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A Classical Analog for Electronic Degrees of Freedom in Non-Adiabatic Collision Processes

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Abstract

It is shown how a formally exact classical analog can be defined for a finite dimensional (in Hilbert space) quantum mechanical system. This approach is then used to obtain a classical model for the electronic degrees of freedom in a molecular collision system, and the combination of this with the usual classical description of the heavy particle (i.e., nuclear) motion provides a completely classical model for the electronic and heavy particle degrees of freedom. The resulting equations of motion are shown to be equivalent to describing the electronic degrees of freedom by the time-dependent Schrödinger equation, the time dependence arising from the classical motion of the nuclei, the trajectory of which is determined by the quantum mechanical average (i.e., Ehrenfest) force on the nuclei. Quantizing the system via classical S-matrix theory is shown to provide a dynamically consistent description of non-adiabatic collision processes; i.e., different electronic transitions have different heavy particle trajectories and, for example, the total energy of the electronic and heavy particle degrees of freedom is conserved. Application of this classical model for the electronic degrees of freedom (plus classical S-matrix theory) to the 2-state model problem shows that the approach provides a good description of the electronic dynamics.

I. Introduction

Recent work[1,2] on the semiclassical theory of electronically non-adiabatic collision processes has emphasized the need for a model that treats all degrees of freedom--heavy particle (i.e., translation, rotation, and vibration) and electronic--on the same dynamical footing. It has been shown[3] that semiclassical approaches which fail to do this can miss important dynamical features in these collision phenomena.

The most straight-forward formulation that combines all degrees of freedom in a consistent way is a completely quantum mechanical treatment, i.e., the coupled-channel Schrödinger equation[4] expanded in the rovibronic states of the collision partners; although this is obviously correct, it is often too difficult to be useful. On the other hand, it is usually feasible, and usefully accurate, to describe all the heavy particle degrees of freedom by classical mechanics, by computing classical trajectories on a potential energy surface, but to be dynamically consistent it is then necessary to treat the electronic degrees of freedom also by classical mechanics. This does not mean that one must treat all the electrons of the molecular system as classical particles orbiting about the nuclei, but that one must construct a classical model for the relevant aspects of the electronic degrees of freedom. Previous papers[1,2] on this topic have shown how this can be done for several special cases and have also reported encouraging results of numerical calculations applying these models.

The purpose of this paper is to present and explore another way of constructing a classical model for the electronic degrees of freedom. Section II develops this classical analog, and Section III discusses its general

properties. In a number of aspects it is seen that the classical analog is formally exact, i.e., involves no approximations at all. When coupled with the classical motion of the nuclei, it is seen that the overall model is equivalent to one that has been used by several other workers[5-7]: the electronic motion is described by the time-dependent electronic Schrödinger equation, where the time-dependence comes from the classical motion of the nuclei, the trajectory of which is determined by the quantum mechanical average of the force on the nuclei. However the boundary conditions usually[5-7] applied to these equations are dynamically inconsistent; e.g., the trajectory of the heavy particle degrees of freedom is independent of the final electronic state, a clearly unphysical situation. By invoking the classical interpretation of these equations and then applying the boundary conditions of classical S-matrix theory, however, a dynamically correct theory is achieved. Finally, Section IV considers the 2-state example to show that the classical electronic Hamiltonian plus classical S-matrix theory provides a good description of the purely electronic aspect of the model.

II. The Classical Analog.

Consider a molecular collision system having F electronic states, for which the quantum mechanical Hamiltonian operator is

$$H = \frac{p^2}{2\mu} + \sum_{k,k'=1}^{F} |k\rangle\, H_{k,k'}(\underset{\sim}{x})\, \langle k'| \quad , \tag{2.1}$$

where $\underset{\sim}{x}$ denotes the coordinates of all the heavy particle degrees of freedom and $\underset{\sim}{p}$ their conjugate momentum operators, and $H_{k,k'}(\underset{\sim}{x})$ is the "diabatic" electronic Hamiltonian matrix. For simplicity of notation, the nuclear coordinates $\underset{\sim}{x}$ are assumed to be scaled so that the mass is the same for all of them.

For the moment we drop the nuclear kinetic energy term in Eq. (2.1) and let $\underset{\sim}{x} = \underset{\sim}{x}(t)$ be some fixed trajectory; the time-dependent electronic Hamiltonian operator is then

$$H_{e\ell}(t) = \sum_{k,k'=1}^{F} |k\rangle\, H_{k,k'}(\underset{\sim}{x}(t))\, \langle k'| \quad . \tag{2.2}$$

If the time-dependent electronic wavefunction $\psi(t)$ is expanded in the electronic basis $\{|k\rangle\}$,

$$|\psi(t)\rangle = \sum_{k=1}^{F} a_k(t)|k\rangle \quad , \tag{2.3}$$

the time-dependent coefficients $\{a_k(t)\}$ satisfy the usual first order equations (with $\hbar = 1$):

$$\dot{a}_k(t) = -i \sum_{k'} H_{k,k'}(\underset{\sim}{x}(t))\, a_{k'}(t) \quad , \tag{2.4}$$

which are derived in the standard way from the time-dependent Schrödinger equation.

The real variables $\{n_k\}$ and $\{q_k\}$ are defined in terms of the complex amplitudes $\{a_k\}$ by

$$a_k(t) = \sqrt{n_k(t)}\, e^{-iq_k(t)} \quad , \tag{2.5}$$

and the function $H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q};t)$ is defined as the expectation value of the operator $H_{e\ell}(t)$,

$$\begin{aligned} H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q};t) &= \langle\psi|H_{e\ell}(t)|\psi\rangle \\ &= \sum_{k,k'} a_k^* a_{k'} H_{k,k'}(\underset{\sim}{x}(t)) \\ &= \sum_{k,k'} \sqrt{n_k n_{k'}}\, e^{i(q_k - q_{k'})} H_{k,k'}(\underset{\sim}{x}(t)) \quad , \end{aligned} \tag{2.6}$$

where $\{n_k\}$ and $\{q_k\}$ are taken here as independent variables. Considering $H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q};t)$ in Eq. (2.6) as the classical electronic Hamiltonian function and $\{n_k\}$ and $\{q_k\}$ as classical action-angle variables,[8] the time-dependence of $n_k(t)$ and $q_k(t)$ is given according to Hamilton's equations[9] by

$$\dot{q}_k(t) = \frac{\partial H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q};t)}{\partial n_k} \tag{2.7a}$$

$$\dot{n}_k(t) = -\frac{\partial H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q};t)}{\partial q_k} \quad . \tag{2.7b}$$

The remarkable, and most important fact, is that these classical equations

of motion, Eqs. (2.7) and (2.6), are identical to Eq. (2.4), the time-dependent Schrödinger equation, with $\{a_k(t)\}$ and $\{n_k(t), q_k(t)\}$ related by Eq. (2.5); i.e., the F complex equations of Eq. (2.4) are identical to the 2 F real equations of Eq. (2.7). This establishes an exact correspondence between the F-state quantum system with the Hamiltonian operator of Eq. (2.2) and the classical system of F degrees of freedom with Hamiltonian function of Eq. (2.6).

The complete classical Hamiltonian function for the collision system is now obtained by adding the classical nuclear kinetic energy to $H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q})$ and by letting $\underset{\sim}{x}$ by independent variables; this gives the complete classical Hamiltonian as

$$H(\underset{\sim}{p},\underset{\sim}{x},\underset{\sim}{n},\underset{\sim}{q}) = \frac{\underset{\sim}{p}^2}{2\mu} + \sum_{k,k'=1}^{F} \sqrt{n_k n_{k'}}\, e^{i(q_k - q_{k'})}\, H_{k,k'}(\underset{\sim}{x}) \quad . \tag{2.8}$$

Hamilton's equations[9] then determine the time evolution of all the coordinates and momenta,

$$\dot{x}_i(t) = \frac{\partial H}{\partial p_i} = p_i/\mu \tag{2.9a}$$

$$\dot{p}_i(t) = -\frac{\partial H}{\partial x_i} = -\sum_{k,k'=1}^{F} \sqrt{n_k n_{k'}}\, e^{i(q_k - q_{k'})}\, \frac{\partial H_{k,k'}(\underset{\sim}{x})}{\partial x_i} \tag{2.9b}$$

$$\dot{q}_k(t) = \frac{\partial H}{\partial n_k} = \sum_{k'=1}^{F} \sqrt{\frac{n_{k'}}{n_k}}\, \mathrm{Re}[e^{i(q_k - q_{k'})}\, H_{k,k'}(\underset{\sim}{x})] \tag{2.9c}$$

$$\dot{n}_k(t) = -\frac{\partial H}{\partial q_k} = \sum_{k'=1}^{F} 2\sqrt{n_k n_{k'}}\, \mathrm{Im}[e^{i(q_k - q_{k'})}\, H_{k,k'}(\underset{\sim}{x})] \quad . \tag{2.9d}$$

Eqs. (2.8)-(2.9) are the semiclassical model that results from this approach: heavy particle degrees of freedom $(\underset{\sim}{p},\underset{\sim}{x})$ and electronic degrees

of freedom $(\underset{\sim}{n},\underset{\sim}{q})$ are described consistently by classical mechanics.

III. Discussion

There are a number of observations one can make concerning the model developed in the previous section.

a. Relation to "Ehrenfest" Model

It is interesting to see that Eqs. (2.9) are equivalent to a semiclassical approach that several other workers have advocated.[5-7] The equations are usually written in terms of the amplitudes $\{a_k(t)\}$, however, rather than the action-angle variables $\{n_k(t), q_k(t)\}$, and the equations are rationalized as follows: the equations for the electronic amplitudes are the time-dependent Schrödinger equation,

$$\dot{a}_k(t) = -i \sum_{k'=1}^{F} H_{k,k'}(\underset{\sim}{x}(t))\, a_{k'}(t) \quad , \tag{3.1a}$$

where $\underset{\sim}{x}(t)$ is the classical trajectory determined from the forces implied by Ehrenfest's theorem,[10]

$$\dot{\underset{\sim}{p}} \equiv \mu\, \ddot{\underset{\sim}{x}}(t) = - \langle \psi(t) | \frac{\partial H_{e\ell}(\underset{\sim}{x})}{\partial \underset{\sim}{x}} | \psi(t) \rangle$$

$$= - \sum_{k,k'} a_k(t)^* \frac{\partial H_{k,k'}(\underset{\sim}{x})}{\partial \underset{\sim}{x}}\, a_{k'}(t) \quad . \tag{3.1b}$$

With Eq. (2.5), it is easy to show that Eqs. (2.9) and (3.1) are equivalent.

The primary problem with this semiclassical approach has to do with the boundary conditions. The initial conditions for the heavy particle degrees of freedom, $(\underset{\sim}{p}_1, \underset{\sim}{x}_1)$,

$$\underset{\sim}{p}(t_1) = \underset{\sim}{p}_1$$

$$\underset{\sim}{x}(t_1) = \underset{\sim}{x}_1 \quad , \tag{3.2}$$

are usually chosen via the quasiclassical prescription, and for the amplitudes $\{a_k(t)\}$ one has

$$a_k(t_1) = \delta_{k,k_1} \quad , \tag{3.3a}$$

where k_1 is the initial electronic state. The final value of $a_{k_2}(t)$ then determines the $k_1 \to k_2$ electronic transition probability,

$$P_{k_2 \leftarrow k_1} = |a_{k_2}(t_2)|^2 \quad , \tag{3.3b}$$

with $t_1 \to -\infty$ and $t_2 \to +\infty$. The problem is that Eqs. (3.1) with the boundary conditions of Eqs. (3.2)-(3.3) determine a <u>single</u>, unique classical trajectory, independent of the final electronic quantum number k_2, whereas each electronic transition $k_1 \to k_2$ should have its own "best" trajectory (or trajectories!).[11,12] The final nuclear kinetic energy, for example, is independent of the final electronic state of the system, a clearly unsatisfactory situation. From this point of view there is no way of overcoming these fundamental inconsistencies of the model. In Section IIIg, however, it is shown how these defects of the model <u>can</u> be overcome by thinking in terms of the equivalent classical analog, Eqs. (2.8)-(2.9), rather than Eq. (3.1), and then "quantizing" the system within classical S-matrix formalism.[12]

b. Generalization

The classical analog developed for the electronic Hamiltonian can be defined quite generally. For any operator A defined on the F-dimensional Hilbert space $\{|k>\}$, k = 1, ..., F, its classical analog $A(\underset{\sim}{n},\underset{\sim}{q})$ is defined by

$$A(\underset{\sim}{n},\underset{\sim}{q}) = \sum_{k,k'=1}^{F} \sqrt{n_k n_{k'}}\; e^{i(q_k - q_{k'})} A_{k,k'} \quad , \tag{3.4}$$

and one notes that $A(\underset{\sim}{n},\underset{\sim}{q})$ is real if A is hermitian. One can also show (see Appendix A) that if $A(\underset{\sim}{n},\underset{\sim}{q})$ and $B(\underset{\sim}{n},\underset{\sim}{q})$ are the classical analogs of operators A and B, then the classical analog of the commutator [A,B] is equal to the Poisson bracket[13] of $A(\underset{\sim}{n},\underset{\sim}{q})$ and $B(\underset{\sim}{n},\underset{\sim}{q})$, i.e.,

$$i\{A(\underset{\sim}{n},\underset{\sim}{q}),B(\underset{\sim}{n},\underset{\sim}{q})\} = [A,B](\underset{\sim}{n},\underset{\sim}{q}) \quad . \tag{3.5}$$

The equivalence of Eqs. (2.9) and (3.1) is a special case of this more general relation.

It is also shown in Appendix A that a quantum mechanical basis set transformation $\{|k>\} \rightarrow \{|K>\}$ corresponds in general to the classical canonical transformation[14] $(\underset{\sim}{n},\underset{\sim}{q}) \rightarrow (\underset{\sim}{N},\underset{\sim}{Q})$, where the old and new classical variables are related by

$$\sum_k e^{-iq_k}\sqrt{n_k}\ |k\rangle = \sum_K e^{-iQ_k}\sqrt{N_K}\ |K\rangle \quad ,$$

so that

$$e^{-iQ_K}\sqrt{N_K} = \sum_k e^{-iq_k}\sqrt{n_k}\ \langle K|k\rangle \quad , \tag{3.6a}$$

or inversely

$$e^{-iq_k}\sqrt{n_k} = \sum_K e^{-iQ_K}\sqrt{N_K}\ \langle k|K\rangle \quad . \tag{3.6b}$$

An example of this is the transformation from the "diabatic" representation of the Hamiltonian in Eq. (2.8) to the adiabatic representation, the basis set that diagonalizes $H_{e\ell}$ at fixed $\underset{\sim}{x}$. If $(\underset{\sim}{N},\underset{\sim}{Q})$ are action-angle variables corresponding to these adiabatic electronic states, then it is shown in Appendix B that the classical Hamiltonian is given in the adiabatic representation by

$$H(\underset{\sim}{p},\underset{\sim}{x},\underset{\sim}{N},\underset{\sim}{Q}) = \frac{\underset{\sim}{p}^2}{2\mu} + \underset{\sim}{p}\cdot\underset{\sim}{F}(\underset{\sim}{N},\underset{\sim}{Q};x)/\mu + |\underset{\sim}{F}(\underset{\sim}{N},\underset{\sim}{Q};\underset{\sim}{x})|^2/2\mu$$

$$+ \sum_{K=1}^{F} E_K(\underset{\sim}{x})\ N_K \quad , \tag{3.7}$$

where

$$\underset{\sim}{F}(\underset{\sim}{N},\underset{\sim}{Q};x) = -i \sum_{K,K'=1}^{F} \sqrt{N_K N_{K'}}\ e^{i(Q_K - Q_{K'})}\ \underset{\sim}{T}_{K,K'}(\underset{\sim}{x}) \quad ; \tag{3.8}$$

$\underset{\sim}{T}_{K,K'}(\underset{\sim}{x})$ and $E_K(\underset{\sim}{x})$ are the adiabatic coupling elements and the adiabatic eigenvalues, respectively.

c. Semiclassical Eigenvalues.

Another general consequence of the canonical transformation property of Eq. (3.6) is that the semiclassical eigenvalues of the classical analog of a Hamiltonian--e.g., $H(\underset{\sim}{n},\underset{\sim}{q})$ of Eq. (2.6) for fixed $\underset{\sim}{x}$--are identical to the eigenvalues of the matrix $\{H_{k,k'}\}$, i.e., to the quantum mechanical eigenvalues.

To see this, let the basis $\{|K\rangle\}$ in Eq. (3.6) be the eigenvectors of $\{H_{k,k'}\}$, i.e., the eigenstates of the quantum Hamiltonian. The classical Hamiltonian is expressed in terms of the new variables $(\underset{\sim}{N},\underset{\sim}{Q})$ by using Eq. (3.6b):

$$
\begin{aligned}
H(\underset{\sim}{N},\underset{\sim}{Q}) &= \sum_{k,k'} \sqrt{n_k n_{k'}}\; e^{i(q_k - q_{k'})}\; H_{k,k'} \\
&= \sum_{k,k'} \sum_{K,K'} \sqrt{N_K N_{K'}}\; e^{i(Q_K - Q_{K'})}\; \langle K|k\rangle\, H_{k,k'}\, \langle k'|K'\rangle \\
&= \sum_{K,K'} \sqrt{N_K N_{K'}}\; e^{i(Q_K - Q_{K'})}\; H_{K,K'} \quad . \qquad (3.9)
\end{aligned}
$$

But since $H_{K,K'}$ is diagonal,

$$H_{K,K'} = \delta_{K,K'}\, E_K \quad , \qquad (3.10)$$

Eq. (3.9) becomes

$$H(\underset{\sim}{N},\underset{\sim}{Q}) = \sum_K N_K E_K \quad . \qquad (3.11)$$

The semiclassical eigenvalues are obtained by requiring the "good" action variables $\{N_K\}$ to be integral, and since conservation of probability (see next section) requires that they sum to unity,

$$\sum_K N_K = 1 \quad , \tag{3.12}$$

this means all but one of the action variables must be zero, and the non-zero one must be unity. These conditions, with Eq. (3.11), show that the semiclassical eigenvalues are $\{E_K\}$, the quantum mechanical ones.

d. Conservation of Probability.

It is quite straight-forward to show that the classical Hamiltonian of Eq. (2.8) conserves the total electronic probability, i.e.,

$$\begin{aligned} -\frac{d}{dt}\left(\sum_{k=1}^{F} n_k(t)\right) &= \sum_{k=1}^{F} \dot{n}_k(t) \\ &= -\sum_{k=1}^{F} \frac{\partial H}{\partial q_K} = 0 \quad , \end{aligned} \tag{3.13}$$

so that only (F-1) of the F variables $\{n_k\}$ are independent. It is thus possible to make a canonical transformation to a new set of variables, one of which is a conserved and thus time-independent quantity.

The new variables $\{n_k'\}$ are defined by

$$n_1' = \sum_{k=1}^{F} n_k \tag{3.14a}$$

$$n_k' = n_k \ , \ k = 2, \ldots, F \quad , \tag{3.14b}$$

and the generating function[14] which effects the transformation $(\underset{\sim}{n},\underset{\sim}{q}) \rightarrow (\underset{\sim}{n}',\underset{\sim}{q}')$ is

$$F_2(\underset{\sim}{q},\underset{\sim}{n}') = q_1 n_1' + \sum_{k=2}^{F} (q_k - q_1) n_k' \quad . \tag{3.15}$$

The transformation relations[15]

$$q_k' = \frac{\partial F_2(\underset{\sim}{q},\underset{\sim}{n}')}{\partial n_k'} \tag{3.16a}$$

$$n_k = \frac{\partial F_2(\underset{\sim}{q},\underset{\sim}{n}')}{\partial q_k} \quad , \tag{3.16b}$$

reproduce Eqs. (3.14) and then lead to the following definition of the new angle variables:

$$q_1' = q_1 \tag{3.17a}$$

$$q_k' = q_k - q_1 \ , \ k = 2, \ \ldots, \ F \quad . \tag{3.17b}$$

The Hamiltonian of Eq. (2.8), expressed in terms of the new variables $(\underset{\sim}{n}',\underset{\sim}{q}')$, is independent of q_1', so that n_1' is time-dependent and appears in the Hamiltonian only as a parameter. Since the initial conditions of Eq. (3.3) correspond to n_1' having the initial value 1, i.e.,

$$n_1' \equiv \sum_{k=1}^{F} n_k = 1 \quad ,$$

and since this value is conserved, one concludes in general that conservation of probability implies that n_1' should be set to 1.

e. Example: Two States.

It is illustrative to see the specific form of the classical electronic Hamiltonian function for the simplest case F = 2. Eq. (2.6) is

$$H_{e\ell}(n_1,n_2,q_1,q_2) = n_1H_{11} + n_2H_{22} + 2\sqrt{n_1n_2}\cos(q_2-q_1)H_{12} \quad , \qquad (3.18)$$

where the $\underset{\sim}{x}$ dependence is not denoted explicitly and where $H_{k,k'}$ is assumed real so that $H_{12} = H_{21}$. In terms of the new variables $(\underset{\sim}{n}',\underset{\sim}{q}')$ of Eqs. (3.14) and (3.17),

$$n_1 = n_1'-n_2' = 1-n_2'$$

$$n_2 = n_2'$$

and

$$q_2-q_1 = q_2' \quad ,$$

so that Eq. (3.18) becomes a system with only one degree of freedom $(n_2',q_2') \equiv (n,q)$,

$$H_{e\ell}(n,q) = (1-n)H_{11} + nH_{22} + 2\sqrt{n(1-n)}\cos q\, H_{12} \quad , \qquad (3.19)$$

which one recalls is identical to the form obtained for the two state case by Miller and McCurdy[1] on more heuristic grounds.

f. A 3-State Example.

For F > 2 the classical analog developed in this paper provides a different classical model for the electronic degrees of freedom than the ones suggested earlier.[1,2] The case of a P-state atom A colliding with a

closed shell $^1\Sigma$ diatomic molecule BC is a 3-state system, corresponding to the unpaired p-orbital of the atom having projection m = -1, 0 or +1. For fixed nuclear positions, the diabatic electronic matrix has the form[1]

$$[H_{m,m'}] = \begin{array}{c} \\ -1 \\ 0 \\ +1 \end{array} \begin{array}{c} \begin{array}{ccc} -1 & 0 & +1 \end{array} \\ \begin{pmatrix} \bar{H} & -i\frac{H_{yz}}{\sqrt{2}} & \Delta \\ i\frac{H_{yz}}{\sqrt{2}} & H_{zz} & -i\frac{H_{yz}}{\sqrt{2}} \\ \Delta & i\frac{H_{yz}}{\sqrt{2}} & \bar{H} \end{pmatrix} \end{array} . \qquad (3.20)$$

We denote the three action variables by $n_{+1} \equiv n_+$, n_0, and $n_{-1} \equiv n_-$, rather than n_1, n_2, and n_3, and as discussed above, only two of them are independent; e.g., we take $n_0 \equiv 1-n_+-n_-$. It is not hard to show that Eq. (2.6), with the transformations of Eqs. (3.14) and (3.17) to eliminate (n_0,q_0), gives the classical analog of this Hamiltonian matrix as

$$\begin{aligned} H(n_+,n_-,q_+,q_-) &= (n_++n_-)\bar{H} + (1-n_+-n_-)H_{zz} \\ &+ 2\sqrt{n_+n_-}\,\Delta\cos(q_+-q_-) + \sqrt{2n_-(1-n_+-n_-)}\,H_{yz}\sin q_- \\ &- \sqrt{2n_+(1-n_+-n_-)}\,H_{yz}\sin q_+ \quad . \end{aligned} \qquad (3.21)$$

The classical analogs of the three components of electronic orbital angular momentum are also needed in order to construct other terms in the Hamiltonian (e.g., spin-orbit and coriolis coupling), and since their matrices are

$$(L_z)_{m,m'} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (3.22a)$$

$$(L_y)_{m,m'} = \begin{pmatrix} 0 & i/\sqrt{2} & 0 \\ -i/\sqrt{2} & 0 & i/\sqrt{2} \\ 0 & -i/\sqrt{2} & 0 \end{pmatrix} \tag{3.22b}$$

$$(L_x)_{m,m'} = \begin{pmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{pmatrix} \tag{3.22c}$$

Eq. (3.4) gives the following expressions for their classical analogs:

$$L_z(n_+,n_-,q_+,q_-) = n_+ - n_- \tag{3.23a}$$

$$L_y(n_+,n_-,q_+,q_-) = \sqrt{2\,n_+(1-n_+-n_-)}\,\sin q_+ - \sqrt{2n_-(1-n_+-n_-)}\,\sin q_- \tag{3.23b}$$

$$L_x(n_+,n_-,q_+,q_-) = \sqrt{2\,n_+(1-n_+-n_-)}\,\cos q_+ + \sqrt{2n_-(1-n_+-n_-)}\,\cos q_- \quad . \tag{3.23c}$$

Eqs. (3.21) and (3.23) clearly constitute a different classical model for the electronic states of the A(P) + BC system than the one obtained earlier[1,2] in that it consists of <u>two</u> degrees of freedom whereas the earlier one involved only <u>one</u> degree of freedom. Because of the many desirable features of the classical analog that have been discussed in this paper, we feel that the above model will probably be a more accurate model than our earlier one, but this must be tested by calculations.

g. <u>Classical S-Matrix</u>.

So far we have added little to the well-known[5-7] approximation of solving the time-dependent Schrödinger equation along the classical path determined by the average (i.e., Ehrenfest) force, other than presenting a new "classical" way of looking at it. Here, however, we show how the principal defect of the model, as discussed at the end of Section IIIa--i.e., that a <u>single</u>

trajectory determines all electronic transitions, rather than each transition having a different trajectory--can be overcome by using this new classical interpretation. One thinks in terms of the classical analog, Eqs. (2.8)-(2.9), rather than Eq. (3.1), and "quantizes" the classical system within the framework of classical S-matrix theory.[12]

To describe the specific $k_1 \to k_2$ electronic transition one thus needs to integrate the classical equations of motion Eq. (2.9) with the initial conditions

$$n_k(t_1) = \delta_{k,k_1} \tag{3.24a}$$

$$q_k(t_1) = ? \quad , \tag{3.24b}$$

where the F initial angle variables $\{q_k(t_1)\}$ are chosen so that the final action variables $\{n_k(t_2)\}$ are

$$n_k(t_2) = \delta_{k,k_2} \quad . \tag{3.24c}$$

The electronic transition probability is then given, for example in the completely classical version of this theory, by the determinant of the Jacobian of the final action variables with respect to the initial angles:

$$P_{k_2 \leftarrow k_1} = [(2\pi)^F \, |\frac{\partial \underset{\sim}{n}(t_2)}{\partial \underset{\sim}{q}(t_1)}|]^{-1} \quad . \tag{3.24d}$$

If more than one trajectory satisfies the boundary conditions of Eq. (3.24), then the transition probability also involves the differences in the action integrals for the trajectories (cf. Section IV).

For the case of two electronic states, for example, the boundary conditions for the $1 \rightarrow 2$ transition are

$$n_1(t_1) = 1$$

$$n_2(t_1) = 0 \quad ,$$

with $q_1(t_1)$ and $q_2(t_1)$ chosen so that

$$n_1(t_2) = 0$$

$$n_2(t_2) = 1 \quad ,$$

with $t_1 \to -\infty$ and $t_2 \to +\infty$. The boundary conditions for the heavy particle degrees of freedom are chosen as in conventional classical S-matrix theory,[12] or one may want to "partially average"[15] over them in which case they would be chosen by the quasiclassical prescription.

It is clear that these boundary conditions based on classical S-matrix theory provide a dynamically consistent description of the electronic transition: different electronic transitions involve different classical trajectories, and since the classical Hamiltonian of Eq. (2.8) conserves the total energy of the system, it is clear that energy conservation is correctly obeyed; e.g., for the trajectory or trajectories determined by the boundary conditions of Eq. (3.24) the nuclear degrees of freedom will gain (or loose) the amount of energy lost (or gained) by the electronic transition. It is also clear from classical S-matrix theory that the electronic transition probability will be microscopically reversible.

There is a flaw, however, in the model as it stands: with the Hamiltonian of Eq. (3.28) and the boundary conditions of Eq. (3.24), the final action variables $\{n_k(t_2)\}$ are actually <u>independent</u> of the initial angle variables $\{q_k(t_1)\}$, so that one cannot satisfy Eqs. (3.24) by varying them. (One can see this most easily by referring to the equivalent time-dependent Schrödinger equation, Eqs. (2.3)-(2.5); since all the initial amplitudes $\{a_k(t_1)\}$ are zero except for $k = k_1$, the final values of the amplitudes cannot depend on the initial phases $\{q_k(t_1)\}$, $k \neq k_1$. Also, $q_{k_1}(t_1)$ appears as an overall phase

factor in the total wavefunction, so nothing can depend on it either.) This defect of the model is corrected by invoking the ubiquitous Langer-type modification to the electronic Hamiltonian, i.e., by adding "$\frac{1}{2}$" to all the action variables $\{n_k\}$. The electronic Hamiltonian then becomes

$$H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q};\underset{\sim}{x}) = \sum_{k,k'=1}^{F} \sqrt{(n_k+\tfrac{1}{2})(n_{k'}+\tfrac{1}{2})}\; e^{i(q_k-q_{k'})}\; H_{k,k'}(\underset{\sim}{x}) \quad , \tag{3.25}$$

but this also is not totally satisfactory because it changes the adiabatic electronic eigenvalues; i.e., in terms of the adiabatic action-angle variables (N_k,Q_k) this Langer-modified Hamiltonian is

$$H_{e\ell}(\underset{\sim}{N},\underset{\sim}{Q};\underset{\sim}{x}) = \sum_{K=1}^{F} (N_K+\tfrac{1}{2})\; E_K(\underset{\sim}{x}) \quad , \tag{3.26}$$

because adding "$\frac{1}{2}$" to all n_k's has the effect of adding "$\frac{1}{2}$" to all N_K's. Thus setting $N_K = \delta_{K,K_1}$ in Eq. (3.26) does <u>not</u> give the adiabatic eigenvalue $E_{K_1}(\underset{\sim}{x})$. This problem is easily remedied, however, by subtracting the term

$$\frac{1}{2}\sum_{K=1}^{F} E_K(\underset{\sim}{x})$$

from Eq. (3.26), so that the desired form of the adiabatic Hamiltonian is recovered:

$$H_{e\ell}(\underset{\sim}{N},\underset{\sim}{Q};\underset{\sim}{x}) = \sum_{K=1}^{F} N_K\; E_K(\underset{\sim}{x}) \quad . \tag{3.27}$$

This term that is subtracted from the Hamiltonian is a constant so far as the electronic action-angle variables are concerned and thus does not

change the electronic dynamics. It must also be subtracted from the Hamiltonian in the diabatic representation, Eq. (3.25), and since

$$\frac{1}{2}\sum_{K=1}^{F} E_K(\underset{\sim}{x}) = \frac{1}{2}\,\mathrm{tr}(\underset{\approx}{H}_{e\ell}(\underset{\sim}{x})) = \frac{1}{2}\sum_{k=1}^{F} H_{k,k}(\underset{\sim}{x}) \quad ,$$

subtracting this term from Eq. (3.25) gives

$$H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q};\underset{\sim}{x}) = \sum_{k=1}^{F} n_k\, H_{k,k}(\underset{\sim}{x}) + \sum_{\substack{k,k'=1 \\ k\neq k'}}^{F} \sqrt{(n_k+\tfrac{1}{2})(n_{k'}+\tfrac{1}{2})}\; e^{i(q_k-q_{k'})}\, H_{k,k'}(\underset{\sim}{x}) \quad . \tag{3.28}$$

Eq. (3.28) is the final form of the Langer-modified electronic Hamiltonian, and one notes that the above analysis has the simple effect of making the Langer modification only in the off-diagonal terms. As noted, it still gives the correct semiclassical eigenvalues, i.e., it is given in adiabatic representation by Eq. (3.27). The complete Hamiltonian for the collision system is obtained by adding the nuclear kinetic energy

$$H(\underset{\sim}{p},\underset{\sim}{x},\underset{\sim}{n},\underset{\sim}{q}) = \frac{p^2}{2\mu} + H_{e\ell}(\underset{\sim}{n},\underset{\sim}{q};\underset{\sim}{x}) \quad , \tag{3.29}$$

with $H_{e\ell}$ of Eq. (3.28). It can now be used in a conventional classical S-matrix treatment which, as discussed above, allows electronic and heavy particle degrees of freedom to interact so that different electronic transitions have different heavy particle trajectories and conserves the total energy correctly for all transitions.

IV. Test of the Semiclassical Electronic Transition Probability.

It is clear from the discussion in Section IIIg that the Langer-modified classical electronic Hamiltonian [Eq. (3.28)], used in conjunction with classical S-matrix theory, treats the coupling between heavy particle motion and electronic degrees of freedom in a consistent way; i.e., different electronic transitions have different heavy particle trajectories and, for example, the heavy particle degrees of freedom gain or loose energy to compensate for the change in electronic energy. As discussed in Section IIIa, this is not the case with conventional classical path models, even those that use the classical path determined by the Ehrenfest force.

There is a price that has been paid for the achievement of this dynamical consistency, however, namely that the electronic degrees of freedom are described by classical rather than quantum mechanics. Therefore although this approach describes the electronic and nuclear dynamics more consistently, it provides a cruder description of the electronic degrees of freedom themselves. An important question, therefore, is how well the classical/semiclassical model for the electronic degrees of freedom can describe the purely electronic aspect of the process, i.e., the electronic transition probability. A simple test of this particular aspect of the model can be made by ignoring the nuclear degrees of freedom and considering just the time-dependent electronic problem.

In this section we thus consider the time-dependent 2-state electronic problem, the goal being to see how well the classical model for the electronic degrees of freedom (with classical S-matrix theory) can describe the electronic transition probability. For two states the Langer-modified classical Hamiltonian of Eq. (3.28) is

$$H_{e\ell}(n_1,q_1,n_2,q_2;t) = n_1\, H_{11}(t) + n_2\, H_{22}(t)$$

$$+ 2\sqrt{(n_1+\tfrac{1}{2})(n_2+\tfrac{1}{2})}\; H_{12}(t)\, \cos(q_2-q_1) \quad , \tag{4.1}$$

and using conservation of probability to eliminate n_1 as in Section IIId (cf. Eq. (3.19)) gives

$$H_{e\ell}(n,q;t) = (1-n)\, H_{11}(t) + n\, H_{22}(t)$$

$$+ 2\sqrt{n+\tfrac{1}{2}}\sqrt{\tfrac{3}{2}-n}\; H_{12}(t)\, \cos q \quad . \tag{4.2}$$

To construct the 1→2 electronic transition probability one integrates Hamilton's equations of motion,

$$\dot{q} = \frac{\partial H}{\partial n} = H_{11}(t) - H_{22}(t) + \frac{1-2n}{\sqrt{n+\frac{1}{2}}\sqrt{\frac{3}{2}-n}}\; H_{12}(t)\, \cos q \tag{4.3a}$$

$$\dot{n} = -\frac{\partial H}{\partial q} = 2\sqrt{n+\tfrac{1}{2}}\sqrt{\tfrac{3}{2}-n}\; H_{12}(t)\, \sin q \quad , \tag{4.3b}$$

with initial conditions

$$q(t_1) = q_1 \tag{4.4a}$$

$$n(t_1) = 0 \quad . \tag{4.4b}$$

The values of n(t) and q(t) at the final time t_2 are denoted $n_2(q_1)$ and $q_2(q_1)$, and one also needs the action integral ϕ,

$$\phi(q_1) = \int_{t_1}^{t_2} dt \quad [-q(t)\,\dot{n}(t) - H(n(t),q(t);t)] \quad , \tag{4.5a}$$

which can also be computed by

$$\phi(q_1) = -\int dq_1 \; q_2(q_1)\; n_2'(q_1) \quad . \tag{4.5b}$$

If q_I and q_{II} are the two roots (as is typically the case) of the equation

$$n_2(q_1) = 1 \quad ,$$

then the <u>primitive</u> <u>classical</u> transition probability is given by

$$P_{2\leftarrow 1}^{\;CL} = p_I + p_{II} \quad , \tag{4.6a}$$

where

$$p = [2\pi |n_2'(q_1)|]^{-1} \tag{4.6b}$$

with $q_1 = q_I$ or q_{II}.

At the completely classical level, however, it is usually better to average the primitive classical result over an integer width about the final quantum number; this gives the quasiclassical or "histogram" result,

$$P_{2\leftarrow 1}^{\;QC} \equiv \int_{I-\frac{1}{2}}^{1+\frac{1}{2}} dn_2 \quad \frac{1}{2\pi \left|\frac{dn_2}{dq_1}\right|} = \frac{\Delta q_1}{2\pi} \quad , \tag{4.7a}$$

where Δq_1 is the increment of the 2π-length interval of q_1 for which

$$|n_2(q_1) - 1| \leq \frac{1}{2} \quad . \tag{4.7b}$$

For the two examples considered below it turns out that

$$p_I = p_{II} \ (\equiv p) \quad ,$$

and in this case the uniform semiclassical approximation to the transition probability takes the simple form

$$P_{2\leftarrow 1}^{USC} = 4p\pi \sqrt{z}\, Ai(-z)^2 \quad , \tag{4.8a}$$

where Ai is the regular Airy function and

$$z = \left(\frac{3}{4} \Delta\phi\right)^{2/3} \tag{4.8b}$$

$$\Delta\phi = \phi(q_{II}) - \phi(q_I)$$

$$= -\int_{q_I}^{q_{II}} dq_1 \ \ q_2(q_1)\, n_2'(q_1) \quad . \tag{4.8c}$$

a. Landau-Zener Model

We consider first the Landau-Zener model, for which the electronic Hamiltonian matrix is

$$H_{11}(t) = 0$$

$$H_{22}(t) = Ft$$

$$H_{12}(t) = H_{12} = \text{constant} \quad , \tag{4.9}$$

and the time interval is $t_1 \to -\infty$, $t_2 \to +\infty$. This model describes the well-known curve-crossing situation and is thus an important example to consider.

Integrating the classical equations of motion with this Hamiltonian gives

$$n_2(\bar{q}_1) = p - \sqrt{3p(1-p)}\,\sin\bar{q}_1 \tag{4.10a}$$

$$\bar{q}_2(\bar{q}_1) = \tan^{-1}\left[(1-2p)\,\tan\bar{q}_1 - 2\sqrt{\frac{p(1-p)}{3}}\,\sec\bar{q}_1\right] \quad , \tag{4.10b}$$

where p is the parameter

$$p = 1 - \exp\left[-\frac{2\pi H_{12}^2}{|F|}\right] \quad , \tag{4.10c}$$

and where $\bar{q}_1$ and $\bar{q}_2$ differ from q_1 and q_2 by irrelevant constants. The action integral ϕ is computed by integrating Eq. (4.5b) numerically. The correct quantum mechanical transition probability is given by

$$P_{2\leftarrow 1}^{QM} = p \quad , \tag{4.11}$$

where p is the parameter defined by Eq. (4.10c).

Figure 1 shows the primitive classical (CL), quasiclassical (QC), and uniform semiclassical (USC) results (computed from Eqs. (4.6)-(4.8) with Eq. (4.10)) compared to the correct quantum mechanical (QM) result, as a function of the parameter p. The primitive classical result shows the typical singularities which mark the transition between "classically allowed" and "classically forbidden" regions. The quasiclassical approximation smoothes out these singularities and in general provides a better description at the completely classical level.

The uniform semiclassical approximation of Eq. (4.8) is in very good agreement with the quantum mechanical result for all values of $p \lesssim \frac{3}{4}$. Figure 2 shows that this good agreement persists into the classically forbidden region where $p << 1$.

For $p \gtrsim \frac{3}{4}$, the Airy uniform approximation breaks down because the quantum number function of Eq. (4.10a) becomes too flat. In this case, however, the Bessel uniform approximation[15,16] is appropriate and gives

$$P_{2\leftarrow 1}^{USC} = \pi p \, \Delta\phi \, J_0(\tfrac{\Delta\phi}{2})^2 \quad . \tag{4.12}$$

As seen in Figure 1, this uniformization works well for large transition probabilities.

b. General Two-State Model

It is interesting to show that the results obtained above for the Landau-Zener model are actually true for any two-state model.

To see this we note that the initial and final values of the amplitudes $\{a_k\}$ are related by an S-matrix,

$$\underset{\sim}{a}(t_2) = \underset{\approx}{S} \cdot \underset{\sim}{a}(t_1) \quad ,$$

or written out explicitly for the 2-state case,

$$\begin{aligned} a_1(t_2) &= S_{11}\, a_1(t_1) + S_{12}\, a_2(t_1) \\ a_2(t_2) &= S_{21}\, a_1(t_1) + S_{22}\, a_2(t_1) \quad . \end{aligned} \tag{4.13}$$

Invoking the relation [Eq. (2.5)] between the amplitudes $\{a_k\}$ and the action-angle variables $\{n_k, q_k\}$ gives

$$\sqrt{n_1(t_2)}\, e^{-iq_1(t_2)} = S_{11}\sqrt{n_1(t_1)}\, e^{-iq_1(t_1)} + S_{12}\sqrt{n_2(t_1)}\, e^{-iq_2(t_1)}$$

$$\sqrt{n_2(t_2)}\, e^{-iq_2(t_2)} = S_{21}\sqrt{n_1(t_1)}\, e^{-iq_1(t_1)} + S_{22}\sqrt{n_2(t_1)}\, e^{-iq_2(t_1)} \quad ,$$

and if conservation of probability is utilized this becomes

$$\sqrt{1-n_2}\, e^{-iQ_2} = S_{11}\sqrt{1-n_1}\, e^{-iQ_1} + S_{12}\sqrt{n_1}\, e^{-iQ_1}\, e^{-iq_1}$$

$$\sqrt{n_2}\, e^{-iQ_2}\, e^{-iq_2} = S_{21}\sqrt{1-n_1}\, e^{-iQ_1} + S_{22}\sqrt{n_1}\, e^{-iQ_1}\, e^{-iq_1} \quad ,$$

where here

$$n_1 = n(t_1)$$

$$n_2 = n(t_2)$$

$$q_1 = q(t_1)$$

$$q_2 = q(t_2)$$

$$Q_1 = Q(t_1)$$

$$Q_2 = Q(t_2) \quad ,$$

and $Q(t)$ is the angle variable conjugate to the conserved quantity $n_1(t) + n_2(t)$. Forming the ratio of the above two equations eliminates the initial and final values of Q,

$$\sqrt{\frac{1-n_2}{n_2}}\, e^{iq_2} = \frac{S_{11}\sqrt{1-n_1}\, e^{iq_1} + S_{12}\sqrt{n_1}}{S_{21}\sqrt{1-n_1}\, e^{iq_1} + S_{22}\sqrt{n_1}} \tag{4.14}$$

The 2 x 2 S-matrix is unitary and symmetric and can in general be parameterized by two angles and a probability,

$$S_{11} = \sqrt{1-p}\, e^{i\alpha_1} \tag{4.15a}$$

$$S_{22} = \sqrt{1-p}\, e^{i\alpha_2} \tag{4.15b}$$

$$S_{12} = S_{21} = i\sqrt{p}\, e^{i(\alpha_1+\alpha_2)/2} \quad , \tag{4.15c}$$

and we note that the parameter p is the quantum mechanical $1 \to 2$ transition probability,

$$P_{2\leftarrow 1} \equiv |S_{12}|^2 = p \quad . \tag{4.16}$$

Using Eq. (4.15), and also making the Langer modification, converts Eq. (4.14) into

$$\sqrt{\frac{\frac{3}{2}-n_2}{n_2+\frac{1}{2}}}\, e^{i\bar{q}_2} = \frac{e^{i\bar{q}_1}\sqrt{1-p}\sqrt{\frac{3}{2}-n_1} + i\sqrt{p}\sqrt{n_1+\frac{1}{2}}}{i\, e^{i\bar{q}_1}\sqrt{p}\sqrt{\frac{3}{2}-n_1} + \sqrt{1-p}\sqrt{n_1+\frac{1}{2}}} \quad , \tag{4.17}$$

where

$$\bar{q}_2 = q_2 + \tfrac{1}{2}(\alpha_2-\alpha_1)$$

$$\bar{q}_1 = q_1 - \tfrac{1}{2}(\alpha_2-\alpha_1) \quad .$$

From Eq. (4.17) one can determine n_2 and $\bar{q}_2$ in terms of $\bar{q}_1$ and n_1,

$$n_2(\bar{q}_1, n_1) = p + n_1(1-2p) - 2\sqrt{p(1-p)}\sqrt{n_1 + \tfrac{1}{2}}\sqrt{\tfrac{3}{2} - n_1}\,\sin\bar{q}_1 \qquad (4.18a)$$

$$\bar{q}_2(\bar{q}_1, n_1) = \tan^{-1}\left[(1-2p)\tan\bar{q}_1 + \frac{(2n_1-1)\sqrt{p(1-p)}}{\sqrt{(n_1+\frac{1}{2})(\frac{3}{2}-n_1)}}\,\sec\bar{q}_1\right] \quad , \qquad (4.18b)$$

and setting $n_1 = 0$ gives Eqs. (4.10a) and (4.10b) of the Section IVa. Since the functions $n_2(\bar{q}_1)$ and $\bar{q}_2(\bar{q}_1)$ determine the classical and semiclassical transition probabilities, the comparisons shown in the previous section will thus be the same for any two-level system.

IV. Concluding Remarks.

We have shown how one can define a formally exact classical analog for a finite dimensional quantum mechanical system. If this is a set of diabatic electronic states to which the nuclear kinetic energy is added as in Eqs. (2.8)-(2.9), then the result is seen to be equivalent to the "Ehrenfest" model, for which the electronic amplitudes obey a time-dependent Schrödinger equation, the time dependence coming from the nuclei which follow a classical trajectory determined by the "Ehrenfest force".

The boundary conditions usually applied to these equations are dynamically inconsistent, but it was seen that the classical interpretation of the equations plus the boundary conditions of classical S-matrix theory (and a Langer-modification of the Hamiltonian) leads to a dynamically consistent model. Application to two simple model systems showed that the electronic dynamics is described quite well by this classical/semiclassical model.

It appears, therefore, that this classical model of electronically non-adiabatic collision systems should provide a usefully accurate description of these processes.

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Appendix A

We wish to prove that

$$\frac{1}{i}[A,B](\underset{\sim}{n},\underset{\sim}{q}) = \{A(\underset{\sim}{n},\underset{\sim}{q}),B(\underset{\sim}{n},\underset{\sim}{q})\} \quad , \tag{A.1}$$

where the commutator $[A,B]$ and Poisson bracket $\{A,B\}$ are

$$[A,B] = AB - BA$$

$$\{A(\underset{\sim}{n},\underset{\sim}{q}),B(\underset{\sim}{n},\underset{\sim}{q})\} = \sum_{j=1}^{F} \left[\frac{\partial A(\underset{\sim}{n},\underset{\sim}{q})}{\partial q_j} \frac{\partial B(\underset{\sim}{n},\underset{\sim}{q})}{\partial n_j} - \frac{\partial A(\underset{\sim}{n},\underset{\sim}{q})}{\partial n_j} \frac{\partial B(\underset{\sim}{n},\underset{\sim}{q})}{\partial q_j}\right] ,$$

with $A(\underset{\sim}{n},\underset{\sim}{q})$ defined by Eq. (3.5), and $B(\underset{\sim}{n},\underset{\sim}{q})$ similarly. Since

$$\frac{\partial A(\underset{\sim}{n},\underset{\sim}{q})}{\partial n_j} = \sum_{\ell} \frac{\sqrt{n_j n_\ell}}{2n_j} \left(e^{i(q_j-q_\ell)} A_{j\ell} + e^{i(q_\ell-q_j)} A_{\ell j}\right)$$

$$\frac{\partial A(\underset{\sim}{n},\underset{\sim}{q})}{\partial q_j} = i\sum_{\ell} \sqrt{n_j n_\ell} \left(e^{i(q_j-q_\ell)} A_{j\ell} - e^{i(q_\ell-q_j)} A_{\ell j}\right) \quad , \tag{A.2}$$

the Poisson bracket yields:

$$\begin{aligned}\{A(\underset{\sim}{n},\underset{\sim}{q}),B(\underset{\sim}{n},\underset{\sim}{q})\} = \frac{i}{2} \sum_{j,\ell,m} \sqrt{n_\ell n_m} \{ & e^{i(q_m-q_\ell)} (B_{mj}A_{j\ell} - A_{mj}B_{j\ell}) \\ & + e^{i(q_\ell-q_m)} (-A_{\ell j}B_{jm} + B_{\ell j}A_{jm}) \\ & + e^{i(2q_j-q_\ell-q_m)} (A_{j\ell}B_{jm} - A_{jm}B_{j\ell}) \\ & e^{-i(2q_j-q_\ell-q_m)} (-A_{j\ell}B_{mj} + A_{mj}B_{\ell j})\} \quad . \end{aligned} \tag{A.3}$$

The last two terms vanish upon summation due to symmetry, and the first two terms are the same. Thus

$$\{A,B\} = -i \sum_{\ell,m} \sqrt{n_\ell n_m}\ e^{i(q_\ell - q_m)} \sum_j (A_{\ell j} B_{jm} - B_{\ell j} A_{jm})$$

$$= -i \sum_{\ell,m} \sqrt{n_\ell n_m}\ e^{i(q_\ell - q_m)} [A,B]_{\ell,m}$$

$$= \frac{1}{i} [A,B](\underset{\sim}{n},\underset{\sim}{q}) \quad . \tag{A.4}$$

It is also useful to note the relation of a canonical transformation between variables of this type to a quantum mechanical basis set transformation. Let $\{|k>\}$ and $\{|K>\}$ each be orthonormal sets; the relations between the "old" and "new" action-angle variables, $(\underset{\sim}{n},\underset{\sim}{q})$ and $(\underset{\sim}{N},\underset{\sim}{Q})$, are given by Eq. (3.6). Thus

$$N_K = \left| \sum_k e^{-iq_k} \sqrt{n_k}\ <K|k> \right|^2 \quad , \tag{A.5}$$

and one calculates

$$\frac{\partial N_K}{\partial q_k} = -\, i\, e^{-iq_k} \sqrt{n_k}\ <K|k> \left[\sum_{k'} e^{-iq_k} \sqrt{n_k}\ <K|k> \right]^*$$

$$+ \text{complex conjugate},$$

$$= 2\ \mathrm{Im}[e^{i(Q_K - q_k)} \sqrt{N_K n_k}\ <K|k>] \quad . \tag{A.6}$$

Similarly,

$$n_k = \left|\sum_K e^{-iQ_k}\sqrt{N_K}\,\langle k|K\rangle\right|^2 \quad , \tag{A.7}$$

and differentiating, one finds

$$\frac{\partial n_k}{\partial Q_K} = 2\ \mathrm{Im}\left[e^{i(q_k - Q_K)}\sqrt{n_k N_K}\,\langle k|K\rangle\right] \quad . \tag{A.8}$$

But since

$$\mathrm{Im}(z) = -\mathrm{Im}(z^*)$$

$$\langle k|K\rangle^* = \langle K|k\rangle \quad ,$$

Eq. (A.8) is equivalent to

$$\frac{\partial n_k}{\partial Q_K} = -\,2\ \mathrm{Im}\left[e^{i(Q_K - q_k)}\sqrt{N_K n_k}\,\langle K|k\rangle\right] \quad , \tag{A.8'}$$

so that Eqs. (A.6) and (A.8') imply that

$$\frac{\partial N_K}{\partial q_k} = -\frac{\partial n_k}{\partial Q_K} \quad . \tag{A.9}$$

Thinking of $\{q_k\}$ and $\{Q_K\}$ as the independent variables, Eq. (A.9) implies the existence of a function $F_1(\underset{\sim}{q},\underset{\sim}{Q})$ such that

$$N_K = -\frac{\partial F_1(\underset{\sim}{q},\underset{\sim}{Q})}{\partial Q_K} \tag{A.10a}$$

$$n_k = \frac{\partial F_1(\underset{\sim}{q},\underset{\sim}{Q})}{\partial q_k} \quad . \tag{A.10b}$$

The existence of such a function (the generating function) guarantees that the $(\underset{\sim}{n},\underset{\sim}{q}) \leftrightarrow (\underset{\sim}{N},\underset{\sim}{Q})$ transformation is canonical.[15]

Proceeding in a similar fashion, one can show more generally that

$$\frac{\partial N_K}{\partial n_k} = \frac{1}{n_k} \mathrm{Re}(A_{K,k}) \tag{A.11a}$$

$$\frac{\partial N_K}{\partial q_k} = 2\ \mathrm{Im}(A_{K,k}) \tag{A.11b}$$

$$\frac{\partial Q_K}{\partial n_k} = \frac{-1}{2N_K n_k} \mathrm{Im}(A_{K,k}) \tag{A.11c}$$

$$\frac{\partial Q_K}{\partial q_k} = \frac{1}{N_K} \mathrm{Re}(A_{K,k}) \quad , \tag{A.11d}$$

where

$$A_{K,k} = e^{i(Q_K - q_k)} \sqrt{N_K n_k}\ \langle K|k\rangle \quad . \tag{A.12}$$

By interchanging $(\underset{\sim}{n},\underset{\sim}{q}) \leftrightarrow (\underset{\sim}{N},\underset{\sim}{Q})$, or by a similar calculation as above, one also finds

$$\frac{\partial n_k}{\partial N_K} = \frac{1}{N_K} \mathrm{Re}(A_{k,K}) \tag{A.13a}$$

$$\frac{\partial n_k}{\partial Q_K} = 2\ \mathrm{Im}(A_{k,K}) \tag{A.13b}$$

$$\frac{\partial q_k}{\partial N_K} = -\frac{1}{2n_k N_K}\ \mathrm{Im}(A_{k,K}) \tag{A.13c}$$

$$\frac{\partial q_k}{\partial Q_K} = \frac{1}{n_k} \mathrm{Re}(A_{k,K}) \quad . \tag{A.13d}$$

Since

$$A_{k,K} = A_{K,k}^{*} \quad , \tag{A.14}$$

Eqs. (A.11) and (A.13) imply that

$$\frac{\partial N_K}{\partial q_k} = - \frac{\partial n_k}{\partial Q_K} \tag{A.15a}$$

$$\frac{\partial Q_K}{\partial q_k} = \frac{\partial n_k}{\partial N_K} \tag{A.15b}$$

$$\frac{\partial N_K}{\partial n_k} = \frac{\partial q_k}{\partial Q_K} \tag{A.15c}$$

$$\frac{\partial q_k}{\partial N_K} = - \frac{\partial Q_K}{\partial n_k} \quad . \tag{A.15d}$$

Eqs. (A.15a)-(A.15d) imply, respectively, the existence of generating functions $F_1(\underset{\sim}{q},\underset{\sim}{Q})$, $F_2(\underset{\sim}{q},\underset{\sim}{N})$, $F_3(\underset{\sim}{n},\underset{\sim}{Q})$, and $F_4(\underset{\sim}{n},\underset{\sim}{N})$ such that

$$n_k = \frac{\partial F_1(\underset{\sim}{q},\underset{\sim}{Q})}{\partial q_k} \quad , \quad N_K = - \frac{\partial F_1(\underset{\sim}{q},\underset{\sim}{Q})}{\partial Q_K} \tag{A.16a}$$

$$p_k = \frac{\partial F_2(\underset{\sim}{q},\underset{\sim}{N})}{\partial q_k} \quad , \quad Q_K = \frac{\partial F_2(\underset{\sim}{q},\underset{\sim}{N})}{\partial N_K} \tag{A.16b}$$

$$q_k = \frac{\partial F_3(\underset{\sim}{n},\underset{\sim}{Q})}{\partial n_k} \quad , \quad N_K = \frac{\partial F_3(\underset{\sim}{n},\underset{\sim}{Q})}{\partial Q_K} \tag{A.16c}$$

$$q_k = -\frac{\partial F_4(\underset{\sim}{n},\underset{\sim}{N})}{\partial n_k} \quad , \quad Q_K = \frac{\partial F_4(\underset{\sim}{n},\underset{\sim}{N})}{\partial N_K} \quad . \tag{A.16d}$$

Any one of the pair of equations in Eq. (A.16) is sufficient to guarantee that the transformation is canonical.[15]

Appendix B

Let $\{|k\rangle\}$ and $\{|K\rangle\}$ denote the diabatic and adiabatic electronic states, respectively; $\{|K\rangle\}$ depend parametrically on the nuclear coordinates $\underset{\sim}{x}$. The coupling elements $\underset{\sim}{T}_{K,K'}(\underset{\sim}{x})$ are

$$\underset{\sim}{T}_{K,K'} = \langle K|\frac{\partial}{\partial \underset{\sim}{x}} K'\rangle = \sum_k \langle K|k\rangle \frac{\partial}{\partial \underset{\sim}{x}} \langle k|K'\rangle \tag{B.1a}$$

$$= -\sum_k (\frac{\partial}{\partial \underset{\sim}{x}} \langle K|k\rangle)\langle k|K'\rangle \quad , \tag{B.1b}$$

and we note that $\underset{\sim}{T}_{K,K'}$ is skew-hermitian

$$\underset{\sim}{T}^{\dagger}_{K,K'} = - \underset{\sim}{T}^{*}_{K',K} \quad . \tag{B.2}$$

It is a lengthy but straight-forward matter to calculate $\frac{\partial N_K}{\partial \underset{\sim}{x}}$ and $\frac{\partial Q_K}{\partial \underset{\sim}{x}}$ for fixed $\underset{\sim}{n}$ and $\underset{\sim}{q}$. One obtains

$$\frac{\partial N_K}{\partial \underset{\sim}{x}} = -2\ \mathrm{Re} \sum_{K'} e^{i(Q_K - Q_{K'})} \sqrt{N_K N_{K'}}\ \underset{\sim}{T}_{K,K'} \tag{B.3a}$$

$$\frac{\partial Q_K}{\partial \underset{\sim}{x}} = \frac{1}{N_K}\ \mathrm{Im} \sum_{K'} e^{i(Q_K - Q_{K'})} \sqrt{N_K N_{K'}}\ \underset{\sim}{T}_{K,K'} \quad . \tag{B.3b}$$

The equations of motion for $\underset{\sim}{N}$ and $\underset{\sim}{Q}$ are then given by

$$\dot{N}_K = \sum_k (\frac{\partial N_K}{\partial q_k} \dot{q}_k + \frac{\partial N_K}{\partial n_k} \dot{n}_k) + \frac{\partial N_K}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{x}} = \frac{\partial N_K}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{x}} \tag{B.4a}$$

$$\dot{Q}_K = \sum_k (\frac{\partial Q_K}{\partial q_k} \dot{q}_k + \frac{\partial Q_K}{\partial n_k} \dot{n}_k) + \frac{\partial Q_K}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{x}} = E_K + \frac{\partial Q_K}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{x}} \quad , \tag{B.4b}$$

where $E_K = E_K(\underset{\sim}{x})$ is the adiabatic eigenvalue, i.e., the adiabatic potential energy surface.

The task is now to find a Hamiltonian that reproduces these equations of motion. It is useful to define the quantity $\underset{\sim}{F}(\underset{\sim}{N},\underset{\sim}{Q};\underset{\sim}{x})$ by

$$\underset{\sim}{F}(\underset{\sim}{x}) = -i \sum_{K,K'} e^{i(Q_K - Q_{K'})} \sqrt{N_K N_{K'}}\, \underset{\sim}{T}_{K,K'}(x) \quad , \tag{B.5}$$

where we note that in light of Eq. (B.2) $\underset{\sim}{F}$ is real. One finds that Eq. (B.3) is equivalent to

$$\frac{\partial N_K}{\partial \underset{\sim}{x}} = - \frac{\partial \underset{\sim}{F}}{\partial Q_K} \tag{B.6a}$$

$$\frac{\partial Q_K}{\partial \underset{\sim}{x}} = \frac{\partial \underset{\sim}{F}}{\partial N_K} \quad . \tag{B.6b}$$

It is then relatively straight-forward to show that the Hamiltonian in Eq. (3.7) produces the equations of motion in Eq. (B.4). More completely, the Hamiltonian of Eq. (3.7) leads to the following equations of motion for electronic and nuclear degrees of freedom in the adiabatic representation:

$$\dot{x}_i = \frac{\partial H}{\partial p_i} = (p_i + F_i)/\mu \tag{B.7a}$$

$$\dot{p}_i = - \frac{\partial H}{\partial x_i} = -\sum_K N_K \frac{\partial E_K}{\partial x_i} - \frac{\partial \underset{\sim}{F}}{\partial x_i} \cdot (\underset{\sim}{p}+\underset{\sim}{F})/\mu \tag{B.7b}$$

$$\dot{Q}_K = \frac{\partial H}{\partial N_K} = E_K + \frac{\partial \underset{\sim}{F}}{\partial N_K} \cdot (\underset{\sim}{p}+\underset{\sim}{F})/\mu \tag{B.7c}$$

$$\dot{N}_K = - \frac{\partial H}{\partial Q_K} = - \frac{\partial \underset{\sim}{F}}{\partial Q_K} \cdot (\underset{\sim}{p}+\underset{\sim}{F})/\mu \quad . \tag{B.7d}$$

References

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Figure Captions

1. Electronic transition probability for the 2-state model, as a function of the parameter p. The primitive classical (-·-·) and quasiclassical (---) results are computed via Eqs. (4.6) and (4.7), respectively, and the uniform semiclassical (····) results via Eqs. (4.8) and (4.12). The correct quantum mechanical transition probability is the solid line (——) $P_{2\leftarrow 1} = p$.

2. Percent error, 100 X ($P_{2\leftarrow 1}^{USC}/P_{2\leftarrow 1}^{QM}$ - 1), in the uniform semiclassical transition probability for the 2-state model in the limit of very small ($p \ll 1$) transition probabilities.

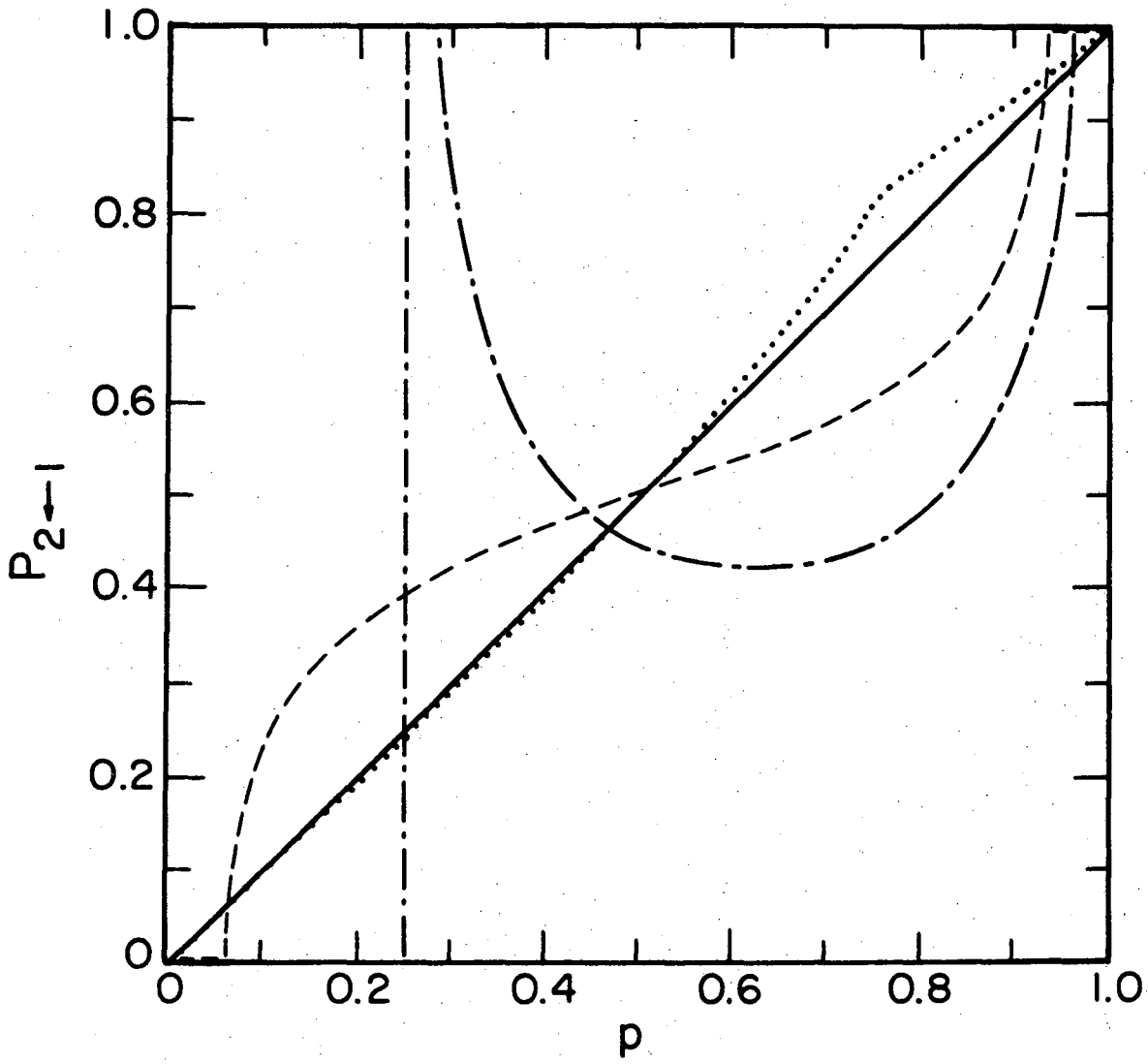

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Figure 1

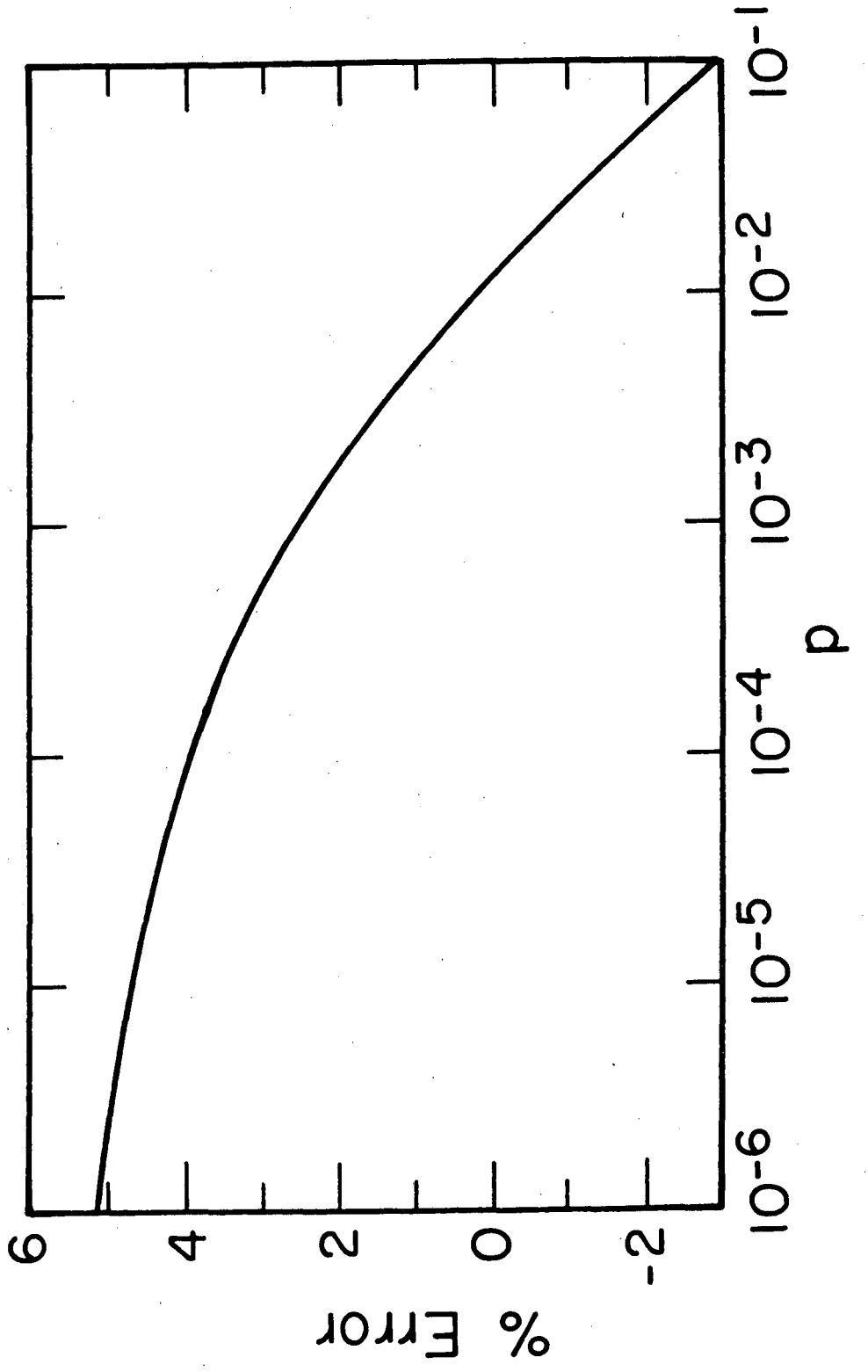

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Figure 2

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