Basis Set and Nuclear Relaxation Effects in Hole and Electron Transfer in a Water Dimer System

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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

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Electronic coupling elements between initial and final-states for a model water dimer system were calculated for hole and electron transfer reactions using the corresponding orbitals method of King, with an extension to allow for differing initial- and final-state nuclear geometries. Three basis sets, 6–311G, 6–311++G and 6–311++G(3pd, 3df), were used, and calculations were performed approximating slow (nuclear relaxation included) or fast (no nuclear relaxation) timescales. Electronic overlaps and coupling elements were observed to decay exponentially and smoothly with separation in the case of hole transfer in all combinations of slow vs. fast and basis sets. In the case of electron transfer, the decay of coupling was strongly basis set dependent, giving rapid and unrealistic decay at short distances with the non-diffuse-extended basis set, and approximately exponential decay with diffuse-extended basis sets. The addition of diffuse functions to the 6–311G basis set is significant and important in these calculations, while the addition of polarization functions seems to have little importance.

The prediction of coupling terms, a vital component of rate determination for hole and electron transfer reactions, is clearly an essential task in modern theoretical chemistry. Several methods are available for the approximation of coupling elements, including various one- and many-electron models.[1] Of the latter, the corresponding orbitals method[2–6] (COM) allows the evaluation of the transfer integral $H_{IF} = \langle \Psi_F | H | \Psi_I \rangle$ without any preconceived notions about the character of the valence or core orbitals, unlike, e.g., Koopmans' theorem[7] (which assumes a static core). From the transfer integral, the overlap integral between initial and final wavefunctions (S_{IF}) and the energies of initial (H_{II}) and final (H_{FF}) states at the particular nuclear configuration we calculate the effective electron transfer coupling[8]

$$H_{eff} = \frac{\{(H_{II} - H_{FF})^2 + 4[H_{IF}^2 - S_{IF}H_{IF}(H_{II} + H_{FF})] + S_{IF}^2 H_{II}H_{FF}\}^{1/2}}{[2(1 - S_{IF}^2)]}$$

COM is not restricted to any particular wavefunction, and can be adapted to correlated wavefunctions as easily as HF wavefunctions; furthermore it does not require

that initial and final states be orthogonal to one another (and is in fact based on the assumption that they are not). The primary disadvantage of COM is that it is a many-electron method, and can require both heavy disk usage and long calculation times for large systems. Correlated procedures within the framework of the CASSCF and RASSCF methods have been developed and utilized for calculating effective electron transfer elements.[9a,b]

We have recently extended our version of the COM in two ways:[8b]

Direct calculation: We have extended our code to allow direct calculation. This allows the method to be used with large systems and/or extended basis sets on machines where disk space is limited, but CPU time is not so dear (note that direct methods generally take longer than disk-based methods for small to moderate sized systems; larger systems may perform faster with the direct method, based on I/O vs. CPU performance).

Non-identical initial and final nuclear geometries: Electronic coupling elements may now be calculated between initial and final states of differing geometries. It must be understood that the COM yields only the electronic portions of the coupling and overlap terms,

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and ignores the contribution of nuclear dynamics to the overall rate. The method calculates the overlap between the orbitals centered at the initial and final state nuclei $(S_{IF} = \langle \Psi_F | \Psi_I \rangle)$ for use in the corresponding orbitals transformation; thus, the overlap is the true electronic overlap between the two states (of differing geometry). However, the one- and two-electronic hamiltonian matrices are generated at the intermediate (transition-state) geometry.

We have restricted our studies to systems in which (a) the initial and final states are mirror images (and therefore of equal energies) and (b) the nuclear rearrangements are relatively minor, as in the present case, where only hydrogens are allowed to move. The current work examines the validity of calculating the coupling elements for these reactions near the crossing point, but with initial and final states on either side of the barrier, as compared to calculations at the crossing point (using broken symmetry solutions of the wavefunction). Off-symmetric nuclear geometries (especially in transfer between like species, as in this case) greatly aid in the calculation of initial and final states, as convergence of the localized wavefunctions is much faster than in symmetric systems.

Calculational details. Wavefunctions for the water dimers were obtained through the use of the Gaussian 92 series of programs.[10] The 6-311G triple-ζ basis set of Pople[11] was used without modification (basis set *a*), with the addition of diffuse functions on oxygen and hydrogen (6-311 + +G, basis set *b*), and with the addition of both diffuse and polarization functions on O and H [6-311 + +G(3pd, 3df), basis set *c*]. All dimers were constrained to lie in a plane, with oxygens facing towards each other, with at least C_{2v} symmetry. In all cases of hole and electron transfer, MP2/6-311G minimized geometries were used. In the case of 'fast' transfer, in which no nuclear relaxation was included, the initial and final state molecules were in the H_2O^0 configuration ($R_{OH} = 0.969$ Å; $A_{HOH} = 109.97°$). In the case of 'slow' transfer, the H_2O^0, H_2O^+ ($R_{OH} = 1.004$ Å; $A_{HOH} = 117.69°$), and H_2O^- ($R_{OH} = 1.035$ Å; $A_{HOH} = 101.89°$) configurations were used, where appropriate, maintaining C_{2v} symmetry. Thus, the initial state for a 'slow' hole transfer reaction appears as $[H_2O]^0$-$[OH_2]^+$, while the final state is $[H_2O]^+$-$[OH_2]^0$, with each $[H_2O]^x$ in its isolated, ground-state configuration. For 'fast' hole and electron transfer cases, where the initial- and final-state nuclear geometries were identical, mirror-image broken-symmetry HF-SCF wavefunctions were obtained for initial and final states by removing electronic symmetry constraints, mixing the HOMO and LUMO to yield an asymmetric distribution of charge density, and minimizing the energy (with respect to electronic degrees of freedom only). (Note, again, that no such mixing is required to yield localized wavefunctions for non-symmetric 'slow' initial and final states.) One- and two-electron integrals were calculated at the geometry corres-

ponding to the midpoint of the linear synchronous path between the initial and final state geometries, corresponding approximately to the transition state geometry. Orbital overlaps were calculated explicitly between the initial and final states, or at the intermediate geometry, as noted.

Results.

Hole transfer. Logarithms of squared effective coupling elements are plotted in Fig. 1 for the case of hole transfer in the model water dimer over a range of 2.5–10 Å. The coupling elements show smooth (exponential) decay in all combinations of basis set and 'slow' vs. 'fast' reactions, with diffuse-extended bases showing more gradual decay. Note that non-diffuse-extended calculations fail to give coupling elements at separations greater than 6.5 Å, due to nearly non-overlapping initial and final states, while diffuse extended basis sets yield data out to 10 Å.

The addition of polarization functions to the 6-311 + +G basis has very little effect on the coupling element over the entire range. However, the addition of diffuse functions to the 6-311G basis decreases the decay of the coupling element with distance (compare a decay of ca. 1.5 orders of magnitude per ångstrom with 0.8 in the case of overlap, and 3.0 orders of magnitude per ångstrom with 1.6 in the case of squared coupling element). Note also that the decay is more nearly exponential in the diffuse-modified basis (the curve-fitting parameter R for an exponential curve fit is 0.9998 for overlap, 0.9999 for coupling) than in the 'plain' 6-311G basis ($R = 0.989$ for overlap, 0.992 for coupling).

As seen in Fig. 1, slow vs. fast transfer yielded essentially identical results, with slightly lower coupling elements for slow vs. fast, as expected (given different nuclear geometries between initial and final states in the slow case, and thus different orbital centers). Localized wavefunctions of states with differing initial and final nuclear geometries were easier to calculate (more readily converged) than the symmetric systems, as seen in the
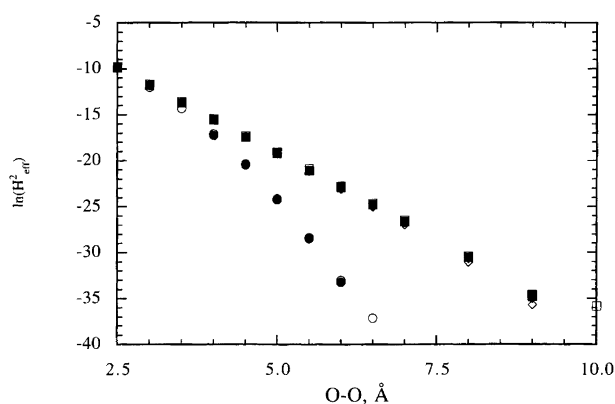

Fig. 1. Effective transfer coupling elements for hole transfer for the three different basis sets (*a*), (*b*) and (*c*) and for the two different nuclear configurations slow (s) and fast (f); see text for further details.

case of basis *a* (more data are available in the slow case than the fast).

Electron transfer. Logarithms of the squared effective coupling elements are plotted in Fig. 2 for the case of electron transfer in the model water dimer over a range of 3–20 Å. Unlike the case of hole transfer (Fig. 1), coupling elements for electron transfer do not show simple, (nearly) exponential decay with distance, except in certain combinations of distance and basis set. Qualitatively, however, the results are similar, in that the addition of diffuse functions greatly decreases the decay of the coupling elements, and generally makes the decay more smooth and nearly exponential, while the addition of polarization functions has little effect.

Diffuse functions are commonly added to gaussian basis sets to describe anions, as 'default' basis sets are defined for neutral, ground-state systems and are not typically adequate to describe the diffuse character of anions (yielding, for example, negative electron affinities for some systems known to have stable anions). Here we observe dramatically different behavior between a relatively flexible but non-diffuse basis set (*a*) and diffuse-modified basis sets (*b* and *c*). Note, in the case of overlaps, the *a* set shows rapid decay in the 3–10 Å range (ca. 1.4 orders of magnitude/Å; $R = 0.997$), and then shows unrealistic behavior at larger separations (10–20 Å). Similar behavior is shown for the squared coupling elements (2.4 orders of magnitude/Å in the 3–10 Å range with $R = 0.997$, unrealistic behavior at > 10 Å). Diffuse-modified basis sets, on the other hand, show strong overlaps in the 3–8 Å range (indicating basically adiabatic transfer, in which case the coupling elements calculated here are inappropriate), and then basically smooth exponential decay over the range 8–18 Å (0.6 orders of magnitude/Å for overlaps with $R = 0.995$, 1.0 orders of magnitude/Å for squared coupling elements with $R = 0.982$). However, the diffuse-modified basis sets appear to fail at extremely large separations (18–20 Å), indicating that perhaps the basis
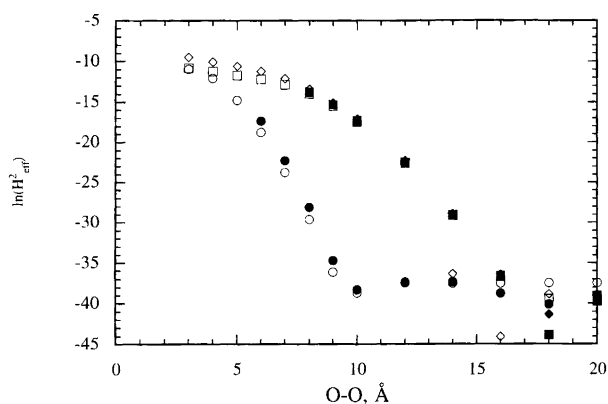
sets should have greater flexibility in the long range (more diffuse functions of differing character).

The comparison of slow vs. fast electron transfer in this model system shows similar behavior to that of hole transfer: slow transfer (with differing nuclear geometries between initial and final states) show generally smaller overlaps and coupling elements, but not significantly so. In the case of coupling elements, the results are basically identical, with the exception of slow transfer with basis set *c*, where basis set superposition error may be influencing the results (see conclusions, below). As with hole transfer, the slow transfer cases are easier to calculate than the fast, due to differing nuclear geometries between initial and final states, and thus easier convergence of localized wavefunctions.

For both the hole and electron transfer we compared the new and improved method for obtaining the overlap matrix between the atomic orbitals of the initial and final nuclear configurations with the method normally used.[3–6] The latter method is not appropriate, as stated previously, for different nuclear inital and final nuclear configurations. The results in Figs. 3A and 3B illustrate clearly that for both the electron and hole transfer the coupling elements as a function of distance are very similar. For the presently investigated transfer systems, having minor changes in the nuclear configuration, the
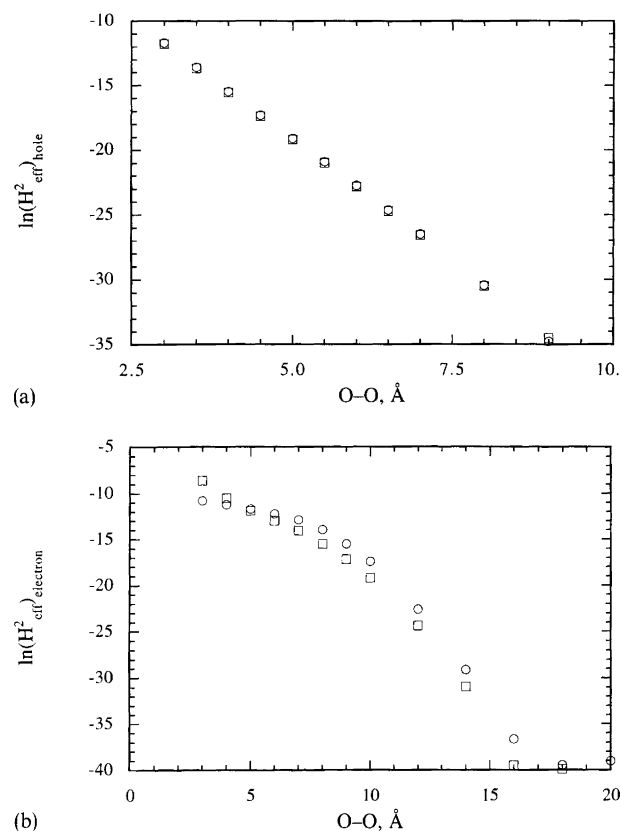

(a)

(b)

Fig. 2. Effective transfer elements for electron transfer for the three different basis sets (*a*), (*b*) and (*c*) and for the two different nuclear configurations slow (s) and fast (f); see text for further details.

Fig. 3. Effective transfer elements for hole (A) and electron transfer (B) for the basis set (*b*) and the slow nuclear configuration; see text for further details.

small differences in the transfer coupling elements from the two different methods are to be expected.

Conclusions.

In both hole and electron transfer, the diffuse-extended basis sets b and c show generally smooth exponential decay for the effective electron transfer coupling elements, while the non-diffuse-extended basis a, although fairly flexible, yields non-exponential and rapid decay over short range and (in the case of electron transfer) unreasonable behavior at long range. The addition of polarization functions has little or no contribution to the overlap or coupling element in all cases considered.

The comparison of slow vs. fast transfer yields nearly identical results in all cases studied, especially with regard to coupling elements. Slow transfer, with differing initial and final nuclear geometries, offers a calculational advantage, in that initial and final localized wavefunctions are easier to converge, and does not require mixing of the HOMO and LUMO in the initial guess to break symmetry, as is the case with identical initial and final (nuclear) states. Much more significantly, the nearly identical results argue that, within the range of geometries probed here, the coupling element is (nearly) invariant with position on the potential energy surface (equivalent to the Condon approximation), even to the point of choosing different initial and final state nuclear geometries. Thus, coupling elements determined at the geometry associated with the initial state (as might be obtained from a Hush analysis of optical excitation spectra)[12] can be used to describe thermal charge transfer, assuming minor changes in (nuclear) geometry between initial and final states.

Failure of the basis sets to provide smooth, exponential decay (of either overlaps or coupling elements) is most likely the result of basis set superposition error[13] (in the case of moderate overlaps, in the short to intermediate separations), or round-off error on the tail of (not adequately diffuse) basis functions (in the case of long-range interactions). The 8–12 Å behavior of the coupling element in the slow, basis c electron transfer case is an example of the former, while the 10–20 Å behavior of basis set a for the electron transfer case is an example of the latter.

Generally, then, flexible and diffuse-extended basis sets are essential to provide realistic behavior for hole and electron transfer. Also, a minor change in nuclear geometry between the initial and final states does not seem to significantly affect the overlaps or coupling elements, while it does allow for greater ease of calculation.

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