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CLASSICAL TRAJECTORY MODELS FOR ELECTRONICALLY NON-ADIABATIC COLLISION PROCESSES: A CLASSICAL VALENCE BOND MODEL FOR ELECTRONIC DEGREES OF FREEDOM

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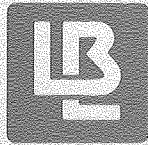VALENCE BOND MODEL FOR ELECTRONIC DEGREES OF
FREEDOM

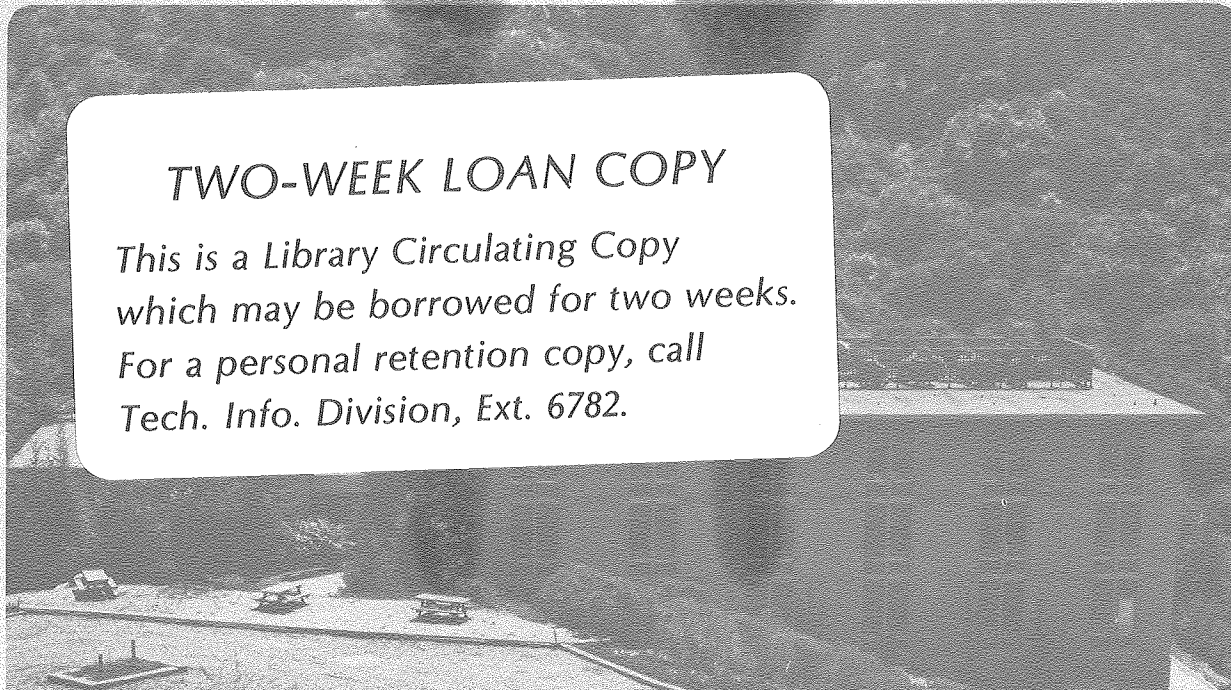William H. Miller and Ann E. Orel

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Classical Trajectory Models for Electronically Non-Adiabatic Collision

Processes: a Classical Valence Bond Model for Electronic Degrees of Freedom

By

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Abstract

A classical interpretation of the Dirac-Van Vleck spin version of valence bond theory is used to obtain a classical model for electronic degrees of freedom within the valence bond framework. The approach is illustrated by deriving the explicit forms of the classical Hamiltonians, involving electronic and heavy particle degrees of freedom, for the $H-H_2$, $F-H_2$, and $O-H_2$ systems. It is also shown how the initial conditions for both electronic and heavy particle degrees of freedom are chosen to carry out a classical trajectory simulation of collision processes. The attractive feature of this model is that it is as easily applicable to electronically non-adiabatic processes as it is to adiabatic ones.

I.   Introduction.

During the last few years a theoretical approach[1] to electronically non-adiabatic collision phenomena has been developed which treats the electronic degrees of freedom, as well as the nuclear degrees of freedom (i.e., translation, rotation, and vibration), by classical mechanics. The advantage of such a model is that a classical trajectory simulation can be carried out which treats the dynamics of all degrees of freedom, the electronic transition and the nuclear motion, in a consistent way. The original motivation for this approach was the realization[2,3] that models which do not treat electronic and heavy particle degrees of freedom on a dynamically consistent footing will fail to describe certain aspects of the process correctly.

Even though these "totally classical" models are more dynamically consistent than others (except, of course, the totally quantum mechanical formulation, i.e., the rovibronic coupled-channel Schrodinger equation), they have the obvious shortcoming that they characterize the electronic degrees of freedom via classical rather than quantum mechanics. Since electrons are usually considered to be highly quantum mechanical entities, it is not obvious that such an approach will be usefully accurate. Several applications,[1] however, have shown that these classical models can describe electronically inelastic processes essentially as well as ordinary classical trajectory approaches describe rotationally and/or vibrationally inelastic processes. It should be noted, too, that the electrons themselves are not treated classically, but rather a classical degree(s) of freedom is introduced to model the _collective_ electronic

degrees of freedom responsible for the electronic states of interest.

The purpose of this paper is to show how the chemical notion of valence bond theory can be given a classical interpretation and then used to construct a classical model for the electronic states of a molecular system. Although this approach to modeling electronic degrees of freedom by classical mechanics has some features in common with our earlier approaches, it is actually quite different. As will be seen, in this approach one never requires the Born-Oppenheimer potential energy surfaces per se; they and all the non-adiabatic couplings between them are all contained implicitly in the classical valence bond model. One of the most promising aspects of this approach is that it provides a classical model for electronic degrees of freedom which incorporates all the chemically important features of valence bond theory, i.e., bond breaking and making, directed valence, etc.

The key to constructing this classical analog to valence bond theory is the Dirac-Van Vleck[4] spin model for electronic degrees of freedom. If the quantum mechanical version of this spin model is used to determine the electronic energy for fixed nuclear geometry (i.e., the Born-Oppenheimer potential energy surfaces), one obtains standard valence bond results, i.e., the familiar London equation[5] if all the atoms are monovalent S-atoms (e.g., H_3), the diatomics-in-molecules[6] result if only one of the monovalent atoms has angular momentum (e.g., FH_2), etc. Most important for present purposes, however, is that this Dirac-Van Vleck version of valence bond theory leads to a elegantly simple classical model for the electronic degrees of freedom, namely one takes the various spins and orbital angular momenta (vide infra) to be classical angular momenta; this will be clear below.

Rather than attempt a more precise statement of the model, we developed it with several examples. Section II considers the simplest example, the H_3 system; it also shows how the initial conditions of the classical spin (i.e., electronic) variables are chosen if one wishes to carry out a trajectory calculation within the usual quasi-classical framework. The results of such a trajectory calculation using the classical valence bond model for the $H + H_2 \rightarrow H_2 + H$ reaction are presented in Section IIc, and the results are reasonably encouraging. Section III then shows how the model can be applied to more complex chemical systems, first the $F-H_2$ system, and then a system involving a multivalent atom, $O-H_2$.

II.   The Model; Application to H_3.

   a. The Classical Hamiltonian and Equations of Motion

The usual quantum mechanical version of the Dirac-Van Vleck[4] spin

model for electronic degrees of freedom is well known. It is essentially

an alternate formulation of valence bond theory. Here we show how the

classical version of this model is defined, taking as first example the

simple case of three hydrogen atoms.

Let r_{12}, r_{13}, and r_{23} be the internuclear distances for the three

hydrogen atoms and $\vec{S}_i$, i=1,2,3 the spin of the electron on atom i. The

electronic Hamiltonian is taken to be the spin Hamiltonian for these three

spins and is a sum of spin-dependent pair interactions between each of

the electrons,

$$H_{e\ell} = H_{12} + H_{13} + H_{23} \qquad , \tag{2.1}$$

where

$$H_{ij} = V_{ij} + \Delta V_{ij}(\vec{S}_i \cdot \vec{S}_j + \frac{3}{4}) \qquad . \tag{2.2}$$

The operators in this quantum mechanical Hamiltonian are the spin

operators for the three spins; the quantities V_{ij} and ΔV_{ij} are numbers

which are functions of the internuclear distance r_{ij}, and because of

the equivalence of the three H atoms,

$$V_{ij} = V(r_{ij}) \tag{2.3a}$$

$$\Delta V_{ij} = \Delta V(r_{ij}) \qquad . \tag{2.3b}$$

Choosing the functions $V(r)$ and $\Delta V(r)$ to be

$$V(r) = {}^1\Sigma(r) \tag{2.4a}$$

$$\Delta V(r) = {}^3\Sigma(r) - {}^1\Sigma(r) \quad , \tag{2.4b}$$

where ${}^1\Sigma(r)$ and ${}^3\Sigma(r)$ are the potential energy curves for the lowest ${}^1\Sigma$ and ${}^3\Sigma$ states of H_2, respectively, ensures that the correct diatomic electronic states are obtained if one of the atoms is removed to infinity. If one diagonalizes the spin Hamiltonian of Eq. (2.1) in the space of total spin 1/2 (a 2 × 2 matrix), the well-known London energy expression[5] is obtained for the ground state Born-Oppenheimer potential energy surface of H_3.

To proceed classically we use the above spin Hamiltonian but take the three spins to be <u>classical</u> spins. To have a complete classical Hamiltonian for nuclear and electronic degrees of freedom the nuclear kinetic energy must be added to this Hamiltonian. Within the overall center of mass of the three-atom system the conventional choice of nuclear variables is $\vec{r}$, the relative coordinate between atoms 1 and 2, say, and $\vec{R}$, the coordinate of atom 3 relative to the center of mass of atoms 1 and 2:

$$\vec{r} = \vec{r}_2 - \vec{r}_1 \tag{2.5a}$$

$$\vec{R} = \vec{r}_3 - \frac{1}{2}(\vec{r}_1 + \vec{r}_2) \quad . \tag{2.5b}$$

If $\vec{p}$ and $\vec{P}$ are the momenta conjugate to $\vec{r}$ and $\vec{R}$, and m and μ the corresponding reduced masses, then the classical Hamiltonian for the complete system is

$$H(\vec{p},\vec{r},\vec{P},\vec{R},\vec{S}_1,\vec{S}_2,\vec{S}_3) = \frac{\vec{P}^2}{2\mu} + \frac{\vec{p}^2}{2m}$$

$$+ V(r_{12}) + \Delta V(r_{12})(\vec{S}_1 \cdot \vec{S}_2 + \frac{3}{4})$$

$$+ V(r_{13}) + \Delta V(r_{13})(\vec{S}_1 \cdot \vec{S}_3 + \frac{3}{4})$$

$$+ V(r_{23}) + \Delta V(r_{23})(\vec{S}_2 \cdot \vec{S}_3 + \frac{3}{4}) \quad , \tag{2.6}$$

where

$$\vec{r}_{12} = \vec{r}$$

$$\vec{r}_{13} = \vec{R} + \frac{1}{2} \vec{r}$$

$$\vec{r}_{23} = \vec{R} - \frac{1}{2} \vec{r} \qquad . \tag{2.7}$$

The classical equations of motion for $\vec{r}(t)$, $\vec{R}(t)$, $\vec{p}(t)$, $\vec{P}(t)$, $\vec{S}_1(t)$, $\vec{S}_2(t)$ and $\vec{S}_3(t)$ are generated by the equations

$$\frac{d}{dt} \vec{r}(t) = \frac{\partial H}{\partial \vec{p}} \tag{2.8a}$$

$$\frac{d}{dt} \vec{R}(t) = \frac{\partial H}{\partial \vec{P}} \tag{2.8b}$$

$$\frac{d}{dt} \vec{p}(t) = - \frac{\partial H}{\partial \vec{r}} \tag{2.8c}$$

$$\frac{d}{dt} \vec{P}(t) = - \frac{\partial H}{\partial \vec{R}} \tag{2.8d}$$

$$\frac{d}{dt} \vec{S}_i(t) = - \vec{S}_i \times \frac{\partial H}{\partial \vec{S}_i} \quad , \quad i = 1,2,3 \quad , \tag{2.8e}$$

and with the classical Hamiltonian of Eq. (2.6) these equations of motion are easily found to be

$$\frac{d}{dt}\,\vec{r} \quad = \vec{p}/m \tag{2.9a}$$

$$\frac{d}{dt}\,\vec{R} \quad = \vec{P}/\mu \tag{2.9b}$$

$$\frac{d}{dt}\,\vec{p} \quad = - \,[V'(r_{12}) + \Delta V'(r_{12})(\vec{S}_1\cdot\vec{S}_2 + \tfrac{3}{4})]\hat{r}_{12}$$

$$- \tfrac{1}{2}\,[V'(r_{13}) + \Delta V'(r_{13})(\vec{S}_1\cdot\vec{S}_3 + \tfrac{3}{4})]\hat{r}_{13}$$

$$+ \tfrac{1}{2}\,[V'(r_{23}) + \Delta V'(r_{23})(\vec{S}_2\cdot\vec{S}_3 + \tfrac{3}{4})]\hat{r}_{23} \tag{2.9c}$$

$$\frac{d}{dt}\,\vec{P} \quad = - \,[V'(r_{13}) + \Delta V'(r_{13})(\vec{S}_1\cdot\vec{S}_3 + \tfrac{3}{4})]\hat{r}_{13}$$

$$- \,[V'(r_{23}) + \Delta V'(r_{23})(\vec{S}_2\cdot\vec{S}_3 + \tfrac{3}{4})]\hat{r}_{23} \tag{2.9d}$$

$$\frac{d}{dt}\,\vec{S}_i \quad = - \sum_{\substack{j=1 \\ j \neq i}}^{3} (\vec{S}_i \times \vec{S}_j)\,\Delta V(r_{ij}) \quad , \quad i = 1,2,3 \tag{2.9e}$$

where

$$\hat{r}_{ij} = \vec{r}_{ij}/|\vec{r}_{ij}| \qquad .$$

Given initial conditions for $\vec{r}$, $\vec{R}$, $\vec{p}$, $\vec{P}$, and $\vec{S}_i$, i=1,2,3, Eq. (2.9) can be integrated numerically with standard trajectory programs[7] to determine the final values of these quantities. Section IIb discusses the initial conditions appropriate to an H + H$_2$ collision.

Rather than characterizing the classical spins by their three

cartesian components, i.e., $\vec{S}_i \equiv (S_{ix}, S_{iy}, S_{iz})$, one may alternatively use the action-angle variables (m_i, q_i). m_i is the component of $\vec{S}_i$ along a space-fixed direction, and q_i is the angle variable conjugate to it. Since the magnitude of the spin is conserved, the spin $\vec{S}_i$ is completely characterized by the pair of action-angle variables (m_i, q_i); specifically, the cartesian components of $\vec{S}_i$ are given in terms of the action-angle variables by[8]

$$\vec{S}_i = \begin{pmatrix} \sqrt{S_i^2 - m_i^2}\, \cos q_i \\ \\ \sqrt{S_i^2 - m_i^2}\, \sin q_i \\ \\ m_i \end{pmatrix} . \tag{2.10}$$

Since

$$\vec{S}_i \cdot \vec{S}_j = m_i m_j + \sqrt{S_i^2 - m_i^2}\,\sqrt{S_j^2 - m_j^2}\, \cos(q_i - q_j) \quad , \tag{2.11}$$

it is easy to express the classical Hamiltonian of Eq. (2.6) in terms of the canonical variables $(\vec{p}, \vec{r}, \vec{P}, \vec{R}, m_1, q_1, m_2, q_2, m_3, q_3)$, and their time dependence is determined by Hamilton's equations, i.e., Eqs. (2.8a)-(2.8d), with (2.8e) replaced by

$$\frac{d}{dt} q_i(t) = \frac{\partial H(\vec{p}, \vec{r}, \vec{P}, \vec{R}, m_1, q_1, m_2, q_2, m_3, q_3)}{\partial m_i}$$

$$\frac{d}{dt} m_i(t) = -\frac{\partial H(\vec{p}, \vec{r}, \vec{P}, \vec{R}, m_1, q_1, m_2, q_2, m_3, q_3)}{\partial q_i} \quad , \tag{2.8e'}$$

$i=1,2,3$. One can verify by direct calculation that, with $\vec{S}_i$ and

(m_i,q_i) related by Eq. (2.10), the equations of motion given by

Eqs. (2.8e) and (2.8e') are identical. Characterizing the spin $\vec{S}_i$

by the two variables (m_i,q_i) rather than the three cartesian components

(S_{ix},S_{iy},S_{iz}) means that there is one less equation in the classical

equations of motion for each spin; i.e., Eq. (2.8a)-(2.8e) consists

of 21 first order differential equations, whereas Eqs. (2.8a)-(2.8d)

plus (2.8e') are only 18 first order differential equations. In

practice, however, 18 is not sufficiently less than 21 to be significant,

and since the equations of motion in terms of the cartesian spin

variables are quite a bit simpler algebraically than the ones in terms

of the action-angle variables, it is actually more convenient and

efficient to carry out numerical trajectory calculations using the

cartesian spin variables rather than the action-angle spin variables.

As seen in the next section, though, the action-angle variables are

necessary for specifying the appropriate initial values of the spins.

b. Initial Conditions

Here we specify the initial conditions for the variables $(\vec{p},\vec{r},\vec{P},\vec{R}$,

and $\vec{S}_i$, $i=1,2,3$) of Eq. (2.9) that are appropriate for an H + H$_2$($^1\Sigma$)

collision within the standard quasi-classical model.[7] Initial values for

the nuclear variables $(\vec{p},\vec{r},\vec{P},\vec{R})$ are determined in the usual way,[7,8] so

no further discussion regarding them is necessary. It remains to specify

the appropriate initial values of the spin variables.

If atoms 1 and 2 are the two that initially form H$_2$($^1\Sigma$), then

$\vec{S}_1$ and $\vec{S}_2$ need to be coupled initially to form a resultant singlet spin

state. This is accomplished by making a canonical transformation from the uncoupled action-angle variables (m_1, q_1, m_2, q_2) to the coupled action-angle variables $(S_{12}, q_{S_{12}}, m_{12}, q_{m_{12}})$, where

$$S_{12} \equiv |\vec{S}_1 + \vec{S}_2|$$

$$m_{12} \equiv m_1 + m_2 \qquad , \qquad\qquad (2.12)$$

and where $q_{S_{12}}$ and $q_{m_{12}}$ are the angle variables conjugate to S_{12} and m_{12}. This transformation is the classical equivalent of a Clebsch-Gordan transformation[9] in quantum mechanics, and the appropriate expressions specifying this canonical transformation have been given before.[8] For the singlet state the quantum mechanical values of S_{12} and m_{12} are $S_{12} = m_{12} = 0$, but we wish to retain the possibility that S_{12} may not be zero (see below). Thus specializing the general expressions to the case $m_{12} = 0$ and $S_1^2 = S_2^2$, the cartesian spins $\vec{S}_1$ and $\vec{S}_2$ are given in terms of the coupled action-angle variables by

$$\vec{S}_1 = \begin{pmatrix} \dfrac{S_{12}}{2} \cos q_{m_{12}} - \sqrt{S_1^2 - \dfrac{S_{12}^2}{4}} \; \sin q_{m_{12}} \; \sin q_{S_{12}} \\[3ex] \dfrac{S_{12}}{2} \sin q_{m_{12}} + \sqrt{S_1^2 - \dfrac{S_{12}^2}{4}} \; \cos q_{m_{12}} \; \sin q_{S_{12}} \\[3ex] -\sqrt{S_1^2 - \dfrac{S_{12}^2}{4}} \; \cos q_{S_{12}} \end{pmatrix} \qquad (2.13a)$$

$$\vec{S}_2 = \text{same as above with} \; \sqrt{S_1^2 - \dfrac{S_{12}^2}{4}} \; \rightarrow \; -\sqrt{S_1^2 - \dfrac{S_{12}^2}{4}} \quad . \quad (2.13b)$$

The third spin, that of the free H atom, is given in terms of its action-angle variables by Eq. (2.10); setting $m_3 = 1/2$ and since $S_3^2 = S_1^2$, this becomes

$$\vec{S}_3 = \begin{pmatrix} \sqrt{S_1^2 - \frac{1}{4}} \cos q_3 \\ \sqrt{S_1^2 - \frac{1}{4}} \sin q_3 \\ \frac{1}{2} \end{pmatrix} \qquad . \qquad (2.13c)$$

The question now arises as to the values for S_1^2 and the initial value of S_{12} in Eq. (2.13). The quantum mechanical values are obviously

$$(S_1^2)_{QM} = \frac{1}{2}(\frac{1}{2} + 1) = \frac{3}{4}$$

$$(S_{12}^2)_{QM} = 0(0 + 1) = 0 \qquad , \qquad (2.14)$$

but it is well-known in classical/semiclassical folklore that a Langer-modification to the magnitude of angular momenta usually gives better results.[8,10] The Langer-modified values are

$$(S_1^2)_{Langer} = (\frac{1}{2} + \frac{1}{2})^2 = 1$$

$$(S_{12}^2)_{Langer} = (0 + \frac{1}{2})^2 = \frac{1}{4} \qquad , \qquad (2.15)$$

and if these values are used then the fraction 3/4 in Eqs. (2.6) and (2.9) must be replaced by 7/8 so that the initial vibrational potential for H_2 is $^1\Sigma(r)$.

With S_1 and S_{12} given by Eq. (2.15), the angle variables $q_{S_{12}}$, $q_{m_{12}}$, and q_3 are chosen by Monte Carlo, i.e., as $2\pi \times$ (random number), and Eq. (2.13) then gives the quasiclassical initial conditions for the Cartesian spin variables. The classical equations of motion, Eq. (2.9), can then be integrated by standard methods.

c. Numerical Test: $H + H_2 \rightarrow H_2 + H$ in 3d

One does not believe that electronically non-adiabatic effects are important in collisions of ground state H and H_2 until very high collision energies, and this fact can be used to provide a first numerical test of the classical valence bond model described above.

Thus the conventional (i.e., electronically adiabatic) quasiclassical treatment of the $H + H_2$ reaction[11] considers it to be classical motion on the lowest Born-Oppenheimer potential surface. This potential surface is the lowest quantum mechanical eigenvalue of the electronic Hamiltonian (for fixed nuclear positions), and with the Hamiltonian of Eq. (2.1)-(2.2) this is, as noted above, the London expression

$$E(r_{12}, r_{13}, r_{23}) = V(r_{12}) + V(r_{13}) + V(r_{23})$$

$$+ \frac{1}{2} [\Delta V(r_{12}) + \Delta V(r_{13}) + \Delta V(r_{23})]$$

$$- \frac{1}{2} [\Delta V(r_{12})^2 + \Delta V(r_{13})^2 + \Delta V(r_{23})^2 - \Delta V(r_{12})\Delta V(r_{13})$$

$$- \Delta V(r_{12}) \Delta V(r_{23}) - \Delta V(r_{13}) \Delta V(r_{23})]^{1/2} \quad , \quad (2.16)$$

where V and ΔV are given by Eq. (2.4). A standard quasiclassical trajectory calculation[7] for the $H + H_2 \rightarrow H_2 + H$ reaction with this potential surface thus provides what we consider to be the "correct" classical result for this system and which we would expect[12] to be in reasonably good agreement with the quantum mechanical results for this surface.

The classical valence bond model, on the other hand, proceeds as described in Section IIb: The classical equations of motion, involving the spin (i.e., electronic) variables as well as the nuclear coordinates and momenta, i.e., Eqs. (2.9), are integrated numerically with the initial conditions given by Eqs. (2.13) and (2.15). As noted in the Introduction, this approach does not involve the Born-Oppenheimer potential energy surface but rather uses the classical valence bond (i.e., spin) Hamiltonian directly. Thus no assumption of electronic adiabaticity is incorporated, and if the actual electronic dynamics is approximately adiabatic (as we expect it to be for $H + H_2$), this must follow from the classical mechanics of the electronic (i.e., spin) degrees of freedom.

Standard Morse and anti-Morse functions were used to represent the $^1\Sigma$ and $^3\Sigma$ potential curves of H_2,

$$^1\Sigma(r) = D_1 [e^{-2\beta_1(r-r_0)} - 2e^{-\beta_1(r-r_0)}] \tag{2.16a}$$

$$^3\Sigma(r) = D_3 [e^{-2\beta_3(r-r_0)} + 2e^{-\beta_3(r-r_0)}] \quad , \tag{2.16b}$$

with parameters

$D_1 = 0.1744$ hartree, $D_3 = 0.1360$ hartree

$\beta_1 = 1.04435 \ a_0^{-1}$, $\beta_3 = 1.032 \ a_0^{-1}$

$r_0 = 1.40083 \ a_0$.

This gives an adiabatic barrier height of 11.1 kcal/mole at $r = 1.76\ a_0$, in reasonable agreement with the accurate value 9.8 kcal/mole also at $r = 1.76\ a_0$. For the present test purposes we are not particularly concerned with representing the true H_3 potential surface extremely accurately.

Figure 1 shows the cross sections as a function of initial translational energy for reaction (R),

$$H + H_2 \rightarrow H_2 + H \qquad , \qquad\qquad\qquad (2.17a)$$

and also for collisional dissociation (D),

$$H + H_2 \rightarrow H + H + H \qquad . \qquad\qquad\qquad (2.17b)$$

The solid curves are the results of the conventional quasiclassical calculation on the London potential surface, presumably the "correct" values, and the broken curves the results of the quasiclassical calculation with the classical valence bond (i.e., spin) Hamiltonian.

We consider these results to be reasonably encouraging; other than the threshold region of the reactive channel the classical valence bond model describes the overall energy dependence of these cross sections quite well. The problem with the reactive threshold seems to stem from the fact that the correct threshold behavior is determined almost entirely by the adiabatic barrier height, and even though the classical spins do evolve essentially adiabatically, the classical adiabatic electronic (i.e., spin) energy in the transition state region does not approximate the quantum mechanical adiabatic electronic energy well. It is not clear, of course, whether this difficulty with threshold is typical of this model or not, a question that can only be settled by further applications. It

should be kept in mind, too, that this classical valence bond model is being developed for systems which, unlike $H + H_2$, $\underline{do}$ involve electronic non-adiabaticity in an essential way, i.e., for processes which involve several, maybe many, different electronic states.

III.   Further Applications.

In this section we show how the Dirac-Van Vleck spin formulation of valence bond theory can be applied to some more interesting molecular systems, thus yielding classical models for the electronic degrees of freedom in these systems.

a.   F-H$_2$

Interest in the reaction F + H$_2$ was the initial motivation for developing classical models for electronic degrees of freedom,[1] so it is of special concern to see how the present classical valence bond model can be applied to it.

Let $\vec{S}_1$ and $\vec{S}_2$ be the spins of the electrons on each of the two H atoms, and $\vec{S}_3$ the spin of the electron (hole) on the F atom; electron 3 (actually an electron hole) is a p-orbital—i.e., F is a ^{2}P atom—so that it also has an orbital angular momentum $\vec{L}$, of magnitude 1. Just as for the H$_3$ system of Section IIa, the classical electronic Hamiltonian for F-H$_2$ is taken to be the spin Hamiltonian which is a sum of pair interactions between all the valence electrons (and electron holes):

$$H_{e\ell} = H_{12} + H_{13} + H_{23} \qquad . \tag{3.1}$$

H_{12}, interaction between the electrons on the hydrogen atoms, is the same as that of Section II, i.e.,

$$H_{12} = V_{H_2}(r_{12}) + \Delta V_{H_2}(r_{12})(\vec{S}_1 \cdot \vec{S}_2 + \tfrac{3}{4}) \qquad , \tag{3.2}$$

where V_{H_2} and ΔV_{H_2} are given by Eq. (2.4) in terms of the $^1\Sigma$ and $^3\Sigma$ potential curves of H$_2$. H_{13} and H_{23} of Eq. (3.1), i.e., the interaction between the electrons on each of the two H atoms and the electron

(hole) on the F atom, has this same form with the generalization that V and ΔV now depend on the orbital angular momentum of the electron (hole) on the F atom—

$$H_{13} = V_{HF}(r_{13}, \vec{L} \cdot \hat{r}_{13}) + \Delta V_{HF}(r_{13}, \vec{L} \cdot \hat{r}_{13})(\vec{S}_1 \cdot \vec{S}_3 + \frac{3}{4}) \tag{3.3a}$$

$$H_{23} = V_{HF}(r_{23}, \vec{L} \cdot \hat{r}_{23}) + \Delta V_{HF}(r_{23}, \vec{L} \cdot \hat{r}_{23})(\vec{S}_2 \cdot \vec{S}_3 + \frac{3}{4}) \quad , \tag{3.3b}$$

where we have noted that due to the diatomic symmetry the interaction can actually depend only on the component of $\vec{L}$ along the relevant diatomic axis.

The functions $V_{HF}(r, \vec{L} \cdot \hat{r})$ and $\Delta V_{HF}(r, \vec{L} \cdot \hat{r})$ of Eq. (3.3) are determined, as before, by the singlet and triplet H-F potential curves [cf. Eq. (2.4)], and their dependence on the projection of orbital angular momentum, $\vec{L} \cdot \hat{r}$, by the Σ and Π potential curves; i.e.,

$$V_{HF}(r, \vec{L} \cdot \hat{r}) = V_0(r) + V_1(r)(\vec{L} \cdot \hat{r})^2 \tag{3.4a}$$

$$\Delta V_{HF}(r, \vec{L} \cdot \hat{r}) = \Delta V_0(r) + \Delta V_1(r)(\vec{L} \cdot \hat{r})^2 \tag{3.4b}$$

where V_0, V_1, ΔV_0, and ΔV, are given in terms of the HF potential curves by

$$V_0(r) = {}^1\Sigma_{HF}(r) \tag{3.5a}$$

$$V_1(r) = {}^1\Pi_{HF}(r) - {}^1\Sigma_{HF}(r) \tag{3.5b}$$

$$\Delta V_0(r) = {}^3\Sigma_{HF}(r) - {}^1\Sigma_{HF}(r) \tag{3.5c}$$

$$\Delta V_1(r) = {}^3\Pi_{HF}(r) - {}^1\Pi_{HF}(r) - [{}^3\Sigma_{HF}(r) - {}^1\Sigma_{HF}(r)] \tag{3.5d}$$

Thus when $(\vec{L}\cdot\hat{r})^2 = 0$ the interaction is determined by the Σ potentials, and Eq. (3.4) gives

$$V_{HF}(r) = {}^1\Sigma_{HF}(r)$$

$$\Delta V_{HF}(r) = {}^3\Sigma_{HF}(r) - {}^1\Sigma_{HF}(r) \quad ,$$

and when $(\vec{L}\cdot\hat{r})^2 = 1$ the interaction is determined by the Π potentials, and Eq. (3.4) becomes

$$V_{HF}(r) = {}^1\Pi_{HF}(r)$$

$$\Delta V_{HF}(r) = {}^3\Pi_{HF}(r) - {}^1\Pi_{HF}(r) \quad .$$

Ths interpolative nature with respect to $m_L \equiv \vec{L}\cdot\hat{r}$, i.e., $\Sigma + (\Pi-\Sigma)m_L^2$, is the same dependence that has appeared in our earlier classical models.[1]

Using Eq. (3.4) in Eq. (3.3) completely specifies the electronic Hamiltonian. If one takes this to be a <u>quantum mechanical</u> Hamiltonian, with $\vec{S}_1, \vec{S}_2, \vec{S}_3$, and $\vec{L}$ being operators, then one can show that this spin Hamiltonian is completely equivalent to the diatomics-in-molecules (DIM) Hamiltonian if only the lowest ${}^1\Sigma$ and ${}^3\Sigma$ states of H_2 and the lowest ${}^1\Sigma, {}^3\Sigma, {}^1\Pi$, and ${}^3\Pi$ states of HF are used. That is, the matrix of this spin Hamiltonian in the basis $|S_1 m_{S_1}\rangle \, |S_2 m_{S_2}\rangle \, |S_3 m_{S_3}\rangle \, |L m_L\rangle$, where $S_1 = S_2 = S_3 = \frac{1}{2}$, $L=1$, is identical to the DIM matrix. (This $2 \times 2 \times 2 \times 3 = 24$ dimensional matrix factors considerably; for states of ${}^2A'$ symmetry, for example, one has a 4×4 matrix, and for ${}^2A''$ states a 2×2 matrix.)

To obtain a classical model for the electronic degrees of freedom of the FH_2 system, however, we proceed as in Section II and take the spins $\vec{S}_1, \vec{S}_2, \vec{S}_3$, and the orbital angular momentum $\vec{L}$ to be <u>classical</u> angular momenta and Eqs. (3.1)-(3.5) thus define the classical electronic Hamiltonian as a function of the nuclear coordinates. Again within the overall center of mass system, the nuclear variables are chosen as in Eq. (2.5), i.e., $\vec{r}$ is the H-H relative coordinate and $\vec{R}$ the coordinate of F relative to the center of mass of H_2. Adding in the nuclear kinetic energy and the spin-orbit interaction between $\vec{L}$ and $\vec{S}_3$ on the fluorine atom, the complete classical Hamiltonian for the F-H_2 system is given explicitly by

$$H(\vec{p}, \vec{r}, \vec{P}, \vec{R}, \vec{S}_1, \vec{S}_2, \vec{S}_3, \vec{L}) = \frac{\vec{P}^2}{2\mu} + \frac{\vec{p}^2}{2m} + B\,\vec{L}\cdot\vec{S}_3$$

$$+ V_{H_2}(r_{12}) + \Delta V_{H_2}(r_{12})(\vec{S}_1\cdot\vec{S}_2 + \tfrac{3}{4})$$

$$+ V_0(r_{13}) + V_1(r_{13})(\vec{L}\cdot\hat{r}_{13})^2$$

$$+ [\Delta V_0(r_{13}) + \Delta V_1(r_{13})(\vec{L}\cdot\hat{r}_{13})^2](\vec{S}_1\cdot\vec{S}_3 + \tfrac{3}{4})$$

$$+ V_0(r_{23}) + V_1(r_{23})(\vec{L}\cdot\hat{r}_{23})^2$$

$$+ [\Delta V_0(r_{23}) + \Delta V_1(r_{23})(\vec{L}\cdot\hat{r}_{23})^2](\vec{S}_2\,\vec{S}_3 + \tfrac{3}{4}) \quad , \quad (3.6)$$

with $\vec{r}_{ij}$ still given by Eq. (2.7) and V_0, V_1, ΔV_0, and ΔV_1 by Eq. (3.5).

The classical equations of motion are generated as before, by Eq. (2.8) with the additional equation for $\vec{L}$,

$$\frac{d}{dt} \vec{L}(t) = -\vec{L} \times \frac{\partial H}{\partial \vec{L}} \qquad (3.7)$$

Again, it is possible to express the Hamiltonian in terms of the action-angle variables of all the angular momenta, (m_1, q_1), (m_2, q_2), (m_3, q_3), (m_L, q_{m_L}), and generate equations of motion for them. Although this leads to fewer first order differential equations, the resulting equations are sufficiently more complex (involving trignometric functions and square roots) that computation with the Cartesian form of the spins is probably more desirable.

Within the standard quasi-classical model, initial conditions for the nuclear variables $(\vec{p}, \vec{r}, \vec{P}, \vec{R})$ are again given in the usual way, and initial conditions for the spins $\vec{S}_1$ and $\vec{S}_2$ of the H atoms are the same

as in Section IIb [i.e., Eq. (2.13)]; i.e., $\vec{S}_1$ and $\vec{S}_2$ are coupled initially to form a singlet spin state of H_2. The spin and orbital angular momentum of the F atom, $\vec{S}_3$ and $\vec{L}$, must be coupled initially to form an eigenstate of total electronic angular momentum of the fluorine atom, and this is again the classical version of a Clebsch-Gordan transformation. Thus the uncoupled action-angle variables of $\vec{S}_3$ and $\vec{L}$, (m_3, q_3) and (m_L, q_{m_L}), are replaced by the coupled action-angle variables (j, q_j) and (m_j, q_{m_j}), where

$$j \equiv |\vec{S}_3 + \vec{L}| \tag{3.8a}$$

$$m_j = m_3 + m_L \quad , \tag{3.8b}$$

with q_j and q_{m_j} their conjugate angle variables, and in terms of the coupled action-angle variables $\vec{S}_3$ and $\vec{L}$ are given by[8]

$$\vec{L} = A \begin{pmatrix} -m_j \cos q_{m_j} \cos q_j - j \sin q_{m_j} \sin q_j \\ -mj \sin q_{m_j} \cos q_j + j \cos q_{m_j} \sin q_j \\ \sqrt{j^2 - m_j^2} \cos q_j \end{pmatrix}$$

$$+ \left(\frac{j^2 + L^2 - S_3^2}{2j^2} \right) \begin{pmatrix} \sqrt{j^2 - m_j^2} \cos q_{m_j} \\ \sqrt{j^2 - m_j^2} \sin q_{m_j} \\ m_j \end{pmatrix} \tag{3.9a}$$

$$\vec{S}_3 = \text{same as above with } A \rightarrow -A \text{ and } (j^2 + L^2 - S_3^2) \rightarrow (j^2 + S_3^2 - L^2) \; , \tag{3.9b}$$

where

$$A = [-j^4-L^4-S_3{}^4+2L^2j^2+2L^2S_3{}^2+2j^2S_3{}^2]^{1/2}/(2j^2) \quad . \qquad (3.9c)$$

Within the usual Monte Carlo procedure the angle variables q_j and q_{m_j}, as well as $q_{S_{12}}$ and $q_{m_{12}}$ for the spins of H_2, are chosen as $2\pi \times$ (random numbers).

For the magnitudes of the angular momenta L^2 and j^2 it is probably desirable also to make a Langer modification. If the initial state of F is the electronically excited state $^2P_{1/2}$, for example, then the quantum mechanical values for L^2 and the initial values of j^2 are

$$(j^2)_{QM} = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4} \qquad (3.10a)$$

$$(L^2)_{QM} = 1(1+1) = 2 \quad , \qquad (3.10b)$$

while the preferred Langer-modified values are

$$(j^2)_{Langer} = (\frac{1}{2} + \frac{1}{2})^2 = 1 \qquad (3.11a)$$

$$(L^2)_{Langer} = (1 + \frac{1}{2})^2 = \frac{9}{4} \quad . \qquad (3.11b)$$

There is no Langer modification to projection quantum numbers so that $m_j = -\frac{1}{2}$ or $+\frac{1}{2}$ initially, and $S_1{}^2 = S_2{}^2 = S_3{}^2$ and $S_{12}{}^2$ are still given as in Section IIb, i.e., by Eq. (2.15).

b. $\underline{O-H_2}$

To show how the model can be extended to deal with atoms involving more than one valence electron (or electron "hole") we consider the $O+H_2$

system.

Let $\vec{S}_1$ and $\vec{S}_2$ be the spins of the electrons on the two hydrogen atoms and $(\vec{S}_3,\vec{L}_3)$ and $(\vec{S}_4,\vec{L}_4)$ be the spin and orbital angular momenta for the two oxygen electrons (holes). The Dirac-Van Vleck spin model takes the Hamiltonian to be the sum of all pair interactions between the valence electrons (and holes), so in this case one has

$$H_{e\ell} = H_{12} + H_{34} + H_{13} + H_{14} + H_{23} + H_{24} \qquad , \qquad (3.12)$$

where H_{ij} is the interaction between electrons i and j.

Each pair interaction H_{ij} in Eq. (3.12) has the same form as in Section II,

$$H_{ij} = V_{ij} + \Delta V_{ij}(\vec{S}_i \cdot \vec{S}_j + \frac{3}{4}) \qquad , \qquad (3.13)$$

where V_{ij} and ΔV_{ij} are functions of the distance between the atoms on which electrons i and j are situated and also the orbital angular momenta of electrons i and j, $\vec{L}_i$ and $\vec{L}_j$, if these are non-zero. Thus H_{12}, the interaction between the electrons on each of the H atoms, is still given by Eq. (3.2). H_{13}, H_{14}, H_{23} and H_{24} are the interactions between an electron on one of the H atoms and one of the p-electrons (holes) on oxygen and are thus of the same form as for the H-F interaction in Eqs. (3.3) and (3.4); i.e.,

$$H_{ij} = V_0(r) + V_1(r)(\vec{L}_j \cdot \hat{r})^2$$

$$+ [\Delta V_0(r) + \Delta V_1(r)(\vec{L}_j \cdot \hat{r})^2](\vec{S}_i \cdot \vec{S}_j + \frac{3}{4}) \qquad , \qquad (3.14)$$

with

$$\vec{r} = \vec{r}_{H_i} - \vec{r}_{Ox}$$

for

$$(i,j) = (1,3), \ (1,4), \ (2,3), \ (2,4) \qquad .$$

The four functions $V_0(r)$, $V_1(r)$, $\Delta V_0(r)$, and $\Delta V_1(r)$ are determined by the diatomic potential curves of OH, but this is more complicated than for the HF case treated in Section IIIa and is deferred to the next section.

The remaining pair interaction, H_{34}, is that between the two electrons (holes) on oxygen. It is also of the general form of Eq. (3.13)

$$H_{34} = V_{Ox}(\vec{L}_3, \vec{L}_4) + \Delta V_{Ox}(\vec{L}_3, \vec{L}_4)(\vec{S}_3 \cdot \vec{S}_4 + \tfrac{3}{4}) \qquad , \qquad (3.15)$$

and since the two electrons are on the same center, the functions V_{Ox} and ΔV_{Ox} are independent of nuclear geometry and thus characteristic of the isolated oxygen atom. Because of spherical symmetry of the atom, V_{Ox} and ΔV_{Ox} can be functions only of $\vec{L}_3 \cdot \vec{L}_4$, and since the electrons (holes) are in p orbitals there can be no higher than quadratic powers of $\vec{L}_3$ and $\vec{L}_4$; i.e., V_{Ox} and ΔV_{Ox} are of the form

$$V_{Ox}(\vec{L}_3, \vec{L}_4) = a_0 + a_1(\vec{L}_3 \cdot \vec{L}_4) + a_2(\vec{L}_3 \cdot \vec{L}_4)^2 \qquad (3.16a)$$

$$\Delta V_{Ox}(\vec{L}_3 \cdot \vec{L}_4) = b_0 + b_1(\vec{L}_3 \cdot \vec{L}_4) + b_2(\vec{L}_3 \cdot \vec{L}_4)^2 \qquad . \qquad (3.16b)$$

Because the two electrons are equivalent, however, $\Delta V_{Ox} \equiv 0$--i.e., there is no exchange interaction between equivalent electrons--so that $b_0 = b_1 = b_2 = 0$. The three constants a_0, a_1, and a_2 are then determined from the

energies of the ^3P, ^1D, and ^1S states of oxygen.

The electronic Hamiltonian of Eq. (3.12) is now completely specified once the prescription is given for determining the four functions V_0, ΔV_0, V_1, and ΔV_1 in Eq. (3.14); this is considered in the next section. Taking all the spins, $\vec{S}_1$, $\vec{S}_2$, $\vec{S}_3$ and $\vec{S}_4$, and orbital angular momenta, $\vec{L}_3$ and $\vec{L}_4$, to be <u>classical</u> angular momenta and adding the nuclear kinetic energy to this classical electronic Hamiltonian as in the previous sections, one obtains the classical Hamiltonian for the complete $O-H_2$ system:

$$H(\vec{P},\vec{R},\vec{p},\vec{r},\vec{S}_1,\vec{S}_2,\vec{S}_3,\vec{S}_4,\vec{L}_3,\vec{L}_4) = \frac{\vec{P}^2}{2\mu} + \frac{\vec{p}^2}{2m}$$

$$+ a_0 + a_1(\vec{L}_3\cdot\vec{L}_4) + a_2(\vec{L}_3\cdot\vec{L}_4)^2$$

$$+ V_{H_2}(r_{12}) + \Delta V_{H_2}(r_{12})(\vec{S}_1\cdot\vec{S}_2+\tfrac{3}{4})$$

$$+ V_0(r_{13}) + V_1(r_{13})(\vec{L}_3\cdot\hat{r}_{13})^2 + [\Delta V_0(r_{13}) + \Delta V_1(r_{13})(\vec{L}_3\cdot\hat{r}_{13})^2](\vec{S}_1\cdot\vec{S}_3+\tfrac{3}{4})$$

$$+ V_0(r_{13}) + V_1(r_{13})(\vec{L}_4\cdot\hat{r}_{13})^2 + [\Delta V_0(r_{13}) + \Delta V_1(r_{13})(\vec{L}_4\cdot\hat{r}_{13})^2](\vec{S}_1\cdot\vec{S}_4+\tfrac{3}{4})$$

$$+ V_0(r_{23}) + V_1(r_{23})(\vec{L}_3\cdot\hat{r}_{23})^2 + [\Delta V_0(r_{23}) + \Delta V_1(r_{23})(\vec{L}_3\cdot\hat{r}_{23})^2](\vec{S}_2\cdot\vec{S}_3+\tfrac{3}{4})$$

$$+ V_0(r_{23}) + V_1(r_{23})(\vec{L}_4\cdot\hat{r}_{23})^2 + [\Delta V_0(r_{23}) + \Delta V_1(r_{23})(\vec{L}_4\cdot\hat{r}_{23})^2](\vec{S}_2\cdot\vec{S}_4+\tfrac{3}{4}) \ ,$$

$$(3.17)$$

where r_{12}, the H-H separation, and r_{13} and r_{23} are defined in terms of $\vec{r}$ and $\vec{R}$ by Eqs. (2.5) and (2.7). To include the effects of spin-orbit coupling in the oxygen atom one would add a term proportional to $(\vec{L}_3+\vec{L}_4)\cdot(\vec{S}_3+\vec{S}_4)$ to Eq. (3.17).

Initial conditions for the classical trajectories of an $O + H_2$

collision are specified, as in the previous sections, by coupling the various angular momenta to correspond to the appropriate initial state. $\vec{S}_1$ and $\vec{S}_2$, the spins on the two hydrogen atoms, are coupled as in Section IIb to form a singlet electronic state of H_2. If the initial electronic state of the oxygen atom is ^1D, for example, then one would couple $\vec{S}_3$ and $\vec{S}_4$ to form a singlet, and $\vec{L}_3$ and $\vec{L}_4$ to form a D state, i.e., $L_{34} \equiv |\vec{L}_3 + \vec{L}_4| = 2$; each of these couplings involves a classical Clebsch-Gordan transformation of the type discussed in Sections IIb and IIIa. In this way one generates all the initial conditions appropriate to an $O(^1D) + H_2(^1\Sigma)$ collision; by the same methods one could generate the initial conditions for $O(^3P) + H_2(^1\Sigma)$, etc.

c. <u>O-H</u>

To determine the functions $V_0(r)$, $\Delta V_0(r)$, $V_1(r)$, and $\Delta V_1(r)$ of Eq. (3.14), which characterize the interaction of an s electron on hydrogen with a p electron (hole) on oxygen, we apply the spin model to O-H and choose these functions so that the <u>quantum mechanical</u> eigenvalues of the spin Hamiltonian agree with the diatomic potential curves of OH, so far as is possible. This is what has been done for the diatomic fragments of the H_3 and FH_2 systems above, except that for these systems the process was so trivial one took little note of it. For the present case, however, which involves a multivalent atom, this process is more involved.

Thus in this section let $(\vec{S}_1, \vec{L}_1)$ and $(\vec{S}_2, \vec{L}_2)$ denote the spin and orbital angular momentum of the two oxygen electrons (holes) and $\vec{S}_3$ the spin of the hydrogen electron. The electronic Hamiltonian for OH is then (ignoring spin-orbit coupling)

$$H_{e\ell} = H_{12} + H_{13} + H_{23} \quad , \tag{3.18}$$

and from Section IIIb one has

$$H_{12} = a_0 + a_1(\vec{L}_1 \cdot \vec{L}_2) + a_2(\vec{L}_1 \cdot \vec{L}_2)^2 \tag{3.19a}$$

$$H_{13} = V_0(r) + L_{1z}^2 V_1(r) + [\Delta V_0(r) + L_{1z}^2 \Delta V_1(r)](\vec{S}_1 \cdot \vec{S}_3 + \tfrac{3}{4}) \tag{3.19b}$$

$$H_{23} = V_0(r) + L_{2z}^2 V_1(r) + [\Delta V_0(r) + L_{2z}^2 \Delta V_1(r)](\vec{S}_2 \cdot \vec{S}_3 + \tfrac{3}{4}), \tag{3.19c}$$

where

$$L_{1z} = \vec{L}_1 \cdot \hat{r}$$

$$L_{2z} = \vec{L}_2 \cdot \hat{r} \quad .$$

To determine the quantum mechanical eigenvalues of this Hamiltonian a matrix representation is constructed in the basis set

$$|L_1 m_{L_1}\rangle |L_2 m_{L_2}\rangle |S_1 m_{S_1}\rangle |S_2 m_{S_2}\rangle |S_3 m_{S_3}\rangle \quad ,$$

with $L_1 = L_2 = 1$, $S_1 = S_2 = S_3 = 1/2$. It is convenient, though, to replace m_{L_1} and m_{L_2} by the coupled variables L, M_L, where

$$L = |\vec{L}_1 + \vec{L}_2|$$

$$M_L = m_{L_1} + m_{L_2} \quad .$$

Also, m_{s_1} and m_{s_2} are replaced by the coupled variables S_{12}, $M_{S_{12}}$,

$$S_{12} = |\vec{S}_1 + \vec{S}_2|$$

$$M_{S_{12}} = m_{s_1} + m_{s_2} \quad ,$$

and then $M_{S_{12}}$ and m_{s_3} are replaced by the total spin and its projection, S and M_S,

$$S = |\vec{S}_{12} + \vec{S}_3| = |\vec{S}_1 + \vec{S}_2 + \vec{S}_3|$$

$$M_S = M_{S_{12}} + m_{s_3} = m_{s_1} + m_{s_2} + m_{s_3} \quad .$$

The basis functions of this basis set are designated

$$|L\ M_L\rangle |S\ M_S\ S_{12}\rangle \qquad ,$$

and are particularly convenient because the electronic Hamiltonian is diagonal in S, M_S, and M_L (and independent of M_S). From Eqs. (3.18) and (3.19) and standard angular momentum properties this Hamiltonian matrix is

$$
\begin{aligned}
H^{S,M_L}_{L'S'_{12},LS_{12}} &= \delta_{L',L}\,\delta_{S'_{12},S_{12}}\,[E_0^{LS_{12}} + 2V_0 + (\tfrac{3}{4} + \tfrac{S(S+1)}{2})\Delta V_0] \\
&\quad + \delta_{S'_{12},S_{12}}\,(V_1 + \tfrac{3}{4}\Delta V_1)\,\langle L'M_L|L_{1z}^2 + L_{2z}^2|LM_L\rangle \\
&\quad + \Delta V_1[\langle L'M_L|L_{1z}^2|LM_L\rangle\langle SM_S S'_{12}|\vec{S}_1\cdot\vec{S}_3|SM_S S_{12}\rangle \\
&\quad + \langle L'M_L|L_{2z}^2|LM_L\rangle\langle SM_S S'_{12}|\vec{S}_2\cdot\vec{S}_3|SM_S S_{12}\rangle] \qquad . \tag{3.20}
\end{aligned}
$$

Since the allowed values of (L,S_{12}) are $(0,0)$, $(1,1)$, and $(2,0)$, this is at most a 3 x 3 matrix; $E_0^{LS_{12}}$ is the atomic energy of the oxygen in the ^1S, ^3P, or ^1D state.

The matrices of the angular momentum operators in Eq. (3.20) can

be calculated by standard angular momentum methodology,[9] so it is a straight-forward procedure to construct this Hamiltonian matrix and find its eigenvalues for the various allowed values of the good quantum numbers S, M_L. We thus simply summarize the results here:

$$^4\Sigma = E_0(^3P) + 2V_0 + 2V_1 + 2\Delta V_0 + 2\Delta V_1 \tag{3.21a}$$

$$^2\Sigma^- = E_0(^3P) + 2V_0 + 2V_1 + \frac{1}{2}\Delta V_0 + \frac{1}{2}\Delta V_1 \tag{3.21b}$$

$$^2\Sigma^+ = \frac{1}{2}\left[E_0(^1D) + E_0(^1S)\right] + 2V_0 + V_1 + \frac{3}{2}\Delta V_0 + \frac{3}{4}\Delta V_1$$

$$\pm \left\{\left[\frac{E_0(^1S)-E_0(^1D)}{2}\right]^2 + \frac{1}{3}\left[E_0(^1S)-E_0(^1D)\right]\left(V_1 + \frac{3}{4}\Delta V_1\right)\right.$$

$$\left. + \left(V_1 + \frac{3}{4}\Delta V_1\right)^2\right\}^{1/2} \tag{3.21c}$$

$$^4\Pi = E_0(^3P) + 2V_0 + V_1 + 2\Delta V_0 + \Delta V_1 \tag{3.21d}$$

$$^2\Pi = \frac{1}{2}\left[E_0(^3P) + E_0(^1D)\right] + 2V_0 + V_1 + V_0 + \frac{1}{2}V_1$$

$$\pm \frac{1}{2}\left\{\left[E_0(^1D)-E_0(^3P) + \Delta V_0 + \frac{1}{2}\Delta V_1\right]^2 + \frac{3}{4}\Delta V_1^2\right\}^{1/2} \tag{3.21e}$$

$$^2\Delta = E_0(^1D) + 2V_0 + 2V_1 + \frac{3}{2}\Delta V_0 + \frac{3}{2}\Delta V_1 \tag{3.21f}$$

where $^4\Sigma$, $^2\Pi$, etc., corresponds to $(S, M_L) = (\frac{3}{2}, 0)$, $(\frac{1}{2}, 1)$, etc.

Eq. (3.21) expresses the _eight_ valence potential curves of OH in terms of only _four_ functions of r. This is a non-trivial test of the valence bond model even here at the diatomic level; i.e., is it possible to choose four functions $V_0(r)$, $V_1(r)$, $\Delta V_0(r)$, and $\Delta V_1(r)$ so that Eq. (3.21) _accurately_ represents the eight true valence potential curves of OH. The answer is affirmative,[13] to a very good approximation.

With the four functions $V_0(r)$, $V_1(r)$, $\Delta V_0(r)$, and $\Delta V_1(r)$ which characterize the interaction between a hydrogen s-electron and an oxygen p-electron (hole) thus determined, the valence bond spin Hamiltonian for the $O-H_2$ system, Eq. (3.17), is now completely defined.

IV.   Concluding Remarks.

The classical valence bond model developed in this paper is the
boldest approach yet attempted for modeling electronic degrees of freedom
classically. Even the intimate chemical features of bonding are characterized
classically. The approach completely obviates the Born-Oppenheimer (i.e.,
electronically adiabatic) approximation by following the classical mechanics
of the electronic (i.e., spin) degrees of freedom along with the nuclear
motion. A classical trajectory simulation using this model can thus deal
as easily with electronically non-adiabatic processes as with adiabatic
ones.

It is difficult to predict how quantitatively accurate the model will
be. The application in Section IIc to the $H + H_2$ reaction is reasonably
encouraging. Calculations for $F + H_2$, including spin-orbit coupling, should
certainly be possible and will be an important test of the approach. The
$O + H_2$ collision system, as described in Sections IIIb,c is an even more
challenging application because of the three electronic states of oxygen
that are involved. These calculations should also be possible.

Finally, we note as an aside that the analysis in Sections IIIb,c
has suggested to us a semiempirical valence bond (SEVB) model for quantum
chemistry, i.e., for Born-Oppenheimer potential energy surfaces. Thus
one can determine quantum mechanical Born-Oppenheimer potential surfaces
for the polyatomic OH_2 system by finding the eigenvalues of the quantum
mechanical version of the spin Hamiltonian for OH_2, Eq. (3.17) minus the
nuclear kinetic energy terms, where the various functions of atom-atom
distances are determined from the diatomic fragments as in
Section IIIc. For the H_3 and FH_2 examples this approach is identical to

the London and DIM models, respectively, but when one of the atoms involved is multivalent, as in OH_2, this SEVB model is different and, moreover, seems to have some important advantages. First, it is more economical than DIM; i.e., there are _eight_ valence potential curves of OH, which are all independent parameters in the DIM approach, whereas the SEVB model involves only _four_ parameters for this case. Also, the SEVB model involves no indeterminant "mixing parameters" that appear in DIM when multivalent atoms are involved.[6,14] Preliminary results[13] for OH_2 are very encouraging, and further work[15] is in progress pursuing the possibilities of this SEVB approach as an approximate quantum chemistry model.

Acknowledgments

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Figure Caption

Cross sections as a function of initial translational energy for the reaction (R) $H + H_2(v=j=0) \rightarrow H_2 + H$ and the collisional dissociation (D) $H + H_2(v=j=0) \rightarrow H + H + H$. The solid curves are the results of the conventional quasiclassical model using the lowest Born-Oppenheimer potential surface, and the broken lines the results given by the classical valence bond model; see text. The error bars indicate the usual Monte Carlo estimates of statistical error.
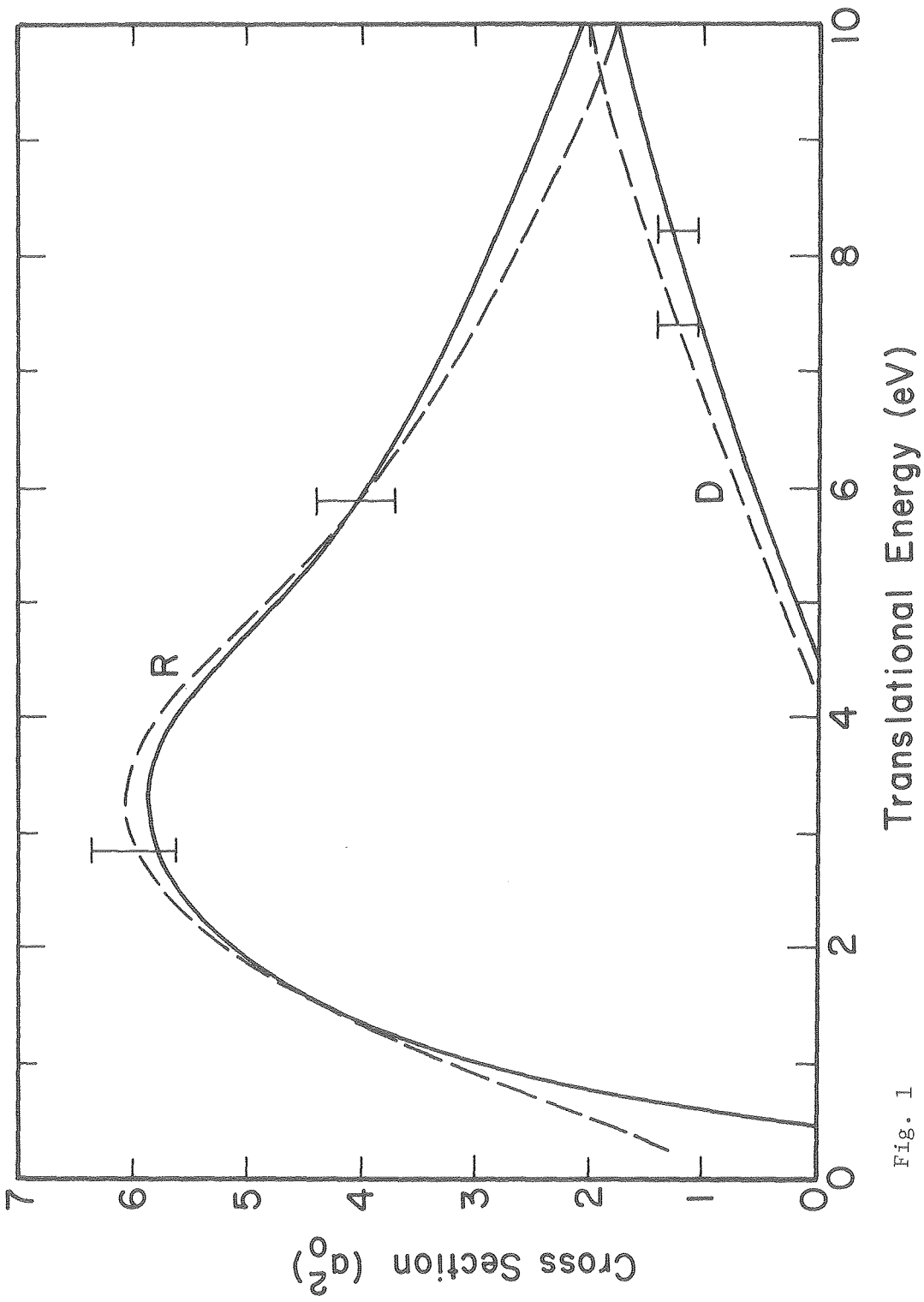
Fig. 1

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