curve, as shown in Figure 3. The more proper way of handling this problem is to use more sophisticated methods such as MRCI (multireference CI) or MCSCF (multiple configuration SCF) that reflect the multiple configurations arising upon twisting the biphenyl molecule. While the UCIS does not yield the correct dipole/transition moments, MRCI or MCSCF certainly will.

The variation of the H_{ab} curve as a function of geometry is a clear breakdown of the Condon approximation. Orbital mixing control due to symmetry-changing torsions will be important for some electron transfers. MH/GMH, though correct and useful, puts severe demands on the level of computational theory. Primitive EH results are qualitatively correct but with more precise ab initio techniques, artifacts can arise due to strong changes in ground-state character upon twisting. These require close attention and a consistent level of theory.[48−50]

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(46) The CIS default settings yield the ground-state dipole moment and the transition dipole moment, but not the excited-state dipole moment. As a result, the force field option was chosen for the JOBTYPE in the $rem block. (Note that this option is not available for ROCIS, and therefore the $multipole_field block, along with the finite difference method, has to be utilized in order to compute the excited-state dipole moment.). Both methods, however, were used to compute ground and excited sates dipole moments, for confirmation purposes, yielding exact agreement. While Zindo is not set up to compute dipole moments for charged molecules, Q-Chem is.

(47) A problem occurred involving the RPA instability at $\theta = 90°$. Use of the RPA leads to accurate transition properties for many systems, but it can also produce numerical instabilities and complex excitation energies when HF instability occurs. As a result in all the calculations (except EH) we went only up to $\theta = 85°$ (cf., e.g.: Thouless, D. J. *The Quantum Mechanics of Many-Body Systems*; Academic Press: New York and London, 1972.).

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