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Basis set effects on the direct calculation of intermolecular coupling elements for electron transfer reactions

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Abstract

We investigate basis set effects for the direct calculations of coupling elements for electron transfer reactions. We discuss the advantages of direct methods versus indirect methods. Appropriate description of the coupling elements for electron transfer reactions at large intermolecular separation requires flexible basis sets.

Keywords: Calculation; Intermolecular coupling elements; Electron transfer reactions

1. Introduction

Theoretical elucidation of electron transfer events has been the focus of increasing interest and numerous excellent reviews in recent years [1–4]. Such interest has arisen largely from the increasing ease of calculation of such parameters as the electronic coupling element, solvent relaxation effects, calculation of reorganization energies, etc. Procedures for the calculation of coupling elements include simple one particle (either an electron or a 'hole') [2], pseudo-two particle (both electron and hole which may interfere con- or destructively) [3], and many particle methods [4], employing extended Hückel [2e–g,4b,l] various NDO (neglect of differential overlap) [4b,d,k] or ab initio [4a–j,m] techniques for the definition of electronic states. Methods may be indirect (e.g. change in self consistent field calculated total energies (ΔSCF) [2e], Koopmans [5,4b,f] or (less commonly) employ direct calculations [4a–j,m]. In all such calculations, careful selection of basis sets is necessary to adequately describe the system in question. However, as shown by Cave et al. [4f] and Newton [4d], to adequately define long range interactions (such as electron transfer at distances greater than 5 Å), currently available Gaussian-type orbital basis sets such as those of Pople [6] or Huzinaga [7] must be augmented by diffuse terms. Here we carefully consider the addition of basis functions, both diffuse (s-type) and polarizable (p or d), to a number of symmetric electron transfer systems. We also consider the contributions of both one and two electron integrals to the overall coupling element expression. The indirect methods have within recent years been utilized for obtaining information about the dependence of the electronic transfer element as a function of distance and orientation of the charge transfer system [2h–l].

2. Theory

SCF calculations on symmetric open shell dimer systems can yield solutions of two types: the symmetric solution, and the broken symmetry solutions [8], in which the odd electron is localized on either the 'left' or 'right' half of the system. The broken symmetry solutions can be obtained by removing symmetry restraints, mixing the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) to yield an unsymmetric distribution of charge density, and minimizing the energy.

The two broken symmetry solutions, corresponding to initial and final states (ψ_i and ψ_f) of an electron transfer event at the avoided crossing, have orbitals which are not orthogonal to one another. We therefore used the corresponding orbitals method [9] based upon a pairing theorem of Löwdin [10] to obtain overlaps and coupling elements between these two states. Thus, in the Hartree–Fock (HF) case we start with two

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wavefunctions ψ_i and ψ_f which are defined as non-orthogonal Slater determinants of spin orbitals:

$$|\psi_\mathrm{i}\rangle=\prod_{j=1}^{N_\alpha}a^\dagger_{\alpha,K^\mathrm{i}_j}\prod_{k=1}^{N_\beta}a^\dagger_{\beta,K^\mathrm{i}_k}|\mathrm{vac}\rangle$$

$$|\psi_\mathrm{f}\rangle=\prod_{j=1}^{N_\alpha}a^\dagger_{\alpha,K^\mathrm{f}_j}\prod_{k=1}^{N_\beta}a^\dagger_{\beta,K^\mathrm{f}_k}|\mathrm{vac}\rangle \qquad (1)$$

where N_α and N_β refer to the number of α and β electrons, respectively, $a^\dagger_\alpha$ is an α-electron creation operator, K^i_j (K^f_j) refers to the jth molecular orbital (MO) of the initial (final) state i (f), and vac refers to the vacuum state. The creation operators are written in ascending order. The MOs are formed from the given basis set of atomic orbitals (AOs). The MOs for the initial and final states are given by:

$$|K^\mathrm{i}_{x,j}\rangle=a^\dagger_{x,K^\mathrm{i}_j}|\mathrm{vac}\rangle$$

$$|K^\mathrm{f}_{x,j}\rangle=a^\dagger_{x,K^\mathrm{f}_j}|\mathrm{vac}\rangle \qquad (2)$$

in which $a^\dagger_{x,k}$ creates an electron with spin x in the kth orbital. Thus, the character of the MOs and the overall character of the initial and final states are defined by our choice of basis sets. Note that the orbitals within the spin orbital sets for the given electronic state are orthogonal; we then express the non-orthogonality between the MOs of the different states by the overlap matrix **D**, whose elements are as follows:

$$\mathbf{D}^x_{jk}=\langle K^\mathrm{f}_{x,j}|K^\mathrm{i}_{x,k}\rangle\neq\delta_{jk} \qquad (3)$$

Hereafter the spin state x will not be written, but it is understood that α and β MOs must be dealt with separately. We may then perform unitary transformations on the sets of spin orbitals $|K^\mathrm{i}\rangle$ and $|K^\mathrm{f}\rangle$:

$$|\hat{K}^\mathrm{i}_j\rangle=\mathbf{V}|K^\mathrm{i}_j\rangle \qquad (4)$$

and

$$|\hat{K}^\mathrm{f}_k\rangle=\mathbf{U}|K^\mathrm{f}_k\rangle \qquad (5)$$

which leave ψ_i and ψ_f invariant except in phase. The overlap matrix **D** is then transformed according to

$$\langle\hat{K}^\mathrm{f}|\hat{K}^\mathrm{i}\rangle=\hat{\mathbf{d}}=\mathbf{U}^\dagger\mathbf{D}\mathbf{V} \qquad (6)$$

The transformation matrices **U** and **V** are obtained along with the (diagonal) eigenvalue matrix Λ from the equations

$$\mathbf{D}^\dagger\mathbf{D}\mathbf{V}=\mathbf{V}\Lambda \qquad (7)$$

and

$$\mathbf{U}=\mathbf{D}\mathbf{V}\Lambda^{-1/2} \qquad (8)$$

(It should be understood that **U** is defined as the eigenvector matrix of $\mathbf{D}\mathbf{D}^\dagger$, and can thus be obtained in two ways.) Given that (from Eq. (7))

$$\Lambda=\mathbf{V}^\dagger\mathbf{D}^\dagger\mathbf{D}\mathbf{V} \qquad (9)$$

it follows that

$$\begin{aligned}\hat{\mathbf{d}}&=\mathbf{U}^\dagger\mathbf{D}\mathbf{V}\\&=\Lambda^{-1/2}\mathbf{V}^\dagger\mathbf{D}^\dagger\mathbf{D}\mathbf{V}\\&=\Lambda^{1/2}\end{aligned} \qquad (10)$$

which has the required diagonal form.

The overlap integral between ψ_i and ψ_f is then given by

$$S_\mathrm{fi}=\left\langle\prod_{k=1}^{N}K^\mathrm{f}_k\middle|\prod_{j=1}^{n}K^\mathrm{i}_j\right\rangle$$

$$=(\det\mathbf{U})(\det\mathbf{V}^\dagger)\prod_{j=1}^{N}\hat{d}_{jj} \qquad (11)$$

Given the general energy operator Ω_op

$$\Omega_\mathrm{op}=\Omega_0+\Omega_1+\tfrac{1}{2}\Omega_2 \qquad (12)$$

in which Ω_0 is the nuclear repulsion operator, Ω_1 is the one-electron operator, and Ω_2 is the two-electron operator, we can obtain the various components of the energy as follows:

$$\Omega^{(0)}_\mathrm{fi}=\left\langle\prod_{k=1}^{N}K^\mathrm{f}_k|\Omega_0|\prod_{j=1}^{N}K^\mathrm{i}_j\right\rangle$$

$$=\Omega_0(\det\mathbf{U})(\det\mathbf{V}^\dagger)\prod_{j=1}^{N}\hat{d}_{jj} \qquad (13)$$

$$\Omega^{(1)}_\mathrm{fi}=(\det\mathbf{U})(\det\mathbf{V}^\dagger)\sum_{j=1}^{N}\langle\hat{K}^\mathrm{f}_j|\omega|\hat{K}^i_j\rangle\prod_{k\neq j}^{N}\hat{d}_\mathrm{kk} \qquad (14)$$

$$\Omega^{(2)}_\mathrm{fi}=(\det\mathbf{U})(\det\mathbf{V}^\dagger)\sum_{j<k}\prod_{m\neq j,k}^{N}\hat{d}_\mathrm{mm}$$

$$\times\langle\hat{K}^\mathrm{f}_j\hat{K}^\mathrm{f}_k|\omega(1,2)(1-P_{12})|\hat{K}^\mathrm{i}_j\hat{K}^\mathrm{i}_k\rangle \qquad (15)$$

in which ω is the kinetic plus nuclear attraction energy, $\omega(1,2)$ is $1/R_{12}$ (the distance between the electrons in atomic units), and P_{12} is the exchange operator:

$$P_{12}|\hat{K}^\mathrm{i}_j\hat{K}^\mathrm{i}_k\rangle=|\hat{K}^\mathrm{i}_k\hat{K}^\mathrm{i}_j\rangle \qquad (16)$$

If we then define

$$H_\mathrm{ii}=\langle\psi_\mathrm{i}|\Omega_\mathrm{op}|\psi_\mathrm{i}\rangle \qquad (17)$$

$$H_\mathrm{ff}=\langle\psi_\mathrm{f}|\Omega_\mathrm{op}|\psi_\mathrm{f}\rangle \qquad (18)$$

and

$$H_\mathrm{fi}=\langle\psi_\mathrm{f}|\Omega_\mathrm{op}|\psi_\mathrm{i}\rangle \qquad (19)$$

the coupling element T_fi (or one half the splitting between the symmetric and anti-symmetric solutions at the transition state) is given by

$$T_\mathrm{fi}=\frac{H_\mathrm{fi}-S_\mathrm{fi}H_\mathrm{ii}}{1-S^2_\mathrm{fi}} \qquad (20)$$

This T_fi corresponds to the off-diagonal element in the non-orthogonal two-state CI problem [11].

The procedure outlined above describes the direct calculation of the coupling element between two different and non-orthogonal electronic states. One of us has developed another procedure for direct calculation of coupling elements between initial and final states for the ET reaction which employs the Löwdin symmetric orthogonalization scheme for taking account of the non-orthogonality [4m].

The schemes used most frequently for calculating the coupling element involve various indirect methods. The ΔSCF method [2e–g] involves the calculation of total energies of ground and first excited states at a given geometry; the coupling element is then given by half the energy difference between the two states at the transition state configuration. This total energy difference is frequently approximated by the use of Koopmans theorem [5], which makes the assumption that the spin orbitals in the $(N\pm1)$-electron states are identical with those of the N-electron state. Therefore the energy splitting between the two states is approximated by the difference in energy between the HOMO and the LUMO, or the initial MO and the final MO.

The scheme for indirect calculation of the coupling element can be expressed by considering the diabatic representation for the electronic wave functions (ψ_i and ψ_f). These wave functions are the broken symmetry solutions and represent electronic states where the excess electron is either located on the donor (ψ_i) or acceptor (ψ_f). The adiabatic representation for the electronic wave functions are given by the ansatz

$$\Psi(Q)=C_i(Q)\psi_i(Q)+C_f(Q)\psi_f(Q) \tag{21}$$

where Q is the generalized reaction coordinate. The energies for the two states in the adiabatic representation are obtained from

$$H(Q)\Psi(Q)=\Psi(Q)E(Q) \tag{22}$$

and making use of Eq. (21) the following secular equation is obtained

$$\begin{pmatrix} H_{ii}-E & H_{if}-S_{if}E \\ H_{fi}-S_{fi}E & H_{ff}-E \end{pmatrix}\begin{pmatrix} C_i \\ C_f \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{23}$$

where $S_{fi}(Q)=S_{if}(Q)=S_{if}=\langle\psi_i(Q)|\psi_f(Q)\rangle$, $H_{jj}(Q)=H_{jj}=\langle\psi_j(Q)|H(Q)|\psi_j(Q)\rangle$, and $H_{fi}(Q)=H_{if}(Q)=H_{if}=\langle\psi_f(Q)|H(Q)|\psi_i(Q)\rangle$. The energies are then given by

$$E(Q)^{\pm}=\frac{H_{ii}+H_{ff}-2H_{if}S_{if}}{2(1-S_{if}^2)}\pm\frac{\sqrt{D}}{2(1-S_{if}^2)} \tag{24}$$

where

$$D=(H_{ii}-H_{ff})^2+4[H_{if}^2-H_{if}S_{if}(H_{ii}+H_{ff})+S_{if}^2H_{ii}H_{ff}] \tag{25}$$

Therefore for a given nuclear configuration the energy difference between the two adiabatic states is given by

$$\Delta E(Q)=\frac{\sqrt{D}}{1-S_{if}^2} \tag{26}$$

At the transition state configuration Q^*, the diabatic energy surfaces cross and $H_{ii}(Q^*)=H_{ff}(Q^*)$; then D is reduced to $4(H_{if}(Q^*)-S_{if}(Q^*)H_{ii}(Q^*))^2$, and the energy splitting is given by

$$\Delta E(Q^*)=2\,\frac{H_{if}-S_{if}H_{ii}}{1-S_{if}^2} \tag{27}$$

where H_{if}, S_{if}, and H_{ii} are all evaluated at Q^*. It is clearly seen from Eqs. (25)–(27) that the energy splitting is equal to twice the coupling element for the ET reaction at only those nuclear configurations at which $H_{ii}(Q)=H_{ff}(Q)$, i.e. the transition state configuration(s). For the indirect calculations it is extremely important to use the approximate calculation for the difference in total energy given in Eq. (27) only at the appropriate nuclear configuration; otherwise, it is necessary to employ the full expression for D as seen in Eq. (25). The location of the transition state is given by the topology of the energy surfaces and not by the model concept that the transferring electron should be distributed equally between the donor and acceptor sites. This model concept was introduced by Marcus for simplifying the statistical mechanical calculations, but it is not necessarily valid for the more detailed electronic descriptions. It is true that this model works well for symmetric systems, and for large systems it is a practical method for the determination of the appropriate nuclear configuration for indirect methods. Nevertheless, indirect methods remain highly inaccurate and the direct methods offer clear advantages. Direct methods simply require some non-standard techniques and implementation of computer code and assumes that the reacting system is approximated by a linear combination of two Slater determinants.

3. Calculational details

Wavefunctions for the various systems under study were obtained through the use of the Gaussian 88 series of programs [12]. Basis sets used included Pople's 21G and 31G sets for H and He [6c,d,f], with and without added p or diffuse s [13] functions (see below), and Pople's 6-31G set for O [6d,e], with and without added d or diffuse sp [13] functions (see below). In all cases the ground state of the fully symmetric system was calculated. All symmetry restrictions were removed, and slight mixing of the HOMO and LUMO before the SCF iterations yielded localized results as long as the distances between the 'right' and 'left' portions were sufficiently large (⩾3 Å). We restricted out studies to fully symmetric systems in which the right and left halves differed only in charge density. The geometries used for the bimolecular systems (H_4^{+} and $[H_2O]_2^{+}$) were obtained from geometry minimizations at 5.0 Å (using Pople's 6-31G basis), with the constraint that both molecules have equivalent geometries (maintaining at least C_{2v} symmetry).

Note that ψ_i and ψ_f for an unsymmetric system must be obtained by two separate calculations. However, as we have constrained our systems to be of at least C_{2v} symmetry, the initial and final electronic states are mirror images of one another. Therefore, only one calculation was needed to obtain the MO coefficients, and our computation time was reduced by half.

4. Results and discussion

4.1. He_2^+

The first and simplest system we studied was the three-electron He_2^+ system. Our results are shown in Fig. 1. Five different basis sets were used over the internuclear separation range 3–9 Å: Pople's 21G, 31G, 31G+*p* $(\gamma=1.1)$[1] 31G+s $(\gamma=0.04)$[2] and 31G+s, p and one centered ('c') s-type 'ghost' orbital ($\gamma_s=0.3129$, $\gamma_p=0.3541$, $\gamma_c=0.03555$; coefficients chosen to yield a minimum energy at 5.0 Å) [6c,d,f]. Fig. 1(a) and (b) shows overlaps and coupling elements, respectively, between initial and final states over the indicated range of internuclear separations. Note that each basis set save the last (31G+spc) has a limited range in which results are reasonable. For the 21G, 31G and 31G+p sets, such limited range is the result of basis functions whose tails (at large distances) have amplitudes which do not decay in a regular fashion, yielding spurious data. The 31G+s, on the other hand, seems to yield reasonable results at separations greater than 7 Å; however, there is a node at close to 6 Å at which both the overlap and coupling terms drop suddenly to 0. This occurs because of a negative coefficient on the diffuse function for the unoccupied site (at distances greater than 5.5 Å) which is larger than the sum of the positive coefficients for the other s functions on that site. This results in a wavefunction with a large positive charge density on one site, and a small negative charge density on the other. Switching the electron and integrating the overlap between the initial and final states then gives the nodal behavior shown.

Addition of a lone p-type function to He centers seems to have little effect on overlap or coupling terms. However, to adequately describe polarization of electron shells by ions, etc., both diffuse s and p functions should be used, with additional centered functions, as shown in the 31G+spc case, which yields the most smooth and reasonable results. Of course, the more functions within a basis set, the more flexible it becomes and the better the results, as long as basis functions chosen are appropriate for the system (i.e. yield lowest energies).

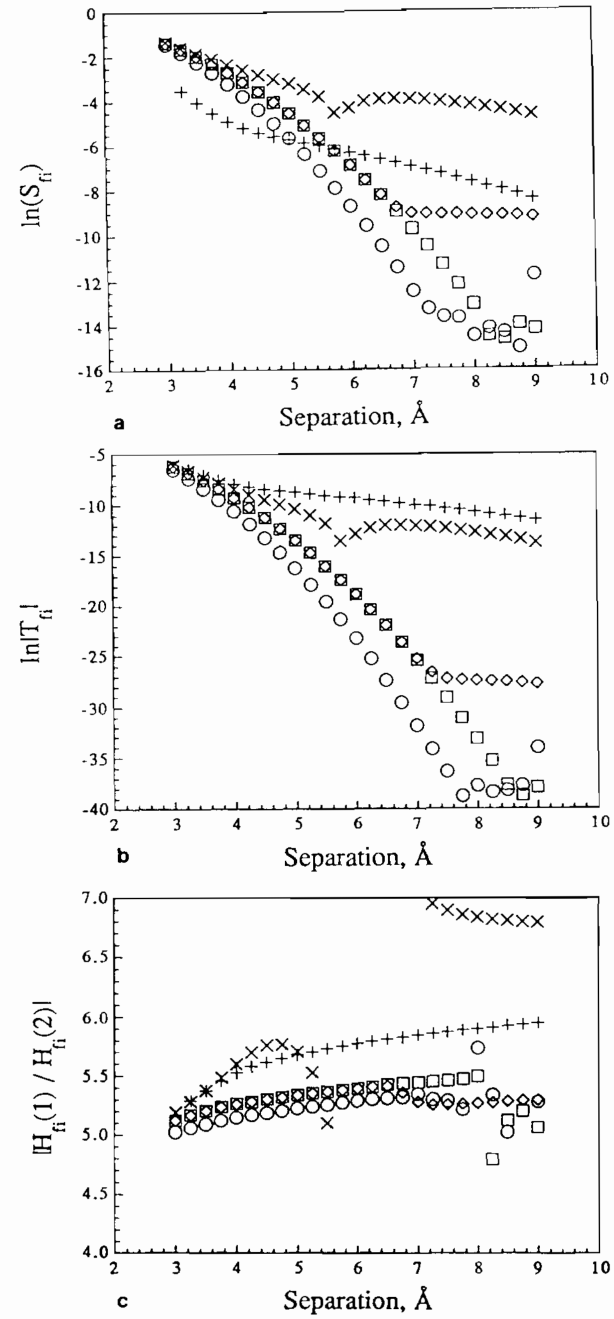

Fig. 1. (a) Overlaps, (b) coupling elements and (c) ratios of one- to two-electron terms for the He_2^+ system. ○, 21G; □, 31G; ◇, 31G+p; ×, 31G+s; +, 31G+spc; details of basis sets are in the text. T_{fi} is in a.u.

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[1] γ refers to the coefficient of the exponent in a Gaussian type orbital: a $e^{\gamma r}$, where r is the distance from the nucleus. Note that γ is given in a.u.$^{-1}$.

[2] γ here was chosen based on a comparable diffuse s for H; see Ref. [13].

As shown in Fig. 1(c), the 21G, 31G and 31G+p cases yielded ratios of the one-electron versus two-electron parts of the coupling elements which were nearly constant at 5.25. Thus, methods which neglect two-electron terms (such as extended Hückel) neglect a significant contribution to the coupling element for this simple three-electron system. The 31G+s set again gave nodal behavior around 6 Å.

In addition to studying the changes in overlap and coupling elements with distance and with various basis sets, we studied the addition of a range of diffuse Gaussians at a fixed geometry (5.0 Å separation), shown in Fig. 2. For this study we used Pople's 31G basis set [6c,d,f]. To this we added a single s-type Gaussian function, with an exponential coefficient varied over the range 10^3 to 10^{-6}. Note that (at 5.0 Å) significant changes to the coupling element occur only over a narrow range of exponential coefficients (10^0 to 10^{-4}). The largest coupling element at 5.0 Å was found to occur with an s-type Gaussian with $\gamma = 0.013$; with this additional basis we obtained a coupling element of 4.1985×10^{-5} a.u.[3], as opposed to the value without the additional basis, 1.4474×10^{-6} a.u. It should be noted that the lowest total energy at 5.0 Å was obtained with the addition of a basis function with $\gamma = 0.3072$, which gave a coupling element of 1.6854×10^{-6} a.u. (Corresponding overlaps and HF energies are: for no additional basis, overlap 2.9396×10^{-5}, energy -4.8488 a.u.; for $\gamma = 0.013$, overlap 8.2939×10^{-4}, energy -4.8491 a.u.; for $\gamma = 0.3072$, overlap 3.3384×10^{-5}, energy -4.8507 a.u.)

4.2. H_4^+

Three different configurations of the bimolecular $[H_2]_2^+$ system were examined over a range of geometries. The first configuration, labeled H_4^+(R) (Fig. 3), consisted of two H_2 molecules parallel to one another and lying in a plane, with the intramolecular bond distances held fixed at 0.855 Å, while the intermolecular distance was varied (rectangular). The second configuration, H_4^+(L) (Fig. 4), consisted of two H_2 molecules lined up (linear), with the intramolecular bond distances held at 0.884 Å, and the intermolecular (inner H–inner H) distance varied. The third configuration, H_4^+(X) (Fig.

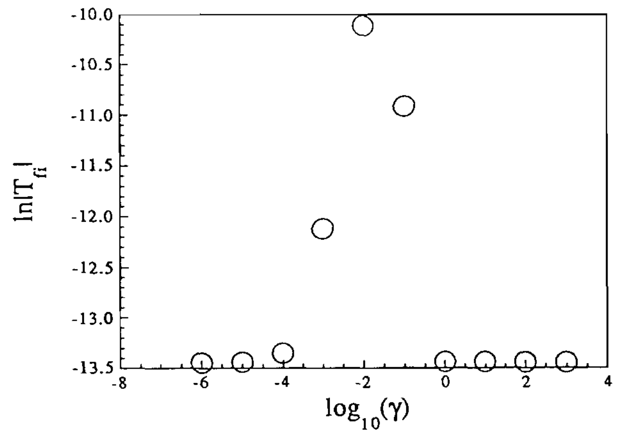

Fig. 2. Coupling elements vs. $\log_{10}(\gamma)$ for He_2^+ 31G+s (γ on added s) at 5.0 Å. T_{fi} is in a.u.

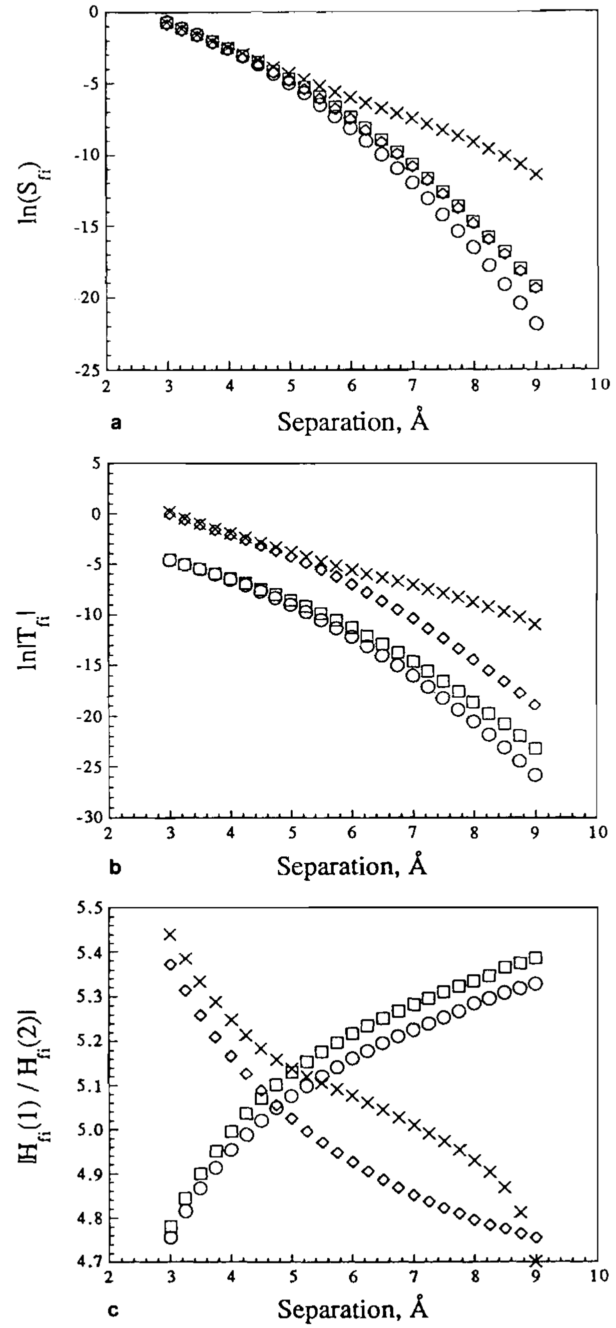

Fig. 3. (a) Overlaps, (b) coupling elements and (c) ratios of one- to two-electron terms for the H_4^+(R) system (see text). ○, 21G; □, 31G; ◇, 31G+p; ×, 31G+s; details of basis sets are in the text. T_{fi} is in a.u.

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[3] Throughout the text we report the absolute values of the coupling elements.

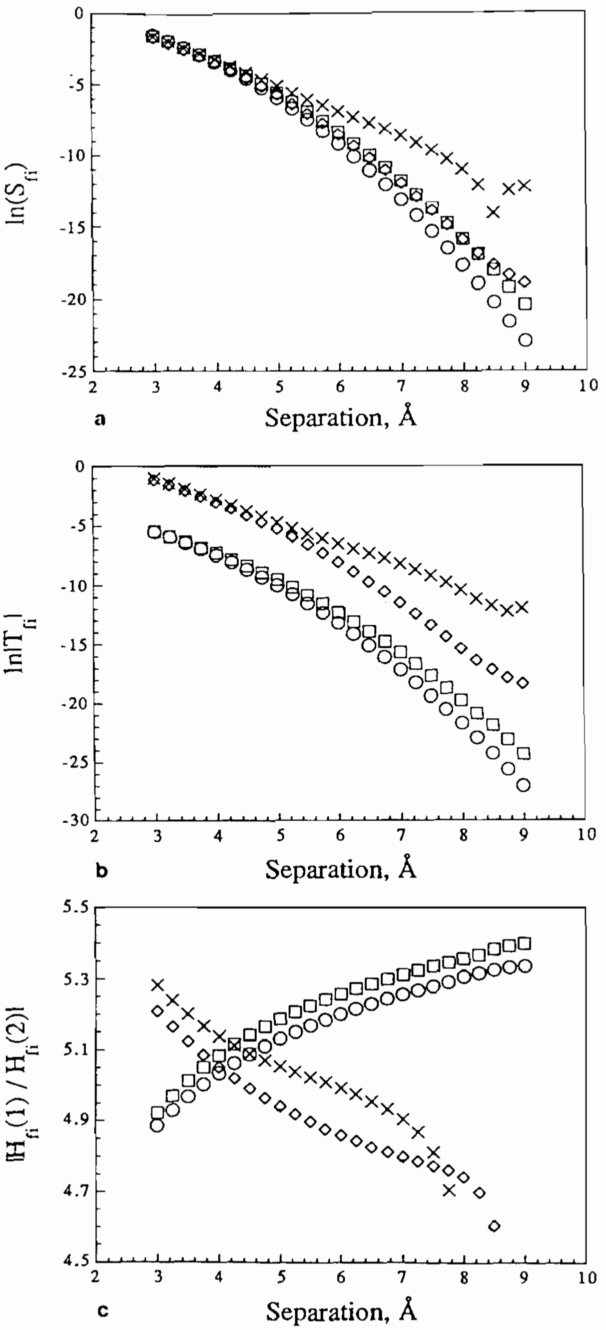

Fig. 4. (a) Overlaps, (b) coupling elements and (c) ratios of one- to two-electron terms for the $H_4^+(L)$ system (see text). ○, 21G; □, 31G; ◇, 31G+p; ×, 31G+s; details of basis sets are in the text. T_{fi} is in a.u.

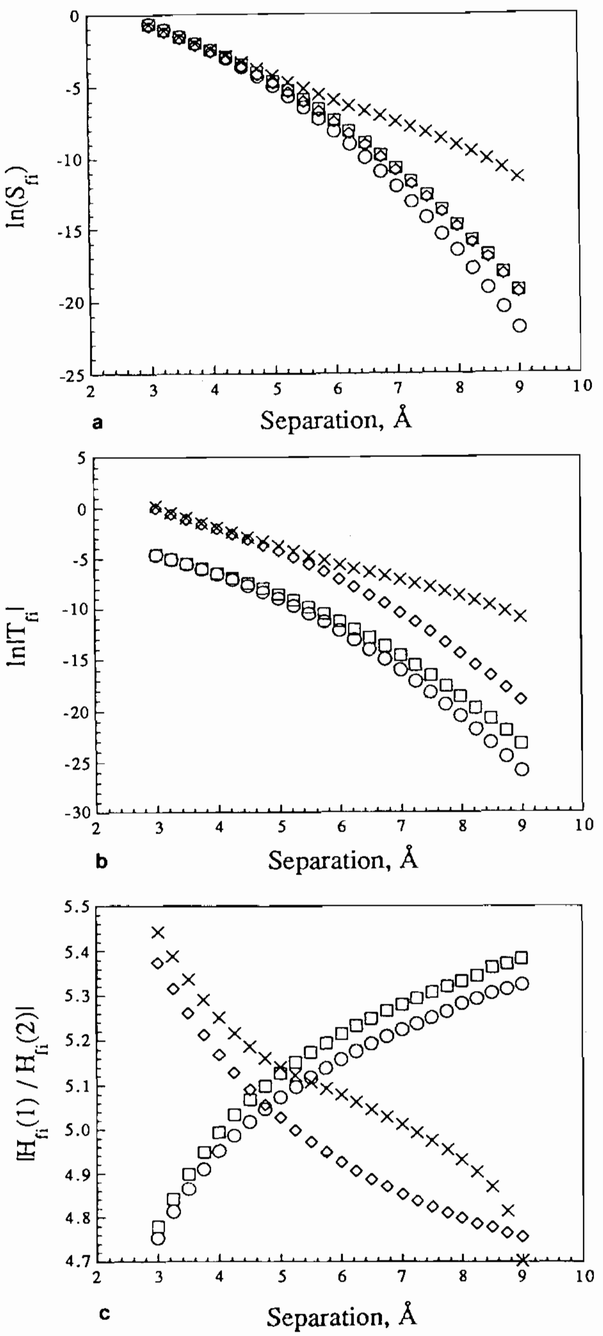

Fig. 5. (a) Overlaps, (b) coupling elements and (c) ratios of one- to two-electron terms for the $H_4^+(X)$ system (see text). ○, 21G; □, 31G; ◇, 31G+p; ×, 31G+s; details of basis sets are in the text. T_{fi} is in a.u.

5), was similar to the first, except that the two hydrogen molecules were twisted 90° relative to one another. The intramolecular bond distances were held at 0.855 Å.

The results for each H_4^+ system were similar: $H_4^+(R)$ and $H_4^+(X)$ were basically identical, differing by less than 0.5% in all values (see Figs. 3 and 5), while $H_4^+(L)$ was similar but with lower overlaps and coupling elements ($\sim 40\%$ of the $H_4^+(R)$ values) (see Fig. 4) for a given intermolecular distance. With this in mind, we will discuss the results for $H_4^+(R)$ as the general case. We examined four different basis sets over the intermolecular separation range 3–9 Å: Pople's 21G, 31G, 31G+p ($\gamma=1.1$) and 31G+s ($\gamma=0.036$) [6c,d,f,13].

Overlaps and coupling elements are shown in Figs. 3(a) and (b), respectively. Note that all basis sets give

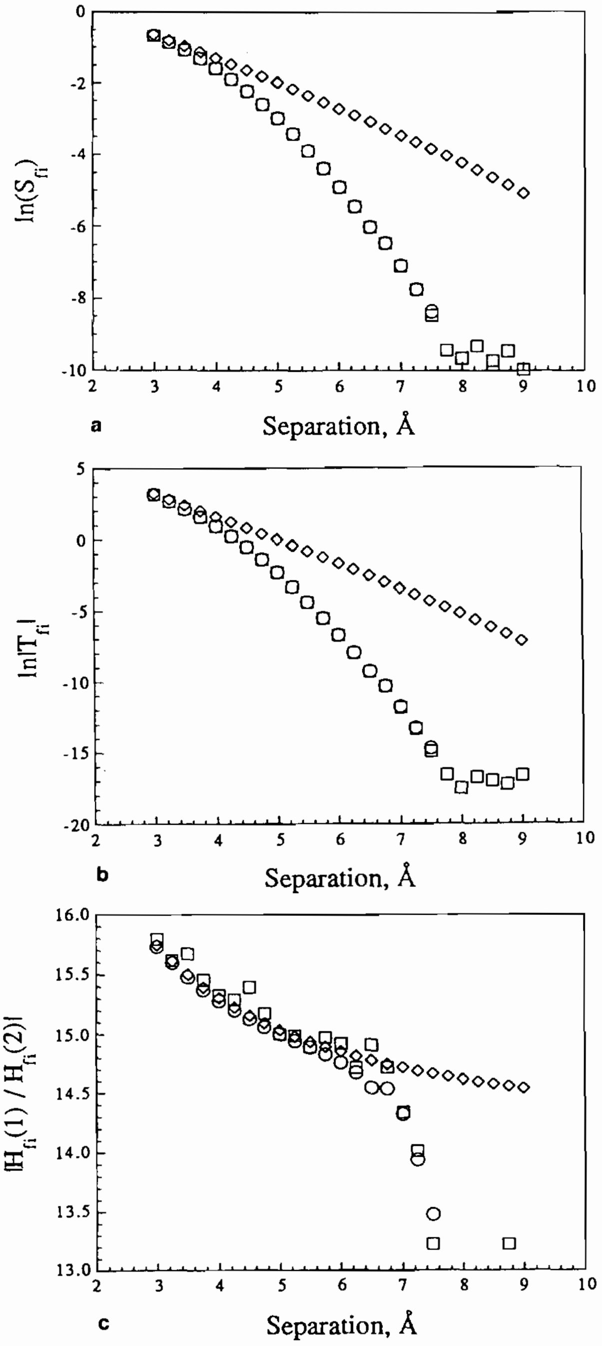

Fig. 6. (a) Overlaps, (b) coupling elements and (c) ratios of one- to two-electron terms for the $[H_2O]_2^+$(**1**) system (see text). ○, 6-31G; □, 6-31G+d; ◇, 31G+sp; details of basis sets are in the text. T_{fi} is in a.u.

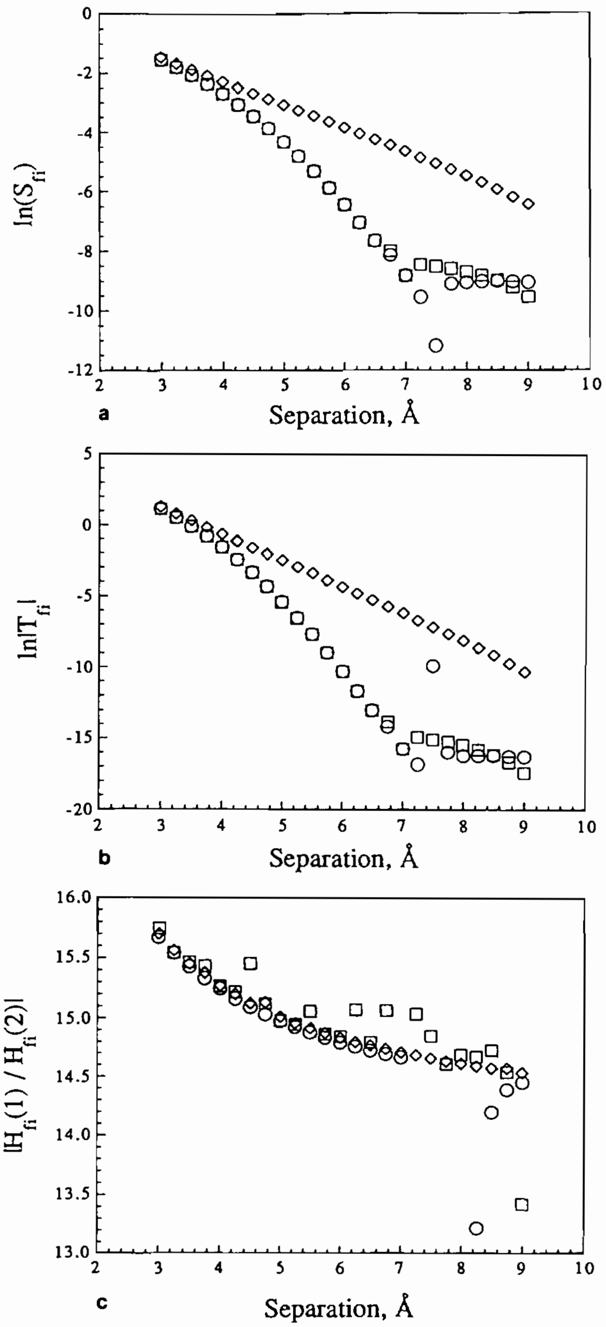

Fig. 7. (a) Overlaps, (b) coupling elements and (c) ratios of one- to two-electron terms for the $[H_2O]_2^+$(**2**) system (see text). ○, 6-31G; □, 6-31G+d; ◇, 31G+sp; details of basis sets are in the text. T_{fi} is in a.u.

smooth behavior over the range shown, but that 31G+s gives basically exponential decay over the full range (3–9 Å), while the other sets give a more rapid decay. Energies at 5.0 Å are, for 21G = −1.6890 a.u., 31G = −1.6942 a.u., 31G+s = −1.6952 a.u. and 31G+p = −1.7091 a.u. Contrary to the He_2^+ system, the p-type orbitals are well populated and contribute to both intermolecular σ bonding as well as intramolecular coupling.

The ratios of one-electron versus two-electron integrals are shown in Fig. 3(c). Note that two-electron terms decline with respect to one-electron terms in systems without additional functions (21G, 31G), while the opposite is true with systems with added functions (31G+p, 31G+s).

$[H_2O]_2{}^+$

Two configurations of the bimolecular system $[H_2O]_2{}^+$ were studied: $[H_2O]_2{}^+$(**1**) (Fig. 6) consisted of two water molecules whose planes were parallel and whose hydrogens eclipsed one another (H–O distance 0.9675 Å; ∠HOH 115.215°), while $[H_2O]_2{}^+$(**2**) (Fig. 7) consisted of two water molecules lying in a plane, with the oxygens pointing at one another (H–O distance 0.9675 Å; ∠HOH 114.975°). Intermolecular distances for both systems are O–O nuclear separations. We examined three different basis sets over the intermolecular separation range 3–9 Å: Pople's 6-31G (1s2sp on O, 2s on H), 6-31G+d (on O only; $\gamma=0.8$) and 6-31G+sp (on O only; $\gamma=0.0845$) [6d,e,13].

The results for the two different systems of $[H_2O]_2{}^+$ were similar. Overlaps for the $[H_2O]_2{}^+$(**1**) system were generally 10 times larger than those of $[H_2O]_2{}^+$(**2**), while coupling elements were 10–100 times larger for $[H_2O]_2{}^+$(**1**), but the trends were consistent between the two cases. We will therefore describe $[H_2O]_2{}^+$(**1**) as the general case. Note that both systems failed to yield suitable data at separations greater than 7 Å, except when the diffuse sp basis was added.

Overlaps and coupling elements are shown in Figs. 6(a) and 6(b), respectively. Note that 6-31G and 6-31G+d give basically identical results, yielding a faster-than-exponential decay with distance, while 6-31G+sp is basically exponential for both overlap and coupling terms.

Ratios of one- versus two-electron terms are shown in Fig. 6(c). Though less significant than in the $He_2{}^+$ or $H_4{}^+$ systems, the two-electron term remains important enough in systems with heavy atoms that its neglect may cause significant errors in calculated coupling elements.

5. Conclusions

We have examined a series of symmetric, two-site electron exchange systems with a series of different basis sets, observing the changes with the addition of diffuse and polarizable basis functions. We have directly calculated, using the corresponding orbitals scheme, the overlaps and coupling elements for the initial and final states of an electron transfer event occurring over a range of internuclear and intermolecular separations.

Our results indicate that, without the addition of diffuse functions, Gaussian type basis sets yield overlaps and coupling elements whose decay rates at large internuclear or intermolecular separations become non-exponential, dropping off too rapidly with distance. Furthermore, such basis sets have a limited 'useful range', beyond which results become nonsensical (>7 Å for $He_2{}^+$ 31G or $[H_2O]_2{}^+$ 6-31G). Addition of polarizable (p or d) functions to systems such as $He_2{}^+$ (purely s-type) or $[H_2O]_2{}^+$ (which already has occupied p orbitals) gives little change to overlaps or coupling terms, while in a system such as $H_4{}^+$ (bimolecular; pseudo-p character) addition of polarizable functions increases coupling at large distances (but has little effect on overlap) and alters the ratio of one- versus two-electron terms in the coupling element. Addition of diffuse functions in all cases yields the most dramatic effects, giving for both overlap and coupling basically exponential decays with distance which are much less rapid than for systems without diffuse functions.

It must be stressed that the 'best' choice for a basis set should take into consideration both flexibility and minimization of energy. Arbitrarily adding diffuse functions to atomic centers may increase coupling terms dramatically, and yet may not be appropriate for the system in question. Addition of a suitable number of both diffuse and polarizable functions and minimization of energy terms should yield the 'best' results, giving both lower energies and a more extended range of geometries over which calculations are valid.

In addition, we have carefully examined the contribution of one- and two-electron terms to the overall coupling expression. In all systems studied, the two-electron term is a significant contribution to the coupling element, and its neglect could not fail to adversely affect an adequate description of intermolecular coupling. Another aspect to consider is the small range by which the ratio of one and two electronic contributions varies. This indicates that semi-empirical calculations that grossly neglect two-electronic terms can be parametrized for each homolog series of charge transfer systems and thereby provide good estimates of the electron transfer coupling elements. This will of course extend the direct scheme of calculating coupling elements to very large systems.

At present we have not considered the effects of off-centre basis functions and we have limited ourselves to the commonly available basis sets in order to illustrate the problems that are connected to the use of these when calculating electron transfer coupling elements.

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