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A Simple Model for the Interaction Potentials in Electron-Transfer Reactions: Application to the H_2^+/H_2 System

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Abstract: This paper presents a rigorous diabatic formulation for the electron transfer between two deformable structured ion cores. The electronic overlaps and interaction matrix elements are evaluated within a model that considers only the active electron explicitly. The exact relationship between the diabatic matrix elements and the adiabatic electronic energies of the total system is used to compare the results of our model with those from previous ab initio calculations. The agreement for the H_2^+/H_2 system at various geometries strongly supports the adequacy of the one-active-electron model. Within this model the electronic–vibrational interaction matrix elements can be evaluated directly and efficiently, thus allowing the first detailed test of the Franck–Condon approximation for electron-transfer processes. It is shown that the Franck–Condon approximation leads to inaccuracies of less than 10% except at very small center of mass separations.

I. Introduction

The role of vibrational and electronic energy in gas-phase electron-transfer reactions is a topic of increasing interest both experimentally[1-12] and theoretically.[13-18] Experimental measurements have succeeded in providing either initial state selected total integral cross sections or final state selected integral and differential cross sections. Fully resolved state-to-state data have not been determined, but are expected in the near future.

In theoretical investigations, the dynamics of electron transfer can be treated rigorously within the arrangement channel formulation of chemical reactions.[19-21] This has been presented in a totally quantum mechanical formalism for heavy-atom reactions by Diestler,[19] and later for electron-transfer reactions by Schmalz, Stechel, and Light.[20] Further developments can be found in the recent article of Top and Shapiro.[21] The semiclassical impact parameter treatment, predating the above work by a few years, was presented in the seminal paper of Bates and Reid.[17] Their procedure used the time-dependent Schrödinger equation for the internal motion and a straight line classical path for the relative translational motion. Flannery, Moran, and co-workers[18] developed a better description of the trajectory in this semiclassical formulation. Recently, Becker[16] has provided accurate quantum mechanical results for reaction 1 using a model potential. These

$$\begin{aligned} O_2^+(v_1) + O_2(v_2) &\rightarrow O_2^+(v_1') + O_2(v_2') \text{ direct (D)} \\ &\rightarrow O_2(v_2') + O_2^+(v_1') \text{ exchange(X)} \quad (1) \end{aligned}$$

have been reproduced with quantitative accuracy by the semiclassical energy conserving trajectory (SCECT) procedure,[14] which is formally identical with the multistate orbital treatment of Flannery, Moran, and co-workers.[18]

Although the dynamics can be treated accurately at modest computational expense (especially within the SCECT procedure),

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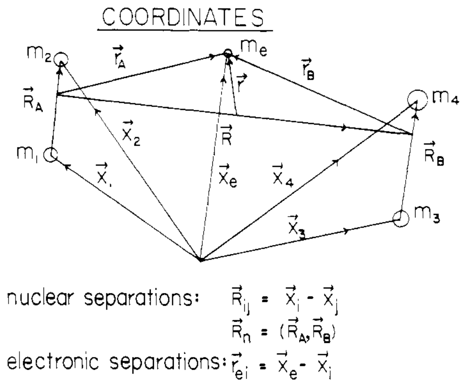

Figure 1. Coordinates and masses for the electron transfer between two diatomic ion cores A^+ and B^+.

the agreement with experimental total cross sections[2b] is unsatisfactory even for the simple symmetric charge-transfer reaction[15] in eq 1. This points to the inadequacy of the present models for the interaction potentials in electron-transfer reactions.

In this article, we focus on symmetric electron-transfer processes for which two basic assumptions[17] about the interaction potentials are generally invoked: (1) the interactions are only weakly dependent on the neutral's and ion's bond lengths; and (2) the interactions are independent of the neutral's and ion's orientation. The former yields vibrational coupling matrix elements as the direct overlap of ion and neutral vibrational wave functions, while the latter leads to spherically symmetric interactions. On the basis of these approximations, Bates and Reid[17] evaluated the interactions for the H_2^+/H_2 system using the accurate single-center Slater orbital expansion of Joy and Parr[22] for the H_2 wave functions and the exact prolate spheroidal wave functions[23] for H_2^+. Arguing quite correctly that such a procedure would be extremely difficult for heavier systems, Flannery, Cosby, and Moran[18a] introduced two further assumptions, both concerned with the dependence of these spherically symmetric interactions on relative translational separation, R: (3) the interactions that do not couple the different electronic arrangements are Morse functions; (4) the interactions responsible for electron exchange are determined from the difference between Sato anti-Morse and Morse functions.

The central purpose of this paper is to remove these approximations through the development of a simple but accurate model interaction for the exchange of a single active electron between two *deformable*, *structured* cores. This is accomplished without parametrization by using a two-term LCAO for each molecule combined with enforcement of the correct *asymptotic* long-range form[24] for the atomic orbitals. Comparison to ab initio CI results[25] for the H_2^+/H_2 system demonstrates the predictive ability of the model even at small separations.

In the next section we present the dynamical equations governing electron-transfer reactions in the diabatic or chemical reaction formulation. The model for the interaction potential is then developed; the diabatic results are related to the standardly computed adiabatic interaction energies; and the integrals are explicitly evaluated for the H_2^+/H_2 system. We compare the predictions to the ab initio results of the Borkman and Cobb[25] in section III. Section IV contains a detailed test of the adequacy of the Franck–Condon approximation for electron-transfer reactions. A brief conclusion appears in section V.

II. Theory

A. Dynamical Equations. We consider the exchange of one active electron between two deformable, structured ion cores, A^+ and B^+. The two arrangements are direct, $D = (A,B^+)$, and exchange, $X = (A^+,B)$, and will be denoted by the index α. In this paper both cores are considered to be diatomic ions, but extension to other systems may be made in a similar way. The coordinates and masses of the system are defined in Figure 1. Various mass combinations are defined as follows:

heavy particles

$$M_A = m_1 + m_2 \tag{2a}$$

$$\mu_A = m_1 m_2 / M_A \tag{2b}$$

$$M_B = m_3 + m_4 \tag{2c}$$

$$\mu_B = m_3 m_4 / M_B \tag{2d}$$

$$M = M_A + M_B \tag{2e}$$

$$\mu = M_A M_B / M \tag{2f}$$

electron

$$\mu_e = m_e M / (m_e + M) \tag{3a}$$

$$\mu_\alpha = \begin{matrix} m_e M_A/(m_e + M_A) & \alpha = D \\ m_e M_B/(m_e + M_B) & \alpha = X \end{matrix} \tag{3b}$$

We shall use atomic units throughout, but m_e will be shown explicitly. The total Hamiltonian in the center of mass system is given by

$$H(\vec{r},\vec{R},\vec{R}_n) = T(\vec{R}) + T(\vec{R}_n) + H^{(el)}(\vec{r},\vec{R},\vec{R}_n) \tag{4}$$

where

$$T(\vec{R}) = -\frac{1}{2\mu}\nabla_{\vec{R}}^2 \tag{5}$$

$$T(\vec{R}_n) = -\frac{1}{2\mu_A}\nabla_{\vec{R}_A}^2 - \frac{1}{2\mu_B}\nabla_{\vec{R}_B}^2 \tag{6}$$

$H^{(el)}$ is the electronic Hamiltonian which may be written as

$$H^{(el)}(\vec{r},\vec{R},\vec{R}_n) = T(\vec{r}) + V^{(A^+)} + V^{(B^+)} + V^{(A^+,B^+)} + V^{(e,A^+)} + V^{(e,B^+)} \tag{7}$$

with

$$T(\vec{r}) = -\frac{1}{2\mu_e}\nabla_{\vec{r}}^2 \tag{8}$$

$$V^{(A^+)} = \text{frozen core potential for } A^+ \tag{9a}$$

$$V^{(B^+)} = \text{frozen core potential for } B^+ \tag{9b}$$

$$V^{(A^+,B^+)} = \text{interaction between the two frozen cores} \tag{9c}$$

$$V^{(e,A^+)} = \text{interaction of the active electron with } A^+ \tag{9d}$$

$$V^{(e,B^+)} = \text{interaction of the active electron with } B^+ \tag{9e}$$

Equation 7 can be rewritten in terms of the isolated ($R \rightarrow \infty$) molecular Hamiltonian in the αth arrangement:

$$H^{(el)}(\vec{r},\vec{R},\vec{R}_n) = H^{(el)}(\vec{r}_\alpha,\vec{R}_n) + V_\alpha^{(op)}(\vec{r}_\alpha,\vec{R},\vec{R}_n) \tag{10}$$

which defines the interaction *operator*, $V_\alpha^{(op)}$, in the αth arrangement as the difference between $H^{(el)}(\vec{r},\vec{R},\vec{R}_n)$ and $H^{(el)}(\vec{r}_\alpha,\vec{R}_n)$. The latter is given explicitly as

$$H^{(el)}(\vec{r}_\alpha,\vec{R}_n) = -\frac{1}{2\mu_\alpha}\nabla_{\vec{r}_\alpha}^2 + V^{(A^+)} + V^{(B^+)} + V^{(\alpha)} \tag{11}$$

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where

$$V^{(\alpha)} = \begin{matrix} V^{(\mathrm{e,A^+})} & \alpha = \mathrm{D} \\ V^{(\mathrm{e,B^+})} & \alpha = \mathrm{X} \end{matrix} \qquad (12\mathrm{a,b})$$

Due to the coordinate transformation of the electronic kinetic energy operators[20] in eq 8 and 11, the interaction $V_\alpha^{(\mathrm{op})}$ contains an explicit cross-derivative operator of the form $\vec{\nabla}_{\vec{r}_\alpha}\cdot\vec{\nabla}_{\vec{R}}$). We will symbolize the interaction *without* this cross-derivative operator by the term V_α.

The isolated molecular eigenfunctions are assumed to satisfy the Born–Oppenheimer approximation, which implies

$$[H^{(\mathrm{el})}(\vec{r}_\alpha,\vec{R}_\mathrm{n}) - \epsilon_{\alpha N}(\vec{R}_\mathrm{n})]\Phi_N{}^\alpha(\vec{r}_\alpha;\vec{R}_\mathrm{n}) = 0 \qquad (13)$$

$$[T(\vec{R}_\mathrm{n}) + \epsilon_{\alpha N}(\vec{R}_\mathrm{n}) - \epsilon_{\alpha NV}]\phi_V{}^{\alpha,N}(\vec{R}_\mathrm{n}) = 0 \qquad (14)$$

The electronic and vibration–rotation quantum numbers of the entire system are denoted by the collective indices N and V, respectively.

Expansion of the total wave function as

$$\Psi_{\alpha NV}(\vec{r},\vec{R},\vec{R}_\mathrm{n}) = \sum_{\alpha'N'V'} F_{\alpha'N'V',\alpha NV}(\vec{R})\Phi_{N'}{}^{\alpha'}(\vec{r}_{\alpha'};\vec{R}_\mathrm{n})\ \phi_{V'}{}^{\alpha',N'}(\vec{R}_\mathrm{n}) \qquad (15)$$

and substitution into the time-independent Schrödinger equation leads via standard techniques to the matrix equations

$$(\mathbf{1}T(\vec{R}) + \mathbf{S}^{-1}\vec{\mathbf{\Pi}}\cdot\vec{\nabla}_{\vec{R}} + \mathbf{S}^{-1}\mathbf{V} + \epsilon - \mathbf{1}E)\mathbf{F}(\vec{R}) = 0 \qquad (16)$$

$$[\mathbf{S}]_{\alpha'N'V',\alpha NV} = \langle\Phi_{N'}{}^{\alpha'}\phi_{V'}{}^{\alpha',N'}|\Phi_N{}^\alpha\phi_V{}^{\alpha,N}\rangle \qquad (17)$$

$$[\vec{\Pi}]_{\alpha'N'V',\alpha NV} = \begin{cases} -\dfrac{1}{M_\mathrm{A}}<\Phi_{N'}{}^{\alpha'}\phi_{V'}{}^{\alpha',N'}|\vec{\nabla}_{\vec{r}_\mathrm{A}}|\Phi_N{}^\alpha\phi_V{}^{\alpha,N}> & \alpha = \mathrm{D}\ (18\mathrm{a}) \\ \dfrac{-1}{M_\mathrm{B}}<\Phi_{N'}{}^{\alpha'}\phi_{V'}{}^{\alpha',N'}|\vec{\nabla}_{\vec{r}_\mathrm{B}}|\Phi_N{}^\alpha\phi_V{}^{\alpha,N}> & \alpha = \mathrm{X}\ (18\mathrm{b}) \end{cases}$$

$$[\mathbf{V}]_{\alpha'N'V',\alpha NV} = \langle\Phi_{N'}{}^{\alpha'}\phi_{V'}{}^{\alpha',N'}|V_\alpha(\vec{r}_\alpha,\vec{R},\vec{R}_\mathrm{n})|\Phi_N{}^\alpha\phi_V{}^{\alpha,N}\rangle \qquad (19)$$

$$[\epsilon]_{\alpha'N'V',\alpha NV} = \delta_{\alpha\alpha'}\delta_{NN'}\delta_{VV'}\epsilon_{\alpha NV} \qquad (20)$$

Equations 16–20 provide the fundamental time-independent theory of electron-transfer reactions for two possible arrangements with any number of electronic–vibrational–rotational states in each arrangement. These equations are the generalization to diatomic molecules of the forms given for electron transfer between atoms in ref 20. (Note that the matrices Q and $\mathrm{H^e}$ in that paper can be combined through the use of the electron reduced mass μ_α in the different arrangements.)

In the time-dependent semiclassical theory, the expansion in eq 15 is replaced by

$$\Psi_{\alpha NV}(\vec{r},\vec{R}(t),\vec{R}_\mathrm{n}) = \sum_{\alpha'N'V'} C_{\alpha'N'V',\alpha NV}(t)\Phi_{N'}{}^{\alpha'}(\vec{r}_{\alpha'},\vec{R}_\mathrm{n})\phi_{V'}{}^{\alpha',N'}(\vec{R}_\mathrm{n})\ \exp(-\mathrm{i}\epsilon_{\alpha'N'V'}t) \qquad (21)$$

which yields the dynamical equations in standard form

$$\mathrm{i}\ \exp(\mathrm{i}\epsilon t)\ \mathbf{S}\ \exp(-\mathrm{i}\epsilon t)\ \dot{\mathbf{C}} = \exp(\mathrm{i}\epsilon t)\ \mathbf{V}\ \exp(-\mathrm{i}\epsilon t)\ \mathbf{C} \qquad (22\mathrm{a})$$

which can obviously be rewritten as

$$\mathrm{i}\mathbf{C} = \exp(\mathrm{i}\epsilon t)\ \mathbf{S}^{-1}\mathbf{V}\ \exp(-\mathrm{i}\epsilon t)\ \mathbf{C} \qquad (22\mathrm{b})$$

Equation 22b must be supplemented by Hamilton's equations to determine the trajectory and thus the time dependence of $\vec{R}(t)$. This can be accomplished at various levels of sophistication, e.g., straight-line and curved trajectory, etc., but this is not of central importance to the present development of an accurate model for S and V.

Inherent in this semiclassical formulation is the neglect of the cross-derivative term, $\mathbf{S}^{-1}\vec{\mathbf{\Pi}}\cdot\vec{\nabla}_{\vec{R}}$ in eq 16. Assuming $F_{\alpha NV}(\vec{R}) \propto \exp(\mathrm{i}\vec{P}\cdot\vec{R})$ and noting that $\mathrm{M_A}$, $\mathrm{M_B}$, and μ are on the same order lead to the justification of this approximation when the relative translational velocity in atomic units is much less than one:

$$(2E/\mu)^{1/2} \ll 1 \qquad (23)$$

For $\mathrm{H_2^+/H_2}$ the velocity is ~0.2 at 1 keV while for heavier systems this approximation is even better. Hence we focus on determining S and V in this article, but for completeness the matrix $\vec{\mathbf{\Pi}}$ is evaluated in the appendix for our model of the $\mathrm{H_2^+/H_2}$ system. The particular combination $\mathbf{S}^{-1}\mathbf{V}$, appearing in the dynamical eq 22b, shall be referred to as the "effective interaction potential" and denoted by W; i.e.,

$$\mathbf{W} \equiv \mathbf{S}^{-1}\mathbf{V} \qquad (24)$$

B. Model for the Interaction Matrix. For the remainder of this article, we asume that a single electronic level suffices to describe each arrangement, and hence the index N is suppressed. Expanding each molecular electronic wave function in a two-term LCAO yields

$$\Phi^\mathrm{D}(\vec{r}_\mathrm{A};\vec{R}_\mathrm{n}) = C_1\zeta_1(\vec{r}_\mathrm{e1}) + C_2\zeta_2(\vec{r}_\mathrm{e2}) \qquad (25\mathrm{a})$$

$$\Phi^\mathrm{X}(\vec{r}_\mathrm{B};\vec{R}_\mathrm{n}) = C_3\zeta_3(\vec{r}_\mathrm{e3}) + C_4\zeta_4(\vec{r}_\mathrm{e4}) \qquad (25\mathrm{b})$$

The electronic–vibrational wave functions are simply products of eq 25a and 25b with $\phi_V{}^{(\mathrm{A,B^+})}(\vec{R}_\mathrm{n})$ and $\phi_V{}^{(\mathrm{A^+,B})}(\vec{R}_\mathrm{n})$, respectively. The matrix elements with respect to these vibrational coordinates can be evaluated after first performing the integration over electronic coordinates. We signify all quantities resulting from electronic integration by suppression of the argument "$\vec{r}_\alpha$".

The overlap matrix is given by

$$\mathrm{S}(\vec{R},\vec{R}_\mathrm{n}) \doteq \begin{bmatrix} 1 & S_\mathrm{DX} \\ S_\mathrm{XD} & 1 \end{bmatrix} \qquad (26)$$

where

$$S_\mathrm{DX}(\vec{R},\vec{R}_\mathrm{n}) = \int \mathrm{d}\vec{r}_\mathrm{A}\ \Phi^\mathrm{D}(\vec{r}_\mathrm{A};\vec{R}_\mathrm{n})^*\ \Phi^\mathrm{X}(\vec{r}_\mathrm{B};\vec{R}_\mathrm{n}) \qquad (27\mathrm{a})$$

$$= S_\mathrm{XD}(\vec{R},\vec{R}_\mathrm{n})^* \qquad (27\mathrm{b})$$

The integration in eq 27 requires only two-center integrals, which can be performed quite easily for Slater type orbitals.[26]

The non-cross-derivative parts of the interaction potentials in the D and X arrangements are

$$V_\mathrm{D}(\vec{r}_\mathrm{A},\vec{R},\vec{R}_\mathrm{n}) = V^{(\mathrm{A^+,B^+})} + V^{(\mathrm{e,B^+})} \qquad (28)$$

$$V_\mathrm{X}(\vec{r}_\mathrm{B},\vec{R},\vec{R}_\mathrm{n}) = V^{(\mathrm{A^+,B^+})} + V^{(\mathrm{e,A^+})} \qquad (29)$$

The electron–core interaction is assumed to be a point-charge interaction, with each nucleus plus nonactive electrons having an effective charge q_i.

$$V^{(\mathrm{e,A^+})} = -\frac{q_1}{r_\mathrm{e1}} - \frac{q_2}{r_\mathrm{e2}} \qquad (30)$$

$$V^{(\mathrm{e,B^+})} = -\frac{q_3}{r_\mathrm{e3}} - \frac{q_4}{r_\mathrm{e4}} \qquad (31)$$

For singly charged homonuclear ion cores, the effective charge on each nucleus must be $^1/_2$ in order to satisfy charge conservation. For heteronuclear ion cores, the effective charge may be estimated by taking into account the electron affinity at each nucleus. The electronically integrated effective interaction potential matrix is

$$\mathrm{W}(\vec{R},\vec{R}_\mathrm{n}) = V^{(\mathrm{A^+,B^+})}1 + \mathrm{S}^{-1}\begin{bmatrix} V_\mathrm{DD}{}^{(\mathrm{e,B^+})} & V_\mathrm{DX}{}^{(\mathrm{e,A^+})} \\ V_\mathrm{XD}{}^{(\mathrm{e,B^+})} & V_\mathrm{XX}{}^{(\mathrm{e,A^+})} \end{bmatrix} \qquad (32)$$

with obvious notation.

It is interesting to note that the core–core interaction, $V^{(\mathrm{A^+,B^+})}$, appears only in the diagonal terms of the effective interaction matrix. If a straight-line trajectory is used in the dynamical equation 22b, $V^{(\mathrm{A^+,B^+})}$ can be ignored for symmetric systems where $V_\mathrm{DD}{}^{(\mathrm{e,B^+})} = V_\mathrm{XX}{}^{(\mathrm{e,A^+})}$, since in such cases the diagonal terms can be eliminated by a phase transformation[17] on the amplitudes C. For a realistic trajectory,[14,15,18] one must specify $V^{(\mathrm{A^+,B^+})}$ even

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though it does *not* couple the two different electronic arrangements. In the present model, we assume

$$V^{(A^+,B^+)} = \sum_{i=1}^{2} \sum_{j=3}^{4} \left(\frac{q_i q_j}{R_{ij}} + \gamma e^{-\eta R_{ij}} \right) \tag{33}$$

The first term in the parentheses is simply the point charge interaction and the second term represents the short-range repulsion[27] due to added electron–electron repulsions. The parameters γ and η may be obtained from a simple model proposed by Böhm and Ahlrichs.[27]

From eq 25, and 30, and 31, we have

$$V_{DD}^{(e,B^+)} = -\sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{k=3}^{4} q_k C_i C_j I_{ijk} \tag{34a}$$

$$V_{XX}^{(e,A^+)} = -\sum_{i=3}^{4} \sum_{j=3}^{4} \sum_{k=1}^{2} q_k C_i C_j I_{ijk} \tag{34b}$$

$$V_{DX}^{(e,A^+)} = -\sum_{i=1}^{2} \sum_{j=3}^{4} \sum_{k=1}^{2} q_k C_i C_j I_{ijk} \tag{34c}$$

$$V_{XD}^{(e,B^+)} = -\sum_{i=3}^{4} \sum_{j=1}^{2} \sum_{k=3}^{4} q_k C_i C_j I_{ijk} \tag{34d}$$

where

$$I_{ijk} \equiv \int d\vec{r}_{ei}\ \zeta_i^*(\vec{r}_{ei})\ \zeta_j(\vec{r}_{ej}) \frac{1}{r_{ek}} \tag{35}$$

is in general a three-center integral. For the cases that $i = j$, $k = i$, or $k = j$, eq 35 reduces to a two-center integral, which we evaluate analytically.[26] In other cases, we make the Mulliken type approximation:[28]

$$I_{ijk} \approx \frac{1}{2} \left(\frac{1}{R_{ik}} + \frac{1}{R_{jk}} \right) \int d\vec{r}_{ei}\ \zeta_i^*(\vec{r}_{ei})\ \zeta_j(\vec{r}_{ej}) \tag{36}$$

if i and j belong to the same molecule, and

$$I_{ijk} \approx I_{ijj} \tag{37}$$

if i and j belong to different molecules. These approximations are expected to be more accurate when either the bond length of the diatom decreases or the separation of the two molecules increases. In the next section we demonstrate that for H_2^+/H_2 the approximation is still fairly good even at small separation.

III. Application to H_2^+/H_2

Borkman and Cobb[25] have performed ab initio calculations for the ground and first excited state of the H_4^+ system. For a symmetric configuration these correspond to gerade and ungerade levels and we shall use this terminology throughout even though for asymmetric configurations the mirror plane symmetry is absent. Since ab initio calculations are performed at fixed nuclear geometries, the terms involving $T(\vec{R})$ and $\vec{V}_{\vec{R}}$ in eq 16 vanish and the vibration–rotation index V can be suppressed. The g–u energies are then the solution of the 2 × 2 secular equation,

$$|\mathbf{W}(\vec{R},\vec{R}_n) + \epsilon(\vec{R}_n) - \mathbf{1}E(\vec{R},\vec{R}_n)| = 0 \tag{38}$$

with the result

$$E_g(\vec{R},\vec{R}_n) = \frac{1}{2}(W_{XX} + W_{DD} + \epsilon_X + \epsilon_D) - \frac{1}{2}[(W_{XX} - W_{DD} + \epsilon_X - \epsilon_D)^2 + 4W_{DX}W_{XD}]^{1/2} \tag{39}$$

$$E_u(\vec{R},\vec{R}_n) = \frac{1}{2}(W_{XX} + W_{DD} + \epsilon_X + \epsilon_D) + \frac{1}{2}[(W_{XX} - W_{DD} + \epsilon_X - \epsilon_D)^2 + 4W_{DX}W_{XD}]^{1/2} \tag{40}$$

Since $W_{\alpha\alpha'}$ vanishes at $R \rightarrow \infty$, the values of ϵ_D and ϵ_X can be identified as the asymptotic values of E_g and E_u, respectively.

From eq 32, 39, and 40, we see that the energy splitting, $E_u - E_g$, is independent of $V^{(A^+,B^+)}$. Therefore, to predict the $\vec{R}$ and $\vec{R}_n$ dependencies of the energy splitting, we need to specify only the atomic orbitals involved in eq 25 and not the parameters γ and η in eq 33. A reasonable choice is

$$\zeta_i(\vec{r}_{ei}) = \xi^{3/2} \pi^{-1/2} e^{-\xi r_{ei}} \tag{41}$$

$$\xi = (2\mathrm{IP})^{1/2} \tag{42}$$

where IP is the ionization potential (in atomic units) of H_2. Equation 42 is based on the long-range behavior of molecular electronic wave functions.[24,29] The ionization potential has also been incorporated in the interaction matrix for charge transfer in atom/atom systems.[30,31] When the model presented in section IIB is used, the effective interaction matrix elements can be evaluated as

$$W_{DD} = V^{(A^+,B^+)} + \frac{1}{1 - S_{DX}S_{XD}}[V_{DD}^{(e,B^+)} - S_{DX}V_{XD}^{(e,B^+)}] \tag{43a}$$

$$W_{XX} = V^{(A^+,B^+)} + \frac{1}{1 - S_{DX}S_{XD}}[V_{XX}^{(e,A^+)} - S_{XD}V_{DX}^{(e,A^+)}] \tag{43b}$$

$$W_{DX} = \frac{1}{1 - S_{DX}S_{XD}}[V_{DX}^{(e,A^+)} - S_{DX}V_{XX}^{(e,A^+)}] \tag{43c}$$

$$W_{XD} = \frac{1}{1 - S_{DX}S_{XD}}[V_{XD}^{(e,B^+)} - S_{XD}V_{DD}^{(e,B^+)}] \tag{43d}$$

where the particular quantities are given by

$$S_{DX} = S_{XD} = C_A C_B \sum_{i=1}^{2} \sum_{j=3}^{4} F(\xi R_{ij}) \tag{44a}$$

$$C_A \equiv C_1 = C_2 = [2 + 2F(\xi R_A)]^{-1/2} \tag{44b}$$

$$C_B \equiv C_3 = C_4 = [2 + 2F(\xi R_B)]^{-1/2} \tag{44c}$$

$$F(x) \equiv \left(1 + x + \frac{1}{3}x^2 \right) \exp(-x) \tag{44d}$$

$$V_{DD}^{(e,B^+)} = -\sum_{i=1}^{2} \sum_{j=3}^{4} \frac{1}{4R_{ij}} + \frac{C_A^2}{R_{ij}}(1 + \xi R_{ij}) \exp(-2\xi R_{ij}) \tag{44e}$$

$$V_{XX}^{(e,A^+)} = -\sum_{i=1}^{2} \sum_{j=3}^{4} \frac{1}{4R_{ij}} + \frac{C_B^2}{R_{ij}}(1 + \xi R_{ij}) \exp(-2\xi R_{ij}) \tag{44f}$$

$$V_{DX}^{(e,A^+)} = -\xi C_A C_B \sum_{i=1}^{2} \sum_{j=3}^{4} (1 + \xi R_{ij}) \exp(-\xi R_{ij}) \tag{44g}$$

$$V_{XD}^{(e,B^+)} = V_{DX}^{(e,A^+)} \tag{44h}$$

As in the ab initio calculations, the bond lengths are set to the equilibrium values ($R_A = 1.401$ au, $R_B = 1.988$ au), and $\epsilon_X - \epsilon_D = 0.0681$ au due to the difference in vibrational potentials of H_2 and H_2^+. The ionization potential of H_2 is known[32] to be 0.567 au, which yields $\xi = 1.065$ au. We have evaluated the energy splitting as a function of intermolecular separation at four geometries A, C, F, and I as defined by Borkman and Cobb[25] and reproduced in Figure 2. Table I compares the results of this model with the ab initio SD-CI calculations. (Note that the 2 × 2 CI results, which were calculated for the other geometries in ref 25, are not accurate except for very small R.) Despite its simplicity, the present model provides splittings in fairly good agreement with the ab initio calculation. Except for geometry A at very short distances where extreme overlap of the atomic orbitals occurs, the predictions of the order of energy splitting, A > F > C, is in

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(27) Bohm, H. J.; Alrichs, R. *J. Chem. Phys.* **1982**, *77*, 2028.

(28) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 792.

(29) The long-range wave function is exactly proportional to $r^{(1-\xi)/\xi}$ exp($-\xi r$) but $\xi = 1.065$ so that the power of r is nearly 0.

(30) Rapp, D.; Francis, W. E. *J. Chem. Phys.* **1962**, *37*, 2631.

(31) Olson, R. E.; Smith, F. T.; Bauer, E. *Appl. Opt.* **1977**, *10*, 1848.

(32) Huber, K. P.; Herzberg, G. "Constants of Diatomic Molecules"; Van Nostrand–Reinhold: New York, 1976.

Table I. Energy Splitting as a Function of Intermolecular Distance and Orientation[a] for H_2^+/H_2

	A		C		F		I	
R	approx[b]	ab initio[c]	approx	ab initio	approx	ab initio	approx	ab initio
1.25	0.6914		0.8179	0.7930	0.8330		0.7724	
1.50	0.6967		0.6567		0.7009	0.7238	0.6186	0.7758
1.75	0.6556	0.9246	0.5296	0.5430	0.5894		0.5019	
2.00	0.5833	0.8021	0.4306	0.4453	0.4942	0.5011	0.4112	0.4977
2.50	0.4262	0.5779	0.2914	0.2872	0.3463	0.3122	0.2822	0.2979
3.00	0.3007	0.3649	0.2029	0.1969	0.2436	0.2157	0.1984	0.2027
3.50	0.2120	0.2191	0.1460	0.1398	0.1738	0.1504	0.1438	0.1387
4.00	0.1521	0.1539	0.1103	0.1054	0.1280	0.1093	0.1093	0.1049
5.00	0.0911	0.0931	0.0781	0.0765	0.0834	0.0749	0.0779	0.0764
6.00	0.0728	0.0766	0.0700	0.0705	0.0711	0.0686	0.0700	0.0705
∞	0.0681	0.0681	0.0681	0.0681	0.0681	0.0681	0.0681	0.0681

[a] All quantities are given in atomic units. [b] Predictions of the present model. [c] Results from ref 25.

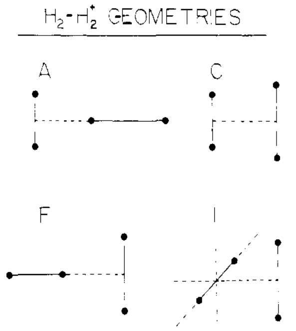

Figure 2. Geometries of the H_2^+/H_2 system used for comparison to the *ab initio* calculations of ref 25.

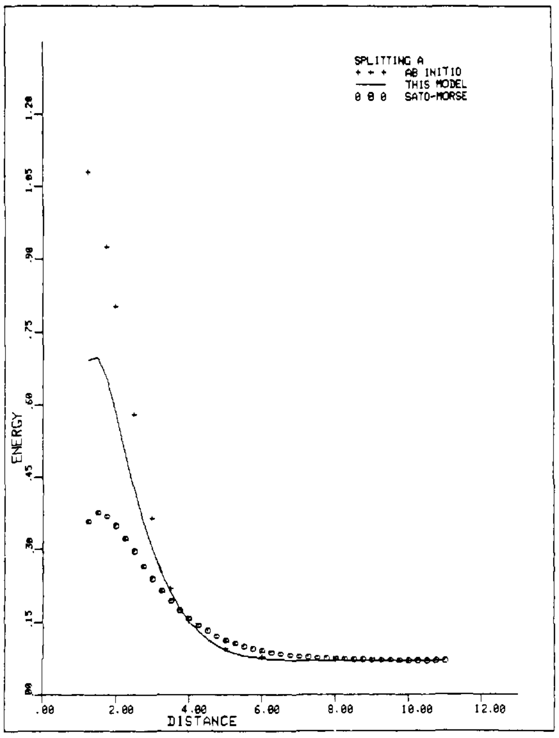

Figure 3. Energy splittings predicted by this model (—), ab initio SD-CI (+++) calculations,[25] and Sato anti-Morse minus Morse potential (O O O) for geometry A in Figure 2.

accord with the ab initio results. Judging from the excellent agreement of geometry C and the correct orientation dependence, we believe that the one-active-electron model is quite adequate. The poor agreement in geometry A at small separation is most likely due to the approximation of the three-center integrals as two-center integrals, i.e., eq 36, 37.

Because accurate ab initio calculations of the energy differences between ground and excited electronic states are so difficult for more complex systems, following Sato, several researchers[18] assumed that the ungerade energy could be approximated by

$$E_u(R) = \frac{1}{2}D_e\{\exp[-2\beta(R - R_e)] + 2\exp[-\beta(R - R_e)]\} \quad (45)$$

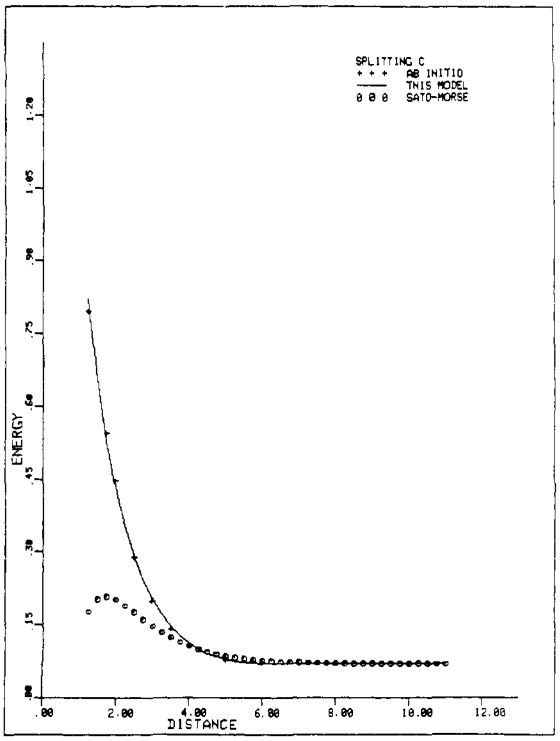

Figure 4. Energy splittings predicted by this model (—), ab initio SD-CI (+++) calculations,[25] and Sato anti-Morse minus Morse potential (O O O) for geometry C in Figure 2.

where the gerade energy is represented by a Morse potential,

$$E_g(R) = D_e\{\exp[-2\beta(R - R_e)] - 2\exp[-\beta(R - R_e)]\} \quad (46)$$

In order to eliminate any influence of orientation averaging, we considered eq 45 and 46 for each orientation separately. We found that for H_2^+/H_2 the ab initio results can indeed be fitted extremely well by eq 46 by using the following parameters: $D_e = 0.0682$, $\beta = 0.75$, $R_e = 3.00$ for geometry A and $D_e = 0.0291$, $\beta = 0.85$, $R_e = 3.00$ for geometry C. However, as shown in Figures 3 and 4, eq 45 yielded quite poor values for the ungerade energy and energy splitting even with the good accuracy for the gerade energy.

In the present model, the gerade energy can also be calculated from eq 39, together with the knowledge of $V^{(A^+,B^+)}$. In eq 33, we choose $\gamma = 1$ and $\eta = 2\xi$, which is the same exponent that occurs in the D-D and X-X terms. The strength parameter γ could be determined by comparison to SCF calculations of E_g, as suggested in ref 27; since this only requires the ground energy at small internuclear separations, it is a viable procedure. In the

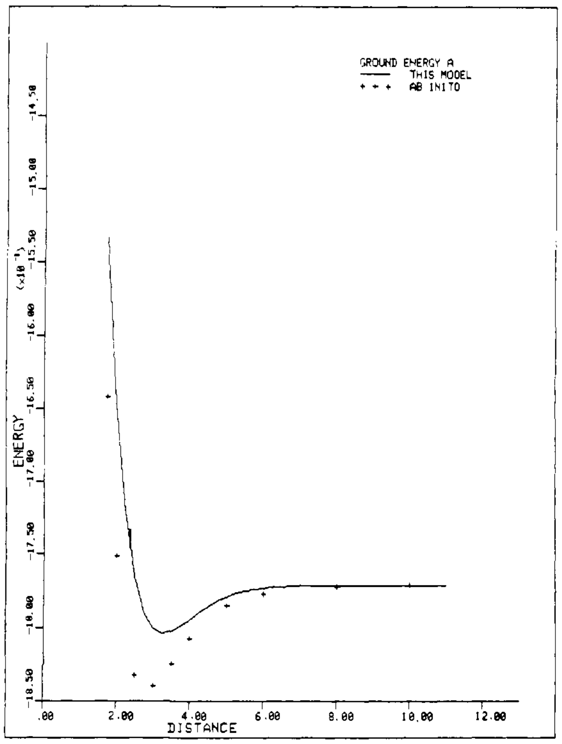

Figure 5. Ground-state energies predicted by this model (—) and ab initio SD-CI (+++) calculations[25] for geometry A in Figure 2.

present study, we used $\gamma = 1$ and 1.5 with little difference in the results, which are shown in Figures 5 and 6 for the former value. The general agreement is good, which is entirely adequate for the present purposes, since the electron-transfer reaction is mainly determined by the energy splitting, not the ground-state intermolecular potential.

IV. A Test of the Franck-Condon Approximation

The model for the diabatic interactions, presented and tested in the previous sections, allows for a detailed computational study of the accuracy of the Franck-Condon (FC) approximation in electron-transfer reactions. In terms of the "effective" interaction, the FC assumption is simply

$$\langle(\alpha,N)v|[\mathbf{W}(\vec{R},\vec{R}_n)]_{\alpha N,\alpha'N'}|(\alpha',N')v'\rangle \approx \langle(\alpha,N)v|(\alpha',N')v'\rangle[\mathbf{W}(\vec{R},\hat{R}_n,\bar{R}_n)]_{\alpha N,\alpha'N'} \quad (47)$$

Here, the integration *refers only to vibrational coordinates* with the translational and molecular orientation variables fixed. In order to emphasize this, we use lower case v's in the bra's and kets. Note that the right-hand side of eq 47 must be evaluated at *some* arbitrary bond length, $\bar{R}_n$. Although a reasonable value is simply the average of the neutral and ion equilibrium bond lengths, other values could be utilized. In order to eliminate such ambiguity in the test of the FC approximation, we consider the ratio

$$R_{\alpha Nv,\alpha'N'v'}(\vec{R},\hat{R}_n) \equiv \frac{\langle(\alpha,N)v|[\mathbf{W}(\vec{R},\vec{R}_n)]_{\alpha N,\alpha'N'}|(\alpha',N')v'\rangle}{\langle(\alpha,N)v|(\alpha',N')v'\rangle} \quad (48)$$

as a function of vibrational states v and v′ for specific rearrangement and electronic indices.

The electron-transfer reaction for which the detailed tests of the diabatic interaction model are presented is

$$H_2^+(v_1) + H_2(v_2) \rightarrow H_2(v_2') + H_2^+(v_1') \quad (49)$$

For this reaction, eq 48 becomes

$$R_{Dv_1v_2,Xv_1'v_2'}(\vec{R},\hat{R}_A,\hat{R}_B) = \frac{\langle(D)v_1v_2|W_{DX}(\vec{R},\vec{R}_A,\vec{R}_B)|(X)v_1'v_2'\rangle}{\langle(D)v_1v_2|(X)v_1'v_2'\rangle} \quad (50)$$

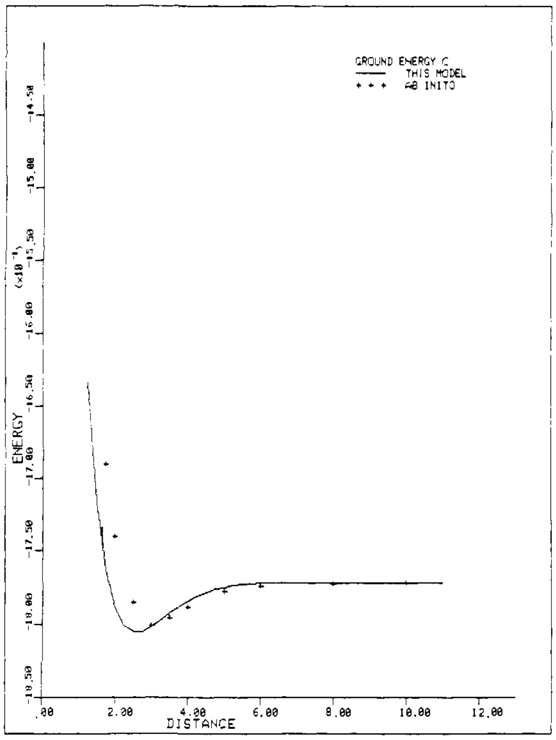

Figure 6. Ground-state energies predicted by this model (—) and ab initio SD-CI (+++) calculations[25] for geometry C in Figure 2.

Note that the core-core interaction, $V^{(A^+,B^+)}$, does not influence this ratio.

The H_2^+ and H_2 vibrational eigenfunctions were approximated by Morse wave functions, by using the parameters (D_e, α_e, R_e, μ) = (2.63779 eV, 1.3614 Å^{-1}, 1.052 Å, 0.503775 amu) and (4.9679 eV, 1.9006 Å^{-1}, 0.74144 Å, 0.50391 amu) for the ion and neutral, respectively.[33] Both the (simple product of two) one-dimensional overlap integrals in the denominator of eq 50 and the more complicated two-dimensional integral in the numerator of eq 50 were evaluated by using high-order (up to 30 points) Gauss-Laguerre integration in each dimension.

The results of the above procedure are displayed in Figures 7 and 8 for two different orientations of the neutral and ion and for $v_1 = v_2$. The total number of quanta, $v_1 + v_2 + v_1' + v_2'$, provides a convenient measure of the overall variations in bond lengths due to vibrational motion. It is clear that the increase of $R_{Dv_1v_2,Xv_1'v_2'}$ with total vibrational quanta signifies a breakdown of the FC approximation, but except at very small ion-molecule separations the inaccuracy is slight. (Note that the decreasing magnitude of the ratio with translational separation reflects only the variation of $W_{DX}(\vec{R},\vec{R}_A,\vec{R}_B)$ with increasing R and is irrelevant for testing the FC approximation.)

V. Conclusions

We have presented a simple one-active-electron model for the effective interaction matrix $\mathbf{S}^{-1}\mathbf{V}$ in electron-transfer processes between two deformable, structured cores. The prediction of the coupling between different arrangements required only the electron-ion core interactions, $V^{(e,A^+)}$ and $V^{(e,B^+)}$, and the wave functions for the active electron in the two arrangements. The core-core interaction does not participate directly in the electron-transfer process but only influences the collisional trajectory. It was approximated by a point-charge interaction plus steric repulsion. For valence s-orbitals of the atomic cores, the wave function of the active electron can be expressed in a linear combination of two atomic orbitals with correct asymptotic forms.[24] In more complicated cases involving p-orbitals, more than two such atomic orbitals need to be retained, and for asymmetric electron transfer it may be necessary to allow more than a single

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[33] Nicholls, R. W. *J. Phys. B* **1968**, *1*, 1192.

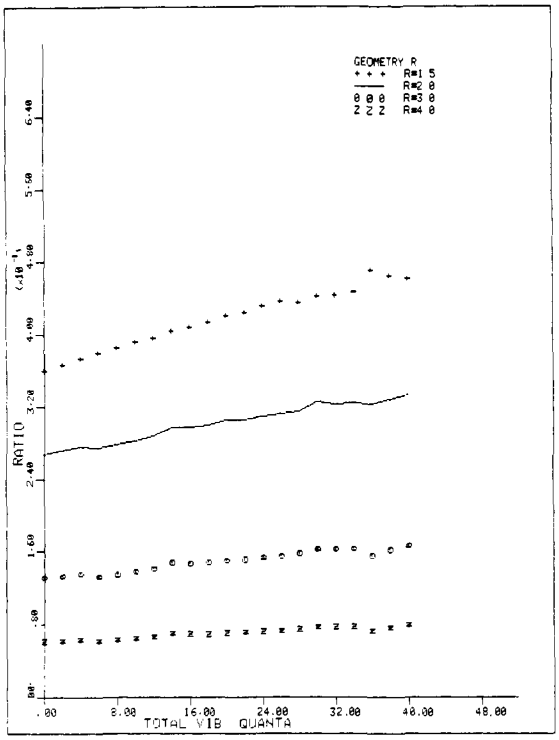

Figure 7. Test of the Franck–Condon approximation using the present model for the D–X coupling in the H_2^+/H_2 system in geometry A of Figure 2. The "ratio" is given by eq 50. Each curve represents the ratio vs. total vibrational quanta for a specific intermolecular separation *R*. The small variation of the ratio with total vibrational quanta indicates a slight breakdown of the FC approximation. (The decrease of the ratio with increasing *R* simply reflects the decrease of the interaction potential with *R*.)

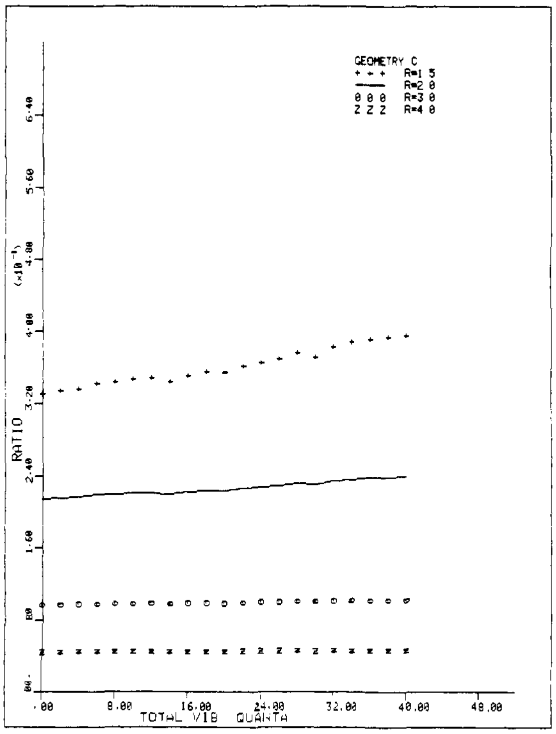

Figure 8. Same as Figure 7 except for geometry C in Figure 2.

electronic state N. Testing of the utility and accuracy of the present approach is these situations must await suitable ab initio CI calculations.

An initial test of this approach was presented for the H_2^+/H_2 system. The exact relationship between the diabatic matrix elements and the adiabatic gerade–ungerade energies was utilized for comparison of the results of this model with those from ab initio calculations.[25] The agreement for the energy splittings in the H_2^+/H_2 system supports this one-active-electron picture. As an application we tested the Franck–Condon approximation for the vibrational-state dependencies and found it to be generally accurate except at very small intermolecular separations.

We expect the present model to be most useful in the treatment of the dynamics of electron-transfer processes for three reasons. First, both orientation and bond-length dependencies are included in the overlap and potential matrices, **S** and **V**, respectively, thus allowing for a complete treatment of all dynamical degrees of freedom. Second, the correct description of the long-range interaction potentials is incorporated, which is most important for symmetric electron transfer in which large cross sections are found. Third, the evaluation of **S** and **V** and their derivatives is not unduly complicated or time-consuming, which is an important consideration since thousands of such evaluations are required for each impact parameter in the semiclassical trajectory calculations. Detailed studies of the dynamics are now under way and will be reported in future publications.

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VI. Appendix: Evaluation of the Matrix Elements of $\vec{\Pi}$

We are concerned here only with the integration over electronic coordinates. The integration over vibrational coordinates can be carried out with numerical methods, as mentioned in section IV. According to eq 18 the integrals involved in $\vec{\Pi}$ have the following form:

$$\vec{I}_{\alpha'\alpha} = \int d\tau\ \Phi^{\alpha'}\vec{\nabla}_{\vec{r}_a}\Phi^{\alpha} \tag{A.1}$$

For the H_2^+/H_2 system, Φ^α is given by eq 25, 41, and 44b–d. Thus,

$$\begin{aligned}\vec{I}_{XD} &= C_AC_B\sum_{i=3}^{4}\sum_{j=1}^{2}\int d\tau\ \zeta_i\vec{\nabla}_{\vec{r}_{ej}}\zeta_j \\ &= -\xi C_AC_B\sum_{i=3}^{4}\sum_{j=1}^{2}\int d\tau\ \zeta_i\zeta_j\hat{r}_{ej}\end{aligned} \tag{A.2,A.3}$$

The unit vector $\hat{r}_{ej}$ may be expressed in terms of fixed cartesian coordinates. Letting $\hat{R}_{ji}$ (pointing from j to i) be the z-axis, we find that integration over x and y coordinates ($\hat{x}_{ej}$ and $\hat{y}_{ej}$) vanishes. Equation A.3 then becomes

$$\vec{I}_{XD} = -\xi C_AC_B\sum_{i=3}^{4}\sum_{j=1}^{2}\hat{R}_{ji}\int d\tau\ \zeta_i\zeta_j\cos\theta \tag{A.4}$$

where θ is the angle between $\hat{R}_{ji}$ and $\hat{r}_{ej}$. Using spheroidal coordinates, one can obtain, using $\hat{R}_{ij} = -\hat{R}_{ji}$,

$$\vec{I}_{XD} = \frac{1}{3}\xi^2C_AC_B\sum_{i=3}^{4}\sum_{j=1}^{2}\vec{R}_{ij}(1 + \xi R_{ij})\exp(-\xi R_{ij}) \tag{A.5}$$

Similarly, we find

$$\vec{I}_{DX} = -\vec{I}_{XD} \tag{A.6}$$

$$\vec{I}_{DD} = 0 \tag{A.7}$$

$$\vec{I}_{XX} = 0 \tag{A.8}$$

We note that the magnitudes of $\vec{I}_{DX}$ and $\vec{I}_{XD}$ are comparable with $V_{DX}^{(e,A^+)}$ and $V_{XD}^{(e,B^+)}$ given in eq 44g–h. Thus, the off-diagonal terms of $\vec{\Pi}$ are smaller than those of **V** by a factor of molecular mass (M_A or M_B), which is about 2000 for the H_2^+/H_2 system.

Registry No. H_2, 1333-74-0; H_2^+, 12184-90-6.