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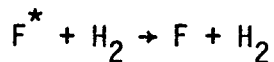https://escholarship.org/uc/item/9sk38770

Author
Meyer, H-D.

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CLASSICAL MODELS FOR ELECTRONIC DEGREES OF FREEDOM: DERIVATION VIA SPIN ANALOGY AND APPLICATION TO

$$F^* + H_2 \rightarrow F + H_2$$

Hans-Dieter Meyer and William H. Miller

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Classical Models for Electronic Degrees of Freedom:

Derivation via Spin Analogy and Application to

$$F^* + H_2 \rightarrow F + H_2$$

Hans-Dieter Meyer[‡] and William H. Miller[‡‡]

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

Abstract

By invoking the formal equivalence of a finite level quantum mechanical system to a quantum spin in an external field, this paper shows how a classical model can be constructed for an arbitrary finite level quantum system. For the 2-state and 3-state cases this leads to the same classical Hamiltonian that was obtained earlier by other more heuristic methods, but it shows how to treat the general F-state case. The purpose of this overall approach is to be able to represent the electronic states in electronically non-adiabatic collision processes by a classical degree of freedom so that all degrees of freedom, electronic and heavy particle (i.e., translation, rotation, and vibration), can be treated on a consistent dynamical footing. Application of this model to the quenching of $F^*(^2P_{1/2})$ by collisions with H_2 is described, and this completely classical approach is seen to give excellent agreement with the quantum mechanical coupled channel calculations of Rebentrost and Lester.

I. Introduction.

In several recent papers[1-3] it has been shown how the electronic degrees of freedom in a molecular collision system can be modeled classically. The motivation for this work has been to develop an approach in which all the degrees of freedom, electronic and nuclear (i.e., translation, rotation, and vibration), are treated on the same dynamical footing. This is important if one is to have a unified theoretical description of electronically non-adiabatic collision processes, for it has been noted[4] that dynamically inconsistent models--i.e., those which describe some degrees of freedom by quantum mechanics and other degrees of freedom by classical mechanics-- can sometimes miss significant features in these processes. One can, of course, achieve dynamical consistency by resorting to a fully quantum mechanical formulation--i.e., the complete rovibronic coupled-channel Schrödinger equation--but this is often impractical because of the large number of strongly coupled rotational and vibrational states in a molecular collision system. To retain the facility of a classical description of the heavy particle degrees of freedom and to achieve dynamical consistency, one is thus forced to model the electronic degrees of freedom also by classical mechanics.

This paper presents some additional formal developments in this approach and also the results of its application to a problem of considerable interest, the quenching of $F^*(^2P_{1/2})$ by H_2,

$$F^*(^2P_{1/2}) + H_2 \rightarrow F(^2P_{3/2}) + H_2 \quad . \tag{1.1}$$
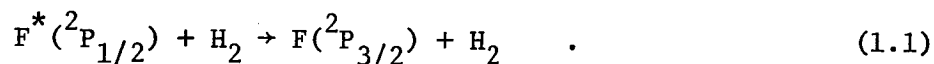
It was the desire to describe the prominent resonance effect[4] in this process that was the initial motivation for this entire line of work, and it is gratifying to see in Section III that this completely classical model for electronic and nuclear degrees of freedom does indeed describe this effect correctly, in fact, giving reasonably good agreement with the quantum mechanical coupled-channel scattering calculations of Rebentrost and Lester.[5] Section II first shows an alternate methodology for deriving classical models for finite level quantum systems, i.e., for replacing a finite level quantum system by a classical degree of freedom. For the 2-state and 3-state cases this new more solidly based derivation gives the same classical models that were obtained earlier[1,2] on more heuristic grounds, and it shows a definite procedure for extending the approach to 4-state, 5-state, etc., cases. Section III then describes the application of these procedures to reaction (1.1) and the results obtained.

II. Derivation of Classical Model via Analogy with Spin.

The goal here is to replace a finite quantum mechanical Hamiltonian matrix representation of a system, $\{H_{n',n}\}$, by a classical Hamiltonian function $H_{CL}(n,q)$, where the quantum number labels (n',n) are discrete integer values, i.e., $n = 0,1,2, \ldots$, and (n,q) are classical action-angle variables.[6] The action variable n has continuous values $\geq -1/2$ and the angle variable q varies over the interval $(0,2\pi)$. For the application we have in mind the quantum states are electronic states and the matrix elements depend parametrically on the nuclear coordinate $\underset{\sim}{x}$, $\{H_{n',n}(\underset{\sim}{x})\}$. The classical electronic Hamiltonian thus also depends parametrically on $\underset{\sim}{x}$, and once $H_{CL}(n,q;\underset{\sim}{x})$ is obtained the classical Hamilton function for the complete system, including electronic and nuclear degrees of freedom, is

$$H(\underset{\sim}{p},\underset{\sim}{x},n,q) = \frac{p^2}{2m} + H_{CL}(n,q;\underset{\sim}{x}) \quad . \tag{2.1}$$

The key to this formulation is thus learning how $H_{CL}(n,q)$ is obtained from the matrix elements $\{H_{n',n}\}$ (the dependence on the nuclear coordinate $\underset{\sim}{x}$ will be suppressed when it is not necessary). Although we have electronic states in mind, there is nothing in the results we obtain which restricts the treatment to this. Section IIa and IIb treat the 2-state and general F-state cases, respectively, while Section IIc shows a simple example.

(a) 2-State Case

It is well-known that a quantum mechanical 2-state system can without restriction be regarded as an angular momentum, or spin 1/2 system in an

external field, the two state being spin up and spin down, i.e., $m = + 1/2$ or $- 1/2$. Furthermore, the most general form of the Hamilton operator for a spin 1/2 system is

$$H = A_0 + \vec{A} \cdot \vec{S}$$

$$= A_0 + A_x S_x + A_y S_y + A_z S_z \tag{2.2}$$

where S_x, S_y, S_z are the usual angular momentum operators and A_0, A_x, A_y, A_z are real numbers; i.e., the operators 1, S_x, S_y, S_z are a complete set of linearly independent operators in the space of spin 1/2.

It is then a straightforward matter to obtain the classical Hamiltonian corresponding to Eq. (2.2) by replacing the operators S_x, S_y, S_z by the corresponding classical functions of the canonical variables. A classical angular momentum consists of two degrees of freedom for which the action-angle variables are (s, q_s) and (m, q_m): s is the magnitude of the angular momentum and m its projection onto a space-fixed axis (the z-axis), and q_s and q_m are their conjugate angle variables. The projections of the angular momentum onto the three cartesian axes--i.e., S_x, S_y, S_z--are given by[7]

$$S_x = \sqrt{s^2 - m^2} \cos q_m \tag{2.3a}$$

$$S_y = \sqrt{s^2 - m^2} \sin q_m \tag{2.3b}$$

$$S_z = m \quad . \tag{2.3c}$$

Using Eqs. (2.3), the classical Hamiltonian corresponding to the Hamiltonian operator in Eq. (2.2) is thus

$$H_{CL}(m,q_m) = A_0 + A_x \sqrt{s^2-m^2} \cos q + A_y \sqrt{s^2-m^2} \sin q + A_z m \quad . \quad (2.4)$$

Since H_{CL} is not a function of q_s, s is a constant of the motion and for the present case has the value $s = \frac{1}{2}$. Since q_m is the only interesting angle variable left, the index m will be dropped from it for the remainder of this section.

Eq. (2.4) gives the general <u>form</u> of the classical Hamiltonian for the spin 1/2 system, but to make the construction complete one needs to express the parameters A_0, A_x, A_y, A_z in terms of the matrix elements $\{H_{n',n}\}$. Since the matrix representations of the operators S_x, S_y, S_z are

$$S_x = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \quad (2.5a)$$

$$S_y = \begin{pmatrix} 0 & +i/2 \\ -i/2 & 0 \end{pmatrix} \quad (2.5b)$$

$$S_z = \begin{pmatrix} -1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \quad (2.5c)$$

one finds from Eq. (2.2) that

$$H_{-1/2,-1/2} = A_0 - \frac{1}{2} A_z \quad (2.6a)$$

$$H_{1/2,1/2} = A_0 + \frac{1}{2} A_z \quad (2.6b)$$

$$H_{-1/2,1/2} = \frac{1}{2}(A_x + iA_y) \tag{2.6c}$$

$$H_{1/2,-1/2} = \frac{1}{2}(A_x - iA_y) \quad . \tag{2.6d}$$

These relations are easily inverted to give

$$A_0 = \frac{1}{2}(H_{1/2,1/2} + H_{-1/2,-1/2}) \tag{2.7a}$$

$$A_z = H_{1/2,1/2} - H_{-1/2,-1/2} \tag{2.7b}$$

$$A_x = 2 \operatorname{Re}(H_{-1/2,1/2}) \tag{2.7c}$$

$$A_y = 2 \operatorname{Im}(H_{-1/2,1/2}) \quad , \tag{2.7d}$$

and using Eqs. (2.7) in Eq. (2.4) then gives the classical Hamiltonian explicitly in terms of the matrix elements themselves:

$$H_{CL}(m,q) = (\tfrac{1}{2}+m) H_{1/2,1/2} + (\tfrac{1}{2}-m) H_{-1/2,-1/2}$$

$$+ 2\sqrt{\tfrac{1}{4}-m^2} \operatorname{Re}(H_{-1/2,1/2})\cos q + 2\sqrt{\tfrac{1}{4}-m^2} \operatorname{Im}(H_{-1/2,1/2})\sin q \quad .$$

$$\tag{2.8}$$

The classical variable m varies over the interval $(-1/2, 1/2)$, but to make better connection with earlier work it is useful to have an action variable defined on the interval $(0,1)$. The action variable n is thus defined by

$$n = m + \frac{1}{2}$$

or

$$m = n - \frac{1}{2}$$

and it is also useful to label the matrix elements $H_{-1/2,-1/2}$, $H_{1/2,1/2}$, $H_{-1/2,1/2}$ as H_{00}, H_{11}, H_{01}, respectively. Since $\frac{1}{4} - m^2 = n(1-n)$, the final expression for the classical Hamiltonian for the 2-state system is

$$H_{CL}(n,q) = (1-n)H_{00} + n\, H_{11} + 2\, Re(H_{01})\, \sqrt{n(1-n)}\, \cos q$$

$$+ 2\, Im(H_{01})\, \sqrt{n(1-n)}\, \sin q \qquad (2.9)$$

which we note is identical to the formula obtained earlier by Miller and McCurdy,[1] by invoking the Heisenberg correspondence principle and heuristic arguments, and by Meyer and Miller[3] from their "classical analog" analysis. The Meyer-Miller analysis showed, in fact, that in a certain sense this classical Hamiltonian is _exactly_ equivalent to the quantum 2-state system.

As discussed in our earlier papers,[1-3] for actual calculations one should replace s by $s + \frac{1}{2}$ in Eq. (2.3) ($\frac{1}{4}$ by 1 in Eq. (2.8)), i.e., make use of the Langer modification. With this modification Eq. (2.9) becomes

$$H_{CL}(n,q) = (1-n)\, H_{00} + n\, H_{11} + 2\, Re(H_{01})\, \sqrt{(n+\frac{1}{2})(\frac{3}{2}-n)}\, \cos q$$

$$+ 2\, Im(H_{01})\, \sqrt{(n+\frac{1}{2})(\frac{3}{2}-n)}\, \sin q \qquad . \quad (2.10)$$

The action variable n can now vary over the interval $(-\frac{1}{2}, \frac{3}{2})$, and the integral values n = 0 and n = 1 thus occur at the centers of the "boxes"

$(-\frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{3}{2})$ required for the standard quasiclassical histogram procedure.

(b) F-State Case

An F-state quantum mechanical system can without restriction be considered to be a spin $\frac{F-1}{2}$ system in an external field. The four matrices 1, S_x, S_y, S_z, however, do not form a complete set of $F \times F$ matrices for $F > 2$. To expand an $F \times F$ Hamiltonian matrix as a sum of angular momentum operators, one must introduce products of $(F-1)$ operators, and these operator products must be symmetrized in order to be hermitian. We use brackets to denote the properly symmetrized products

$$<A_1 \cdot A_2 \cdots A_{F-1}> = \frac{1}{(F-1)!} \sum_\sigma A_{\sigma(1)} \cdot A_{\sigma(2)} \cdots A_{\sigma(F-1)} \qquad (2.11)$$

where the sum goes over all permutation σ, and the A_i are members of the set $\{1, S_x, S_y, S_z\}$. There are, however, $\frac{1}{6} F(F+1)(F+2)$ such symmetrized operator products while a $F \times F$ hermitian matrix has only F^2 independent real parameters. For $F > 2$ the set of symmetrized operator products is therefore overcomplete (linearly dependent), and the question arises which operators should one choose in which to expand the Hamiltonian.

From the Heisenberg correspondence principle one can conclude that the _form_ of the corresponding classical Hamiltonian function is[1]

$$H_{CL}(n,q) = f(n) + \sum_{\ell=1}^{F-1} g_\ell(n) \cos(\ell q) + h_\ell(n) \sin(\ell q) \qquad ; \qquad (2.12)$$

the task is thus to determine the functions $f(n)$, $\{g_\ell\}$, and $\{h_\ell\}$. It is

also clear from the Heisenberg correspondence principle that[1] $f(n)$ depends only on the diagonal elements of the Hamiltonian, while $g_\ell(n)$ and $h_\ell(n)$ are determined by the real and imaginary part, respectively, of the matrix elements $H_{k,k\pm\ell}$

We therefore choose the independent set of matrices in which the Hamiltonian will be expanded to be those whose corresponding classical functions show a simple harmonic dependence on the angle variable q. These functions and their corresponding matrices are (cf. Eq. (2.3))

$$m^j \leftrightarrow S_z^j$$

$$m^j(s^2-m^2)^{1/2}\cos q \leftrightarrow <S_z^j S_x>$$

$$m^j(s^2-m^2)^{1/2}\sin q \leftrightarrow <S_z^j S_y>$$

$$m^j(s^2-m^2)\cos 2q = m^j(s^2-m^2)(\cos^2 q - \sin^2 q) \leftrightarrow <S_z^j(S_x^2 - S_y^2)>$$

$$m^j(s^2-m^2)\sin 2q = m^j(s^2-m^2)\cdot 2\sin q\,\cos q \leftrightarrow <S_z^j\,2\,S_x S_y>$$

$$m^j(s^2-m^2)^{3/2}\cos 3q = m^j(s^2-m^2)^{3/2}(\cos^3 q - 3\sin^2 q\,\cos q) \leftrightarrow <S_z^j(S_x^3 - 3\,S_y^2 S_x)>$$

$$m^j(s^2-m^2)^{3/2}\sin 3q = m^j(s^2-m^2)^{3/2}(3\cos^2 q\,\sin q - \sin^3 q) \leftrightarrow <S_z^j(3\,S_x^2 S_y - S_y^3)>$$

$$(2.13)$$

and so on.

The general classical function of this type has the form:

$$m^j$$

or

$$m^j (s^2-m^2)^{\ell/2} \cos(\ell q)$$

or

$$m^j (s^2-m^2)^{\ell/2} \sin(\ell q) \quad .$$

Since $\ell = 0,1,2, \ldots, F-1$ and $j = 0,1, \ldots, F-1-\ell$, one obtains F q-independent terms, $\frac{F(F-1)}{2}$ cos-terms and $\frac{F(F-1)}{2}$ sin-terms, and thus F^2 functions altogether. The F^2 corresponding operators form a complete and linearly independent set of hermitian matrices. Table I shows these matrices for $F = 2,3,4$ and the Appendix shows a simple way to construct them in general.

As in the 2-state case one now expands the Hamiltonian in terms of the matrices. For the 3-state case, F=3, one obtains

$$\underline{\underline{H}} = \begin{pmatrix} H_{-1,-1} & H_{-1,0} & H_{-1,1} \\ H_{0,-1} & H_{0,0} & H_{0,1} \\ H_{1,-1} & H_{1,0} & H_{1,1} \end{pmatrix}$$

$$= (1-s_z^2)H_{00} + \frac{1}{2} (s_z^2+s_z)H_{11} + \frac{1}{2} (s_z^2-s_z)H_{-1,-1}$$

$$+ \frac{\sqrt{2}}{2} (S_x + \langle 2s_z s_x\rangle) \, Re(H_{01}) + \frac{\sqrt{2}}{2} (S_y + \langle 2s_z s_y\rangle) \, Im(H_{01})$$

$$+ \frac{\sqrt{2}}{2} (S_x - \langle 2s_z s_x\rangle) \, Re(H_{-1,0}) + \frac{\sqrt{2}}{2} (S_y - \langle 2s_z s_y\rangle) \, Im(H_{-1,0})$$

$$+ \langle s_x^2 - s_y^2\rangle \, Re(H_{-1,1}) + \langle 2s_x s_y\rangle \, Im(H_{-1,1}) \quad , \tag{2.14}$$

or

$$\underline{\underline{H}} = H_{00} \cdot 1 + \frac{H_{11} - H_{-1-1}}{2} S_z + (\frac{H_{11} + H_{-1-1}}{2} - H_{00}) S_z^2$$

$$+ \frac{\sqrt{2}}{2} Re(H_{0,1} + H_{-1,0}) S_x + \frac{\sqrt{2}}{2} Im(H_{0,1} + H_{-1,0}) S_y$$

$$+ \sqrt{2} Re(H_{0,1} - H_{-1,0}) <S_z S_x> + \sqrt{2} Im(H_{0,1} + H_{-1,0}) <S_z S_y>$$

$$+ Re(H_{-1,1}) <S_x^2 - S_y^2> + Im(H_{-1,1}) <2 S_x S_y> \qquad . \qquad (2.15)$$

The classical Hamiltonian function for the 3-state system is then obtained by simply replacing the matrices (operators) by their corresponding classical functions:

$$H_{CL}(m,q) = H_{00} + \frac{H_{11} - H_{-1-1}}{2} m + (\frac{H_{11} + H_{-1-1}}{2} - H_{00}) m^2$$

$$+ \frac{\sqrt{2}}{2} \sqrt{s^2 - m^2} \{Re(H_{0,1} + H_{-1,0}) \cos q + Im(H_{0,1} + H_{-1,0}) \sin q\}$$

$$+ \sqrt{2} m \sqrt{s^2 - m^2} \{Re(H_{0,1} - H_{-1,0}) \cos q + Im(H_{0,1} - H_{-1,0}) \sin q\}$$

$$+ Re(H_{-1,1})(s^2 - m^2) \cos 2q + Im(H_{-1,1})(s^2 - m^2) \sin 2q \qquad . \qquad (2.16)$$

(c) Example: Collinear Atom-Diatom Collision System

It is illustrative to test the general formulae obtained in the previous section on a known example. Thus consider the collinear atom-diatom (harmonic oscillator) collision system for which the Hamiltonian

is

$$H = \frac{p^2}{2\mu} + \frac{p^2}{2m} + \frac{1}{2} m\omega^2 r^2 + V(R,r) \qquad . \qquad (2.17)$$

(For example, if the interaction $V = \exp[-\alpha(R-r)]$, this is the well-known Secrest-Johnson[8] model.) For the test purposes of this section 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. For fixed translational coordinate R the vibrational Hamiltonian is thus

$$h = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 r^2 + V(R,r) \qquad . \qquad (2.18)$$

If the classical variables (p,r) are replaced by the harmonic action-angle variables $(\hbar n, q)$, where $\hbar$ is introduced to make n dimensionless (i.e., the "classical quantum number"), then the classical vibrational Hamiltonian is given in terms of its action-angle variable by

$$h_{CL}(n,q) = \hbar\omega(n + \frac{1}{2}) + V(R, \sqrt{\frac{\hbar(2n+1)}{m\omega}} \cos q) \qquad . \qquad (2.19)$$

The "test" is then as follows: choosing as basis the unperturbed harmonic oscillator states $\{|n>\}$, the matrix of the vibrational Hamiltonian operator in Eq. (2.17), $h_{n',n}$, is first constructed. Then considering this matrix $\{h_{n',n}\}$ as given, one uses the general results of Section IIB to determine the classical Hamiltonian function corresponding to it. If the methodology of Section IIb is correct, one should regain the classical Hamiltonian in Eq. (2.19).

To keep the arithmetic simple the interaction potential $V(R,r)$ is expanded in a Taylor's series in r through terms in r^2. The correct

classical Hamiltonian, Eq. (2.19), thus becomes

$$h_{CL}(n,q) = \hbar\omega(n+\tfrac{1}{2}) + V_0(R) + V_1(R)\sqrt{\frac{\hbar(2n+1)}{m\omega}}\cos q + \frac{1}{2}V_2(R)\frac{\hbar(2n+1)}{m\omega}\cos^2 q$$

$$= V_0(R) + \hbar\omega(n+\tfrac{1}{2})[1 + \frac{V_2(R)}{2m\omega^2}] + V_1(R)\sqrt{\frac{\hbar(2n+1)}{m\omega}}\cos q$$

$$+ V_2(R)\frac{\hbar(n+\tfrac{1}{2})}{2m\omega}\cos 2q \quad , \qquad (2.19')$$

where

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

The matrix representation of the vibrational Hamiltonian operator is

$$\{h_{n',n}\} = \frac{\hbar\omega}{2}\begin{pmatrix} 1 & 0 & 0 & 0\ldots \\ 0 & 3 & 0 & 0\ldots \\ 0 & 0 & 5 & 0\ldots \\ 0 & 0 & 0 & 7\ldots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix} + V_0\begin{pmatrix} 1 & 0 & 0 & 0\ldots \\ 0 & 1 & 0 & 0\ldots \\ 0 & 0 & 1 & 0\ldots \\ 0 & 0 & 0 & 1\ldots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix} + V_1\sqrt{\frac{\hbar}{2m\omega}}\begin{pmatrix} 0 & 1 & 0 & 0\ldots \\ 1 & 0 & \sqrt{2} & 0\ldots \\ 0 & \sqrt{2} & 0 & \sqrt{3}\ldots \\ 0 & 0 & \sqrt{3} & 0 \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

$$+ \frac{1}{2}V_2\frac{\hbar}{2m\omega}\begin{pmatrix} 1 & 0 & \sqrt{2} & 0\ldots \\ 0 & 3 & 0 & \sqrt{6}\ldots \\ \sqrt{2} & 0 & 5 & 0\ldots \\ 0 & \sqrt{6} & 0 & 7\ldots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix} \qquad (2.20)$$

If these infinite matrices are now truncated to $F \times F$ matrices and equated
to the appropriate spin matrices as in Section IIb, one then obtains a
family of approximate classical Hamiltonian functions $h_F(n,q)$, each of
which has the form

$$h_F(n,q) = V_0 \hbar\omega(n + \tfrac{1}{2})[1 + \frac{V_2}{2m\omega^2}]$$

$$+ \sqrt{\frac{\hbar}{m\omega}} \; V_1 f_F(n) \; \cos q$$

$$+ \frac{\hbar}{2m\omega} \; V_2 g_F(n) \; \cos 2q \qquad . \qquad (2.21a)$$

where

$$f_F(n) = \frac{\sqrt{2}}{2} \; \sqrt{(s + \tfrac{1}{2})^2 - m^2} \; \sum_{j=0}^{F-2} m^j \sum_{k=1}^{F-1} W_{jk}^{(1)} \; \sqrt{k} \qquad (2.21b)$$

$$g_F(n) = \frac{1}{2} \; [(s + \tfrac{1}{2})^2 - m^2] \; \sum_{j=0}^{F-3} m^j \sum_{k=1}^{F-2} W_{jk}^{(2)} \; \sqrt{k(k+1)} \qquad (2.21c)$$

and

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

s and $W_{jk}^{(\ell)}$ are defined in the appendix. Comparing Eq. (2.21) to the correct classical Hamiltonian, Eq. (2.19'), one sees that the diagonal, i.e. q-independent, parts are identical, as are the forms of the q-dependent terms. For the comparison to be exact, however, one would need $f_F(n)$ and $g_F(n)$ to be equal to the exact functions,

$$f_{exact}(n) = \sqrt{2n+1} \qquad (2.22a)$$

$$g_{exact}(n) = n + \frac{1}{2} \qquad , \qquad (2.22b)$$

and this is <u>not</u> the case.   Figures 1 and 2 show $f_F(n)$ and $g_F(n)$ compared to the correct functions [Eq. (2.22)].   One sees that $f_F(n)$ and $g_F(n)$ become better approximations to the correct functions as F increases and indeed appear to converge to the correct functions as $F \to \infty$.

For this example the methodology of Section IIb is thus seen to reproduce the correct classical Hamiltonian, the only error seeming to originate from truncating the matrix representation of the quantum Hamiltonian.   This example has no practical significance, of course, since one already has a classical model for vibrational degrees of freedom.   The interesting applications of the approach are to those finite level quantum states for which one does not know the appropriate classical model <u>a priori</u>, e.g., to a finite number of electronic states.

III. Application to $F^* + H_2$.

a. Derivation of the Hamiltonian

The diabatic electronic potential matrix for the $F-H_2$ system has been calculated by Rebentrost and Lester[9] in the cartesian basis set $|x\rangle, |y\rangle, |z\rangle$. It has the form:

$$V = \begin{pmatrix} H_{xx} & 0 & 0 \\ 0 & H_{yy} & H_{yz} \\ 0 & H_{yz} & H_{zz} \end{pmatrix} \quad . \tag{3.1}$$

The four real functions H_{xx}, H_{yy}, H_{zz}, H_{yz} depend on R, the distance of the centers of masses of the fluorine atom and the hydrogen molecule, and on γ, the angle between $\vec{R}$ and the internuclear distance vector $\vec{r}$ of the H_2 molecule. There is no r dependence for the present application, i.e., H_2 is treated as a rigid rotor.

It is useful to express the potential matrix Eq. (3.1) in terms of the angular momentum basis set $\{|m\rangle\}$, m=-1,0,1, which is given in terms of the cartesian basis by[10]

$$|0\rangle = |z\rangle$$
$$|1\rangle = -\frac{1}{\sqrt{2}} (|x\rangle + i|y\rangle)$$
$$|-1\rangle = \frac{1}{\sqrt{2}} (|x\rangle - i|y\rangle) \quad .$$

Straight-forward matrix multiplication yields V in the angular momentum basis set

$$V = \begin{pmatrix} \bar{H} & i\frac{H_{yz}}{\sqrt{2}} & -\Delta \\ -i\frac{H_{yz}}{\sqrt{2}} & H_{zz} & -i\frac{H_{yz}}{\sqrt{2}} \\ -\Delta & i\frac{H_{yz}}{\sqrt{2}} & \bar{H} \end{pmatrix} \tag{3.2}$$

where $\bar{H}$ and Δ are given by

$$\bar{H} = \frac{1}{2}(H_{xx} + H_{yy}) \qquad (3.3a)$$

$$\Delta = \frac{1}{2}(H_{xx} - H_{yy}) \qquad . \qquad (3.3b)$$

Using Eq. (2.16) one then obtains the corresponding classical electronic Hamiltonian

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

$$- (L^2-m_L^2)\Delta\,\cos 2q_{m_L} \qquad , \qquad (3.4)$$

where we have changed the symbols s,m,q to L,m_L,q_{m_L} and also indicated the dependence on R and γ in order to avoid confusion. Eq. (3.4) is identical to a result obtained from a different approach by McCurdy, Meyer and Miller.[2]

The full classical Hamiltonian was also derived earlier[1,2] and has the form

$$H_{J,L,S}(P,R,N,q_N,m_N,q_{m_N},m_L,q_{m_L},m_S,q_{m_S}) =$$

$$\frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + B_{rot}\,N^2 + B\,j^2 + V(R,\gamma,m_L,q_{m_L}+\phi) \qquad (3.5)$$

where ℓ denotes the orbital angular momentum of relative F-H$_2$ motion, and N and m_N the rotational angular momentum of the diatom and it's projection onto $\vec{R}$, respectively. j is the total electronic angular

momentum, and S, L, m_S, m_L are the electron spin and orbital angular momenta and their projection onto the $\vec{R}$ axis. J, finally, is the total angular momentum. Since J,L,S are conserved quantities they appear in the Hamiltonian only as parameters and not as variables. The quantities ℓ^2, j^2, γ, and ϕ are given in terms of the canonical variables of the Hamiltonian by

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

$$= J^2 + N^2 + L^2 + S^2 - 2m_N^2 - 2m_L^2 - 2m_S^2 - 2m_N m_L - 2m_N m_S - 2m_L m_S$$

$$- 2\sqrt{J^2 - (m_N + m_L + m_S)^2}\sqrt{N^2 - m_N^2}\cos q_{m_N}$$

$$- 2\sqrt{J^2 - (m_N + m_L + m_S)^2}\sqrt{L^2 - m_L^2}\cos q_{m_L}$$

$$- 2\sqrt{J^2 - (m_N + m_L + m_S)^2}\sqrt{S^2 - m_S^2}\cos q_{m_S}$$

$$+ 2\sqrt{N^2 - m_N^2}\sqrt{L^2 - m_L^2}\cos(q_{m_N} - q_{m_L})$$

$$+ 2\sqrt{N^2 - m_N^2}\sqrt{S^2 - m_S^2}\cos(q_{m_N} - q_{m_S})$$

$$+ 2\sqrt{L^2 - m_L^2}\sqrt{S^2 - m_S^2}\cos(q_{m_L} - q_{m_S}) \qquad (3.6)$$

$$j^2 = |\vec{L} + \vec{S}|^2 = L^2 + S^2 + 2m_L m_S + 2\sqrt{L^2 - m_L^2}\sqrt{S^2 - m_S^2}\cos(q_{m_L} - q_{m_S}) \quad (3.7)$$

$$\cos\gamma = \sqrt{1 - m_N^2/N^2}\cos q_N \qquad , \qquad (3.8)$$

while the azimuth angle ϕ is determined by the relation

$$\sin\gamma \cdot \sin(\phi + q_{m_L}) = \sin q_N \cdot \sin(q_{m_L} - q_{m_N})$$
$$+ \frac{m_N}{N}\cos q_N \cdot \cos(q_{m_L} - q_{m_N}) \qquad . \qquad (3.9)$$

The Hamiltonian of Eq. (3.5) is in the uncoupled representation, i.e., it depends on the variables (m_L, q_{m_L}) and (m_S, q_{m_S}). Using the generating function given before,[1,7] one can couple $\vec{L}$ and $\vec{S}$, i.e., replace (m_L, q_{m_L}) and (m_S, q_{m_S}) by the coupled variables (j, q_j) and (m_j, q_{m_j}), where

$$j^2 = |\vec{L} + \vec{S}|^2$$

$$m_j = m_L + m_S \quad .$$

The Hamiltonian in this coupled representation,

$$H_{J,L,S}(P, R, N, q_N, m_N, q_{m_N}, j, q_j, m_j, q_{m_j}) \quad ,$$

is given still by Eq. (3.5), but with ℓ^2, m_L, q_{m_L} now expressed in the terms of the coupled variables:

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

$$- 2\sqrt{J^2 - (m_N + m_j)^2} \sqrt{N^2 - m_N^2} \cos q_{m_N}$$

$$- 2\sqrt{J^2 - (m_N + m_j)^2} \sqrt{j^2 - m_j^2} \cos q_{m_j}$$

$$+ 2\sqrt{N^2 - m_N^2} \sqrt{j^2 - m_j^2} \cos(q_{m_N} - q_{m_j}) \tag{3.10}$$

$$m_L = \frac{1}{2j^2} \{\alpha\sqrt{j^2 - m_j^2} \cos q_j + m_j (j^2 + L^2 - S^2)\} \tag{3.11}$$

$$q_{m_L} = q_{m_j} + \tan^{-1} \left[\frac{\alpha j \sin q_j}{\alpha m_j \cos q_j - \sqrt{j^2 - m_j^2}(j^2 + L^2 - S^2)}\right] \tag{3.12}$$

where

$$\alpha = \sqrt{(L+S)^2 - j^2} \sqrt{j^2 - (L-S)^2} \quad . \tag{3.13}$$

It was found that calculating the trajectories in the coupled representation takes only $\sim 1/6$ of the time of doing so in the uncoupled representation. Also, it is the coupled variables (j, m_j) which are asymptotically the "good quantum numbers" between which one is determining transitions. It was, however, a useful check to compute some trajectories in both representation and verify that the same results were indeed obtained.

We also note a useful trick to simplify the calculation in the coupled representation; it avoids the necessity of calculating $\sin\gamma$, ϕ, and q_{m_L} individually as functions of the canonical variables. The four matrix elements H_{zz}, $\bar{H}$, H_{yz}, and Δ depend on R and γ in such a way that

$$H_{zz}$$

$$\bar{H}$$

$$\hat{H}_{yz} = \frac{H_{yz}}{\sin\gamma} \tag{3.14a}$$

$$\hat{\Delta} = \frac{\Delta}{\sin^2\gamma} \tag{3.14b}$$

depend only on R and $\cos\gamma$. Using Eq. (3.4) we therefore write the electronic Hamiltonian as

$$V(R, \gamma, m_L, q_{m_L} + \phi) = V(R, \cos\gamma, m_L, a) = (1 - m_L^2) H_{zz}(R, \cos\gamma) + m_L^2 \bar{H}(R, \cos\gamma)$$

$$-2a\sqrt{L^2 - m_L^2} \, \hat{H}_{yz}(R, \cos\gamma) - (L^2 - m_L^2)(1 - \cos^2\gamma - 2a^2)\hat{\Delta}(R, \cos\gamma) \tag{3.15}$$

where a is given by:

$$a \equiv \sin\gamma \cdot \sin(\phi + q_{m_L})$$

$$= \sin q_N \, \sin(q_{m_L} - q_{m_N}) + \frac{m_N}{N} \, \cos q_N \cdot \cos(q_{m_L} - q_{m_N}) \quad . \quad (3.16)$$

Eqs. (3.15) and (3.16) then replace Eqs. (3.4), (3.9) and (3.12).

b. Computational Aspects

The calculations were carried out within the framework of the standard quasiclassical trajectory model. The Langer modification was also consistently made throughout, i.e., wherever J,N,L,S or j appears in Eqs. (3.5)-(3.16) one makes the replacements

$$J \to J + \frac{1}{2}$$

$$N \to N + \frac{1}{2}$$

$$L \to L + \frac{1}{2}$$

$$S \to S + \frac{1}{2}$$

$$j \to j + \frac{1}{2} \quad .$$

The cross section for the $(j_1, N_1) \to (j_2, N_2)$ transition, summed over m_{N_2}, m_{j_2} and averaged over m_{N_1}, m_{j_1}, is given by

$$\sigma_{j_2, N_2 \leftarrow j_1, N_1} = \frac{\pi}{k^2_{j_1, N_1}} \sum_{J = \frac{1}{2}, \frac{3}{2}, \ldots}^{\infty} (2J+1) \, \bar{P}_{j_2, N_2 \leftarrow j_1, N_1}(J) \quad (3.17)$$

where the wavenumber k_{j_1, N_1} is related to the initial kinetic energy E_{j_1, N_1} in the usual way,

$$E_{j_1,N_1} = \frac{\hbar^2 k_{j_1,N_1}^2}{2\mu} \quad .$$

The classical histogram approximation to the average transition probability is

$$\bar{P}_{j_2,N_2 \leftarrow j_1,N_1}(J) = (2N_1+1)^{-1}(2j_1+1)^{-1} \sum_{m_{N_1}=-N_1}^{N_1} \sum_{m_{j_1}=-j_1}^{j_1}$$

$$(2\pi)^{-4} \int_0^{2\pi} dq_{j_1} \int_0^{2\pi} dq_{m_{j_1}} \int_0^{2\pi} dq_{N_1} \int_0^{2\pi} dq_{m_{N_1}}$$

$$\chi \left[j_2(N_1, q_{N_1}, m_{N_1}, q_{m_{N_1}}, j_1, q_{j_1}, m_{j_1}, q_{m_{j_1}}) - j_2 \right]$$

$$\chi \left[\frac{1}{2} \{ N_2(N_1, q_{N_1}, m_{N_1}, q_{m_{N_1}}, j_1, q_{j_1}, m_{j_1}, q_{m_{j_1}}) - N_2 \} \right] \qquad (3.18)$$

where $\chi(x)$ is the "histogram function"

$$\chi(x) = 1 \quad \text{if} \quad |x| < \frac{1}{2}$$

$$= 0 \quad \text{if} \quad |x| \geq \frac{1}{2} \quad .$$

The functions $j_2(N_1,\ldots)$ and $N_2(N_1,\ldots)$ in Eq. (3.18) are the final values of the variables j and N, respectively, that result from the classical trajectory with the indicated initial conditions. The factor 1/2 in the second histogram function results from the fact that, since H_2 is homonuclear, one has $\Delta N = 2$ rather than $\Delta N = 1$ transitions.

The integrals in Eq. (3.18) are then evaluated together with the sum in Eq. (3.17) (which is approximated by an integral) by the usual Monte Carlo method.

c. Results

The relevant energy levels for the infinitely separated F atom and H_2 molecule are indicated in Figure 3, where we have chosen the zero of energy to be the $(\frac{1}{2},0)$ state, as is done for the rest of the paper. Since the transition $(\frac{1}{2},0) \to (\frac{3}{2},2)$ is almost resonant we expect a large cross section for this transition, while all other transitions involved should have much smaller cross sections (at least at collision energies below 100 meV). The quantum mechanical close-coupling calculations of Rebentrost and Lester[5] show this expected behavior.

Calculating the classical cross sections via the histogram procedure described above [i.e., via Eqs. (3.17) and (3.18)], however, gives quite poor agreement with the (correct) quantum mechanical results of reference 5. The $(\frac{1}{2},0) \to (\frac{1}{2},2)$ transition, which is an energetically closed channel for energies below 43.9 meV, is especially poor since a large cross section is obtained for all energies between 10 and 80 meV.

The difficulty is easily understood, though, when one looks at the contour plots of the distribution of the final values of N and j. Figures 4 and 5 show these plots for E = 10 meV and E = 50 meV. There are no trajectories that end with final (j,N) values outside the outermost closed loop. The dashed line indicates the resonance line, i.e., the line for which the loss of electronic energy exactly cancels the gain in rotational energy. One sees quite clearly that the resonance effect plays an important

role: most of the final (j,N) values lie near the resonance line. But in doing so, some trajectories fall in the $(\frac{1}{2},2)$ "box" even though almost all the rotational energy gained comes from de-exiting the electronic degrees of freedom rather than from translation. This makes the $(\frac{1}{2},0) \rightarrow (\frac{1}{2},2)$ cross section much too large. The failure is therefore an artifact of the classical histogram approximation and <u>not</u> a failure of the classical approximation to the Hamiltonian. Exactly the same failure is to be expected for a nearly resonant rigid-rotor rigid-rotor classical trajectory calculation.

The failure can be (partly) overcome by recognizing that the contour plots are almost "separable" in the new quantum numbers X and Y,

$$X = (j - \frac{1}{2}) + N/2 \qquad\qquad (3.19a)$$

$$Y = (j - \frac{1}{2}) - N/2 \qquad . \qquad (3.19b)$$

Applying the usual histogram procedure to X and Y i.e., replacing the χ-functions of Eq. (3.18) by

$$\chi[X_2(N_1,q_{N_1}, \ldots, q_{m_{j_1}})-X_2] \times \chi[Y_2(N_1, \ldots, q_{m_{j_1}})-Y_2] \qquad ,$$

is equivalent to using the "new boxes" in (j,N)-space which are shown in Figure 6.

An other important observation was that microreversibility is poorly obeyed, i.e., the classical cross sections

$$\sigma_{j_1,N_2 \leftarrow j_1,N_1}(E)$$

and

$$\hat{\sigma}_{j_2,N_2 \leftarrow j_1,N_1}(E) = \frac{E_{j_2,N_2}(2j_2+1)(2N_2+1)}{E_{j_1,N_1}(2j_1+1)(2N_1+1)} \sigma_{j_1,N_1 \leftarrow j_2,N_2}(E)$$

$$(3.20)$$

where $E_{j,N}$ denotes the energy with respect to the (j,N)-state and E is the total energy, could differ by an order of magnitude. We therefore defined the average cross section $\bar{\sigma}$ (which does obey microreversibility) by

$$\bar{\sigma} = \sqrt{\sigma \cdot \hat{\sigma}} \qquad . \qquad (3.21)$$

Symmetrizing the cross sections via a geometric average is much to be preferred to the arithmetic average,

$$\bar{\bar{\sigma}} = \frac{1}{2}(\sigma + \hat{\sigma}) \qquad , \qquad (3.22)$$

which also obeys microreversibility. This is because Eq. (3.21) gives a much better description of a threshold behavior than Eq. (3.22) does. Consider, for example, the troublesome non-resonant transition $(\frac{1}{2},0) \rightarrow (\frac{1}{2},2)$. Below the threshold of 43.9 meV there will be no trajectory starting from the $(\frac{1}{2},2)$ state and hence $\hat{\sigma} \equiv 0$. Thus the geometric average cross section gives $\bar{\sigma} = 0$, the correct result, but the arithmetic average cross section yields $\bar{\bar{\sigma}} = \frac{1}{2}\sigma \neq 0$.

Using the "new boxes" and the geometric average cross section, Eq. (3.21), results in a quite good agreement with the quantum mechanical results,

as seen in Figure 7. Shown are the quenching cross sections,

$$F(^2P_{1/2})^* + H_2(N_1=0) \rightarrow F(^2P_{3/2}) + H_2(N) \quad ,$$
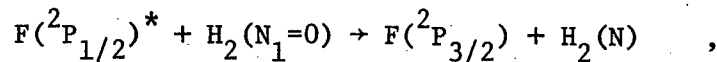
for N = 0,2, and one sees how prominent the resonance effect is at these low collision energies (i.e., H_2 emerges primarily in the N=2 state). The cross sections for quenching by rotationally excited H_2--i.e., the transitions $(\frac{1}{2},2) \rightarrow (\frac{3}{2},2),(\frac{3}{2},0)$--have quantum cross sections[5] $< 1 \text{ Å}^2$ in this energy region, and the quasiclassical results also yield this. The quasiclassical model is, of course, not capable of describing these very weak transitions quantitatively, but it is consistent in giving small values for these cross sections as, for example, for the non-resonant transition in Figure 7.

The important conclusion of these calculations is that the classical model for the electronic degrees of freedom provides a correct description of their dynamics and their interaction with the heavy particle degrees of freedom. Thus even at this completely classical level the resonance effect which dominates this quenching process at low collision energies is correctly described. Furthermore, the somewhat modified quasiclassical histogram model is capable of a reasonably quantitative description of all transitions. There is always the possibility, too, that alternate ways of extracting quantum results from classical trajectories--e.g., the classical moment method,[11] or most rigorously, classical S-matrix theory[7]--may be of use.

IV.   CONCLUDING REMARKS.

In Section II we have presented a new method, based on the equivalence of a finite level quantum system to a quantum spin system in an external field, for deriving a classical Hamiltonian which corresponds to a given matrix representation of a finite level quantum system. For the 2- and 3-state cases it gives essentially the same classical Hamiltonian obtained earlier[1-3] but is somewhat better founded and also shows how to proceed in the general F-level case. (For the 2-level system we have now obtained the same classical Hamiltonian from four completely different approaches!)

One should note that this formal procedure always models the F-level system with one classical degree of freedom. In some cases this may be unphysical. Consider, for example, the Rydberg states of an atom or molecule, for which the states are labeled with quantum numbers n, ℓ and m_{ℓ}. Although it may be possible to construct a classical Hamiltonian with one degree of freedom which will reproduce all these energy levels, one does not expect this to be useful. The reason, of course, is that the states correspond physically to a classical system with three degrees of freedom, i.e., one particle (the electron) in 3-dimensional space.

The classical pseudo-potential analysis of reference 2 is more physically based than the method devised in Section II and, for example, would clearly lead to the correct model for the Rydberg case mentioned above. The pseudo-potential approach in general has the advantage that if one has identified underlying physical origin of the states correctly, then it will provide the correct form of the classical Hamiltonian. It has the disadvantage, though, that it cannot always uniquely give the dependence of the parameters in the classical Hamiltonian on the quantum matrix elements.

In general, therefore, there is still somewhat of an art involved in constructing a classical model for an arbitrary set of electronic states. The method of Section II of this paper give a definite, unambiguous result, but it could be unphysical, while the pseudopotential analysis[2] is physically based but does not always completely define the classical Hamiltonian. When attacking a new electronically non-adiabatic process it is likely that one may need to use some aspects of both these approaches in order to arrive at the "best" classical model for the electronic degrees of freedom. For example, the pseudopotential analysis may be used to determine the _form_ of classical Hamiltonian, and some aspects of the methodology in Section II of this paper may be helpful in uniquely determining the various functions which appear in the classical Hamiltonian determined by the pseudopotential approach.

For the process that we have treated so far, however, e.g., $F^* + H^+$,Xe $\rightarrow$ $F + H^+$,Xe in reference 2, and $F^* + H_2 \rightarrow F + H_2$ in this paper, the origin of the electronic states is sufficiently simple that there is no ambiguity about the correct classical model. Indeed, all roads lead to the same result in these cases.

The results reported in Section III for the quenching of F^* by H_2 are quite good, perhaps surprisingly so in light of the fact that the quantum numbers involved are so small. It is particularly gratifying to see that the resonance effect is described correctly since it was the failure of the "surface hopping" model of Tully and Preston[12] to describe it[4] which was largely responsible for the line of thinking that has lead to the development of these totally classical models for electronically non-adiabatic collision processes.

APPENDIX

The evaluation of the symmetrized matrix products in Eq. (2.11) by straightforward matrix multiplication becomes extremely cumbersome for $F \geq 4$. This appendix shows a simple way to do this for the general case.

First we explain the notation to be used. The spin matrix elements are labeled by $m = -s, -s+1, \ldots, s-1, s$, but it is often more convenient to relabel them by $k = 1, 2, \ldots, F$, where the relations between m and k and s and F are given by

$$F = 2s + 1 \tag{A.1}$$

$$m = k - 1 - s \tag{A.2a}$$

or

$$m = k - \frac{F+1}{2} \tag{A.2b}$$

Sometimes m will be used with a subscript, m_k, to denote the dependence on k, and the following relation is then useful,

$$m_{k+\nu} = m_k + \nu \tag{A.3}$$

The properly symmetrized matrix products are denoted by $\underline{\underline{M}}^{(j)}$, $\underline{\underline{C}}^{(j,\ell)}$ and $\underline{\underline{S}}^{(j,\ell)}$, where the correspondence to the classical functions is

$$m^j \quad \leftrightarrow \quad \underline{\underline{M}}^{(j)} \tag{A.4a}$$

$$m^j (s^2 - m^2)^{\ell/2} \cos\ell q \quad \leftrightarrow \quad \underline{\underline{C}}^{(j,\ell)} \tag{A.4b}$$

$$m^j (s^2 - m^2)^{\ell/2} \sin\ell q \quad \leftrightarrow \quad \underline{\underline{S}}^{(j,\ell)} \tag{A.4c}$$

Upon examining Table I, it is suggestive to write $\underline{\underline{M}}, \underline{\underline{C}}$ and $\underline{\underline{S}}$ as

$$M^{(j)}_{k',k} = \delta_{k',k} \, m_k^{\,j} \tag{A.5a}$$

$$C^{(j,\ell)}_{k',k} = \delta_{k'-\ell,k} \, V^{(j,\ell)}_k + \delta_{k',k-\ell} \, V^{(j,\ell)}_{k'} \tag{A.5b}$$

$$S^{(j,\ell)}_{k',k} = -i \, \delta_{k'-\ell,k} \, V^{(j,\ell)}_k + i \, \delta_{k',k-\ell} \, V^{(j,\ell)}_{k'} \tag{A.5c}$$

Eq. (A.5a) is trivial and Eq. (A.5bc) obviously hold for $\ell=1$. It will become clear shortly that they hold for all $\ell \leq F-1$. Eq. (A.5) enables us to work with vectors $\underline{V}^{(j,\ell)}$ rather than with matrices. From the elementary treatment of angular momentum operators one knows,

$$C^{(0,1)}_{k',k} = (S_x)_{k',k} = \delta_{k'-1,k} \, \frac{1}{2} \sqrt{(s-m_k)(s+m_k+1)}$$

$$+ \delta_{k',k-1} \, \frac{1}{2} \sqrt{(s-m_{k'})(s+m_{k'}+1)} \tag{A.6}$$

and a similar equation holds for $\underline{\underline{S}}^{(0,1)} = \underline{\underline{S}}_y$. Thus,

$$V^{(0,1)}_k = \frac{1}{2} \sqrt{(s-m_k)(s+m_k+1)}$$

$$= \frac{1}{2} \sqrt{k(F-k)} \qquad\qquad k = 1,2, \ldots, F-1 \tag{A.7}$$

To simplify notation we will consistently drop the upper index if it is $(0,1)$, i.e., $\underline{\underline{C}} = \underline{\underline{C}}^{(0,1)}$, $\underline{\underline{S}} = \underline{\underline{S}}^{(0,1)}$, $\underline{V} = \underline{V}^{(0,1)}$.

It is now useful to introduce the matrix $\underline{\underline{E}}$,

$$\underline{\underline{E}} = \underline{\underline{C}} + i\,\underline{\underline{S}} \quad . \tag{A.8}$$

$\underline{\underline{E}}$ corresponds to the classical function e^{iq}. $\underline{\underline{E}}$ and $\underline{\underline{E}}^+$, it's hermitian conjugate, are the usual lowering and raising operators. $\underline{\underline{E}}$ is given in terms of $\underline{V}$ by

$$E_{k',k} = 2\,\delta_{k'-1,k}\,V_k \quad . \tag{A.9}$$

$\underline{\underline{C}}$ and $\underline{\underline{S}}$ are given in terms of $\underline{\underline{E}}$ and $\underline{\underline{E}}^+$ by

$$\underline{\underline{C}} = \frac{1}{2}\,(\underline{\underline{E}} + \underline{\underline{E}}^+) \tag{A.10a}$$

$$\underline{\underline{S}} = \frac{1}{2i}\,(\underline{\underline{E}} - \underline{\underline{E}}^+) \quad . \tag{A.10b}$$

We now evaluate

$$\frac{1}{2}\,(\underline{\underline{E}}^\ell + \underline{\underline{E}}^{+\ell}) = \frac{1}{2}\,((\underline{\underline{C}} + i\underline{\underline{S}})^\ell + (\underline{\underline{C}} - i\underline{\underline{S}})^\ell)$$

$$= \frac{1}{2}\,[\,\sum_{\nu=0}^{\ell} \binom{\ell}{\nu} <\underline{\underline{C}}^{\ell-\nu}\underline{\underline{S}}^\nu> (i^\nu + (-i)^\nu)]$$

$$= \sum_{\nu=0,2,4}^{\ell} \binom{\ell}{\nu} (-1)^{\nu/2} <\underline{\underline{C}}^{\ell-\nu}\underline{\underline{S}}^\nu> \tag{A.11}$$

where the brackets $<\cdots>$ denote again symmetrization via Eq. (2.11). Comparison with Eq. (2.13) shows that Eq. (A.11) is exactly the matrix which corresponds to $(s^2-m^2)^{\ell/2}\cos\ell q$, i.e., $\underline{\underline{C}}^{(0,\ell)}$. Since a similar argument applies to $\underline{\underline{S}}^{(0,\ell)}$ one obtains the following equations

$$\underline{\underline{C}}^{(0,\ell)} = \frac{1}{2} \, (\underline{\underline{E}}^{\ell} + \underline{\underline{E}}^{+\ell}) \qquad\qquad\qquad\qquad (A.12a)$$

$$\underline{\underline{S}}^{(0,\ell)} = \frac{1}{2i} \, (\underline{\underline{E}}^{\ell} - \underline{\underline{E}}^{+\ell}) \qquad . \qquad\qquad\qquad (A.12b)$$

$\underline{\underline{E}}^{\ell}$ is now easy to evaluate:

$$E^{\ell}_{k',k} = \sum_{\substack{n_1=1 \\ \vdots \\ n_{\ell-1}=1}}^{F} \delta_{k'-1,n_1} \, 2V_{n_1} \, \delta_{n_1-1,n_2} \, 2V_{n_2} \cdots \delta_{n_{\ell-1}-1,k} \, 2V_k$$

$$= 2^{\ell} \, \delta_{k'-\ell,k} \prod_{\nu=0}^{\ell=1} V_{k+\nu} \qquad . \qquad\qquad\qquad (A.13)$$

Using Eqs. (A.12) and (A.13) one is able to show that Eqs. (A.5) indeed hold for all ℓ. They also hold for all j since multiplication of a matrix with a diagonal one does not change the location of zeros in that matrix. From Eqs. (A.5), (A.12), and (A.13) it also follows that

$$V_k^{(0,\ell)} = 2^{\ell-1} \prod_{\nu=0}^{\ell-1} V_{k+\nu} \qquad , \qquad\qquad\qquad (A.14)$$

and similar to Eq. (A.9) one has

$$E^{\ell}_{k',k} = 2 \, \delta_{k'-\ell,k} \, V_k^{(0,\ell)} \qquad . \qquad\qquad\qquad (A.15)$$

We have thus derived all matrices which correspond to $\cos\ell q$ and $\sin\ell q$. The remaining task is to find the matrices which corresponds to those

functions multiplied by m^j. Consider therefore the following symmetrized matrix product:

$$\langle \underline{\underline{E}}^{\ell} \underline{\underline{M}}^J \rangle_{k',k} = \frac{J!\ell!}{(J+\ell)!} \sum_{\substack{j_0=0 \\ j_1=0 \\ \vdots \\ j_\ell=0}}^{J} (\underline{\underline{M}}^{j_0} \underline{\underline{E}} \underline{\underline{M}}^{j_1} \underline{\underline{E}} \ldots \underline{\underline{M}}^{j_{\ell-1}} \underline{\underline{E}} \underline{\underline{M}}^{j_\ell})_{k',k} \delta_{J,j_0+j_1\ldots+j_\ell} \quad .$$

$$= \frac{J!\ell!}{(j+\ell)!} 2 \delta_{k'-\ell,k} V_k^{(0,\ell)} \sum_{\substack{j_0=0 \\ \vdots \\ j_\ell=0}}^{J} m^{j_0}(m+1)^{j_1}(m+2)^{j_2}\ldots$$

$$\times (m+\ell)^{j_\ell} \delta_{J,j_0+j_1+\ldots+j_\ell} \quad . \tag{A.16}$$

Since the matrix elements of this symmetrized product are by definition $2 \delta_{k'-\ell,k} V_k^{(J,\ell)}$, we obtain

$$V_k^{(j,\ell)} = V_k^{(0,\ell)} \frac{j!\ell!}{(j+\ell)!} B(m_k,j,\ell) \tag{A.17}$$

where $B(m,J,\ell)$ is given by

$$B(m,J,\ell) = \sum_{\substack{j_0=0 \\ \vdots \\ j_\ell=0}}^{J} m^{j_0}(m+1)^{j_1}\ldots(m+\ell)^{j_\ell} \delta_{J,j_0+j_1+\ldots+j_\ell} \quad . \tag{A.18}$$

The problem is now completely solved, but it is useful to find a simpler expression for B. For $\ell=1$ B is given by

$$B(m,J,\ell=1) = \sum_{j=0}^{J} m^j (m+1)^{J-j} = (m+1)^J \frac{1-(\frac{m}{m+1})^{J+1}}{1-(\frac{m}{m+1})}$$

$$= (m+1)^{J+1} - m^{J+1} \quad . \tag{A.19}$$

This can be generalized to all ℓ, yielding

$$B(m,j,\ell) = \frac{1}{\ell!} \sum_{\nu=0}^{\ell} (-1)^{\nu+\ell} \binom{\ell}{\nu} (m+\nu)^{j+\ell} \quad , \tag{A.20}$$

where $\binom{\ell}{\nu}$ is the binominal coefficient. Eq. (A.20) can be proved by induction over ℓ using the recursion formula

$$B(m,J,\ell+1) = \sum_{j=0}^{J} (m+\ell+1)^j B(m,J-j,\ell) \tag{A.21}$$

which follows directly from Eq. (A.18). By appling the binominal theorem to $(m+\nu)^{j+\ell}$ Eq. (A.20) can be transformed to

$$B(m,j,\ell) = \frac{1}{\ell!} \sum_{\mu=0}^{j} \binom{j+\ell}{\mu+\ell} m^{j-\mu} \sum_{\nu=0}^{\ell} (-1)^{\nu+\ell} \binom{\ell}{\nu} \nu^{\mu+\ell} \quad . \tag{A.22}$$

For large ℓ Eq. (A.22) is easier to use than Eq. (A.20). Since the second sum in Eq. (A.22) depends neither on m nor j, it should be--for fixed ℓ and $\mu=0,1, \ldots, F-\ell$--evaluated once, stored and used to evaluate $B(m,j,\ell)$ for all m and j. In fact, the second sum in Eq. (A.22) can be done analytically, but this becomes increasingly cumbersome for large μ; for the lowest μ values it is

$$\sum_{\nu=0}^{\ell} (-1)^{\nu+\ell} \binom{\ell}{\nu} \nu^{\mu+\ell} = \begin{cases} 0, \quad -\ell \leq \mu \leq -1 \\[2mm] \ell! \, , \qquad\qquad\qquad \mu=0 \\[2mm] (\ell+1)! \, \frac{\ell}{2}, \qquad\qquad \mu=1 \\[2mm] (\ell+2)! \, \frac{\ell}{24}(3\ell+1), \quad \mu=2 \\[2mm] (\ell+3)! \, \frac{\ell^2}{48}(\ell+1), \quad \mu=3 \end{cases} \qquad (A.23)$$

Using Eqs. (A.17), (A.22), and (A.23), one can now evaluate $V^{(j,\ell)}$ for $j = 1,2,3$.

$$V_k^{(1,\ell)} = (m_k + \ell/2) \, V_k^{(0,\ell)} \qquad (A.24a)$$

$$V_k^{(2,\ell)} = (m_k^2 + \ell m_k + \frac{\ell(3\ell+1)}{12}) V_k^{(0,\ell)}$$

$$= \{(m_k + \frac{\ell}{2})^2 + \frac{\ell}{12}\} \, V_k^{(0,\ell)} \qquad (A.24b)$$

$$V_k^{(3,\ell)} = (m_k^3 + \frac{3}{2} \ell m_k^2 + \frac{\ell(3\ell+1)}{4} m_k + \frac{\ell^2(\ell+1)^2}{8}) V_k^{(0,\ell)}$$

$$= \{(m_k + \frac{\ell}{2})^3 + \frac{\ell}{4} (m_k + \frac{\ell}{2})\} \, V_k^{(0,\ell)} \qquad (A.24c)$$

To summarize, in this Appendix we have derived simple expressions for the matrices $\underline{\underline{M}}^{(j)}$, $\underline{\underline{C}}^{(j,\ell)}$, $\underline{\underline{S}}^{(j,\ell)}$. To obtain the classical Hamiltonian function $H(m,q)$ it is necessary to expand the given Hamiltonian matrix $\underline{\underline{H}}$ in a sum of

these matrices, i.e.,

$$\underline{\underline{H}} = \sum_{j=0}^{F-1} d_j \underline{\underline{M}}^{(j)} + \sum_{\ell=1}^{F-1} \sum_{j=0}^{F-\ell-1} a_{j\ell} \underline{\underline{C}}^{(j,\ell)} + b_{j,\ell} \underline{\underline{S}}^{(j,\ell)} \tag{A.25}$$

where d_j, $a_{j,\ell}$, $b_{j,\ell}$ are the F^2 real coefficients to be determined. Recognizing that matrices of different type and matrices for different ℓ do not mix and using Eqs. (A.5), one finds the following sets of linear equations for d_j, $a_{j,\ell}$ and $b_{j,\ell}$

$$\sum_{j=0}^{F-1} d_j m_k^j = H_{kk} \qquad\qquad k = 1,2, \ldots, F \tag{A.26a}$$

$$\sum_{j=0}^{F-\ell-1} a_{j,\ell} V_k^{(j,\ell)} = \text{Re}(H_{k,k+\ell}) \qquad\begin{array}{l} \ell = 1,2, \ldots, F-1 \\[4pt] k = 1,2, \ldots, F-\ell \end{array} \tag{A.26b}$$

$$\sum_{j=0}^{F-\ell-1} b_{j,\ell} V_k^{(j,\ell)} = \text{Im}(H_{k,k+\ell}) \qquad\begin{array}{l} \ell = 1,2, \ldots, F-1 \\[4pt] k = 1,2, \ldots, F-\ell \end{array} \tag{A.26c}$$

After solving these linear equations, the classical Hamiltonian is then given by

$$H(m,q) = \sum_{j=0}^{F-1} d_j m^j + \sum_{\ell=1}^{F-1} \sum_{j=0}^{F-\ell-1} m^j (s^2-m^2)^{\ell/2} (a_{j,\ell} \cos\ell q + b_{j\ell} \sin\ell q) . \tag{A.27}$$

It is even possible to express $H(m,q)$ explicitly in terms of the matrix elements $H_{k,k'}$, by the following procedure. One first defines

$$V_k^{(j,0)} = m_k^j \quad , \tag{A.28}$$

and this enables one to include the q independent terms in the sum over the $\cos \ell q$ terms. For fixed ℓ one then considers $V_k^{(j,\ell)}$ as a $(F-\ell) \times (F-\ell)$ matrix. The inverse of this matrix is given by $\underline{\underline{W}}^{(\ell)}$, i.e., $W_{j,k}^{(\ell)}$ is defined by

$$\sum_{k=1}^{F-\ell} W_{j',k}^{(\ell)} \; V_k^{(j,\ell)} = \delta_{j',j} \tag{A.29a}$$

or

$$\sum_{j=0}^{F-\ell-1} V_k^{(j,\ell)} \; W_{j,k'}^{(\ell)} = \delta_{k,k'} \tag{A.29b}$$

With the aid of the matrices $\underline{\underline{W}}^{(\ell)}$, the coefficients d_j, $a_{j,\ell}$ and $b_{j,\ell}$ are easy to evaluate:

$$d_j = \sum_{k=1}^{F} W_{j,k}^{(0)} \; H_{k,k} \tag{A.30a}$$

$$a_{j,\ell} = \sum_{k=1}^{F-\ell} W_{j,k}^{(\ell)} \; \mathrm{Re}(H_{k,k+\ell}) \tag{A.30b}$$

$$b_{j,\ell} = \sum_{k=1}^{F-\ell} W_{j,k}^{(\ell)} \; \mathrm{Im}(H_{k,k+\ell}) \quad . \tag{A.30c}$$

Substituting Eqs. (A.30) into Eq. (A.27) finally yields

$$H(m,q) = \sum_{\ell=0}^{F-1} \sum_{j=0}^{F-\ell-1} m^j (s^2-m^2)^{\ell/2} \cos\ell q \cdot \sum_{k=1}^{F-\ell} W_{j,k}^{(\ell)} \, \text{Re}(H_{k,k+\ell})$$

$$+ \sum_{\ell=1}^{F-1} \sum_{j=0}^{F-\ell-1} m^j (s^2-m^2)^{\ell/2} \sin\ell q \cdot \sum_{k=1}^{F-\ell} W_{j,k}^{(\ell)} \, \text{Im}(H_{k,k+\ell}) \ . \quad (A.31)$$

For all practical applications one then makes a Langer type modification, i.e., replaces s^2 by $(s+\frac{1}{2})^2$ in Eqs. (A.27) and (A.31). Table II lists the matrices $\underline{\underline{W}}^{(\ell)}$ for the cases $F = 2,3,4$.

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Acknowledgments

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‡ Postdoctoral Fellow of the Deutsche Forschungsgemeinschaft.

‡‡ Camille and Henry Dreyfus Teacher-Scholar.

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Table I. Correspondence between Classical Functions and Symmetrized Angular
Momentum Operator Products (and their Matrix Representations).

Matrix Representations

Classical Function	Operator Product	$s = 1/2$	$s = 1$	$s = 3/2$
1	1_{op}	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$
m	S_z	$\dfrac{1}{2}\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\dfrac{1}{2}\begin{pmatrix} -3 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}$
m^2	S_z^2	--	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\dfrac{1}{4}\begin{pmatrix} 9 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 9 \end{pmatrix}$
m^3	S_z^3	--	--	$\dfrac{1}{8}\begin{pmatrix} -27 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 27 \end{pmatrix}$
$(s^2-m^2)^{1/2}\cos q$	S_x	$\dfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\dfrac{\sqrt{2}}{2}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\dfrac{1}{2}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$
$m(s^2-m^2)^{1/2}\cos q$	$\langle S_z S_x\rangle$	--	$\dfrac{\sqrt{2}}{4}\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\dfrac{\sqrt{3}}{2}\begin{pmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$
$m^2(s^2-m^2)^{1/2}\cos q$	$\langle S_z^2 S_x\rangle$	--	--	$\dfrac{1}{24}\begin{pmatrix} 0 & 13\sqrt{3} & 0 & 0 \\ 13\sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & 13\sqrt{3} \\ 0 & 0 & 13\sqrt{3} & 0 \end{pmatrix}$

Table I. continued

| Classical Function	Operator Product	s = 1/2	s = 1	s = 3/2
$(s^2-m^2)^{1/2}\sin q$	S_y	$\dfrac{i}{2}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\dfrac{\sqrt{2}}{2}i\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$	$\dfrac{i}{2}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}$
$m(s^2-m^2)^{1/2}\sin q$	$\langle S_x S_y\rangle$	--	$\dfrac{\sqrt{2}}{4}i\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$	$\dfrac{\sqrt{3}}{2}i\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$
$m^2(s^2-m^2)^{1/2}\sin q$	$\langle S_z^2 S_y\rangle$	--	--	$\dfrac{i}{24}\begin{pmatrix} 0 & 13\sqrt{3} & 0 & 0 \\ -13\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & 13\sqrt{3} \\ 0 & 0 & -13\sqrt{3} & 0 \end{pmatrix}$
$(s^2-m^2)\cos 2q$	$\langle S_x^2 - S_y^2\rangle$	--	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\sqrt{3}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$
$m(s^2-m^2)\cos 2q$	$\langle S_z(S_x^2 - S_y^2)\rangle$	--	--	$\dfrac{\sqrt{3}}{2}\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$
$(s^2-m^2)\sin 2q$	$\langle 2S_x S_y\rangle$	--	$i\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	$i\sqrt{3}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$
$m(s^2-m^2)\sin 2q$	$\langle 2S_x S_y S_z\rangle$	--	--	$\dfrac{\sqrt{3}}{2}i\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$
$(s^2-m^2)^{3/2}\cos 3q$	$\langle S_x^3 - 3S_x S_y^2\rangle$	--	--	$3\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$
$(s^2-m^2)^{3/2}\sin 3q$	$\langle 3S_y S_x^2 - S_y^3\rangle$	--	--	$3i\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$

Table II. The Matrices $\underset{=}{W}^{(\ell)}$ Appearing in Eq. (A.31).

	F=2	F=3	F=4
$\ell=0$	$\dfrac{1}{2}\begin{pmatrix} 1 & 1 \\ -2 & 2 \end{pmatrix}$	$\dfrac{1}{2}\begin{pmatrix} 0 & 2 & 0 \\ -1 & 0 & 1 \\ 1 & -2 & 1 \end{pmatrix}$	$\dfrac{1}{48}\begin{pmatrix} -3 & 108 & 108 & -3 \\ 2 & -216 & 216 & -2 \\ 12 & -48 & -48 & 12 \\ -8 & 96 & 96 & 8 \end{pmatrix}$
$\ell=1$	2	$\dfrac{\sqrt{2}}{2}\begin{pmatrix} 1 & 1 \\ -2 & 2 \end{pmatrix}$	$\dfrac{\sqrt{3}}{36}\begin{pmatrix} -1 & 13\sqrt{3} & -1 \\ -12 & 0 & 12 \\ 12 & -12\sqrt{3} & 12 \end{pmatrix}$
$\ell=2$		1	$\dfrac{\sqrt{3}}{6}\begin{pmatrix} 1 & 1 \\ -2 & 2 \end{pmatrix}$
$\ell=3$			$\dfrac{1}{3}$

Figure Captions

1. The functions $f_F(n)$ (solid lines) of Eq. (2.21), for F = 2,3,4, compared to the exact function (dashed line) of Eq. (2.22).

2. The functions $g_F(n)$ (solid lines) of Eq. (2.21), for F = 3,4 ($g_2(n) \equiv 0$), compared to the exact function (dashed line) of Eq. (2.22).

3. Lowest energy levels for infinitely separated collidants $F(^2P_j)$ and $H_2(N)$, where j is the total electronic angular momentum quantum number of F and N the rotational quantum number of H_2.

4. Contour plot of the distinction of final (j,N)-values resulting from the classical trajectory calculation with $(j_1,N_1) = (\frac{1}{2},0)$ and energy E = 10 meV. The dashed line is the "resonance line" $\varepsilon_F(j) + \varepsilon_{H_2}(N) = 0$, and the dotted lines correspond to 10 meV increments off resonance. The points are the locations of the discrete quantum values of j and N. No classical trajectories give (j,N)-values outside the largest contour (solid line).

5. Same as Figure 4 except for energy E = 50 meV.

6. Solid lines show the quantum number "boxes" for the conventional histogram method, and the dashed lines show the "modified boxes" described in the text.

7. Cross sections for quenching of $F^*(^2P_{1/2})$ by non-rotating (i.e., N_1 = 0) H_2, as a function of initial translational energy E. The solid curves are the quantum mechanical results of reference 5, and the points are the results of the quasiclassical trajectory calculation (with Monte Carlo error estimates indicated). Note the break in the scale.
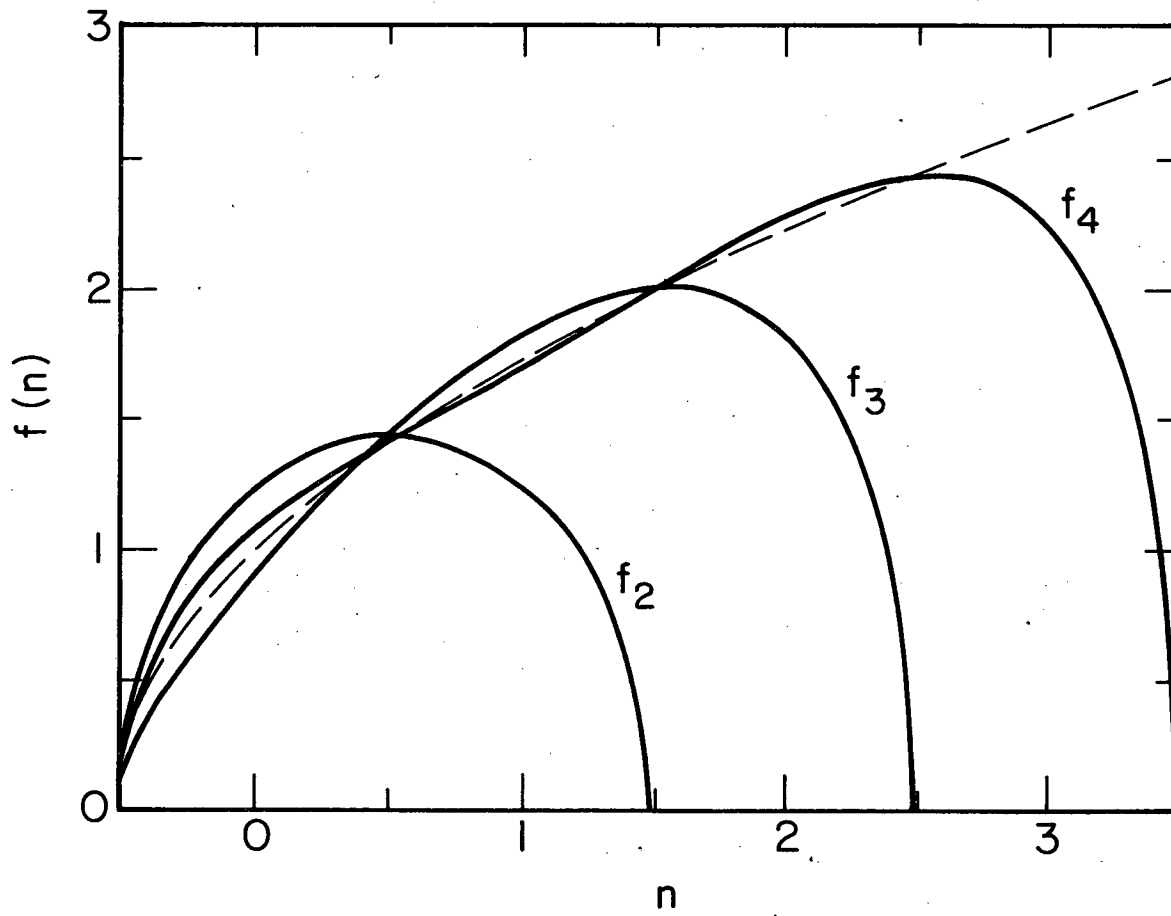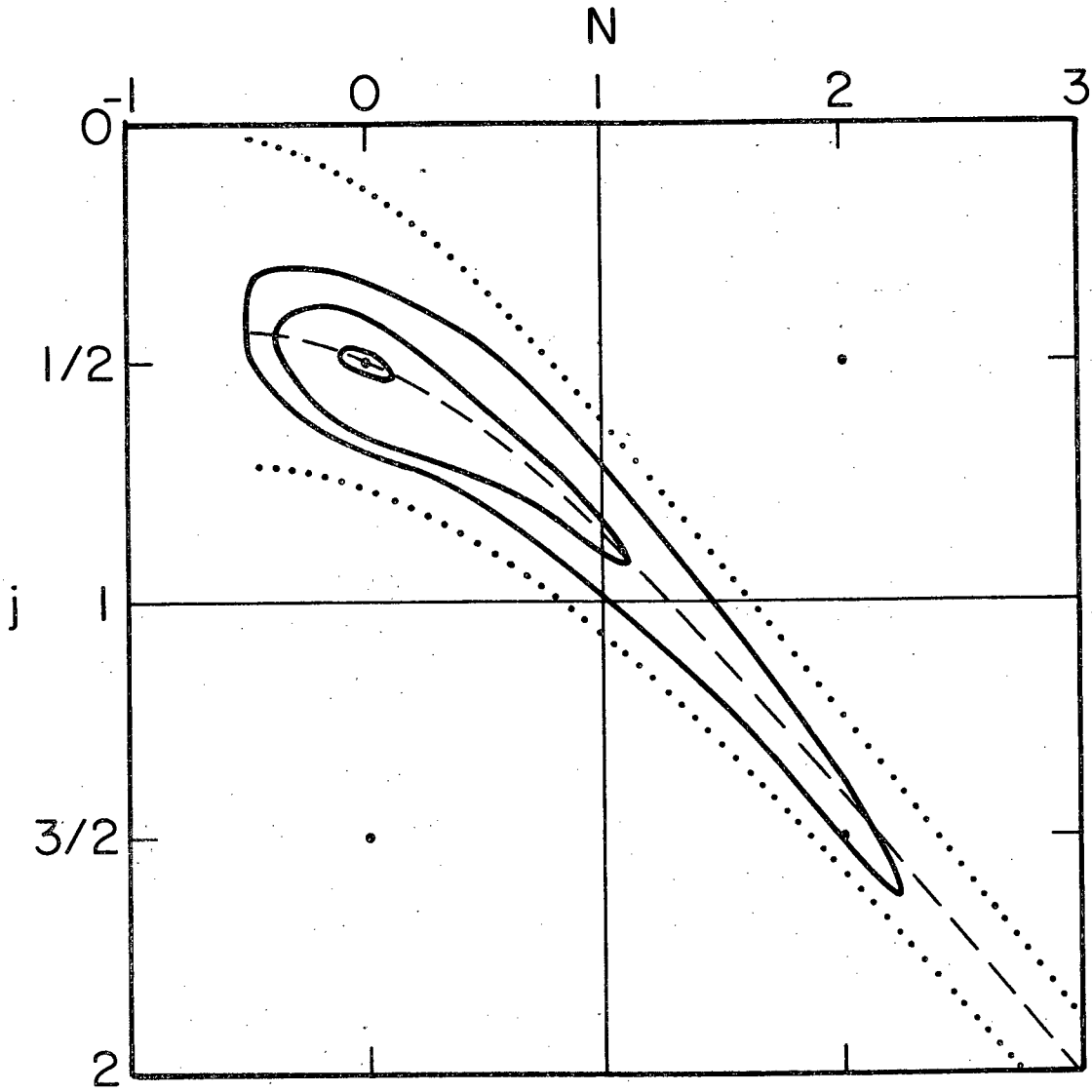
Figure 1

XBL 795-9573

Figure 2
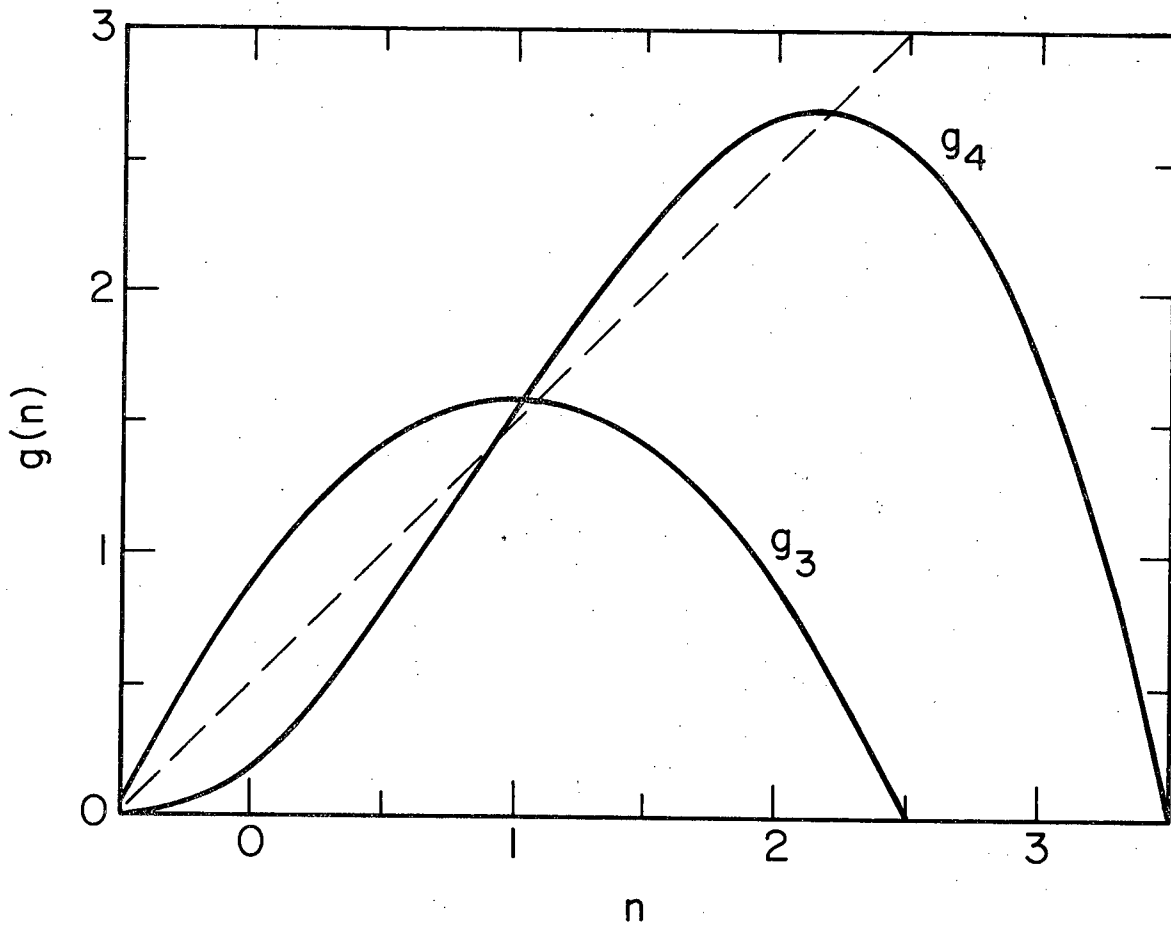
XBL 795-9572

Energy (meV)	State (j,N)
43.9 ——	(1/2,2)
0 ——	(1/2,0)
-6.2 ══	(3/2,2)
-50.1 ——	(3/2,0)

XBL 795-9571

Figure 3

XBL 795-9569

Figure 4

XBL 795-9568

Figure 5

XBL 795-9570

Figure 6

Figure 7

XBL 795-9567