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Author

Miller, W.H.

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W. H. Miller and C. W. McCurdy

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CLASSICAL TRAJECTORY MODEL FOR ELECTRONICALLY NON-ADIABATIC COLLISION PHENOMENA; A CLASSICAL ANALOG FOR ELECTRONIC DEGREES OF FREEDOM

W. H. Miller and C. W. McCurdy*

Department of Chemistry and Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, University of California
Berkeley, CA 94720

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*Present address: Department of Chemistry, Ohio State University, Columbus, Ohio.

Abstract

A theoretical model of electronically non-adiabatic collision processes is proposed which describes all degrees of freedom, electronic and heavy particle (translation, rotation, and vibration), by classical mechanics. The advantage of such an approach is that since all degrees of freedom are treated on the same dynamical footing (i.e., via classical mechanics), all dynamical effects are described correctly (even resonance effects in electronic to vibrational/rotational energy transfer). Calculations can be carried out within the framework of the standard quasi-classical trajectory method. The key element in making this approach successful is being able to construct a classical model for the electronic degrees of freedom, and several approaches for doing this are described.

I. Introduction

It is well-known that classical trajectory methods[1] are extremely useful for describing atomic and molecular collision processes that take place on one electronically adiabatic potential energy surface, i.e., that stay within one adiabatic (Born-Oppenheimer) electronic state throughout the collision. This usefulness stems from the fact that trajectory methods are general, simple to apply, and need involve no approximations other, of course, than the use of classical rather than quantum mechanics. (The errors introduced by using classical rather than quantum mechanics are well understood[2]--i.e., interference and tunneling effects are missed--but these quantum mechanical effects can in principle, and to some extent in practice, be incorporated by semiclassical methods.[2])

In attempting to extend these types of methods to the treatment of electronically non-adiabatic collision processes, i.e., those that involve more than one Born-Oppenheimer potential energy surface, one is faced with considerable difficulty.[3] It is desirable to retain the facility and accuracy of using classical mechanics to describe the heavy particle degrees of freedom (i.e., translation, rotation, and vibration), but it seems clear that the electronic degrees of freedom must be described quantum mechanically, i.e., as states. One is thus forced to mix dynamical descriptions--i.e., to describe some degrees of freedom by quantum mechanics and others by classical mechanics--and it is in general not possible to do this without introducing inherent dynamical approximations. Any theory, therefore, that treats the heavy particle motion classically, i.e., via trajectories, and the electronic degrees of freedom quantum mechanically, i.e., as states, will contain dynamical approximations and thus fail to describe certain aspects of these collision processes correctly.

Tully and Preston's surface hopping model[4] for treating non-adiabatic collision processes is of the type mentioned above: the heavy particle degrees of freedom are described classically, as trajectories moving on a potential energy surface, and transitions from one potential energy surface (i.e., electronic state) to another are accomplished by localized "hops" that take place with a probability determined semiclassically. Although this model is a considerable improvement over earlier approaches that treated both electronic and vibrational degrees of freedom quantum mechanically (the vibronic representation)--for it is usually more important to treat the interaction between translation and vibration (and rotation) consistently (and therefore by classical mechanics) rather than to treat vibrational motion by quantum mechanics--the model has some failings because it does not treat <u>all</u> degrees of freedom on the same dynamical footing. One failure of the surface hopping model is its inability to describe <u>resonance effects</u> in energy transfer between electronic degrees of freedom and heavy particle degrees of freedom,[5,6] for example, near-resonance in electronic-rotational energy transfer,

$$F^* + H_2(j=0) \rightarrow F + H_2(j=2) \quad , \tag{1.1}$$

and in electronic-vibrational energy transfer,

$$Br^* + H_2(v=0) \rightarrow Br + H_2(v=1) \quad . \tag{1.2}$$

It is clear also that the model will fail if the non-adiabatic transitions are not localized.

The generalized Stueckelberg model devised by Miller and George[7] is essentially a more sophisticated version of the surface hopping model that incorporates interference effects between different trajectories that "hop" from one potential energy surface to another. Although this semiclassical theory is more satisfactory and internally consistent in some ways than the Tully-Preston model--it is capable, for example, of describing the above resonance effects correctly[6]--it, too, has inherent limitations: the generalized Stueckelberg model is essentially adiabatic perturbation theory and is thus rigorously valid only if the non-adiabatic transition probabilities are exponentially small.[7,8]

To have a truly correct dynamical theory of non-adiabatic collision processes one thus needs to treat all the degrees of freedom, electronic and heavy particle (translation, rotation, and vibration), on the same dynamical footing. It would be best, of course, to treat them all quantum mechanically, but this typically leads to such an enormous number of coupled channel Schrödinger equations that it is out of the question. In most cases, too, the results desired from a calculation are not sufficiently detailed to justify a completely quantum mechanical scattering calculation.

The opposite extreme, which is explored in this paper, is to treat all the degrees of freedom, electronic and heavy particle, by classical mechanics. This approach is one step further down the road of classical mechanics than the Tully-Preston and Miller-George models in that electronic, as well as the heavy particle degrees of freedom are to be treated classically. The electronic states are thus replaced by coordinates and momenta (more precisely, by action-angle variables) whose time evolution will be determined, along with that of the heavy particle coordinates and momenta, by Hamilton's equations of motion.

It may at first seem absurd to think that electronic degrees of freedom can be treated classically, and indeed we do not plan to follow the classical orbits of all 11 electrons, for example, in the F + H_2 collision system. For non-adiabatic transitions to have significant probabilities, however, the electronic energy spacing must be comparable (at least locally) to vibrational/rotational energy level spacings. Energy level spacings, however, correspond to frequencies (i.e., $\omega = \Delta E/\hbar$) of classical motion. This implies that there is at least some aspect of the electronic motion that is slow, i.e., that corresponds to the classical motion of something that varies on the same time scale as the coordinates and momenta of the heavy particle degrees of freedom. From this point of view, therefore, it does not seem completely unreasonable that one should be able to construct a classical model for the <u>relevant aspects</u> of the electronic degrees of freedom. This paper is a first attempt in showing how this can be done.

Section II considers first the specific case of fine structure transitions in a ^2P atom caused by collision with a ^1S atom or a $^1\Sigma$ diatomic molecule. The specific examples we have in mind are

$$F(^2P_j) + X \rightarrow F(^2P_{j'}) + X \quad , \tag{1.3}$$

where X is a rare gas atom or a diatomic molecule such as H_2; j and j' can have the values 1/2 or 3/2. As will be seen, it is relatively simple to construct a classical model for the relevant electronic degrees of freedom in this case because the origin of the different electronic states (i.e., spin-orbit coupling) has a simple classical analogue.

In Section III it is shown how a classical model for a general two (electronic) state system can be constructed. For an atom-atom or atom-diatom collision system, for example, in which two adiabatic electronic states are involved, it is shown how the two electronic states can be replaced by a generalized coordinate and momentum. It is seen that this can be done in both a diabatic electronic representation or the adiabatic electronic representation. It is also suggested how this scheme can be generalized to an arbitrary number of states.

For the cases discussed in both Sections II and III the idea is that non-adiabatic transitions will be described by computing the complete classical trajectories involving all the degrees of freedom, electronic as well as heavy particle. Transitions between specific electronic states can be determined by the usual quasi-classical prescription,[1] namely the action variable corresponding to the electronic degree of freedom is initially set to an integer, and its final (non-integral) value is assigned to the nearest integer quantum number "box". Since all the degrees of freedom are treated on the same (i.e., classical) dynamical footing, one expects this approach to describe all dynamical effects correctly. Even the resonance effects of Eqs. (1.1) and (1.2) should be described correctly since resonance energy transfer occurs in classical as well as quantum mechanics; the Tully-Preston surface hopping model misses these effects[5,6] only because electronic and heavy particle degrees of freedom are described on different dynamical footings, i.e., by quantum and by classical mechanics, respectively. There are, of course, the purely quantum mechanical interference and tunneling effects that this completely classical model will miss.

These effects can in principle, however, be incorporated by using classical S-matrix theory.[2]

In concluding this Introduction it should be noted that there are other contexts in which classical models have been used to describe electronic degrees of freedom. Perhaps the most common situation is to describe highly excited Rydberg states classically,[9] for these states can be modeled as one-electron systems. Work by Green and Zare,[10] showing that the electronic states arising from the interaction of a $^2\Pi$ diatomic molecule and a ^1S atom can be modeled as a symmetric top molecule plus an atom, is an example of the general correspondence we are trying to develop here, but they did not proceed to construct the actual classical Hamiltonian for this system.

II. Fine Structure Transitions in ^2P Atoms

a. ^2P Atom + ^1S Atom

The goal here is to construct a classical Hamiltonian that describes the collision of a ^2P atom and a ^1S atom, where one is interested in transitions between the $^2P_{1/2}$ and the $^2P_{3/2}$ states of the atom.

For the isolated ^2P atom we thus introduce two classical angular momenta, $\vec{L}$ and $\vec{S}$, each of which consists of two degrees of freedom characterized by the usual action-angle variables:[11,12] (L,q_L), (m_L,q_{m_L}), (S,q_S), (m_S,q_{m_S}), where L,S,m_L, and m_S are the magnitudes of $\vec{L}$ and $\vec{S}$ and their projections onto the interatomic axis, respectively, and the q's are their conjugate angle variables. $\vec{L}$ and $\vec{S}$ are the electronic orbital and spin angular momentum, respectively, of the ^2P atom, so that $L = 1$ and $S = 1/2$. The classical Hamiltonian for the isolated ^2P atom is

$$B|\vec{L}+\vec{S}|^2 = B(L^2 + S^2 + 2\vec{L}\cdot\vec{S}) \quad , \tag{2.1}$$

where B is a constant, and $\vec{L}\cdot\vec{S}$ is given in terms of the canonical variables by[13]

$$\vec{L}\cdot\vec{S} = m_L m_S + \sqrt{L^2-m_L^2}\sqrt{S^2-m_S^2}\ \cos(q_{m_L}-q_{m_S}) \quad . \tag{2.2}$$

As shown in the Appendix, the electronic energy for the two-atom system is given in terms of the canonical variables by

$$H_{e\ell} = (1-m_L^2)\ V_\Sigma(R) + m_L^2\ V_\Pi(R) \quad , \tag{2.3}$$

where $V_\Sigma(R)$ and $V_\pi(R)$ are the $^2\Sigma$ and $^2\Pi$ potential curves for the $^2P + {}^1S$ diatomic system. One may simply think of Eq. (2.3) as an interpolation formula: when m_L (which is called Λ in usual spectroscopic notation) is 0, the energy is V_Σ, and when m_L ± 1 it is V_π.

The complete classical Hamiltonian for the system is thus

$$H = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + B|\vec{L}+\vec{S}|^2 + (1-m_L{}^2)\, V_\Sigma(R) + m_L{}^2\, V_\pi(R) \quad , \tag{2.4}$$

where (P,R) are the momentum and coordinate for the relative translational motion of the two atoms and ℓ is the orbital angular momentum for relative motion of the atoms. Since the <u>total</u> angular momentum $\vec{J}$,

$$\vec{J} = \vec{\ell} + \vec{L} + \vec{S} \quad , \tag{2.5}$$

is conserved, it can be used to eliminate $\vec{\ell}$ from the Hamiltonian; i.e.,

$$\vec{\ell} = \vec{J} - (\vec{L}+\vec{S}) \quad . \tag{2.6}$$

(Table I summarizes the different angular momenta that appear in this system.) Also, one notes that the Hamiltonian does not involve the angle variables q_L and q_S, so that L and S are conserved quantities. The Hamiltonian thus becomes

$$H_{JLS}(P,R,m_L,q_{m_L},m_S,q_{m_S}) = \frac{P^2}{2\mu} + \frac{|\vec{J}-(\vec{L}+\vec{S})|^2}{2\mu R^2}$$

$$+ B|\vec{L}+\vec{S}|^2 + (1-m_L{}^2)\, V_\Sigma(R) + m_L{}^2\, V_\pi(R) \quad , \tag{2.7}$$

where the variables J,L,S are conserved and appear in the Hamiltonian only as parameters.

Before going further it is useful to make a canonical transformation to the "good" action-angle variables of the ^{2}P atom; i.e., since the atomic Hamiltonian of Eqs. (2.1) and (2.2) involves q_{m_L} and q_{m_S}, the action variables m_L and m_S are not constants of the motion of the isolated ^{2}P atom. The desired canonical transformation replaces the momenta m_L and m_S by j and m_j, where $j \equiv |\vec{L}+\vec{S}|$ is the magnitude of the total electronic angular momentum of the ^{2}P atom and m_j its projection onto the interatomic axis. This canonical transformation has been discussed in considerable detail by Miller;[11] it is the classical analogue of the Clebsch-Gordan transformation of quantum mechanics. With (m_L, q_{m_L}) and (m_S, q_{m_S}) replaced by (j, q_j) and (m_j, q_{m_j}), the Hamiltonian of Eq. (2.7) becomes

$$H_{JLS}(P,R,j,q_j,m_j,q_{m_j}) = \frac{P^2}{2\mu} + \frac{|\vec{J}-\vec{j}|^2}{2\mu R^2} + Bj^2$$

$$+ (1-m_L{}^2)\ V_\Sigma(R) + m_L{}^2\ V_\pi(R) \quad , \tag{2.8}$$

where m_L is now a function of the "new" variables j, q_j, m_j, q_{m_j}; the explicit expression for it is

$$m_L = [\alpha\sqrt{j^2-m_j{}^2}\cos q_j + m_j(j^2+L^2-S^2)]/(2j^2) \quad , \tag{2.9a}$$

where

$$\alpha = \sqrt{(L+S)^2-j^2}\ \sqrt{j^2-(L-S)^2} \quad . \tag{2.9b}$$

Proceeding further, one has

$$|\vec{J}-\vec{j}|^2 = J^2 + j^2 - 2\vec{J}\cdot\vec{j} \quad , \tag{2.10}$$

and in terms of the action-angle variables one has[13]

$$\vec{J}\cdot\vec{j} = m_J m_j + \sqrt{J^2-m_J^2}\sqrt{j^2-m_j^2}\,\cos(q_{m_J}-q_{m_j}) \quad , \tag{2.11}$$

where m_J is the projection of J onto the interactomic axis, and q_{m_J} is its conjugate angle. Since the Hamiltonian is independent of m_J, q_{m_J} is a constant and can be set to 0. (This is possible since the 2π-length interval chosen for the domain of q_{m_j} is arbitrary.) Furthermore, since the interatomic axis has been chosen as the quantization axis, it must be that m_ℓ, the projection of $\vec{\ell}$ along it, is 0 (because $\vec{\ell} = \vec{R} \times \vec{P}$); since by Eq. (2.6),

$$\vec{\ell} = \vec{J}-\vec{j} \quad ,$$

one has

$$\begin{aligned} m_\ell &= m_J - m_j \\ &= 0 \quad , \end{aligned}$$

which implies that

$$m_J = m_j \quad . \tag{2.12}$$

Using Eqs. (2.12) and (2.11) in Eq. (2.10) gives

$$\ell^2 \equiv |\vec{J}-\vec{j}|^2 = J^2+j^2-2m_j^2 - 2\sqrt{J^2-m_j^2}\sqrt{j^2-m_j^2}\,\cos q_{m_j} \quad , \tag{2.13}$$

which may be recognized as the expression obtained earlier[12] for the atom-diatom system in the helicity representation.

The classical Hamiltonian of Eq. (2.8) can now be written in its final form

$$H_{JLS}(P,R,j,q_j,m_j,q_{m_j}) = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + Bj^2 + (1-m_L{}^2)\ V_\Sigma(R) + m_L{}^2\ V_\pi(R) \quad , \tag{2.14}$$

with ℓ^2 and m_L given in terms of the canonical variables by Eqs. (2.13) and (2.9), respectively.

The various terms in Eq. (2.14) have rather obvious interpretations as coriolis interactions, etc. This classical Hamiltonian is, in fact, the direct analogue of the quantum mechanical Hamiltonian Mies[14] obtained for describing this same problem quantum mechanically, and the two Hamiltonian's are essentially identical in structure.

With this Hamiltonian one can carry out completely classical trajectory calculations for all the degrees of freedom. According to the standard quasiclassical procedure,[1] the electronic angular momentum j is initially set to an integer, 1/2 or 3/2, and q_j is chosen as a random number in the interval $(0,2\pi)$, etc.

It could turn out to be easier in practice to compute the classical trajectories in the uncoupled representation, i.e., with (m_L,q_{m_L}) and (m_S,q_{m_S}) as the dynamical variables, rather than in the coupled representation described above, i.e., with (j,q_j) and (m_j,q_{m_j}) as the dynamical variables. If so, the Hamiltonian in the uncoupled representation, $H_{JLS}(P,R,m_L,q_{m_L},m_S,q_{m_S})$, is given still by Eq. (2.14) but with j^2 and ℓ^2 expressed in terms of the variables (m_L,q_{m_L}), (m_S,q_{m_S}). From the analysis described above it is not hard to show that these expressions are

$$\begin{aligned} j^2 &= |\vec{L}+\vec{S}|^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S} \\ &= L^2 + S^2 + 2m_L m_S + 2\sqrt{L^2-m_L{}^2}\sqrt{S^2-m_S{}^2}\ \cos(q_{m_L}-q_{m_S}) \quad , \end{aligned} \tag{2.15}$$

and

$$\begin{aligned}
\ell^2 &\equiv |\vec{J}-\vec{L}-\vec{S}|^2 \\
&= J^2 + L^2 + S^2 - 2\vec{J}\cdot\vec{L} - 2\vec{J}\cdot\vec{S} + 2\vec{L}\cdot\vec{S} \\
&= J^2 + L^2 + S^2 - 2m_L^{\;2} - 2m_S^{\;2} - 2m_L m_S \\
&\quad - 2\sqrt{J^2-(m_L+m_S)^2}\,\sqrt{L^2-m_L^{\;2}}\;\cos q_{m_L} \\
&\quad - 2\sqrt{J^2-(m_L+m_S)^2}\;\sqrt{S^2-m_S^{\;2}}\;\cos q_{m_S} \\
&\quad + 2\sqrt{L^2-m_L^{\;2}}\,\sqrt{S^2-m_S^{\;2}}\;\cos(q_{m_L}-q_{m_S}) \quad . \qquad (2.16)
\end{aligned}$$

The results of a classical trajectory calculation are, of course, independent of the representation in which the calculation is carried out.

As a final comment, we note that since J >> L,S,j, it is likely that many of the centrifugal coupling terms in Eq. (2.13) or Eq. (2.16) can be discarded with little error. The simplest such approximation is to take $\ell^2 = J^2$ in both cases; this corresponds to a "helicity conserving" approximation of the type now often used to simplify quantum mechanical scattering calculations.[15]

b. ^2P Atom and $^1\Sigma$ Diatom

Here we show how the above analysis can be generalized to describe a ^2P atom + $^1\Sigma$ diatom collision system, the example we have in mind being $F(^2P) + H_2$. Just as the Hamiltonian of Section IIa is analogous to the quantum mechanical Hamiltonian of Mies,[14] the Hamiltonian of this section is the classical analogue of the quantum mechanical Hamiltonian operator that Rebentrost and Lester[16] derived for the $F(^2P) + H_2$ system. To a large extent, therefore, we follow their notation and approach in constructing the classical Hamiltonian for the system.

$\vec{L}$ and $\vec{S}$ again denote the electronic orbital and spin angular momentum of the ^2P atom, $\vec{j} = \vec{L} + \vec{S}$, and the Hamiltonian for the isolated atom is again given by Eq. (2.1). The diatomic molecule is treated initially as a rigid rotor and thus has only a rotational degree of freedom. N and m_N are the action-angle variables for this rotational angular momentum of the diatom--N is the magnitude of the rotational angular momentum and m_N its projection onto the R axis (see Figure 1)--and q_N and q_{m_N} are their conjugate angle variables. The various angular momenta of the system are summarized in Table II. The Hamiltonian for the isolated diatom is

$$\frac{N^2}{2mr_0^2} \quad , \tag{2.17}$$

where m is the reduced mass of the diatom and r_0 its bound length.

Analogous to Section IIa, the complete Hamiltonian for the system is thus given by

$$H_{JLS}(P,R,N,q_N,q_{m_N},j,q_j,m_j,q_{m_j}) = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + \frac{N^2}{2mr_0^2} + Bj^2 + H_{e\ell} \quad , \tag{2.18}$$

where, as before, total angular momentum conservation can be used to express ℓ^2 in terms of the total angular momentum J and the other angular momenta of the system,

$$\ell^2 = |\vec{J}-\vec{N}-\vec{j}|^2$$

$$= J^2+N^2+j^2 - 2\vec{J}\cdot\vec{N}-2\vec{J}\cdot\vec{j}+2\vec{N}\cdot\vec{j} \quad ; \qquad (2.19)$$

using the general relation in footnote 13 and the fact that $m_\ell \equiv m_J-m_N-m_j = 0$ (since $\vec{R}$ is the quantization axis), which implies that $m_J = m_N + m_j$, the explicit expression for ℓ^2 in terms of the action angle variables is

$$\begin{aligned}\ell^2 &= J^2 + N^2 + j^2 - 2m_N{}^2 - 2m_j{}^2 - 2m_Nm_j \\ &- 2\sqrt{J^2-(m_N+m_j)^2}\sqrt{N^2-m_N{}^2}\ \cos q_{m_N} \\ &- 2\sqrt{J^2-(m_N+m_j)^2}\sqrt{j^2-m_j{}^2}\ \cos q_{m_j} \\ &+ 2\sqrt{N^2-m_N{}^2}\sqrt{j^2-m_j{}^2}\ \cos(q_{m_N}-q_{m_j}) \quad . \qquad (2.20)\end{aligned}$$

It is shown in the Appendix that $H_{e\ell}$, the electronic energy of the system, is given in terms of the canonical variables by

$$\begin{aligned}H_{e\ell}(R,\gamma,m_L,q_{m_L}) &= m_L{}^2\left(\frac{H_{xx}+H_{yy}}{2}\right) + (1-m_L{}^2)\ H_{zz} \\ &+ m_L{}^2\left(\frac{H_{xx}-H_{yy}}{2}\right)\cos 2q_{m_L} - 2m_L\sqrt{1-m_L{}^2}\,H_{yz}\ \sin q_{m_L} \ , \qquad (2.21)\end{aligned}$$

where the electronic matrix H_{xx}, H_{xy}, H_{yz}, etc., is determined by a quantum chemistry calculation; these matrix elements are functions of R and γ. These diabatic potential energy surfaces $H_{xx}(R,\gamma)$, $H_{xy}(R,\gamma)$, etc., have been calculated, for example, by Rebentrost and Lester[16] for the $F(^2P) + H_2$ system.

To complete the specification of the Hamiltonian one needs to express γ, the angle between the center of mass coordinate $\vec{R}$ and the diatomic axis, in terms of the action angle variables; this is the same expression derived earlier[12] for the atom-diatom collision system on a single potential energy surface,

$$\cos\gamma = \sqrt{1-m_N^2/N^2}\,\cos q_N \quad . \tag{2.22}$$

m_L is still given in terms of the canonical variables by Eq. (2.9), and it is also necessary now to express q_{m_L} in terms of the "coupled variables" (j,q_j) and (m_j,q_{m_j}); this expression can also be worked out from the generating function derived by Miller,[11] and one obtains

$$q_{m_L} = q_{m_j} + \tan^{-1}\left[\frac{\alpha j \sin q_j}{\alpha m_j \cos q_j - \sqrt{j^2-m_j^2}\,(j^2+L^2-S^2)}\right] \quad . \tag{2.23}$$

In summarizing the final result we generalize to the case that the diatom is allowed to vibrate. If r is the diatomic coordinate and p its conjugate momentum, this adds the term $p^2/2m$ to the Hamiltonian and r_0 in Eq. (2.17) becomes the variable r. The final result is then

$$H_{JLS}(P,R,p,r,N,q_N,j,q_j,m_j,q_{m_j}) = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2}$$

$$+ \frac{p^2}{2m} + \frac{N^2}{2mr^2} + Bj^2 + H_{e\ell}(R,\gamma,r,m_L,q_{m_L}) \quad , \tag{2.24}$$

where ℓ^2 is given by Eq. (2.20), $H_{e\ell}$ by Eq. (2.21) (the matrix elements H_{xy}, etc., now depend on R,γ, and r), m_L by Eq. (2.9), q_{m_L} by Eq. (2.23), and

γ by Eq. (2.22). With this Hamiltonian one can proceed to compute classical trajectories by numerically integrating Hamilton's equations in the usual way.

We also note the expression for the Hamiltonian if the uncoupled representation, with variables (m_L, q_{m_L}) and (m_S, q_{m_S}), is used instead of the above coupled representation with variables (j, q_j) and (m_j, q_{m_j}). The Hamiltonian $H_{JLS}(P,R,p,r,N,q_N,m_L,q_{m_L},m_S,q_{m_S})$ is the same as that in Eq. (2.24) but with j^2 and ℓ^2 expressed in terms of the appropriate variables. j^2 is given by Eq. (2.15) of the preceeding section, and it is not hard to show (since $m_J = m_N + m_L + m_S$) that

$$\begin{aligned}
\ell^2 &\equiv |\vec{J}-\vec{N}-\vec{L}-\vec{S}|^2 \\
&= J^2 + N^2 + L^2 + S^2 - 2\vec{J}\cdot\vec{N} - 2\vec{J}\cdot\vec{L} - 2\vec{J}\cdot\vec{S} + 2\vec{N}\cdot\vec{L} + 2\vec{N}\cdot\vec{S} + 2\vec{L}\cdot\vec{S} \\
&= J^2 + N^2 + L^2 + S^2 - 2m_N^2 - 2m_L^2 - 2m_S^2 - 2m_N m_L - 2m_N m_S - 2m_L m_S \\
&\quad - 2\sqrt{J^2-(m_N+m_L+m_S)^2}\sqrt{N^2-m_N^2}\cos q_{m_N} \\
&\quad - 2\sqrt{J^2-(m_N+m_L+m_S)^2}\sqrt{L^2-m_L^2}\cos q_{m_L} \\
&\quad - 2\sqrt{J^2-(m_N+m_L+m_S)^2}\sqrt{S^2-m_S^2}\cos q_{m_S} \\
&\quad + 2\sqrt{N^2-m_N^2}\sqrt{L^2-m_L^2}\cos(q_{m_N}-q_{m_L}) \\
&\quad + 2\sqrt{N^2-m_N^2}\sqrt{S^2-m_S^2}\cos(q_{m_N}-q_{m_S}) \\
&\quad + 2\sqrt{L^2-m_L^2}\sqrt{S^2-m_S^2}\cos(q_{m_L}-q_{m_S}) \quad . \qquad (2.25)
\end{aligned}$$

Again, since $J \gg N,L,S,j$ it is likely that many of the angular momentum coupling terms in Eq. (2.20) and Eq. (2.25) can be discarded with little error being introduced. The simplest such approximation is, in both cases, to take $\ell^2 = J^2$.

III. The General Two-State Problem

Here we consider the general problem of a molecular collision system involving heavy particle degrees of freedom $\underset{\sim}{x}$ and $\underset{\sim}{p}$ and two electronic states. We want to show in general--without taking any account of the physical nature of the electronic states as was done above for the examples in Section II--how a classical electronic degree of freedom can be constructed to replace the two electronic states. To include both atom-atom, atom-diatom, etc., systems we omit a detailed specification (i.e., angular momentum coupling, etc.) of the heavy particle degrees of freedom.

a. Diabatic Electronic Representation

We look for a classical Hamiltonian of the form

$$H(\underset{\sim}{p},\underset{\sim}{x},n,q) = \frac{\underset{\sim}{p}^2}{2\mu} + H_{e\ell}(n,q;\underset{\sim}{x}) \quad , \qquad (3.1)$$

where the first term is the kinetic energy of the heavy particle degrees of freedom, and $H_{e\ell}$ is the Born-Oppenheimer electronic energy of the system in terms of the electronic action-angle variables (n,q); $H_{e\ell}$ also depends parametrically on $\underset{\sim}{x}$, the positions of the heavy particles (i.e., nuclei). The goal is to show how the classical function $H_{e\ell}(n,q;\underset{\sim}{x})$ should be constructed from the quantum mechanical 2 x 2 diabatic Hamiltonian matrix

$$\begin{pmatrix} H_{00}(\underset{\sim}{x}) \ , & H_{01}(\underset{\sim}{x}) \\ H_{10}(\underset{\sim}{x}) \ , & H_{11}(\underset{\sim}{x}) \end{pmatrix} \quad ; \qquad (3.2)$$

i.e., suppressing the dependence on $\underset{\sim}{x}$ for the moment, one wants to show how the 2 x 2 Hamiltonian matrix $H_{n',n}$, $n,n' = 0,1$ should--in the most consistent and correct way possible--be replaced by a classical Hamiltonian function H(n,q).

Before proceeding further, it is useful to digress briefly to consider how a diabatic Born-Oppenheimer electronic matrix can be constructed uniquely. This is a topic with a considerable history,[17] and we only wish to make some elementary comments here. The two adiabatic eigenfunctions ψ_0 and ψ_1, and corresponding eigenvalues E_0 and E_1, depend parametrically on the nuclear positions $\underset{\sim}{x}$. It is always possible to define functions ϕ_0 and ϕ_1, and the related electronic Hamiltonian matrix $H_{n',n}$, $n,n' = 0,1$, that are a unitary transformation of the adiabatic quantities:

$$\begin{pmatrix} \phi_0 \\ \phi_1 \end{pmatrix} = \begin{pmatrix} \cos\omega & \sin\omega \\ -\sin\omega & \cos\omega \end{pmatrix} \begin{pmatrix} \psi_0 \\ \psi_1 \end{pmatrix} \tag{3.3a}$$

$$\begin{pmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{pmatrix} = \begin{pmatrix} \cos\omega & \sin\omega \\ -\sin\omega & \cos\omega \end{pmatrix} \begin{pmatrix} E_0 & 0 \\ 0 & E_1 \end{pmatrix} \begin{pmatrix} \cos\omega & -\sin\omega \\ \sin\omega & \cos\omega \end{pmatrix} \tag{3.3b}$$

where E_0, E_1, ω, and $H_{n',n}$ are related by the usual expressions:

$$\omega = \frac{1}{2} \tan^{-1} \left(\frac{2\, H_{10}}{H_{11} - H_{00}} \right) \tag{3.4a}$$

$$E_0 + E_1 = H_{00} + H_{11} \tag{3.4b}$$

$$E_1 - E_0 = \sqrt{(H_{11} - H_{00})^2 + 4\, H_{10}{}^2} \quad . \tag{3.4c}$$

In general, the functions ϕ_0 and ϕ_1 will depend parametrically on $\underset{\sim}{x}$. <u>If</u>, however, there exists a function $\omega(\underset{\sim}{x})$ so that ϕ_0 and ϕ_1 of Eq. (3.3a) are independent of $\underset{\sim}{x}$--or at least approximately so--then all the $\underset{\sim}{x}$ dependence of ψ_0 and ψ_1 is contained in the angle $\omega(\underset{\sim}{x})$:

$$\begin{pmatrix} \psi_0 \\ \psi_1 \end{pmatrix} = \begin{pmatrix} \cos\omega & -\sin\omega \\ \sin\omega & \cos\omega \end{pmatrix} \begin{pmatrix} \phi_0 \\ \phi_1 \end{pmatrix} \quad . \tag{3.5}$$

If this is true, then it is easy to show that the non-adiabatic coupling function is given by

$$\langle\psi_0|\frac{\partial\psi_1}{\partial\underset{\sim}{x}}\rangle = \frac{\partial\omega(\underset{\sim}{x})}{\partial\underset{\sim}{x}} \quad . \tag{3.6}$$

For the case of just one nuclear variable x, for example, it is thus possible to start with the adiabatic potential curves $E_0(x)$, $E_1(x)$, and the non-adiabatic coupling function $\langle\psi_0|\frac{\partial\psi_1}{\partial x}\rangle$, and determine the diabatic Hamiltonian matrix $H_{n',n}(x)$ as follows:

$$\omega(x) \equiv \int_x^\infty dx' \ \langle\psi_0|\frac{\partial\psi_1}{\partial x'}\rangle \quad , \tag{3.7}$$

and then Eq. (3.3b) gives $H_{n',n}(x)$:

$$\begin{pmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{pmatrix} = \begin{pmatrix} E_0\cos^2\omega + E_1\sin^2\omega \ , & (E_1-E_0)\sin\omega\cos\omega \\ (E_1-E_0)\sin\omega\cos\omega \ , & E_0\sin^2\omega + E_1\cos^2\omega \end{pmatrix} . \tag{3.8}$$

Eqs. (3.7) and (3.8) give the diabatic Hamiltonian matrix explicitly in terms of the adiabatic eigenvalues and the non-adiabatic coupling. Whether or not this diabatic Hamiltonian is actually a good representation of the non-adiabatic coupling depends on the extent to which it is physically true that the coupling does arise primarily from the interaction of just two states.

For the present, therefore, we assume that the diabatic electronic Hamiltonian matrix $H_{n',n}(\underset{\sim}{x})$ is provided by quantum chemistry. How then is $H_{e\ell}(n,q;\underset{\sim}{x})$ to be constructed? The basic clue comes from an approximate semiclassical relation sometimes called the Heisenberg Correspondence Principle.[18] Suppressing the $\underset{\sim}{x}$ dependence of all quantities, this relation is

$$H_{n',n} \simeq \frac{1}{2\pi} \int_0^{2\pi} dq \ e^{-i(n'-n)q} \ H(\bar{n},q) \quad , \tag{3.9}$$

where $\bar{n}$ is usually taken to be $\frac{1}{2}$ (n+n'), but this should be viewed only as a rough approximation. If Eq. (3.9) were truly correct, then one could construct H(n,q) as a Fourier series by inverting it:

$$H(n,q) = \sum_{\Delta n=-\infty}^{\infty} e^{i\Delta nq} \ H_{n+\frac{\Delta n}{2},n-\frac{\Delta n}{2}} \quad . \tag{3.10}$$

Since we have only two states, and n,n' = 0 or 1, it is clearly not possible to apply these relations in detail, but they do give some clues as to how H(n,q) should be constructed from the matrix elements $H_{n',n}$. For example, Eq. (3.10) suggests that the q-independent part of H(n,q), i.e., the average of H(n,q) over q, should be such that

$$\frac{1}{2\pi} \int_0^{2\pi} dq \ H(n,q) = H_{n,n} \quad , \tag{3.11}$$

for n = 0,1. The simplest way to accomplish this is to use lowest order (i.e., linear) interpolation, so that the q-independent part of H(n,q) is chosen as

$$(1-n)H_{00} + n\,H_{11} \qquad ; \tag{3.12}$$

for n = 0 and 1 this becomes H_{00} and H_{11}, respectively. (For the 3-state case one would need quadratic interpolation to do the job; i.e., Eq. (3.12) would be replaced by

$$\frac{1}{2}\,(1-n)(2-n)H_{00} + (2-n)n\,H_{11} + \frac{1}{2}\,n(n-1)H_{22} \qquad .)$$

For the two-state case it is clear that only the lowest order terms in Eq. (3.10) should be retained, so that one expects the q-dependent part of H(n,q) to be proportional to cosq; also since $\cos q = \frac{1}{2}e^{iq} + \frac{1}{2}e^{-iq}$, this gives rise to $\Delta n = \pm 1$ coupling, which is physically correct. It is also clear that this term should be proportional to the off-diagonal matrix element H_{01} but it is not clear how it should depend on n. The form that we have chosen for the q-dependent part of H(n,q) is

$$2\,H_{01}\sqrt{n(1-n)}\,\cos q \qquad , \tag{3.13}$$

so that the complete diabatic electronic Hamiltonian function is

$$H_{e\ell}(n,q) = (1-n)H_{00} + n\,H_{11} + 2\,H_{01}\sqrt{n(1-n)}\,\cos q \qquad , \tag{3.14}$$

and it is to be remembered that the matrix elements $H_{n',n}$ depend parametrically on the nuclear coordinates $\underset{\sim}{x}$.

As indicated above, it is not obvious that the n-dependence of the last term in Eq. (3.14) should be chosen as it is, namely as $\sqrt{n(1-n)}$. Indeed, this was not the first thing we tried, but it is the only function we have found that satisfies the criterion discussed below. It does seem reasonable that the function be required to vanish for n = 0 or 1, but there are of course other functional forms that do this.

The primary requirement we make of the classical electronic Hamiltonian function $H_{e\ell}(n,q)$ is that, for fixed $\underset{\sim}{x}$, it *give the correct adiabatic eigenvalues when the system is quantized semiclassically*. If E is the adiabatic electronic energy, therefore, one defines n(q,E) by the equation

$$E = H_{e\ell}(n,q) \quad , \tag{3.15}$$

and then determines the semiclassical eigenvalues E(N), N = 0,1 by the Bohr-Sommerfeld phase integral relation

$$2\pi N = \oint dq\; n(q,E) \quad . \tag{3.16}$$

For $H_{e\ell}(n,q)$ of Eq. (3.14), Eq. (3.15) gives

$$n(q,E) = \left\{ \Delta H(E-H_{00}) + 2\,H_{01}{}^{2}\cos^{2}q \pm 2\,H_{01}\cos q\,[H_{01}{}^{2}\cos^{2}q + \Delta H(E-H_{00}) - (E-H_{00})^{2}]^{1/2} \right\} / (\Delta H^{2} + 4\,H_{01}{}^{2}\cos^{2}q) \quad , \tag{3.17}$$

where $\Delta H = H_{11}-H_{00}$. The phase integral in Eq. (3.16) can be evaluated to give

$$2\pi N = \pi \left\{ 1 - \left[\frac{\Delta H^{2} + 4(E-H_{00})(E-H_{11})}{\Delta H^{2} + 4\,H_{10}{}^{2}} \right]^{1/2} \right\} \quad , \tag{3.18}$$

and this can be algebraically converted to give E(N) as follows:

$$E(N) = \frac{1}{2}\,(H_{00}+H_{11}) + (N-\frac{1}{2})\,\sqrt{\Delta H^2 + 4\,H_{10}^{\;2}} \quad , \tag{3.19}$$

which is seen to be the correct adiabatic eigenvalues for N = 0,1.

It is this above analysis that makes us think that $H_{e\ell}(n,q)$ of Eq. (3.14) is the "best" classical model for the two-state system. There may, of course, be other functions that satisfy this criterion, but we have not found any (and a number have been tried). In the spirit of Ockham's razor, too, one does prefer the simplest, most physically reasonable function that meets this criteria.

In summary, the classical Hamiltonian for the collision system is

$$\begin{aligned} H(\underset{\sim}{p},\underset{\sim}{x},n,q) &= \frac{p^2}{2\mu} + (1-n)\,H_{00}(\underset{\sim}{x}) + n\,H_{11}(\underset{\sim}{x}) \\ &\quad + 2\,H_{01}(\underset{\sim}{x})\,\sqrt{n(1-n)}\ \cos q \quad , \end{aligned} \tag{3.20}$$

for which the classical equations of motion are easily found to be

$$\dot{\underset{\sim}{x}} = \frac{\partial H}{\partial \underset{\sim}{p}} = \underset{\sim}{p}/\mu \tag{3.21a}$$

$$\dot{\underset{\sim}{p}} = -\frac{\partial H}{\partial \underset{\sim}{x}} = -(1-n)\,\frac{\partial H_{00}}{\partial \underset{\sim}{x}} - n\,\frac{\partial H_{11}}{\partial \underset{\sim}{x}} - 2\,\frac{\partial H_{01}}{\partial \underset{\sim}{x}}\sqrt{n(1-n)}\ \cos q \tag{3.21b}$$

$$\dot{q} = \frac{\partial H}{\partial n} = H_{11}-H_{00} + \frac{1-2n}{\sqrt{n(1-n)}}\,\cos q\ H_{01} \tag{3.21c}$$

$$\dot{n} = -\frac{\partial H}{\partial q} = 2\,H_{01}\,\sqrt{n(1-n)}\,\sin q \quad . \tag{3.21d}$$

b. Adiabatic Electronic Representation

Rather than carry out the calculation in the diabatic electronic representation of the previous section, it may be more useful to change to the adiabatic representation. One thus wishes to replace the "old" action-angle variables (n,q) by the "new" variables (N,Q), where N is the adiabatic action variable; i.e., N is defined in terms of (n,q) by the relation

$$H_{e\ell}(n,q) = E(N) \quad , \tag{3.22}$$

where E(N) is the semiclassical eigenvalue function in Eq. (3.19); more specifically, this equation is

$$\begin{aligned}(1-n)H_{00} + n\,H_{11} + 2\,H_{10}\sqrt{n(1-n)}\,\cos q \\ = \tfrac{1}{2}\,(H_{11}+H_{00}) + (N-\tfrac{1}{2})\,\sqrt{\Delta H^2 + 4\,H_{10}{}^2} \quad ,\end{aligned} \tag{3.23}$$

which can be solved for n to give

$$n(q,N) = \frac{1}{2} + \frac{\sqrt{1+t^2}\,(N-\frac{1}{2}) \pm \frac{1}{2}\,t\cos q\,[1 + t^2\cos^2 q - 4(1+t^2)(N-\frac{1}{2})^2]^{1/2}}{1 + t^2\cos^2 q} \quad , \tag{3.24}$$

where $t = 2\,H_{10}/\Delta H$.

The generating function which accomplishes this canonical transformation is of the F_2-type,[19]

$$F_2(\underset{\sim}{x},q;\underset{\sim}{p}',N) = \underset{\sim}{p}'\cdot\underset{\sim}{x} + \int dq\; n(q,N;\underset{\sim}{x}) \quad , \tag{3.25}$$

where $\underset{\sim}{p}'$ and $\underset{\sim}{x}'$ are the "new" canonical variables for the heavy particle degrees of freedom; the function $n(q,N;\underset{\sim}{x})$ is given by Eq. (3.24), and it has been emphasized that n also depends on the nuclear coordinates $\underset{\sim}{x}$ because the matrix elements $H_{n',n}$ do. The canonical transformation is specified by the usual derivative relations[19]

$$\underset{\sim}{p} = \frac{\partial F_2}{\partial \underset{\sim}{x}} = \underset{\sim}{p}' + \frac{\partial}{\partial \underset{\sim}{x}} \int dq \; n(q,N;\underset{\sim}{x}) \tag{3.26a}$$

$$n = \frac{\partial F_2}{\partial q} = n(q,N;\underset{\sim}{x}) \tag{3.26b}$$

$$\underset{\sim}{x}' = \frac{\partial F_2}{d\underset{\sim}{p}'} = \underset{\sim}{x} \tag{3.26c}$$

$$Q = \frac{\partial F_2}{\partial N} = \frac{\partial}{\partial N} \int dq \; n(q,N;\underset{\sim}{x}) \quad . \tag{3.26d}$$

Eq. (3.26c) shows that $\underset{\sim}{x}' = \underset{\sim}{x}$, but Eq. (3.26c) shows that the nuclear momenta are changed; i.e.,

$$\underset{\sim}{p} = \underset{\sim}{p}' + \Delta\underset{\sim}{p} \tag{3.27}$$

where

$$\Delta\underset{\sim}{p} = \frac{\partial}{\partial \underset{\sim}{x}} \int dq \; n(q,N;x) \tag{3.28}$$

with q replaced (after differentiation with respect to $\underset{\sim}{x}$) by what it is in terms of the "new" variables (this is determined from Eq. (3.26d)). The classical Hamiltonian is still given by Eq. (3.20) but with the "old" variables $\underset{\sim}{p},\underset{\sim}{x},n,q$ replaced by what they are in terms of the "new" variables $\underset{\sim}{p}',\underset{\sim}{x}',N,Q$; this gives

$$H(\underset{\sim}{p}',\underset{\sim}{x}',N,Q) = |\underset{\sim}{p}'+\Delta\underset{\sim}{p}|^2/2\mu + E(N) \quad , \tag{3.29}$$

where E(N) is the adiabatic eigenvalue function of Eq. (3.19). Carrying out the calculation for $\Delta\underset{\sim}{p}$, the nonadiabatic correction to the nuclear momenta, is extremely tedious, but the answer is extremely simple. We leave it as an interesting (but not trivial) exercise for the reader to show that

$$\Delta\underset{\sim}{p} = -\,2\,\frac{\partial\omega(\underset{\sim}{x})}{\partial\underset{\sim}{x}}\,\sqrt{N(1-N)}\,\sin Q \quad , \tag{3.30}$$

where $\omega(\underset{\sim}{x})$ is the rotation angle that diagonalizes the 2 x 2 quantum mechanical matrix:

$$\omega(\underset{\sim}{x}) = \frac{1}{2}\tan^{-1}\left[\frac{2\,H_{01}(\underset{\sim}{x})}{H_{11}(\underset{\sim}{x})-H_{00}(\underset{\sim}{x})}\right] \quad . \tag{3.31}$$

Dropping the prime from the "new" heavy particle variables, one thus obtains the complete Hamiltonian in the adiabatic representation as

$$H(\underset{\sim}{p},\underset{\sim}{x},N,Q) = \frac{1}{2\mu}\left|\underset{\sim}{p} - 2\,\frac{\partial\omega(\underset{\sim}{x})}{\partial\underset{\sim}{x}}\sqrt{N(1-N)}\,\sin Q\right|^2$$

$$+\,(1-N)\,E_0(\underset{\sim}{x}) + N\,E_1(x) \quad , \tag{3.32a}$$

or

$$H(\underset{\sim}{p},\underset{\sim}{x},N,Q) = \frac{p^2}{2\mu} - 2\,\frac{\underset{\sim}{p}}{\mu}\cdot\frac{\partial\omega(\underset{\sim}{x})}{\partial\underset{\sim}{x}}\sqrt{N(1-N)}\,\sin Q$$

$$+\,\frac{2}{\mu}\left|\frac{\partial\omega(\underset{\sim}{x})}{\partial\underset{\sim}{x}}\right|^2 N(1-N)\,\sin^2 Q + (1-N)\,E_0(\underset{\sim}{x}) + N\,E_1(\underset{\sim}{x}) \ . \tag{3.32b}$$

This classical Hamiltonian function has essentially the identical structure as the quantum mechanical Hamiltonian operator in the adiabatic representation: identifying

$$\frac{\partial \omega}{\partial \underset{\sim}{x}} \leftrightarrow \langle \psi_0 | \frac{\partial \psi_1}{\partial \underset{\sim}{x}} \rangle \quad ,$$

one sees that the principal non-adiabatic coupling, the second term in Eq. (3.32b), looks just like the quantum mechanical non-adiabatic coupling operator,

$$\langle \psi_0 | \frac{\partial \psi_1}{\partial \underset{\sim}{x}} \rangle \cdot \frac{\underset{\sim}{p}}{\mu} \quad ;$$

where here $\underset{\sim}{p}$ is the momentum operator $-i\hbar \frac{\partial}{\partial \underset{\sim}{x}}$; the sinQ dependence corresponds to $\Delta N = \pm 1$ coupling, and the N dependence, $\sqrt{N(1-N)}$, is of precisely the same form guessed in Section IIIa for the off-diagonal part of the diabatic classical Hamiltonian. Since

$$\sin^2 Q = \frac{1}{2} - \frac{1}{2}\cos(2Q) \quad , \tag{3.33}$$

the third term in Eq. (3.32b) gives a small correction to the adiabatic potential curves (from the first term in Eq. (3.33), the "diagonal" part of this term), just as in the corresponding quantum mechanical case; the cos(2Q) part gives rise to $\Delta N = \pm 2$ transitions and is thus presumably unimportant since N cannot vary below 0 or above 1. Under most conditions one would thus expect that this term could be discarded with little error, as is usually done quantum mechanically.

The advantage of carrying out the classical trajectory calculations in the adiabatic representation is that if the non-adiabatic transitions are localized, N(t) will be constant and Q(t) will be a linear function of t except in the region where non-adiabatic transitions occur. This would mean that the time dependence of the electronic variables would not significantly slow down the trajectory calculation.

Another, perhaps more important advantage of using the classical Hamiltonian in the electronic adiabatic representation, Eq. (3.32), is that one can completely by-pass the possible ambiguity of constructing an electronic diabatic Hamiltonian matrix. In Eq. (3.32) one can thus take the adiabatic potential curves $E_0(\underset{\sim}{x})$ and $E_1(\underset{\sim}{x})$ directly from a quantum chemistry calculation, as well as replace the function $\frac{\partial\omega(\underset{\sim}{x})}{\partial\underset{\sim}{x}}$ by the non-adiabatic coupling function $\langle\psi_0|\frac{\partial\psi_1}{\partial\underset{\sim}{x}}\rangle$ that also comes directly from a quantum chemistry calculation.

c. Generalization to N States

In concluding this section we show how the correspondence established in Section IIIa can be extended to the case of an N x N diabatic Hamiltonian matrix $H_{n',n}$, $n',n = 1, \ldots, N$.

Note that the classical Hamiltonian in Eq. (3.14) can be written as the diagonal matrix element of the Hamiltonian matrix

$$H_{e\ell}(n,q) = \underset{\sim}{v}^{+}\cdot\underset{\approx}{H}\cdot\underset{\sim}{v} = \sum_{k,k'=0}^{1} v_{k'}^{*}\, H_{k',k}\, v_k \quad , \qquad (3.34)$$

where $\underset{\approx}{H}$ is the 2 x 2 Hamiltonian matrix and $\underset{\sim}{v}$ is the complex vector with components

$$v_k = p_k(n)\, e^{-ikq} \quad , \qquad (3.35)$$

k = 0,1, where

$$p_0(n) = \sqrt{1-n} \tag{3.36a}$$

$$p_1(n) = \sqrt{n} \quad . \tag{3.36b}$$

It is easy to show that Eq. (3.34), with Eqs. (3.35) and (3.36), reproduces Eq. (3.15).

It is this above observation that suggests the generalization to the N x N case. We thus take

$$H_{e\ell}(n,q) = \sum_{k,k'=1}^{N} v^*_{k'} \, H_{k',k} \, v_k \quad , \tag{3.37}$$

where

$$v_k = p_k(n) \, e^{-ikq} \quad . \tag{3.38}$$

It is easy to see that this then gives

$$H_{e\ell}(n,q) = \sum_{k,k'=1}^{N} e^{i(k'-k)q} \, p_{k'}(n) \, p_k(n) \, H_{k',k} \quad , \tag{3.39}$$

and if we generalize to allow for the case that the matrix elements $H_{k',k}$ are complex ($H_{k',k}$ is hermitian: $H^*_{k',k} = H_{k,k'}$), this becomes

$$H_{e\ell}(n,q) = \sum_{k=1}^{N} p_k(n)^2 \, H_{k,k}$$

$$+ 2 \sum_{k<k'=1}^{N} p_{k'}(n) p_k(n) \left\{ \mathrm{Re}(H_{k',k}) \cos[(k'-k)q] - \mathrm{Im}(H_{k',k}) \sin[(k'-k)q] \right\} \tag{3.39'}$$

The coefficients $p_k(n)$ are chosen via the logic of Section IIa, i.e., so that

$$\frac{1}{2\pi}\int_0^{2\pi} dq\ H_{e\ell}(n,q) = H_{n,n} \tag{3.40}$$

when n is an integer. This is achieved simplest if $\{p_k(n)^2\}$ are the Lagrangian interpolation coefficients,[20]

$$p_k(n)^2 = \prod_{\substack{m=1\\ m\neq k}}^{N} \left(\frac{n-m}{k-m}\right) \quad . \tag{3.41}$$

Eqs. (3.39) and (3.41) define the classical Hamiltonian function in terms of the N x N Hamiltonian matrix.

This presciption satisfies the desirable property of Eq. (3.40), and it also has the correct feature that the matrix element $H_{k',k}$ in Eq. (3.39) is proportional to $e^{i(k'-k)q}$, as suggested by the Fourier inversion relation in Eq. (3.10). It would be good, of course, to apply the "adiabatic eigenvalue test" to this classical Hamiltonian, i.e., to see how the semiclassical eigenvalues obtained from it agree with those obtained by diagonalizing the matrix. It is clear that this cannot be done algebraically in closed form as it was for the two-state case, but numerically tests should be possible.

IV. Concluding Remarks

The motivation for constructing these classical models of electronic degrees of freedom is to allow one to carry out completely classical trajectory calculations involving electronic and heavy particle degrees of freedom. To the extent that the classical model of the electronic degrees of freedom is realistic, this classical trajectory approach should describe all the dynamical effects in non-adiabatic collision phenomena correctly since all the degrees of freedom are treated on the same dynamical footing. Applications are underway to test this.

Sections II, III, and the Appendix describe one way of constructing a classical model of the electronic degrees of freedom. Another approach to this that we are also exploring is based on the idea of a classical pseudo-potential, and for the cases discussed in Sections II and III it leads to precisely the same classical Hamiltonian obtained there. This classical pseudo-potential analysis will be developed fully in a future paper,[21] along with other approaches to constructed classical models of electronic degrees of freedom.

The ability to construct a realistic classical model for the relevant electronic degrees of freedom is clearly the key element in the model proposed in this paper. More formal and applied (i.e., computation) research on this aspect of the approach is needed to see how the idea works and how generally it can be carried out.

Appendix: $H_{e\ell}$ of Section II

Here we show how $H_{e\ell}$, the electronic part of the classical Hamiltonian of Section II, is obtained. Since this part of the Hamiltonian is from purely coulombic interactions of the electrons, it is independent of spin and is thus a function only of the canonical variables (L,q_L) and (m_L,q_{m_L}). Also, since the variable L is a conserved quantity in this model--e.g., for a P atom one has L=1--$H_{e\ell}$ must be independent of q_L. For L=1, therefore, we seek the function $H_{e\ell}(m_L,q_{m_L})$. Since no other angular momenta are involved in the present discussion, we simplify notation by dropping the subscript "L"--i.e., $(m_L,q_{m_L}) \rightarrow (m,q_m)$--for the remainder of this Appendix.

The diabatic electronic matrix H_{xx}, H_{xy}, etc., is the matrix of the electronic interaction in the basis set of cartesian p-orbitals p_x, p_y, p_z; i.e.,

$$H_{xx} = \langle p_x|H|p_x\rangle$$

$$H_{xy} = \langle p_x|H|p_y\rangle$$

$$H_{xz} = \langle p_x|H|p_z\rangle \quad , \qquad (A.1)$$

etc.

--where the x,y,z axes are as shown in Figure 1. The angles θ_F,ϕ_F (cf. Figure 1) specify the orientation of the "hybrid" p-orbital p_F,

$$|p_F\rangle = \sin\theta_F \cos\phi_F\ |p_x\rangle + \sin\theta_F \sin\phi_F|p_y\rangle + \cos\theta_F|p_z\rangle \quad , \qquad (A.2)$$

and the electronic energy in this general hybrid state is easily found to be

$$\langle p_F|H|p_F\rangle = \sin^2\theta F \cos^2\phi_F H_{xx} + \sin^2\theta_F \sin^2\phi_F H_{yy} + \cos^2\theta_F H_{zz}$$

$$+ 2 \sin^2\theta_F \sin\phi_F \cos\phi_F H_{xy} + 2 \sin\theta_F \cos\theta_F \cos\phi_F H_{xz}$$

$$+ 2 \sin\theta_F \cos\theta_F \sin\phi_F H_{yz} \qquad \text{(A.3a)}$$

$$\equiv H_{e\ell}(\theta_F,\phi_F) \quad . \qquad \text{(A.3b)}$$

Eq. (A.3) gives the electronic energy as a function of the orientation of the p-orbital, and the task now is to deduce what θ_F and ϕ_F are in terms of the action-angle variables (m,q_m).

To do this we first transform the electronic matrix H_{xx}, H_{xy}, etc., from the cartesian basis set (p_x, p_y, p_z) to the polar basis $\{p_m\}$, $m = -1,0,+1$, where as usual

$$p_0 = p_z$$
$$p_1 = \frac{p_x+ip_y}{\sqrt{2}}$$
$$p_{-1} = \frac{p_x-ip_y}{\sqrt{2}} \quad , \qquad \text{(A.4)}$$

or inversely,

$$p_x = \frac{p_1+p_{-1}}{\sqrt{2}}$$
$$p_y = \frac{p_1-p_{-1}}{i\sqrt{2}}$$
$$p_z = p_0 \quad . \qquad \text{(A.5)}$$

Straight-forward matrix multiplication gives

$$H_{m',m} = \begin{array}{c|ccc} & -1 & 0 & 1 \\ \hline -1 & \frac{H_{xx}+H_{yy}}{2}, & \frac{H_{xz}-iH_{yz}}{\sqrt{2}}, & \frac{H_{xx}-H_{yy}}{2} - iH_{xy} \\ 0 & \frac{H_{xz}+iH_{yz}}{\sqrt{2}}, & H_{zz}, & \frac{H_{xz}-iH_{yz}}{\sqrt{2}} \\ 1 & \frac{H_{xx}-H_{yy}}{2} + iH_{xy}, & \frac{H_{xz}+iH_{yz}}{\sqrt{2}}, & \frac{H_{xx}+H_{yy}}{2} \end{array} . \qquad (A.6)$$

The quantum number m of this representation is clearly the quantum mechanical analog of the classical variable m, the component of the electronic orbital angular momentum about the z-axis. Eq. (A.6) thus gives the matrix $H_{m',m}$, and we desire the classical function of the action-angle variables, $H_{e\ell}(m,q_m)$, which corresponds to it.

To find the classical function $H_{e\ell}(m,q_m)$ from the quantum mechanical matrix $H_{m',m}$ in Eq. (A.6), we appeal to the precription discussed in Section IIIa and IIIc. For the present 3-state situation Eq. (3.39') gives

$$\begin{aligned} H_{e\ell}(m,q_m) = {} & \frac{m(m-1)}{2}\left(\frac{H_{xx}+H_{yy}}{2}\right) + (1-m^2)\, H_{zz} + \frac{m(m+1)}{2}\left(\frac{H_{xx}+H_{yy}}{2}\right) \\ & + \sqrt{\frac{m(m-1)}{2}\,(1-m^2)}\left[\frac{H_{xz}-iH_{yz}}{\sqrt{2}}\, e^{-iq_m} + \frac{H_{xz}+iH_{yz}}{\sqrt{2}}\, e^{iq_m}\right] \\ & + \sqrt{\frac{m(m+1)}{2}\,(1-m^2)}\left[\frac{H_{xz}-iH_{yz}}{\sqrt{2}}\, e^{-iq_m} + \frac{H_{xz}+iH_{yz}}{\sqrt{2}}\, e^{iq_m}\right] \\ & + \sqrt{\frac{m^2(m^2-1)}{4}}\left[\left(\frac{H_{xx}-H_{yy}}{2} - iH_{xy}\right) e^{-2iq_m} + \left(\frac{H_{xx}-H_{yy}}{2} + iH_{xy}\right) e^{2iq_m}\right] \\ = {} & m^2\left(\frac{H_{xx}+H_{yy}}{2}\right) + (1-m^2)\, H_{zz} \end{aligned}$$

$$+ \sqrt{1-m^2}\sqrt{m(m-1)} \quad (H_{xz} \cos q_m - H_{yz} \sin q_m)$$

$$+ \sqrt{1-m^2}\sqrt{m(m+1)} \quad (H_{xz} \cos q_m - H_{yz} \sin q_m)$$

$$+ \sqrt{m^2(m^2-1)} \left[\frac{H_{xx}-H_{yy}}{2} \cos(2q_m) - H_{xy} \sin(2q_m)\right] \quad . \qquad (A.7)$$

As discussed in Sections IIIa and IIIc, one is quite confident that the prescription described there gives the q-independent part of $H_{e\ell}(m,q_m)$ correctly--i.e., the first two terms of Eq. (A.7)--and also that the off-diagonal matrix elements H_{xy}, H_{xz}, H_{yz} appear in the correct combination with the trigonometric functions of q_m. One is <u>not</u> sure, however, that the prescription gives the correct m-dependence of the q-dependent terms in $H_{e\ell}(m,q_m)$; i.e., one cannot be sure that this prescription gives the m-dependent factors in the last three terms of Eq. (A.7) correctly.

To determine the correct functions of m in the last three terms of Eq. (A.7) we equate $H_{e\ell}(\theta_F,\phi_F)$ of Eq. (A.3) and $H_{e\ell}(m,q_m)$ of Eq. (A.7); i.e., we require that the coefficients of each matrix element H_{xx}, H_{xy}, etc., be identical. This criterion determines both the relation between (θ_F,ϕ_F) and (m,q_m) and also how the m-dependent coefficients of last three terms of Eq. (A.7) should be modified. One readily concludes that the following three factors in the last three terms of Eq. (A.7), respectively, should be modified as

$$\sqrt{m(m-1)} \rightarrow m$$

$$\sqrt{m(m+1)} \rightarrow m$$

$$\sqrt{m^2-1} \rightarrow m \quad ,$$

so that Eq. (A.7) then becomes

$$H_{e\ell}(m,q_m) = m^2\left(\frac{H_{xx}+H_{yy}}{2}\right) + (1-m^2)H_{zz}$$

$$+ 2m\sqrt{1-m^2}\,(H_{xz}\cos q_m - H_{yz}\sin q_m)$$

$$+ m^2\left(\frac{H_{xx}-H_{yy}}{2}\right)\cos 2q_m - m^2 H_{xy}\sin 2q_m \quad . \qquad (A.7')$$

Eqs. (A.3) and (A.7') are then identical if one makes the following identification between (θ_F,ϕ_F) and (m,q_m):

$$\sin\theta_F = m \qquad (A.8a)$$

$$\phi_F = -q_m \quad .$$

This completes the task, Eq. (A.7') being the desired classical electronic Hamiltonian function.

For the case the ^{2}P-atom interacts with a ^{1}S atom, one has

$$H_{xx} = H_{yy} \equiv V_\pi$$

$$H_{zz} \equiv V_\Sigma$$

$$H_{xy} = H_{xz} = H_{yz} = 0 \quad ,$$

so that Eq. (A.7') becomes

$$H_{e\ell}(m,q_m) = m^2 V_\pi + (1-m^2)V_\Sigma \quad , \qquad (A.9)$$

where V_Σ and V_π are the Σ and π potential curves for the ^{1}S-^{2}P system.

For the case the ^{2}P atom interacts with a $^1\Sigma$ diatomic molecule (cf. Figure 1) one has[16]

$$H_{xy} = H_{xz} = 0 \quad ,$$

so that in this case Eq. (A.7') becomes

$$H_{e\ell}(m,q_m) = m^2\left(\frac{H_{xx}+H_{yy}}{2}\right) + (1-m^2)H_{zz}$$

$$+ m^2\left(\frac{H_{xx}-H_{yy}}{2}\right) \cos 2q_m - 2m\sqrt{1-m^2}\, H_{yz} \sin q_m \quad . \qquad \text{(A.10)}$$

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has $\vec{j}_1 \cdot \vec{j}_2 = m_1 m_2 + \sqrt{j_1^2 - m_1^2}\sqrt{j_2^2 - m_2^2}\cos(q_{m_2} - q_{m_1})$; see reference 2a, p. 92.

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Table I. Various Angular Momenta in the ^2P Atom + ^1S Atom Collision System.

$\vec{L}$ = electronic orbital angular momentum of the ^2P atom.

$\vec{S}$ = electronic spin angular momentum of the ^2P atom.

$\vec{j} \equiv \vec{L}+\vec{S}$ = total electronic angular momentum of the ^2P atom.

$\vec{\ell}$ = orbital angular momentum of relative motion of the two atoms.

$\vec{J} = \vec{\ell}+\vec{L}+\vec{S} = \vec{\ell}+\vec{j}$ = total angular momentum

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Table II. Various Angular Momenta in the ^2P Atom + $^1\Sigma$ Diatom Collision System.

$\vec{L}$ = electronic orbital angular momentum of the atom.

$\vec{S}$ = electronic spin angular momentum of the atom.

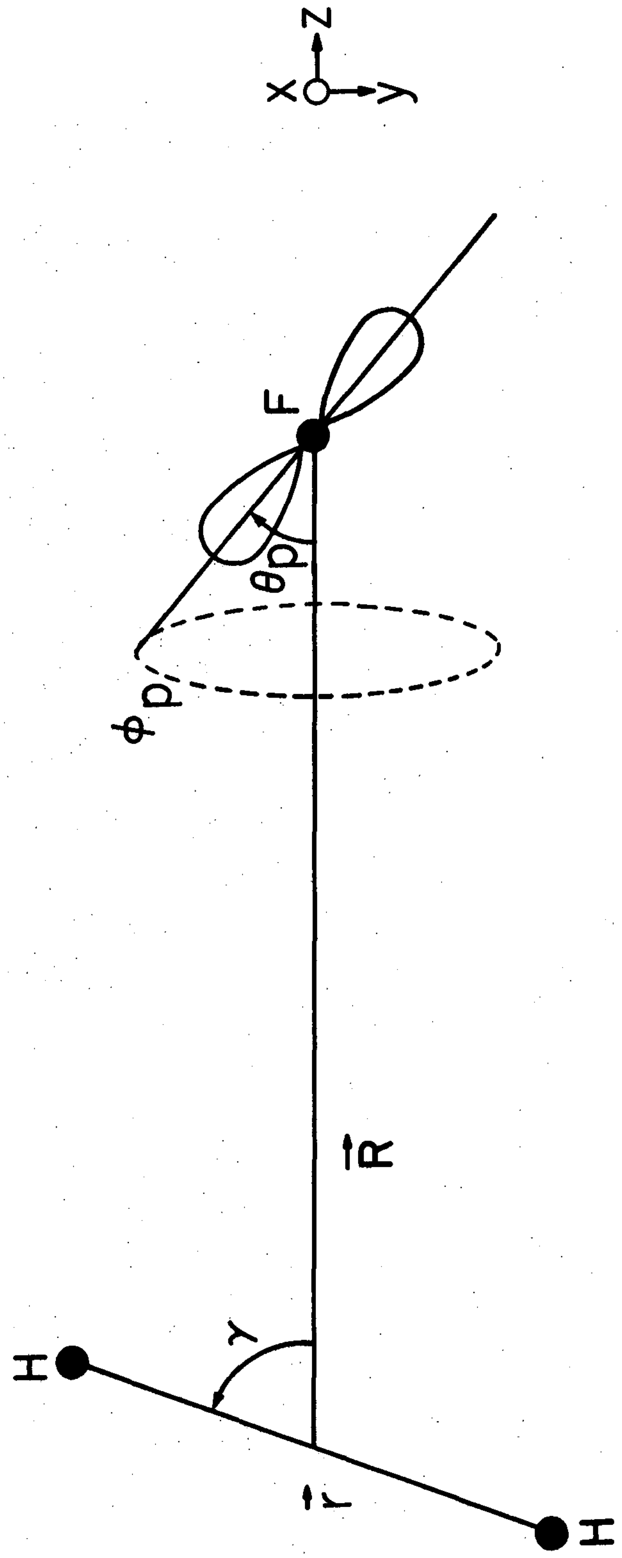
$\vec{j} \equiv \vec{L}+\vec{S}$ = total electronic angular momentum of the atom.

$\vec{N}$ = rotational angular momentum of the diatom.

$\vec{\ell}$ = orbital angular momentum of relative motion of the atom and the center of mass of the diatom.

$\vec{J} = \vec{\ell}+\vec{N}+\vec{L}+\vec{S} = \vec{\ell}+\vec{N}+\vec{j}$ = total angular momentum.

Figure Caption. Coordinate System for the $F(^2P) + H_2$ System. $\vec{r}$,R, and γ are the usual coordinates that specify the relative positions of the nuclei in an atom-diatom system. For fixed nuclei, the axis $\hat{z}$ is along $\vec{R}$, $\hat{x}$ is perpendicular to the plane of the three nuclei, and $\hat{y}$ is in the plane. θ_F and ϕ_F are the polar and azimuthal angles, respectively, of the p-orbital of F in this body-fixed coordinate system.



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