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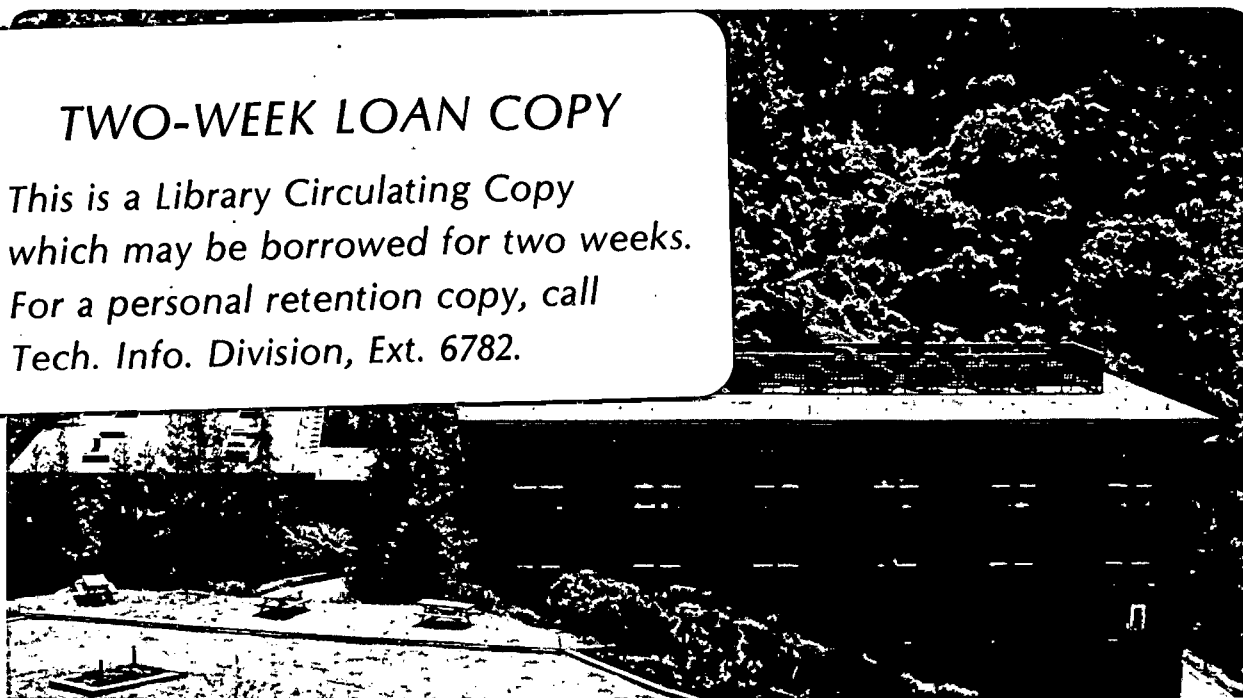Hans-Dieter Meyer and William H. Miller

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ANALYSIS AND EXTENSION OF SOME

RECENTLY PROPOSED CLASSICAL MODELS

FOR ELECTRONIC DEGREES OF FREEDOM

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Abstract

This paper analyzes various methods that have been developed recently for constructing a classical model for a finite set of quantum mechanical states (_electronic_ states for our applications) and also shows how one of them, the spin matrix mapping method of Meyer and Miller, can be generalized in two aspects. First, it is shown how the methodology can be modified to obtain a classical model of any desired number of degrees of freedom, rather than only one degree of freedom as before. Second, it is shown how the method can be applied in the adiabatic representation, so as to be able to use directly the adiabatic potential energy surfaces and non-adiabatic coupling elements produced by a quantum chemistry calculation.

I. Introduction

In recent papers[1-4] several methods have been introduced to model classically the electronic degrees of freedom in a molecular collision. The motivation for this work is to combine the usefulness of a classical mechanical description of heavy particle motion (i.e., translation, rotation, and vibration) with a dynamically consistent approach that treats all degrees of freedom, electronic and heavy particle, on the same dynamical footing (and thus classically). It has been noted that models which fail to treat all degrees of freedom on the same dynamical footing will not describe certain dynamical effects correctly. Encouraging results have been obtained in applications of this model to quenching of fluorine atoms, $F(^2P_{1/2}) \rightarrow F(^2P_{3/2})$, by collisions with H^+, Xe, and H_2. The purpose of the present paper is to generalize and extend these methods for obtaining a classical Hamiltonian that corresponds to a finite set of quantum mechanical states (electronic states for the applications we have in mind, although this is of course not necessary).

There are basically two methods that have been used to derive the classical Hamiltonian for a non-adiabatic collision system (both of which lead to the same results for the applications made thus far): the classical pseudo-potential (CPP) method[2] and the spin matrix mapping (SMM) method.[4] The classical analog of Meyer and Miller,[3] which seems to be more exact but more difficult to apply in general, gives a different Hamiltonian from the methods mentioned above in the general case, although for the specific case of two states all the various methods lead to precisely the same result, i.e., the same classical Hamiltonian.

The SMM method, as it was derived by Meyer and Miller,[4] has the

disadvantage of always leading to a classical electronic Hamiltonian

with only one degree of freedom.   The CPP method of McCurdy,

Meyer and Miller,[2] on the other hand, yields as many electronic degrees

of freedom as are physically meaningful. This latter method, briefly,

consists of four steps:

    1. Write down the full classical Hamiltonian, treating all the

electrons and nuclei as classical particles. (One may simplify things

by considering only the _active_ electrons, the result is the same.)

    2. Change all the coordinates and momenta of the electronic part

of the Hamiltonian to the appropriate set of action-angle variables.

    3. Identify the "relevant" electronic degrees of freedom--i.e., those

whose action variable can be changed by the collision--and average the

Hamiltonian over all the angle variables of the other electronic degrees

of freedom. By so doing the Hamiltonian becomes independent of all the

angle variables one has averaged over, and their canonically conjugate

action variables become constants of motion on which the Hamiltonian depends

only parametrically.

    4. Equate the potential functions, which due to the averaging process

now depend only on the "relevant" electronic degrees of freedom, to the

quantal diabatic potential matrix.

    The fourth step is usually the most difficult part, and there seems to

be no totally unambiguous way to determine the dependence of the parameters

in the classical Hamiltonian for the general case, although it can be done

for some special cases.

    The general idea of the CPP approach, however, is clear. Although one

starts with a Hamiltonian that treats all the electrons classically--which

of course might be a very poor approximation--one arrives at a perfectly

reasonable classical Hamiltonian since one concentrates on the few degrees

of freedom

which are relevant to the scattering process. The motion of these few

degrees of freedom (often a collective degree of freedom, such as the

z-component of the angular momentum of all the electrons of one molecule)

is governed by potentials which are generated not only by the pair-potentials

(i.e., the Coulomb potentials) but also by the motion of all the degrees of

freedom that have been excluded. The many body problem to obtain these

potentials is, of course, solved quantum mechanically, i.e., one makes

use of the potential energy surfaces supplied by quantum chemistry. A

very trivial example may be illustrative. Suppose none of the electronic

states are excited during the collision. The prescription is then to

average over all the angle variables, and the averaged potential will

depend only on the nuclear coordinates. Step four of the procedure

described above becomes trivial since one simply identifies this potential

with the adiabatic Born-Oppenheimer potential surface. Thus one arrives

at the Hamiltonian which is commonly used to study collision

induced rotational and vibrational transitions in molecules. This example

also shows that one may indeed neglect all the "inactive" electrons from

the very beginning.

In a way the SMM-method accomplishes much the same result as the

CPP-method. The quantum chemists "condense" the many body electronic

problem to a small diabatic potential matrix, and the SMM-method "condenses"

this matrix to a classical Hamiltonian of one degree of freedom. Thus

this method achieves the same "reduction of degrees of freedom" but it

does so to the extreme: One always arrives at an electronic Hamiltonian

with one degree of freedom, regardless of how many degrees of freedom are

physically meaningful. In Section III, however, we will show how this

limitation of the SMM-method can be overcome to yield classical Hamiltonians of as many degrees of freedom as the physical problem requires.

As applied thus far, both the CPP-method and the SMM-method make use of the diabatic electronic representation of the scattering process. Quantum chemists, however, usually calculate the (diagonal) matrix of adiabatic potential surfaces and the nonadiabatic coupling elements. Although techniques to transform the adiabatic potential surfaces and the nonadiabatic coupling elements to the diabatic potential matrix are well established in the literature,[5-7] it is desirable to make use of the adiabatic representation directly. How this can be achieved for the SMM-method is shown in Sectin IV.

In the following section we first discuss an ambiguity of the SMM-method, namely the fact that different choices of the basis set which is used to obtain the matrix representation of the Hamiltonian may lead to physically different classical Hamiltonians. How to remove this ambiguity, i.e., how to choose the appropriate basis set, is also discussed in Section II.

II. Quantal and Classical Dynamics--The Effect of a Unitary Transformation.

A classical Hamiltonian derived from a hermitian matrix via the classical analog of Meyer and Miller[3] has the desirable property that a unitary transformation of the Hamiltonian matrix corresponds to a canonical transformation of the classical Hamiltonian. Consequently, different basis sets used to express the quantal Hamiltonian in a matrix representation do not lead to physically different classical Hamiltonians, and thus all results are independent of the particular matrix representation used. Since the classical analog and the SMM-method yield the same classical Hamiltonian for the two state case, F=2, all this holds also for the SMM-method if F=2. For F > 2, however, one is confronted with the problem that for the SMM-method a unitary transformation of the quantal Hamiltonian matrix in general does not correspond to a canonical transformation of the classical Hamiltonian. Hence different choices of the basis set may lead to physically different classical Hamiltonians. This arbitrariness of the choice of the basis set introduces some ambiguity in the classical Hamiltonian which has to be overcome. It is the aim of this section to show how the "best" matrix representation can be found.

The "best" representation is certainly the one in which quantal and corresponding classical motion are most similar. It is therefore useful to investigate the relationship between quantal and classical dynamics, which is most conveniently done by evaluating quantum commutators and classical Poisson brackets.[8] It is shown in Appendix A that the Poisson bracket of the action variable m with H corresponds to -i times the commutator of M and H, where M is the (diagonal) matrix representation of the spin operator S_z. Hence

$$\dot{\underset{\sim}{M}} = -i[\underset{\sim}{M},\underset{\sim}{H}] \leftrightarrow \{m,H\} = \dot{m} \tag{2.1}$$

One therefore obtains an Ehrenfest-like theorem for the quantity m,

$$\frac{d}{dt} m_{CL} = \frac{d}{dt} <m>_{QM} \quad , \tag{2.2}$$

where the bracket denotes the quantum mechanical expectation value. The Ehrenfest theorem does not apply, however, to powers of m, i.e.,

$$\frac{d}{dt} m^2_{CL} \neq \frac{d}{dt} <m^2>_{QM} \tag{2.3a}$$

$$\frac{d}{dt} m^3_{CL} \neq \frac{d}{dt} <m^3>_{QM} \quad , \tag{2.3b}$$

and in general also

$$\frac{d}{dt} f(m,q)_{CL} \neq \frac{d}{dt} <f(m,q)>_{QM} \tag{2.3c}$$

where f denotes some function of m and q.

One can now understand the effect of a unitary transformation quite clearly: The SMM-method always forces the action variable m, i.e., the variable which corresponds to the quantum number labeling of the particular basis set chosen, to behave quantum-like, but functions of the action-angle variables will in general not do so. By changing the basis set, i.e., performing a unitary transformation, one forces another action variable to behave quantum-like. Since this new action variable, which can be thought of being a function of the old action angle variables, did not behave quantum-like in the old representation, the dynamics resulting from applying the SMM-method to the old and new representation must be different. This explains not only the fact that a unitary transformation of the quantal Hamiltonian does

in general not correspond to a canonical transformation of the corresponding

classical Hamiltonian, but is also shows which is the appropriate basis

set to use. One should choose the representation in which the indices are

related in the most direct way possible to the desired quantities (transition

probabilities, etc.).

To be more specific, consider the $F-H_2$ case for which F=3. Rebentrost

and Lester[9] calculated the diabatic potential matrix in the cartesian basis

set $\{|x>, |y>, |z>\}$,

$$\underset{\sim}{V}_{cart} = \begin{pmatrix} H_{xx} & 0 & 0 \\ 0 & H_{yy} & H_{yz} \\ 0 & H_{yz} & H_{zz} \end{pmatrix} \quad , \qquad (2.4)$$

where the four functions H_{xx}, H_{yy}, H_{zz} and H_{yz} are real. Obviously the

cartesian representation is not the appropriate one to use, for the collision

induced transitions occur between states which can be labeled with the

quantum number j--the total electronic angular momentum of the fluorine

atom. j is related to the cartesian basis set in a rather indirect and

complicated fashion. Thus use of the cartesian representation would yield

a classical Hamiltonian which is totally unreliable for studying fine

structure transitions. j, however, depends on m_L--the projection of the

electronic orbital angular momentum onto some quantization axis--in a much

simpler way. It is thus natural--and of course also done in the quantum

mechanical treatments of the problem--to change from the cartesian basis

set to the angular momentum basis set $\{|m_L>\}$, $m_L = -1,0,1$. The unitary matrix

$$\underset{\sim}{U} = \begin{pmatrix} -\frac{\sqrt{2}}{2} & 0 & \frac{\sqrt{2}}{2} \\ -i\frac{\sqrt{2}}{2} & 0 & -i\frac{\sqrt{2}}{2} \\ 0 & 1 & 0 \end{pmatrix} \qquad (2.5)$$

effects this transformation, as discussed in reference 4. Thus one
obtains for the potential matrix in the angular momentum representation

$$\mathbf{V} = \mathbf{U}^{\dagger}\mathbf{V}_{cart}\mathbf{U} = \begin{pmatrix} \bar{H} & i\dfrac{H_{yz}}{\sqrt{2}} & -\Delta \\ -i\dfrac{H_{yz}}{\sqrt{2}} & H_{zz} & -i\dfrac{H_{yz}}{\sqrt{2}} \\ -\Delta & i\dfrac{H_{yz}}{\sqrt{2}} & \bar{H} \end{pmatrix} \tag{2.6}$$

where $\bar{H}$ and Δ are given by

$$\bar{H} = \frac{1}{2}(H_{xx} + H_{yy}) \tag{2.7a}$$

$$\Delta = \frac{1}{2}(H_{xx} - H_{yy}) \quad . \tag{2.7b}$$

Applying the SMM-method to Eq. (2.6) then gives the corresponding
classical function

$$V(m_L, q_{m_L}) = (1 - m_L^2)H_{zz} + m_L^2\bar{H}$$
$$- 2m_L\sqrt{L^2 - m_L^2}\, H_{yz}\sin q_{m_L} - (L^2 - m_L^2)\Delta\cos 2q_{m_L} \tag{2.8}$$

where s, m, and q are replaced by L, m_L and q_{m_L} in order to be consistent
with Section III of reference 4.

There is, however, more than one angular momentum representation.
Consider, for example, a rotation by an angle ϕ around the z axis
(i.e., the quantization axis). The unitary matrix which performs this
transformation—for this topic we are again discussing the general F-level
case—is given by

$$U_{k',k}(\phi) = \delta_{k',k} \, e^{-i\phi m_k} \qquad (2.9)$$

where

$$m_k = k - 1 - s = k - \frac{F+1}{2}$$

as defined in the Appendix of reference 4. Since

$$\underset{\approx}{M}^{(j)'} \equiv \underset{\approx}{U}^{\dagger}(\phi) \cdot \underset{\sim}{M}^{(j)} \cdot \underset{\approx}{U}(\phi) = \underset{\approx}{M}^{(j)} \qquad (2.10a)$$

$$\underset{\approx}{C}^{(j,\ell)'} \equiv \underset{\approx}{U}^{\dagger}(\phi) \cdot \underset{\approx}{C}^{(j,\ell)} \cdot \underset{\approx}{U}(\phi) = \cos\ell\phi \, \underset{\approx}{C}^{(j,\ell)} - \sin\ell\phi \, \underset{\approx}{S}^{(j,\ell)} \qquad (2.10b)$$

$$\underset{\approx}{S}^{(j,\ell)'} \equiv \underset{\approx}{U}^{\dagger}(\phi) \cdot \underset{\approx}{S}^{(j,\ell)} \cdot \underset{\approx}{U}(\phi) = \cos\ell\phi \, \underset{\approx}{S}^{(j,\ell)} + \sin\ell\phi \, \underset{\approx}{C}^{(j,\ell)} \qquad (2.10c)$$

where again $\underset{\approx}{M}^{(j)}$, $\underset{\approx}{C}^{(j,\ell)}$ and $\underset{\approx}{S}^{(j,\ell)}$ are defined in the Appendix of
reference 4, one sees that this unitary transformation corresponds
to the transformation

$$m' = m \qquad (2.11a)$$

$$q' = q + \phi \qquad (2.11b)$$

which, of course, is a canonical one.   Hence all the angular momentum
representations which differ by just a rotation around the quantization
axis are physically identical.   One may use this fact and choose $\phi = \pi/2$
in order to make the diabatic potential matrix [Eq. (2.6)] real,

$$\underset{\approx}{V}' = \underset{\approx}{U}^{\dagger}(\pi/2) \cdot \underset{\approx}{V} \cdot \underset{\approx}{U}(\pi/2) = \begin{pmatrix} \bar{H} & \dfrac{H_{yz}}{\sqrt{2}} & \Delta \\ \dfrac{H_{yz}}{\sqrt{2}} & H_{zz} & \dfrac{H_{yz}}{\sqrt{2}} \\ \Delta & \dfrac{H_{yz}}{\sqrt{2}} & \bar{H} \end{pmatrix} \quad . \qquad (2.12)$$

There are, however, other unitary transformations which map an angular momentum basis set onto an angular momentum basis set. One may, for example, choose the x-axis to be the quantization axis rather than the z-axis. In the F-H_2 case this corresponds to the quantization axis being perpendicular to the plane of the three atoms rather than being along the vector between F and the center of mass of H_2. The unitary transformation from the cartesian representation to this new angular momentum representation is defined by the matrix

$$\underset{\approx}{\hat{U}} = \begin{pmatrix} 0 & 1 & 0 \\ -\dfrac{\sqrt{2}}{2} & 0 & \dfrac{\sqrt{2}}{2} \\ -i\dfrac{\sqrt{2}}{2} & 0 & -i\dfrac{\sqrt{2}}{2} \end{pmatrix} \qquad (2.13)$$

which leads to the diabatic potential matrix

$$\underset{\approx}{\hat{V}} = \underset{\approx}{\hat{U}}^{\dagger} \cdot \underset{\approx}{V}_{cart} \cdot \underset{\approx}{\hat{U}} = \begin{pmatrix} \dfrac{H_{zz} + H_{yy}}{2} & 0 & \dfrac{H_{zz} - H_{yy}}{2} + i\,H_{yz} \\ 0 & H_{xx} & 0 \\ \dfrac{H_{zz} - H_{yy}}{2} - i H_{yz} & 0 & \dfrac{H_{zz} + H_{yy}}{2} \end{pmatrix}$$

$$(2.14)$$

and to the corresponding classical function

$$\hat{V}(\hat{m}_L, \hat{q}_{m_L}) = (1-\hat{m}_L^2)H_{xx} + \hat{m}_L^2 \frac{H_{zz} + H_{yy}}{2}$$

$$+ (L^2 - \hat{m}_L^2)[\frac{H_{zz} - H_{yy}}{2} \cos 2\hat{q}_{m_L} + H_{yz} \sin^2 \hat{q}_{m_L}] \quad . \qquad (2.15)$$

On the otherhand, with the aid of the generator[12]

$$F_2(q_{m_L}, \hat{m}_L) = -L \cos^{-1} (\frac{L \sin q_{m_L}}{\sqrt{L^2 - \hat{m}_L^2}})$$

$$+ \hat{m}_L \cos^{-1} (\frac{\hat{m}_L \tan q_{m_L}}{\sqrt{L^2 - \hat{m}_L^2}}) \qquad (2.16)$$

the classical function Eq. (2.8) can be transformed to

$$V(\hat{m}_L, \hat{q}_{m_L}) = (1-\hat{m}_L^2)H_{xx} + \hat{m}_L^2 \frac{H_{zz} + H_{yy}}{2}$$

$$+ (L^2 - \hat{m}_L^2)[\frac{H_{zz} - H_{yy}}{2} \cos 2\hat{q}_{m_L} + H_{yz} \sin 2\hat{q}_{m_L}]$$

$$+ (L^2 - 2) \frac{H_{xx} - H_{zz}}{2} \quad . \qquad (2.17)$$

Comparing Eqs. (2.15) and (2.17), one sees that changing the quantization axis corresponds to a canonical transformation only if L^2 is replaced by its quantum mechanical value

$$L^2 \to L(L+1) = 2 \quad ,$$

rather than making the semiclassical Langer-modification

$$L^2 \to (L + \frac{1}{2})^2 = 2.25 \quad .$$

Since the choice $L^2 \to L(L+1)$ would give raise to uneven "boxes" used in

the classical histogram approximation (cf. Section III of reference 4),

it is probably desirable to retain the Langer modification and live with

the small ambiguity due to the various possible choices of the quantization

axis. For the three state case, F=3, it can in fact be shown that for

arbitrary rotations of the quantization axis, a quantum unitary transformation

does correspond to a classical canonical transformation if one replaces s^2

by $s(s+1)$; i.e., with this replacement all angular momentum representations

are equivalent. This comes from the fact that, for F=3 and s^2 replaced by

$s(s+1)$, not only m but also $(s^2-m^2)^{1/2}\cos q$ and $(s^2-m^2)^{1/2}\sin q$ follow the

quantal motion, i.e.,

$$\frac{d}{dt} m_{CL} = \frac{d}{dt} <m>_{QM} = \frac{d}{dt} <S_z>$$

$$\frac{d}{dt} [(s^2-m^2)^{1/2}\cos q]_{CL} = \frac{d}{dt} <(s^2-m^2)^{1/2}\cos q>_{QM} = \frac{d}{dt} <S_x>$$

$$\frac{d}{dt} [(s^2-m^2)^{1/2}\sin q]_{CL} = \frac{d}{dt} <(s^2-m^2)^{1/2}\sin q>_{QM} = \frac{d}{dt} <S_y>$$

For F > 3, however, this is no longer the case.

To summarize, the classical model obtained via the SMM-method for the

general F-level case depends on the particular representation one chooses

for the quantum Hamiltonian matrix; i.e., a unitary transformation of the

Hamiltonian matrix does not in general correspond to a canonical transforma-

tion of the classical Hamiltonian. The resolution of this indefinite

situation is a qualitative one: one chooses the matrix representation of

the Hamiltonian to be one for which the quantum numbers (i.e., matrix indices)

are most closely related to the physical quantities of interest, such as angular momentum quantum numbers. For the 2-state case (F=2), however, this ambiguity does not exist, and for the 3-state case the ambiguity is removed if the replacement $(s^2)_{CL} \to s(s+1)$, s=1 is made and if the unitary transformations in question are rotations in space, e.g., if the various representations in question are all angular momentum representations.

Even for F=3, however, we consider it preferable to use the Langer modification, $(s^2)_{CL} \to (s + \frac{1}{2})^2$, s=1, and live with the minor dependence on the choice of quantization axis.

III. The SMM-Method for More than One Degree of Freedom.

The SMM-method makes use of the matrix representation of the electronic Hamiltonian

$$H_{\alpha',\alpha} = \langle \psi_{\alpha'} | H | \psi_{\alpha} \rangle \tag{3.1}$$

where H denotes the electronic Hamiltonian operator and ψ_{α} the electronic wavefunction. In general α will be a composite index. Consider for example the collision of an F-atom with a closed shell atom or molecule. The electronic wavefunction, and hence the matrix, may be thought of as labeled by

$$\alpha = (\beta, S, L, m_S, m_L) \quad , \tag{3.2}$$

where β is a composite index containing all the quantum numbers of the closed shell molecule, the quantum numbers of the inner shell of the fluorine atom, and the principal quantum number of its outer shell. S, L, m_S, m_L are the electronic spin and orbital angular momenta and their projections onto the intermolecular axis, respectively. The fluorine atom is assumed to be in the ^2P state and the collision energy so low that only m_S and m_L may change during the collision. Thus the multi-index β and the indices S and L are "frozen", i.e., have the values $\beta = \beta_0$, $S = \frac{1}{2}$ and L = 1 throughout the collision. Hence α is essentially a double index and instead of considering $H_{\alpha',\alpha}$ one should consider $H_{m_S',m_L',m_S m_L}$. To be physically correct, therefore, the classical Hamiltonian must have two degrees of freedom, namely the classical counterparts of m_S and m_L.

To make all this more precise, suppose on physical grounds the index α can be written as a multi-index

$$\alpha = (\beta, k_1, k_2, \ldots, k_r)$$

where β represents all the "frozen" quantum numbers. The corresponding classical Hamiltonian should thus depend on r degrees of freedom, i.e.,

$$H_{\alpha',\alpha} = H_{k_1',k_2', \ldots, k_r', k_1 k_2, \ldots, k_r} \rightarrow H(n_1, q_1, n_2, q_2, \ldots, n_r, q_r) \quad .$$

To be specific, consider the case $r=2$; the generalization to arbitrary r will be obvious. The Hamiltonian matrix will be written as

$$H_{K'k',Kk} \quad ,$$

with

$$K',K = 1,2, \ldots, F \qquad (3.3a)$$

$$k',k = 1,2, \ldots, f \quad ; \qquad (3.3b)$$

i.e., there are F states associated with the K degree of freedom and f states with the k degree of freedom, so that H is an $(F \cdot f) \times (F \cdot f)$ matrix. To obtain a classical Hamiltonian one first considers $H_{K'k',Kk}$ as a $F \times F$ matrix of $f \times f$ submatrices. One then applies the SMM-method to all the F^2 $f \times f$ submatrices and obtains a $F \times F$ matrix whose matrix elements are functions of m and q. One then applies the SMM-method to this $F \times F$ matrix $H_{K',K}(m,q)$, yielding the desired function $H(m,q,M,Q)$. It is shown in Appendix B how to proceed in detail. It is also shown there that considering $H_{K'k',Kk}$ as a $F \times F$ matrix of $f \times f$ submatrices or as a $f \times f$ matrix of $F \times F$ submatrices leads to the same classical Hamiltonian.

Let us return to the example of fine-structure transitions in the fluorine atom. The electronic Hamiltonian is

$$H = 2B\vec{L}\cdot\vec{S} + V \quad , \tag{3.4}$$

where V is the interaction operator, and $\vec{L}$ and $\vec{S}$ are the orbital and spin angular momentum operators, respectively, i.e., $2B\,\vec{L}\cdot\vec{S}$ is the spin-orbit-coupling operator and the constant B is chosen to give the correct term splitting. Taking matrix elements yields

$$H_{m_S',m_L',m_S m_L} = 2B[(L_x)_{m_L'm_L} \cdot (S_x)_{m_S'm_S} +$$

$$(L_y)_{m_L'm_L} (S_y)_{m_S'm_S} + (L_z)_{m_L'm_L} \cdot (S_z)_{m_S'm_S}]$$

$$+ V_{m_L'm_L} \delta_{m_S'm_S} \tag{3.5}$$

where L_x, S_x, etc., are the matrix representations of the angular momentum operators for $S = \frac{1}{2}$ and $L = 1$, and the matrix V is given by Eq. (2.6). Applying the (generalized) SMM-method described above and in Appendix B to Eq. (3.5) yields

$$H(m_S, q_{m_S}, m_L, q_{m_L}) = 2B[m_L\, m_S + \sqrt{L^2 - m_L^2}\,\sqrt{S^2 - m_S^2}\,\cos(q_{m_L} - q_{m_S})]$$

$$+ (1 - m_L^2)H_{zz} + m_L^2\,\bar{H} - 2m_L\sqrt{L^2 - m_L^2}\,H_{yz}\,\sin q_{m_L}$$

$$- (L^2 - m_L^2)\,\Delta\,\cos 2q_{m_L} \tag{3.6}$$

which one recalls is identical to the electronic Hamiltonian of references 2 and 4, except for the constant, and hence unimportant, term $B(L^2 + S^2)$. Adding this term to the Hamiltonian, the spin orbit

interaction can be written as

$$B\ j^2 \tag{3.7}$$

with

$$j^2 = |\vec{L} + \vec{S}|^2 \quad , \tag{3.8}$$

in both the quantal and the classical Hamiltonian.

The electronic Hamiltonian was derived here in the uncoupled (cf. reference 4) $|m_S m_L\rangle$ representation, whereas the object of the method is to describe Δj-transitions. Thus, in light of the discussion of Section II, the coupled representation $|j, m_j\rangle$ should be the better one. Unfortunately the SMM-method does not work in the $|j, m_j\rangle$ representation because m_j varies from $-j$ to j rather than between fixed numbers. The electronic Hamiltonian in the $|j, m_j\rangle$ representation is thus a matrix of submatrices of which some are non-square matrices, and the SMM-method can obviously not be applied to non-square matrices.

In reference 4 we derived the classical function which corresponds to the interaction operator V via the simpler minded version of the SMM-method which always gives Hamiltonians of one degree of freedom. It worked because $V_{m_S', m_L', m_S m_L}$ is diagonal in and independent of m_S. Hence the corresponding function $V(m_S, q_{m_S}, m_L, q_{m_L})$ depends on neither q_{m_S} nor m_S. For the spin-orbit coupling term, however, one must use the generalized SMM-method and in reference 4 this was circumvented by making use of the CPP-analysis. The structure of this term is so simple, however, that it is clear from the very beginning what the corresponding classical function must be.

IV. The Adiabatic Representation.

This section shows how the SMM-method can make use of the adiabatic representation directly. The idea is simply to apply the SMM-method to the matrix of nonadiabatic coupling elements.

F. T. Smith[5] has shown that in the adiabatic representation the Schrödinger Equation can be written in matrix form as

$$\frac{1}{2M} [\frac{\hbar}{i} \frac{\partial}{\partial R} \underset{\approx}{1} + \underset{\approx}{T}]^2 \cdot \underset{\sim}{\chi} + \underset{\approx}{U} \cdot \underset{\sim}{\chi} = E\underset{\sim}{\chi} \qquad (4.1)$$

where $\underset{\sim}{\chi}$ denotes the vector of heavy particles wavefunctions, $\underset{\approx}{U}$ the adiabatic potential matrix, and $\underset{\approx}{T}$ is the matrix of coupling elements defined by

$$T_{k',k}(R) = \int \psi_{k'}^*(r,R) \frac{\hbar}{i} \frac{\partial}{\partial R} \psi_k(r,R) dr \qquad . \qquad (4.2)$$

Here ψ_k stands for the kth adiabatic electronic wavefunction, and r and R represent all electronic and nuclear coordinates, respectively. $\underset{\approx}{T}$ can be shown to be hermitian.

In order to keep the notation simple we assume that the electronic Hamiltonian has only one "relevant" degree of freedom. After applying the SMM-method to both $\underset{\approx}{T}$ and $\underset{\approx}{U}$, Eq. (4.1) strongly suggest that the classical Hamiltonian in the adiabatic representation is given by

$$H(P,R,n,q) = \frac{1}{2M} [P + T(n,q,R)]^2 + U(n,R) \qquad (4.3)$$

where the classical function U(n,R) is q-independent since $\underset{\approx}{U}$ is diagonal.

The quantal Hamiltonian in the adiabatic representation can be
obtained by applying a unitary transformation to the Hamiltonain in
the diabatic representation. Thus it is tempting to assume that there
exists a canonical transformation which transforms the classical Hamiltonian
of the diabatic representation to the classical Hamiltonian in the adiabatic
representation. In fact for the two state case, F=2, this has already been
proved by Miller and McCurdy[1,10] and--using a different method--by Meyer
and Miller.[3,11] If the number of states F is larger than two, however,
a canonical transformation connecting the Hamiltonians of the diabatic
and the nonadiabatic representation cannot be found. This is due to the
fact, discussed in Section II, that for F > 2 a unitary transformation of
the quantum Hamiltonian does not in general correspond to a canonical
transformation of the corresponding classical Hamiltonian derived via
the SMM-method. The fact that we do get the correct classical Hamiltonian
for the two state case, however, leads to the assumption that Eq. (4.3)
is the correct classical Hamiltonian--i.e., the best possible classical
approximation--for using the adiabatic representation.

To emphasize this point we apply Eq. (4.3) to a known example which
is very much the same as the one studied in our previous paper,[4] namely
the collinear atom-diatom (harmonic oscillator) collision system. The
Hamiltonian of this system is

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} + \frac{1}{2}\mu\,\omega_0^2 r^2 + V(R,r) \quad . \qquad (4.4)$$

For test purposes the vibrational degree of freedom will be considered to
be the quantum-like degree of freedom, i.e., to play the role of the

electronic degrees of freedom. Again, $V(R,r)$ is expanded in a Taylor's series in r through terms in r^2, i.e., $V(R,r)$ is replaced by

$$V_0(R) + V_1(R) r + \frac{1}{2} V_2(R) r^2 \qquad (4.5)$$

where

$$V_n(R) = \frac{\partial^n V(R,r)}{\partial r^n}\bigg|_{r=0} \qquad . \qquad (4.6)$$

Assuming this form of the potential, the Hamiltonian Eq. (4.4) can be written as

$$H(R,P,r,p) = \frac{P^2}{2M} + \frac{p^2}{2\mu} + \frac{1}{2}\mu\,\omega^2(R)\,[r - r_0(R)]^2$$

$$+ V_0(R) + [2\mu\,\omega^2(R)]^{-1}\,V_1(R) \qquad (4.7)$$

with

$$\omega^2(R) = \omega_0{}^2 + \mu^{-1}\,V_2(R) \qquad (4.8a)$$

and

$$r_0 = -\,[\mu\,\omega^2(R)]^{-1}\,V_1(R) \qquad . \qquad (4.8b)$$

This form of the Hamiltonian is well suited for the transformation to the adiabatic representation. We first transform the classical Hamiltonian to the adiabatic representation using an F_3-Generator.[12] Denoting the "old" variables as $\{P,R,p,r\}$ and the "new" variables as $\{P',R',\hbar n,q\}$,

where we use $\hbar n$ as action variable rather than n in order to make n dimensionless, the generator is given by

$$F_3(P,R',p,q) = -PR' + \frac{p^2 \, \cot q}{2\mu \, \omega(R')}$$

$$+ \frac{\hbar q}{2} - p \, r_0(R') \quad . \qquad (4.9)$$

The canonical transformation is now specified by the usual derivative relations

$$R = - \frac{\partial F_3}{\partial P} = R' \qquad (4.10a)$$

$$P' = - \frac{\partial F_3}{\partial R'} = P + \frac{d\omega}{dR'} \, \frac{p^2 \, \cot q}{2\mu \, \omega^2} + p \, \frac{dr_0}{dR'} \qquad (4.10b)$$

$$r = - \frac{\partial F_3}{\partial p} = - \frac{p \, \cot q}{\mu \omega} + r_0 \qquad (4.10c)$$

$$\hbar n = - \frac{\partial F_3}{\partial q} = \frac{p^2}{2\mu \, \omega \, \sin^2 q} - \frac{\hbar}{2} \quad . \qquad (4.10d)$$

Thus the "old" variables are given in terms of the "new" ones by

$$r - r_0 = - \hbar \, \frac{\sqrt{2n+1}}{\sqrt{\mu\hbar\omega}} \quad \cos q \qquad (4.11a)$$

$$p = \sqrt{2n+1} \, \sqrt{\mu\hbar\omega} \, \sin q \qquad (4.11b)$$

$$R = R' \qquad (4.11c)$$

$$P = P' - \frac{d\omega}{dR'} \, \frac{\hbar}{2\omega} \, (n + \frac{1}{2}) \, \sin 2q$$

$$- \frac{dr_0}{dR'} \, \sqrt{2n+1} \, \sqrt{\mu\hbar\omega} \, \sin q \quad , \qquad (4.11d)$$

and using Eqs. (4.8) and (4.11c) gives

$$\frac{d\omega}{dR'} = \frac{1}{\mu\omega} \frac{dV_2}{dR'} \tag{4.12a}$$

$$\frac{dr_0}{dR'} = \frac{-1}{\mu\omega^2} \frac{dV_1}{dR'} + \frac{V_1}{\mu^2\omega^4} \frac{dV_2}{dR'} \quad . \tag{4.12b}$$

If one now substitutes Eqs. (4.11) and (4.12) into Eq. (4.2) and drops
the prime from R and P, one obtains the classical Hamiltonian in the
adiabatic representation:

$$H(R,P,n,q) = \frac{1}{2M} [P + \frac{1}{\omega} \sqrt{\frac{\hbar}{\mu\omega}} (\frac{dV_1}{dR} - \frac{V_1}{\mu\omega^2} \frac{dV_2}{dR}) +$$

$$\sqrt{2n+1} \sin q - \frac{dV_2}{dR} \frac{\hbar}{2\mu\omega^2} (n + \frac{1}{2}) \sin 2q]^2$$

$$+ (n + \frac{1}{2})\hbar\omega + [2\mu\omega^2]^{-1} V_1^2(R) + V_0(R) \quad . \tag{4.13}$$

If one now goes back to Eq. (4.7) and looks upon it as the quantum
Hamiltonian, one notices that the (internal) adiabatic eigenfunctions
are always harmonic oscillator eigenfunctions. The interaction merely
shifts the frequency ω and the location of the equilibrium r_0. Thus the
nonadiabatic coupling elements are given by

$$T_{k',k}(R) = -i\hbar \frac{d\omega}{dR} \int \psi_{k'}(r) \frac{\partial}{\partial\omega} \psi_k(r) \, dr$$

$$-i\hbar \frac{dr_0}{dR} \int \psi_{k'}(r) \frac{\partial}{\partial r_0} \psi_k(r) \, dr \tag{4.14}$$

where $\psi_k(r)$ denotes the kth harmonic oscillator eigenfunction

$$\psi_k(r) = (2^k \, k!)^{-1/2} \, (\frac{\mu\omega}{\pi\hbar})^{1/4} \, e^{-1/2 \, z^2} \, H_k(z) \tag{4.15}$$

and

$$z = \sqrt{\frac{\mu\omega}{\hbar}} \, (r - r_0)$$

where $H_k(z)$ is the kth Hermite polynomial. The arithmetic is easily done, and one obtains

$$T_{k',k}(R) = (\frac{dV_1}{dR} - \frac{V_1}{\mu\omega^2} \frac{dV_2}{dR})\sqrt{\frac{\hbar}{2\mu\omega}} \, \frac{i}{\omega} \{\delta_{k',k-1} \sqrt{k'} - \delta_{k'-1,k} \sqrt{k} \}$$

$$- \frac{dV_2}{dR} \frac{\hbar}{4\mu\omega^2} \, i\{\delta_{k',k-2} \sqrt{k'(k'+1)} - \delta_{k'-2,k} \sqrt{k(k+1)}\} \, . \tag{4.16}$$

The adiabatic potential matrix is simpler to evaluate:

$$U_{k',k} = \delta_{k',k} \{(k + \frac{1}{2})\hbar\omega(R) + V_0(R) + [2\mu\omega^2(R)]^{-1} \, V_1^2(R)\} \, . \tag{4.17}$$

Trucating these infinite matrices to F x F matrices and substituting them into Eq. (4.1) yields the usual set of coupled equations in the adiabatic representation. On the other hand, applying the SMM-method to these truncated matrices yields

$$U(n,R) = (n + \frac{1}{2})\hbar\omega(R) + V_0(R) + [2\mu\omega^2(R)]^{-1} \, V_1^2(R) \tag{4.18}$$

$$T(n,q,R) = \frac{1}{\omega} (\frac{dV_1}{dR} - \frac{V_1}{\mu\omega^2} \frac{dV_2}{dR})\sqrt{\frac{\hbar}{\mu\omega}} \, f_F(n) \, \sin q$$

$$- \frac{dV_2}{dR} \frac{\hbar}{2\mu\omega} \, g_F(n) \, \sin 2q \tag{4.19}$$

where, after making the Langer-modification as discussed in reference 4,

$$f_F(n) = \frac{\sqrt{2}}{2} \sqrt{(s + \tfrac{1}{2})^2 - m^2} \sum_{j=0}^{F-2} m^j \sum_{k=1}^{F-1} W_{j,k}^{(1)} \sqrt{k} \qquad (4.20a)$$

$$g_F(n) = \frac{1}{2} [(s + \tfrac{1}{2})^2 - m^2] \sum_{j=0}^{F-3} m^j \sum_{k=1}^{F-2} W_{j,k}^{(2)} \sqrt{k(k+1)} \qquad (4.20b)$$

and

$$m = n - s \qquad .$$

$W_{jk}^{(\ell)}$ and s both depend on the number of states F and are defined in the Appendix of reference 4. The functions $f_F(n)$ and $g_F(n)$ are precisely the functions discussed in Section IIc of reference 4. Substituting Eqs. (4.8) and Eq. (4.19) into Eq. (4.3) gives the classical Hamiltonian via the SMM-method in the adiabatic representation

$$H(R,P,n,q) = \frac{1}{2M} \left[P + \left(\frac{dV_1}{dR} - \frac{V_1}{2\mu\omega^2} \frac{dV_2}{dR} \right) \frac{1}{\omega} \sqrt{\frac{\hbar}{\mu\omega}} f_F(n) \sin q \right.$$

$$\left. - \frac{dV_2}{dR} \frac{\hbar}{2\mu\omega} g_F(n) \sin 2q \right]^2$$

$$+ (n + \tfrac{1}{2})\hbar\omega + V_0 + [2\mu\omega^2]^{-1} V_1^2 \qquad . \qquad (4.21)$$

This Hamiltonian would be identical to the exact one of Eq. (4.13) if the functions $f_F(n)$ and $g_F(n)$ were the exact functions

$$f_{exact}(n) = \sqrt{2n+1}$$

$$g_{exact}(n) = n + \frac{1}{2} \qquad .$$

Figures 1 and 2 of reference 4 show that $f_F(n)$ and $g_F(n)$ seem to converge to the exact functions as $F \rightarrow \infty$, thus indicating that most, and perhaps all, of the error introduced is due to truncation. In any event, the main result of this "test" is that the SMM-method applied to the adiabatic representation gives classical Hamiltonian functions which are of the same "quality" as applying it to the diabatic representation.

V. Concluding Remarks

The Spin-Matrix-Mapping (SMM) method has been re-analyzed in two aspects. First, its relation to the Classical-Pseudo-Potential (CPP) method has been shown. Second, the origin of the ambiguity of the SMM-method which comes from the arbitrariness of the choice of the quantal basis set has been clarified, and a way to identify the appropriate basis set has been proposed. The SMM-method has then been modified to obtain a classical model of any desired number of degrees of freedom. This is an important generalization, since only a very limited number of problems require an electronic Hamiltonian of only one effective degree of freedom. In fact, to derive the electronic Hamiltonian for the F-H_2 collision system, as done in our previous paper,[4] we had to make use of both the SMM-method and the CPP-analysis. Since that electronic Hamiltonian has two degrees of freedom, the SMM-method was applied there to only part of it.

The second generalization was to show how the SMM-method can make use of the adiabatic representation directly. Although for the scattering systems investigated so far we have used a diabatic representation, the direct use of the adiabatic representation might be of great value for other systems. Indeed, more often than not quantum chemistry supplies one with the adiabatic potential curves and the non-adiabatic coupling elements rather than with the diabatic potential matrix. The derivation of the classical Hamiltonian directly from the adiabatic representation not only saves one from having to transform the adiabatic information to the diabatic potential matrix, but the resulting Hamiltonian might also be preferred over the classical Hamiltonian derived from the diabatic representation. This will be the case if the coefficients of the q-dependent part of the Hamiltonian

are significantly smaller in the adiabatic representation than in the diabatic one, i.e., if the electronic dynamics is more nearly adiabatic.

Appendix A

It is useful to introduce non-hermitian matrices and complex functions. One defines the matrices $\underset{\approx}{E}^{(j,\ell)}$ by

$$\underset{\approx}{E}^{(j,\ell)} = \begin{cases} \underset{\approx}{C}^{(j,\ell)} + i\,\underset{\approx}{S}^{(j,\ell)} & \text{if } \ell > 0 \\ M^{(j)} & \text{if } \ell = 0 \\ C^{(j,|\ell|)} - i\,S^{(j,|\ell|)} & \text{if } \ell < 0 \end{cases} \qquad (A.1)$$

and the corresponding classical function by

$$E^{(j,\ell)}(m,q) = m^j (s^2 - m^2)^{|\ell|/2}\, e^{i\ell q} \quad , \qquad (A.2)$$

where the F x F matrices $\underset{\approx}{C}^{(j,\ell)}$, $\underset{\approx}{S}^{(j,\ell)}$ and $\underset{\approx}{M}^{(j)}$ and the number s are defined in the Appendix of reference 4. We also use a notation in which $\hbar = 1$ so that m and q both are dimensionless. One then likewise defines

$$c_{j,\ell} = \begin{cases} \frac{1}{2}(a_{j,\ell} - i\,b_{j,\ell}) & \text{if } \ell > 0 \\ d_j & \text{if } \ell = 0 \\ \frac{1}{2}(a_{j,|\ell|} + i\,b_{j,|\ell|}) & \text{if } \ell < 0 \end{cases} \qquad (A.3)$$

where $a_{j,\ell}$, $b_{j,\ell}$ and d_j are also defined in the Appendix of reference 4. Equivalent to the definitions above are the following equations:

$$
E_{k',k}^{(j,\ell)} = \begin{cases} 2\, V_k^{(j,\ell)}\, \delta_{k'-\ell,k} & \text{if } \ell > 0 \\[2ex] m_k^{\,j}\, \delta_{k',k} & \text{if } \ell = 0 \\[2ex] 2\, V_{k'}^{(j,|\ell|)}\, \delta_{k'-\ell,k} & \text{if } \ell < 0 \end{cases} \qquad \text{(A.4)}
$$

and

$$
c_{j,\ell} = \begin{cases} \dfrac{1}{2} \displaystyle\sum_{k=1}^{F-\ell} W_{j,k}^{(\ell)}\, H_{k+\ell,k} & \text{if } \ell > 0 \\[3ex] \displaystyle\sum_{k=1}^{F} W_{j,k}^{(0)}\, H_{k,k} & \text{if } \ell = 0 \\[3ex] \dfrac{1}{2} \displaystyle\sum_{k=1}^{F-|\ell|} W_{j,k}^{(|\ell|)}\, H_{k,k+|\ell|} & \text{if } \ell < 0 \end{cases} \qquad \text{(A.5)}
$$

where the quantities $V_k^{(j,\ell)}$ and $W_{j,k}^{(\ell)}$ again are defined in the Appendix of reference 4. Using these new matrices and functions, the quantum and corresponding classical Hamiltonian may be written, respectively, as

$$
\underset{\approx}{H} = \sum_{\ell=-F+1}^{F-1} \sum_{j=0}^{F-|\ell|-1} c_{j,\ell}\; \underset{\approx}{E}^{(j,\ell)} \qquad \text{(A.6a)}
$$

$$
H(m,q) = \sum_{\ell=-F+1}^{F-1} \sum_{j=0}^{F-|\ell|-1} c_{j,\ell}\; E^{(j,\ell)}(m,q) \qquad . \qquad \text{(A.6b)}
$$

In order to investigate the classical and quantum mechanical dynamics, we will evaluate Poisson brackets and commutators of the functions $E^{(j,\ell)}(m,q)$ and the matrices $\underset{\approx}{E}^{(j,\ell)}$ with the action variable m and its corresponding matrix $\underset{\sim}{M}$, respectively. Straight-foward differentiation shows that the Poisson bracket[9] is given by

$$\{m, E^{(j,\ell)}(m,q)\} = -i\ell E^{(j,\ell)}(m,q) \quad . \tag{A.7}$$

On the other hand, with Equations (A.1)-(A.4) it follows that

$$(\underset{\approx}{M} \cdot \underset{\approx}{E}^{(j,\ell)})_{k',k} = 2 \, \delta_{k'-\ell,k} \, V_\mu^{(j,\ell)} m_{k'} \tag{A.8a}$$

$$(\underset{\approx}{E}^{(j,\ell)} \cdot \underset{\sim}{M})_{k',k} = 2 \, \delta_{k'-\ell,k} \, V_\mu^{(j,\ell)} m_k \tag{A.8b}$$

where $\mu = k$ if $\ell \geq 0$ and $\mu = k'$ if $\ell < 0$. Since the Kronecker delta requires

$$m_{k'} = m_{k+\ell} = m_k + \ell \quad ,$$

it follows that the commutator is given by

$$[\underset{\approx}{M}, \underset{\approx}{E}^{(j,\ell)}]_{k',k} = 2 \, \delta_{k'-\ell,k} \, V_\mu^{(j,\ell)} (m_k + \ell - m_k) = \ell \, E^{(j,\ell)}_{k',k} \quad . \tag{A.9}$$

Therefore, comparing Eqs. (A.7) and (A.9) one obtains for all $j + |\ell| < F$

$$[\underset{\approx}{M}, \underset{\approx}{E}^{(j,\ell)}] \;\longleftrightarrow\; i \, \{m, \, E^{(j,\ell)}(m,q)\}$$

or in view of Equation (A.6),

$$[\underset{\approx}{M}, \underset{\approx}{H}] \;\longleftrightarrow\; i\{m, H\} \quad . \tag{A.10}$$

Appendix B

In this appendix we shall derive explicit formulas for the classical analog Hamiltonian depending on two degrees of freedom. We also shall use the notation in the Appendix of reference 4.

Assume the (internal) Hamiltonian matrix $H_{K'k',Kk}$ is an $(F \cdot f)$ x $(F \cdot f)$ hermitian matrix with $k',k = 1,2, \ldots, f$ and $K',K = 1,2, \ldots, F$. We first separate the real and imaginary part of H.

$$H_{K'k',Kk} = R_{K'k',Kk} + i \, I_{K'k',Kk} \tag{B.1}$$

where R is a real symmetric and I a real antisymmetric matrix. We now consider $\underset{\sim}{R}$ and $\underset{\sim}{I}$ as F x F matrices which matrix elements are f x f matrices. These f x f submatrices are in general neither symmetric nor antisymmetric, but they can be, of course, uniquely decomposed into a sum of a symmetric and an antisymmetric matrix, i.e., we may write $\underset{\sim}{H}$ as

$$H_{K'k',Kk} = SR_{k',k}^{(K',K)} + AR_{k',k}^{(K',K)}$$

$$+ i(SI_{k',k}^{(K',K)} + AI_{k',k}^{(K',K)}) \tag{B.2}$$

where for fixed K and K' the matrices $\underset{\sim\approx}{SR}$ and $\underset{\approx\sim}{SI}$ are symmetric and $\underset{\approx\approx}{AR}$ and $\underset{\sim\sim}{AI}$ are antisymmetric with respect to k,k'.

Thus $\underset{\sim\sim}{SR}$, $\underset{\sim\sim}{SI}$, $\underset{\sim\sim}{iAR}$, $\underset{\sim\sim}{iAM}$ are hermitian matrices and one may apply the SMM-method to them as described in the Appendix of reference 4. Doing so one obtains an F x F matrix whose matrix elements are functions of m and q, i.e.,

$$H_{K',K}(m,q) = \sum_{\ell=0}^{f-1} \sum_{j=0}^{f-\ell-1} m^j(s^2-m^2)^{\ell/2} \cos\ell q \sum_{k=1}^{f-\ell} W_{j,k}^{(\ell)} SR_{k,k+\ell}^{(K',K)}$$

$$-i \sum_{\ell=1}^{f-1} \sum_{j=0}^{f-\ell-1} m^j(s^2-m^2)^{\ell/2} \sin\ell q \sum_{k=1}^{f-\ell} W_{j,k}^{(\ell)} AR_{k,k+\ell}^{(K',K)}$$

$$+i \sum_{\ell=0}^{f-1} \sum_{j=0}^{f-\ell-1} m^j(s^2-m^2)^{\ell/2} \cos\ell q \sum_{k=1}^{f-\ell} W_{j,k}^{(\ell)} SI_{k,k+\ell}^{(K',K)}$$

$$+ \sum_{\ell=1}^{f-1} \sum_{j=0}^{f-\ell-1} m^j(s^2-m^2)^{\ell/2} \sin\ell q \sum_{k=1}^{f-\ell} W_{j,k}^{(\ell)} AI_{k,k+\ell}^{(K',K)} \quad . \quad \text{(B.3)}$$

To proceed further, we first formulate the following Lemma.

Lemma: The matrices SR, AR, SI and AI as defined above have the following symmetry properties with respect to K,K'.

$$SR_{k',k}^{(K',K)} = SR_{k',k}^{(K,K')} \tag{B.4a}$$

$$AR_{k',k}^{(K',K)} = -AR_{k',k}^{(K,K')} \tag{B.4b}$$

$$SI_{k',k}^{(K',K)} = -SI_{k',k}^{(K,K')} \tag{B.4c}$$

$$AI_{k',k}^{(K',K)} = AI_{k',k}^{(K,K')} \quad . \tag{B.4d}$$

With the aid of this Lemma, which we will prove shortly, it is not difficult to see that $H_{K',K}(m,q)$ is a hermitian matrix. One may thus apply the SMM-technique again and obtain

$$H(m,q,M,Q) = \sum_{L=0}^{F-1} \sum_{\ell=0}^{f-1} \sum_{J=0}^{F-L-1} \sum_{j=0}^{f-\ell-1} M^J m^j (s^2-m^2)^{L/2} (s^2-m^2)^{\ell/2}$$

$$\{\cos LQ \cos \ell q \sum_{K=1}^{F-L} \sum_{k=1}^{f-\ell} W_{J,K}^{(L)} W_{j,k}^{(\ell)} SR_{k,k+\ell}^{(K,K+L)}$$

$$- \sin LQ \sin \ell q \sum_{K=1}^{F-L} \sum_{k=1}^{f-\ell} W_{J,K}^{(L)} W_{j,k}^{(\ell)} AR_{k,k+\ell}^{(K,K+L)}$$

$$+ \cos LQ \sin \ell q \sum_{K=1}^{F-L} \sum_{k=1}^{f-\ell} W_{J,K}^{(L)} W_{j,k}^{(\ell)} AI_{k,k+\ell}^{(K,K+L)}$$

$$+ \sin LQ \cos \ell q \sum_{K=1}^{F-L} \sum_{k=1}^{f-\ell} W_{J,K}^{(L)} W_{j,k}^{(\ell)} SI_{k,k+\ell}^{(K,K+L)}\} \quad . \qquad (B.5)$$

Now consider $\underset{\sim}{H}$ as a f x f matrix of F x F submatrices; the decomposition of $\underset{\sim}{H}$ then reads

$$H_{K'k',Kk} = \hat{SR}_{K',K}^{(k',k)} + \hat{AR}_{K',K}^{(k',k)}$$

$$+ i (\hat{SI}_{K',K}^{(k',k)} + \hat{AI}_{K',K}^{(k',k)}) \qquad (B.6)$$

where $\underset{\approx}{\hat{SR}}$ and $\underset{\approx}{\hat{SI}}$ are symmetric and $\underset{\sim\sim}{\hat{AR}}$ and $\underset{\sim\sim}{\hat{AI}}$ are antisymmetric with respect to K,K'. If we apply the SMM-procedure now first to the F x F matrices and then to the f x f matrix of corresponding classical functions, we arrive at an expression similar to Eq. (B.5) but with $\underset{\sim\sim}{SR}$, $\underset{\sim\sim}{AR}$, $\underset{\sim\sim}{SI}$, and $\underset{\approx}{AI}$ replaced by $\underset{\sim\sim}{\hat{SR}}$, $\underset{\sim\sim}{\hat{AR}}$, $\underset{\sim\sim}{\hat{AI}}$ and $\underset{\approx}{\hat{SI}}$. Thus it remains to show that

$$SR_{k',k}^{(K',K)} = S\hat{R}_{K',K}^{(k',k)} \tag{B.7a}$$

$$AR_{k',k}^{(K',K)} = A\hat{R}_{K',K}^{(k',k)} \tag{B.7b}$$

$$SI_{k',k}^{(K',K)} = A\hat{I}_{K',K}^{(k',k)} \tag{B.7c}$$

$$AI_{k',k}^{(K',K)} = S\hat{I}_{K',K}^{(k',k)} \qquad . \tag{B.7d}$$

With the aid of the Lemma, however, this is evident if one recalls the fact that the decomposition of a real matrix into a sum of a symmetric and an antisymmetric matrix is unique. This thus shows that considering the matrix $H_{K'k',Kk}$ as an F x F matrix of f x f submatrices, or considering it as an f x f matrix of F x F submatrices, yields the same result.

The only remaining task is to prove the Lemma. To do so it is useful to define the matrix $\underset{\sim}{D}$ by

$$D_{k',k}^{(K',K)} = SR_{k',k}^{(K',K)} - SR_{k,k'}^{(K,K')} \qquad . \tag{B.8}$$

Since $\underset{\sim}{R}$ is symmetric with respect to interchange of both indices one obtains

$$SR_{k',k}^{(K',K)} + AR_{k',k}^{(K',K)} = R_{K'k',Kk} = R_{Kk,K'k'}$$

$$= SR_{k,k'}^{(K,K')} + AR_{k,k'}^{(K,K')}$$

$$= SR_{k',k}^{(K',K)} - D_{k',k}^{(K',K)} + AR_{k,k'}^{(K,K')}$$

so that

$$D_{k',k}^{(K',K)} = AR_{k,k'}^{(K,K')} - AR_{k',k}^{(K',K)} \qquad . \tag{B.9}$$

For fixed K,K' $\underset{\sim}{D}$ must be a symmetric matrix with regard to Eq. (B.8) and an antisymmetric matrix with regard to Eq. (B.9), hence it must be zero. With $\underset{\sim}{D} = \underset{\sim}{0}$ it follows from Eqs. (B.8) and (B.9) that $\underset{\approx}{SR}$ and $\underset{\approx}{AR}$ are symmetric with respect to interchange of both sets of variables. Equations (B.4a,b) are then proved by

$$SR_{k',k}^{(K',K)} = SR_{k,k'}^{(K,K')} = SR_{k',k}^{(K,K')}$$

$$AR_{k',k}^{(K',K)} = AR_{k,k'}^{(K,X')} = - AR_{k',k}^{(K,K')} \quad .$$

Equations (B.4d,c) can be proved by the same technique applied to $\underset{\approx}{SI}$ and $\underset{\approx}{AI}$.

It is sometimes convenient to make use of the non-hermitian matrices $\underset{\approx}{E}^{(j,\ell)}$ and the complex functions $E^{(j,\ell)}(m,q)$ as they are defined in Appendix A. Using them the quantum Hamiltonian may be written as

$$\underset{\sim}{H} = \sum_{L=-F+1}^{F-1} \sum_{\ell=-f+1}^{f-1} \sum_{J=0}^{F-|L|-1} \sum_{j=0}^{f-|\ell|-1} c_{JLj\ell} \, \underset{\approx}{E}^{(J,L)} \otimes \underset{\approx}{E}^{(j,\ell)} \quad (B.10)$$

where the tensor product is defined by

$$(\underset{\approx}{A} \otimes \underset{\approx}{B})_{K'k',Kk} = A_{K',K} \cdot B_{k',k} \quad (B.11)$$

and where the coefficients $c_{JLj\ell}$ are given by (cf. Appendix A)

$$c_{JLj\ell} = \sum_{K=1}^{F-L} \sum_{k=1}^{f-\ell} e(L) \, e(\ell) \, W_{JK}^{(L)} \, W_{jk}^{(\ell)} \, H_{K+L,k+\ell,K,k} \quad (B.12a)$$

for $\ell \geq 0$ and $L \geq 0$. If one of the ℓ-indices is negative one must transpose

H with respect to this subset of indices and take the absolute value of $\underset{\approx}{H}$ the negative ℓ-index, e.g.,

$$c_{JLj\ell} = \sum_{K=1}^{F-L} \sum_{k=1}^{f-\ell} e(L)\, e(\ell)\, W_{JK}^{(L)}\, W_{j,k}^{(|\ell|)}\, H_{K+L,k,K,k+|\ell|}$$

$$\text{(B.12b)}$$

for $L \geq 0$, $\ell < 0$. The function $e(\ell)$ is given by

$$e(\ell) = \begin{cases} 1 & \text{if } \ell = 0 \\ \frac{1}{2} & \text{if } \ell \neq 0 \end{cases} \qquad \text{(B.13)}$$

and similar for $e(L)$. Equation (B.12) can be proved by substituting Eq. (B.10) into it. The corresponding classical Hamiltonian is now given by

$$H(M,Q,m,q) = \sum_{L=-F+1}^{F-1} \sum_{\ell=-f+1}^{f-1} \sum_{J=0}^{F-|L|-1} \sum_{j=0}^{f-|\ell|-1}$$

$$c_{JLj\ell}\, E^{(J,L)}(M,Q) \cdot E^{(j,\ell)}(m,q) \qquad \text{(B.14)}$$

which can be shown to be identical to Eq. (B.5). This form of the Hamiltonian is easier to generalize to more than two degrees of freedom. It also shows that the "Ehrenfest theorem" as discussed in Section II holds for all the various m's, i.e., the dynamics is correct for as many action variables as there are (internal) degrees of freedom. This follows from

$$[1 \underset{\approx}{\otimes} \underset{\approx}{E}^{(j',\ell')}\,,\, \underset{\approx}{E}^{(J,L)} \underset{\approx}{\otimes} \underset{\approx}{E}^{(j,\ell)}] = \underset{\approx}{E}^{(J,L)} \underset{\approx}{\otimes} [\underset{\approx}{E}^{(j',\ell')}\,,\, \underset{\approx}{E}^{(j,\ell)}]$$

$$\text{(B.14a)}$$

and

$$\{E^{(j',\ell')}(m,q) \ , \ E^{(J,L)}(M,Q) \ E^{(j,\ell)}(m,q)\} = E^{(J,L)}(M,Q) \cdot \{E^{(j',\ell')}(m,q) \ ,$$

$$E^{(j,\ell)}(m,q)\} \qquad\qquad (B.14b)$$

which, with the aid of the results of Appendix A, shows that

$$-i[\underset{\approx}{1} \ \textcircled{a} \ \underset{\approx}{E}^{(1,0)} \ , \ \underset{\approx}{H}] \ \leftrightarrow \ \{E^{(1,0)}(m,q),H\} = \{m,H\} \qquad (B.15a)$$

and, using an equation similar to Eq. (B.14),

$$-i[\underset{\approx}{E}^{(1,0)} \ \textcircled{a} \ \underset{\approx}{1} \ , \ \underset{\approx}{H}] \ \leftrightarrow \ \{E^{(1,0)}(M,Q),H\} = \{M,H\} \quad . \quad (B.15b)$$

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References

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10. Note that the matrix of nonadiabatic coupling elements for the two-state

    case, F=2, is given by

    $$-i\hbar \, \frac{\partial \omega}{\partial x} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad ,$$

    where $\omega(x)$ is defined by Eq. (3.31) of reference 1.

11. Note that the definition of $T_{k',k}$ used in reference 3 differs from the

    present one by a factor of $-i\hbar$.

12. Reference 8, pp. 237-247.