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### Publication Date

1975-07-01

Submitted to  
Journal of Chemical Physics

LBL-3990  
Preprint **C. 1**

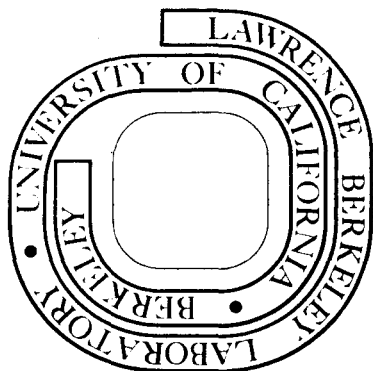
SEMICLASSICAL EIGENVALUES FOR NON-SEPARABLE  
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IN ACTION-ANGLE VARIABLES

Sally Chapman, Bruce C. Garrett and William H. Miller

July 1975

Prepared for the U.S. Energy Research and  
Development Administration under Contract W-7405-ENG-48

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LBL-3990  
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SEMICLASSICAL EIGENVALUES FOR NON-SEPARABLE SYSTEMS:  
NON-PERTURBATIVE SOLUTION OF THE HAMILTON-JACOBI EQUATION  
IN ACTION-ANGLE VARIABLES\*

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ABSTRACT

It is shown how the Hamilton-Jacobi equation for a multi-dimensional non-separable system can be efficiently solved directly in action-angle variables. This allows one to construct the total (classical) Hamiltonian as a function of the "good" action-angle variables which are the complete set of constants of the motion of the system; requiring the action variables to be integers then provides the semiclassical eigenvalues. Numerical results are presented for a two-dimensional potential well, and one sees that the semiclassical eigenvalues are in good agreement with the exact quantum mechanical values even for the case of large non-separable coupling.

I. INTRODUCTION.

Recent years have seen considerable progress in the development of semiclassical methods for describing the dynamics of molecular systems. Most attention has focused on molecular collision processes,<sup>1,2</sup> both elastic and inelastic-reactive scattering of atoms and molecules, but there has also been interest in developing semiclassical methods for determining discrete eigenvalues (i.e., energy levels) of bound molecular systems. It is this latter topic with which the present paper is concerned.

The Bohr-Sommerfeld quantum condition,<sup>3</sup>

$$(n + \frac{1}{2})\pi = \int_{x_{<}}^{x_{>}} dx \{2m[E-V(x)]/\hbar^2\}^{1/2}, \quad (1.1)$$

$n = 0, 1, 2, \dots$ , which defines the eigenvalues  $E(n)$  implicitly, is the semiclassical solution to the eigenvalue problem for one-dimensional potential wells  $V(x)$ ; it is a well-known result and immensely useful in many areas of chemistry and molecular physics. What one desires is the generalization of this result to multi-dimensional, non-separable potential functions.

Einstein<sup>4</sup> was the first to make significant progress in obtaining a semiclassical quantum condition for non-separable multidimensional systems, and Born's<sup>5</sup> book describes the height to which the "Old Quantum Theory" had evolved by 1924, just before the advent of quantum mechanics. More recently a number of workers<sup>6-13</sup> have made contributions to the problem. Keller,<sup>6</sup> following Einstein's approach, has focused attention on the Hamilton-Jacobi equation in cartesian

coordinates, the multivalued structure of its solutions, their caustics, turning surfaces, etc. The work of Maslov,<sup>7</sup> Percival,<sup>10</sup> and Voros<sup>13</sup> has also been along this general line. Marcus,<sup>11</sup> recent work is also an application of Keller's<sup>6</sup> formalism, but he has shown how invariant manifolds generated by quasiperiodic trajectories can be used to construct the multivalued action functions which appear in Keller's theory. Pechukas<sup>9</sup> has attempted a very different approach to the problem, namely mapping the non-separable potential onto a separable one via a generalized Miller-Good transformation. Gutzwiller's<sup>8</sup> approach is also significantly different from the others; it is based on a stationary phase approximation to the trace of the semiclassical propagator. Miller<sup>12</sup> has recently modified and clarified some of the features of Gutzwiller's result and in fact shown that it is an approximate version of Keller's<sup>6</sup> formalism.

The present paper follows the approach of Born:<sup>5</sup> One divides the total Hamiltonian  $H$  into a separable part,  $H_0$ , plus a non-separable interaction  $V$ . The goal is then to construct the canonical transformation from the zero<sup>th</sup> order action-angle variables which correspond to  $H_0$ , to the set of "good" action-angle variables for the total Hamiltonian  $H$ ; in terms of these "good" action-angle variables  $H$  is a function only of the action variables, and this function, for integer values of the action variables, gives the eigenvalues. However, whereas Born's approach is only able to effect this transformation within the framework of perturbation theory--e.g., Born<sup>5</sup> gives explicit expressions for the semiclassical

eigenvalues through second order in the non-separable perturbation V--Sections II and IV below show how it can be carried out efficiently to infinite order, i.e., exactly. Section II first considers the case of a harmonic reference potential, and Section III presents a numerical example to demonstrate how the theory can be applied. Section IV then shows how the approach can be generalized to treat systems with a general (anharmonic) reference potential. The resulting procedure appears to be a powerful and accurate way of constructing semiclassical eigenvalues for non-separable multidimensional systems. Section V concludes by discussing how the approach relates to some of the other recent work discussed above.



## II. HARMONIC REFERENCE POTENTIAL.

The Hamiltonian describing the system is assumed to be of the form

$$H(\underline{p}, \underline{x}) = \frac{\underline{p}^2}{2\mu} + V_0(\underline{x}) + V(\underline{x}) \quad , \quad (2.1)$$

where  $(\underline{x}, \underline{p}) \equiv (x_i, p_i)$ ,  $i=1, \dots, f$  are the cartesian coordinates and momenta and  $f$  is the number of degrees of freedom. (It is no restriction to take all degrees of freedom to have the same mass  $\mu$ .) The reference potential  $V_0(\underline{x})$  is separable,

$$V_0(\underline{x}) = \sum_{i=1}^f v_i(x_i) \quad , \quad (2.2)$$

and in this section it will be assumed that the individual one-dimensional potentials  $v_i(x_i)$  are harmonic:

$$v_i(x_i) = \frac{1}{2} \mu \omega_i^2 x_i^2 \quad . \quad (2.3)$$

The potential  $V(\underline{x})$  is non-separable, the feature which precludes an exact analytic solution to the problem.

Following Born's<sup>5</sup> formulation, one changes from cartesian coordinates and momenta  $(\underline{p}, \underline{x})$  to the action-angle variables<sup>14</sup>  $(\underline{n}, \underline{q})$  which correspond to the reference potential  $V_0$ . For the present case of a harmonic reference potential the cartesian variables  $(\underline{p}, \underline{x})$  are given in terms of the action-angle variables  $(\underline{n}, \underline{q})$  by the following expressions:

$$x_i(n_i, q_i) = \left[ \frac{2n_i+1}{\mu\omega_i} \right]^{1/2} \cos q_i \quad (2.4a)$$

$$p_i(n_i, q_i) = -[(2n_i+1)\mu\omega_i]^{1/2} \sin q_i, \quad (2.4b)$$

$i = 1, 2, \dots, f$ . (The "+1" is added to  $2n_i$  since one knows that half-integer quantum numbers arise in the one-dimensional case--cf. Eq. (1.1)--because of phase contributions from the classical turning points.) If the individual one-dimensional potentials were not harmonic, one could still express  $p_i$  and  $x_i$  in terms of  $n_i$  and  $q_i$ , but the expressions would be different from Eq. (2.4).

In terms of the action-angle variables  $(\underline{n}, \underline{q})$  the Hamiltonian of Eq. (2.1) becomes

$$H(\underline{q}, \underline{n}) = H_0(\underline{n}) + V(\underline{q}, \underline{n}), \quad (2.5)$$

and for the present harmonic case  $H_0$  is given by

$$H_0(\underline{n}) = \sum_{i=1}^f \omega_i \left( n_i + \frac{1}{2} \right) = \underline{\omega} \cdot \left( \underline{n} + \frac{1}{2} \right), \quad (2.6)$$

where one should note that units are being used for which  $\hbar = 1$ .

$V(\underline{q}, \underline{n})$  depends on  $\underline{n}$  and  $\underline{q}$  through Eq. (2.4a); i.e.,

$$V(\underline{q}, \underline{n}) = V(\underline{x}(\underline{n}, \underline{q})) \quad (2.7)$$

If the non-separable interaction  $V$  were absent, i.e.,  $V = 0$ , then the Hamiltonian would depend only on the action variables  $\underline{n}$ ,

$$\lim_{V \rightarrow 0} H(\underline{q}, \underline{n}) = H_0(\underline{n}) \quad , \quad (2.8)$$

and Hamilton's equations

$$\frac{d}{dt} n_i(t) = - \frac{\partial H}{\partial q_i} \quad , \quad (2.9)$$

would thus show the action variables  $\underline{n}$  to be constants of the motion. The eigenvalues of the system would then be obtained by requiring that the action variables only take on integral values, i.e.,

$$E(\underline{n}) = H_0(\underline{n}) \quad , \quad (2.10)$$

with  $\{n_i\}$ ,  $i = 1, 2, \dots, f$  restricted to be integers. The presence of the non-separable interaction  $V(\underline{q}, \underline{n})$ , however, shows via Eq. (2.9) that the  $\{n_i\}$  are not constants of the motion for the total Hamiltonian and thus not the "good" quantum numbers of the system.

What one needs to do, therefore, is to transform from the "unperturbed" action-angle variables  $(\underline{n}, \underline{q})$  to a set of "good" action-angle variables  $(\underline{N}, \underline{Q})$  such that the total Hamiltonian  $H$  depends only on the action variables  $\underline{N}$ . If this can be done, then it is clear that  $\{N_i(t)\}$  will be the constants of the motion for the total Hamiltonian and that the eigenvalues will be given by

$$E(\underline{N}) = H(\underline{N}) \quad ,$$

with the "good quantum numbers"  $\{N_i\}$  required to be integral.

To effect this  $(\underline{n}, \underline{q}) \rightarrow (\underline{N}, \underline{Q})$  transformation, Born<sup>5</sup> introduces a generating function of the  $F_2$ -type,<sup>15</sup> i.e., one which is a function of the "old coordinate"  $\underline{q}$  and the "new momentum"  $\underline{N}$ ,  $F(\underline{q}, \underline{N})$ . The canonical transformation is then defined implicitly by the two differential equations

$$\underline{n}(\underline{q}, \underline{N}) = \frac{\partial F(\underline{q}, \underline{N})}{\partial \underline{q}} \quad (2.11a)$$

$$\underline{Q}(\underline{q}, \underline{N}) = \frac{\partial F(\underline{q}, \underline{N})}{\partial \underline{N}} \quad , \quad (2.11b)$$

which express the other two variables,  $\underline{n}$  and  $\underline{Q}$ , in terms of  $\underline{q}$  and  $\underline{N}$ . The generator  $F$  is determined by substituting Eq. (2.11a) into the Hamiltonian, Eq. (2.5), and requiring that the result be a function only of  $\underline{N}$ :

$$E(\underline{N}) = H_0 \left( \frac{\partial F(\underline{q}, \underline{N})}{\partial \underline{q}} \right) + V \left( \underline{q}, \frac{\partial F(\underline{q}, \underline{N})}{\partial \underline{q}} \right) \quad , \quad (2.12)$$

where  $H(\underline{N})$  has been denoted by  $E(\underline{N})$ . Eq. (2.12) is the Hamilton-Jacobi equation<sup>16</sup> for the generating function  $F$ .

To solve Eq. (2.12) for  $F$  one first notes the solution that would result if  $V$  were set to zero. In that case one would want the "new" action angle variables  $(\underline{N}, \underline{Q})$  to be the same as the "old" ones  $(\underline{n}, \underline{q})$ , and the generator of such an identity transformation is<sup>17</sup>

$$\lim_{V \rightarrow 0} F(\underline{q}, \underline{N}) = \underline{q} \cdot \underline{N} \quad . \quad (2.13)$$

One can easily verify that Eq. (2.11) then gives  $\underline{N} = \underline{n}$  and  $\underline{Q} = \underline{q}$ .

To take explicit account of this separable limit, Eq. (2.13), it is convenient to take  $F$  in the form

$$F(\underline{q}, \underline{N}) = \underline{q} \cdot \underline{N} + G(\underline{q}, \underline{N}) \quad , \quad (2.14)$$

where the function  $G(\underline{q}, \underline{N})$  is to be determined. Using Eq. (2.14), the Hamilton-Jacobi equation, Eq. (2.12), gives the following equation for  $G$ ;

$$E(\underline{N}) = H_0\left(\underline{N} + \frac{\partial G(\underline{q}, \underline{N})}{\partial \underline{q}}\right) + v\left(\underline{q}, \underline{N} + \frac{\partial G(\underline{q}, \underline{N})}{\partial \underline{q}}\right) \quad , \quad (2.15)$$

and for the present case of a harmonic  $H_0$ , this becomes

$$E(\underline{N}) = \omega \cdot \left(\underline{N} + \frac{1}{2}\right) + \omega \cdot \frac{\partial G(\underline{q}, \underline{N})}{\partial \underline{q}} + v\left(\underline{q}, \underline{N} + \frac{\partial G(\underline{q}, \underline{N})}{\partial \underline{q}}\right) \quad . \quad (2.16)$$

At this point Born<sup>5</sup> invokes the boundary conditions which produce quantization. The  $\{N_i\}$  are required to be integers, of course, but in addition  $G(\underline{q}, \underline{N})$  is required to be a periodic function of  $\underline{q}$ . Born's justification for doing this is hard to follow, but it is easy to see why this should be true in light of quantum mechanics: The general semiclassical transformation relations<sup>2</sup> imply that the generator  $F(\underline{q}, \underline{N})$  is related to the wavefunction in  $\underline{q}$ -space by

$$\psi_{\underline{N}}(\underline{q}) \equiv \langle \underline{q} | \underline{N} \rangle \sim \exp\left[\frac{i}{\hbar} F(\underline{q}, \underline{N})\right] \quad , \quad (2.17)$$

and with Eq. (2.14) (and since  $\hbar = 1$  in the present units), this becomes

$$\psi_{\underline{N}}(\underline{q}) \sim \exp(i\underline{q} \cdot \underline{N}) \exp[i \underline{G}(\underline{q}, \underline{N})] \quad (2.18)$$

Single-valuedness of the wavefunction thus implies that the  $\{N_i\}$  should be integers and  $\underline{G}(\underline{q}, \underline{N})$  a periodic function of  $\underline{q}$ .

$\underline{G}(\underline{q}, \underline{N})$  can thus be expanded in a Fourier series

$$\underline{G}(\underline{q}, \underline{N}) = i \sum'_{\underline{k}} B_{\underline{k}} e^{i\underline{k} \cdot \underline{q}} \quad (2.19)$$

where the constant factor  $i$  has been included explicitly for convenience, and where the prime on the summation implies that the constant term  $\underline{k} = (0, 0, 0, \dots, 0) \equiv \underline{0}$  is omitted. ( $B_{\underline{k}}$  is actually a function of  $\underline{N}$  but this functionality will not be explicitly indicated.) Substituting this expansion into Eq. (2.16), multiplying by  $e^{-i\underline{k} \cdot \underline{q}}$ , and integrating over the angles  $\underline{q}$  gives

$$\begin{aligned} E(\underline{N}) \delta_{\underline{k}, \underline{0}} &= \omega \cdot \left(\underline{N} + \frac{1}{2}\right) \delta_{\underline{k}, \underline{0}} - \omega \cdot \underline{k} B_{\underline{k}} \\ &+ (2\pi)^{-f} \int_0^{2\pi} d\underline{q} e^{-i\underline{k} \cdot \underline{q}} V(\underline{q}, \underline{N} - \sum'_{\underline{k}'} \underline{k}' e^{i\underline{k}' \cdot \underline{q}} B_{\underline{k}'}) \quad (2.20) \end{aligned}$$

For  $\underline{k} \neq \underline{0}$  Eq. (2.20) is a set of equations for the Fourier coefficients

$B_{\underline{k}}$ :

$$\omega \cdot \underline{k} B_{\underline{k}} = (2\pi)^{-f} \int_0^{2\pi} d\underline{q} e^{-i\underline{k} \cdot \underline{q}} V(\underline{q}, \underline{N} - \sum'_{\underline{k}'} \underline{k}' e^{i\underline{k}' \cdot \underline{q}} B_{\underline{k}'}) \quad (2.21)$$

and for  $\tilde{k} = 0$  Eq. (2.20) gives the energy eigenvalue  $E(\tilde{N})$  in terms of the Fourier coefficients  $B_{\tilde{k}}$ :

$$E(\tilde{N}) = \tilde{\omega} \cdot (\tilde{N} + \frac{1}{2}) + (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} \, v(\tilde{q}, \tilde{N} - \sum_{\tilde{k}} \tilde{k}' e^{i\tilde{k}' \cdot \tilde{q}} B_{\tilde{k}}) \quad (2.22)$$

The procedure, then, is to solve Eq. (2.21) for the coefficients  $B_{\tilde{k}}$ , and then substitute them into Eq. (2.22) to obtain the energy eigenvalue.

The final formulae are most conveniently expressed if one introduces the coefficients  $A_{\tilde{k}}$  which are defined by

$$A_{\tilde{k}} = (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} \, e^{-i\tilde{k} \cdot \tilde{q}} v(\tilde{q}, \tilde{N} - \sum_{\tilde{k}'} \tilde{k}' e^{i\tilde{k}' \cdot \tilde{q}} B_{\tilde{k}'}) \quad (2.23)$$

From Eq. (2.21) one sees that for  $\tilde{k} \neq 0$ ,  $B_{\tilde{k}}$  is given in terms of  $A_{\tilde{k}}$  by

$$B_{\tilde{k}} = A_{\tilde{k}} / (\tilde{\omega} \cdot \tilde{k}) \quad (2.24)$$

In terms of the coefficients  $A_{\tilde{k}}$ , Eqs. (2.21) and (2.22) thus become

$$A_{\tilde{k}} = (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} \, e^{-i\tilde{k} \cdot \tilde{q}} v(\tilde{q}, \tilde{N} - \sum_{\tilde{k}'} \frac{\tilde{k}' e^{i\tilde{k}' \cdot \tilde{q}}}{\tilde{\omega} \cdot \tilde{k}'} A_{\tilde{k}'}) \quad (2.25a)$$

$$E(\tilde{N}) = \tilde{\omega} \cdot (\tilde{N} + \frac{1}{2}) + A_0 \quad (2.25b)$$

Eq. (2.25) is the final result, and one applies it in the following way: The action variables  $\tilde{N}$  occur in Eq. (2.25) only

as fixed parameters, so they are initially set equal to whichever set of integers one desires, corresponding to whichever eigenvalue one wishes to compute. Eq. (2.25a) must then be solved for the Fourier coefficients  $A_{\tilde{k}}$ , and successive substitution is the most direct way of doing this; i.e., since Eq. (2.25a) is of the form

$$A_{\tilde{k}} = \text{function } [A_{\tilde{k}}] \quad , \quad (2.26)$$

one defines the iteration scheme

$$A_{\tilde{k}}^{(\ell+1)} = \text{function } [A_{\tilde{k}}^{(\ell)}] \quad , \quad (2.27)$$

$\ell = 0, 1, \dots$ , which is initiated by

$$A_{\tilde{k}}^{(0)} = 0 \quad . \quad (2.28)$$

After one iteration, for example, this gives

$$A_{\tilde{k}}^{(1)} = (2\pi)^{-f} \int_0^{2\pi} dq \quad e^{-ik \cdot q} \quad V(q, N) \quad ; \quad (2.29)$$

this result is then substituted into the RHS of Eq. (2.25a) to produce  $A_{\tilde{k}}^{(2)}$ , etc., until  $A_{\tilde{k}}^{(\ell)}$ ,  $\ell \rightarrow \infty$ , takes on a constant value. Since the eigenvalue  $E(N)$ , given by Eq. (2.25b), involves only the  $\tilde{k} = 0$  component of  $A_{\tilde{k}}$ , it is only necessary to carry on this iteration until  $A_0^{(\ell)}$  becomes constant. This, then, is the procedure by which the eigenvalues  $E(N)$  are generated for any set of integers  $\tilde{N} = (N_1, N_2, \dots, N_f)$ .



It is interesting to note that the result of one iteration is equivalent to first order perturbation theory. Eq. (2.29) gives  $A_k^{(1)}$ , so that at this stage Eq. (2.25b) gives the energy as

$$E(\underline{N}) = \underline{\omega} \cdot (\underline{N} + \frac{1}{2}) + (2\pi)^{-f} \int_0^{2\pi} d\underline{q} V(\underline{q}, \underline{N}), \quad (2.30)$$

which is identical to Born's<sup>5</sup> result through first order. Since the RHS of Eq. (2.25a) is a non-linear function of  $A_k$ , however, one can easily verify that the second iterate,  $A_k^{(2)}$ , and the resulting value for  $E(\underline{N})$  given by Eq. (2.25b), is not equivalent to second order perturbation theory.

Although the iteration procedure defined by Eqs. (2.26)-(2.28) is the most convenient way of solving Eq. (2.25a), it may not always be convergent. The Appendix describes an alternate iteration procedure that has superior convergence properties.

### III. NUMERICAL EXAMPLE.

This section applies the procedure developed in Section II to a simple two-dimensional example that has been used as a test case by other workers.<sup>11</sup> The reference potential is harmonic, and the non-separable potential is

$$V(\underline{x}) \equiv V(x_1, x_2) = \lambda x_1 (x_2^2 + \eta x_1^2) \quad , \quad (3.1)$$

where  $\lambda$  and  $\eta$  are constants.

Using Eq. (2.4a) with  $f = 2$ , Eq. (2.25a) reads

$$A_{k_1, k_2} = (2\pi)^{-2} \int_0^{2\pi} dq_1 \int_0^{2\pi} dq_2 e^{-i(k_1 q_1 + k_2 q_2)} V(x_1(q_1, q_2), x_2(q_1, q_2)) \quad , \quad (3.2a)$$

with  $V(x_1, x_2)$  given by Eq. (3.1), where

$$x_1(q_1, q_2) = \left[ \frac{2n_1(q_1, q_2) + 1}{\mu\omega_1} \right]^{1/2} \cos q_1 \quad (3.2b)$$

$$x_2(q_1, q_2) = \left[ \frac{2n_2(q_1, q_2) + 1}{\mu\omega_2} \right]^{1/2} \cos q_2 \quad , \quad (3.2c)$$

with

$$n_1(q_1, q_2) = N_1 - \sum_{k_1, k_2} \frac{k_1 e^{i(k_1 q_1 + k_2 q_2)}}{\omega_1 k_1 + \omega_2 k_2} A_{k_1, k_2} \quad (3.2d)$$

$$n_2(q_1, q_2) = N_2 - \sum_{k_1, k_2} \frac{k_2 e^{i(k_1 q_1 + k_2 q_2)}}{\omega_1 k_1 + \omega_2 k_2} A_{k_1, k_2} \quad (3.2e)$$

For a given set of quantum numbers  $(N_1, N_2)$ , Eq. (3.2) is iterated until  $A_{0,0}$  becomes constant, and then the eigenvalue is given by

$$E(N_1, N_2) = \omega_1(N_1 + \frac{1}{2}) + \omega_2(N_2 + \frac{1}{2}) + A_{0,0} \quad (3.3)$$

Eq. (3.2) may look formidable, but the iteration process is actually a simple procedure operationally because of the availability of Fourier transform and inversion package subroutines. Thus, a grid of  $q_1$  and  $q_2$  values is introduced,

$$q_1^{(\ell_1)} = 2\pi\ell_1/L_1, \quad \ell_1 = 1, \dots, L_1 \quad (3.4)$$

$$q_2^{(\ell_2)} = 2\pi\ell_2/L_2, \quad \ell_2 = 1, \dots, L_2, \quad (3.4b)$$

and the integrals over  $q_1$  and  $q_2$  in Eq. (3.2a) become sums:

$$(2\pi)^{-2} \int_0^{2\pi} dq_1 \int_0^{2\pi} dq_2 f(q_1, q_2) \rightarrow (L_1 L_2)^{-1} \sum_{\ell_1=1}^{L_1} \sum_{\ell_2=1}^{L_2} f(q_1^{(\ell_1)}, q_2^{(\ell_2)}), \quad (3.5)$$

for any function  $f(q_1, q_2)$ . The specific iteration procedure is as follows: Given the matrix of coefficients  $A_{k_1, k_2}$  at any stage of the iteration, the functions  $n_1(q_1, q_2)$  and  $n_2(q_1, q_2)$  of Eqs. (3.2d) and (3.2e) are each evaluated at the complete matrix of grid points

$(q_1^{(\ell_1)}, q_2^{(\ell_2)})$  by a single call of the Fourier inversion subroutine. From these functions the potential  $V$  is evaluated at the matrix of grid points  $(q_1^{(\ell_1)}, q_2^{(\ell_2)})$ , and a single call of the Fourier transform subroutine then generates the matrix  $A_{k_1, k_2}$  via Eq. (3.2a). With this new matrix of coefficients  $A_{k_1, k_2}$ , the functions  $n_1(q_1, q_2)$  and  $n_2(q_1, q_2)$  are re-evaluated at the matrix of grid points  $(q_1^{(\ell_1)}, q_2^{(\ell_2)})$ , etc.

For the numerical results presented below a grid size  $L_1 = L_2 = 8$  was sufficiently large to yield eigenvalues to 4 decimal places, and typically 10-15 iterations were necessary to achieve convergence of  $A_{0,0}$  to this degree of accuracy. Use of the complex fast Fourier transform (CFFT) subroutine of the Computer Library of the Lawrence Berkeley Laboratory made the calculations simple and efficient.

The first calculations were made to compare with the results of Eastes and Marcus<sup>11a</sup> and Noid and Marcus.<sup>11b</sup> This comparison is given in Table I. To the extent that this work<sup>11</sup> based on manifolds of quasi-periodic trajectories and the present work are numerically accurate, one can easily conclude that they should give the same results for the eigenvalues. This is because they are simply different ways of constructing the same thing, the classical Hamiltonian in terms of the two "good" action variables which are constants of the motion. The results in Table I illustrate this conclusion, the small differences in the semiclassical eigenvalues presumably being numerical error.

The semiclassical eigenvalues in Table I are in quite good agreement with the exact quantum mechanical values. The small  $\lambda$  and  $\eta$  values

used in reference 11, however, give only small shifts of the eigenvalues from their unperturbed harmonic values, so the good agreement might not be indicative. Thus another set of calculations was carried out as a function of the non-separable coupling parameters. The quantum mechanical eigenvalues were obtained by diagonalizing the matrix of the Hamiltonian in successively larger harmonic oscillator basis sets.

For the case  $\omega_1 = 0.7$ ,  $\omega_2 = 1.3$ , and  $\eta = -\lambda$ , Table II gives the ground and first two excited state semiclassical and quantum mechanical eigenvalues for  $\lambda = 0 \rightarrow -0.2$ . These results are also displayed in Figure 1. Since this potential function has a relative maximum (i.e., a saddle point) at  $x_1 = \frac{1}{3} (\omega_1/\lambda)^2$ ,  $x_2 = 0$ , of

$$V_{\max} = \frac{\omega_1^6}{54\lambda^4}, \quad (3.6)$$

there can be no eigenvalues above this value. The function  $V_{\max}(\lambda)$  given by Eq. (3.6) is also shown in Figure 1, and one sees that the eigenvalues do tend to break off at this point.

The agreement between the semiclassical and quantum mechanical eigenvalues in Table II and Figure 1 is seen to be quite good. A more severe test of the semiclassical quantum condition, however, is to focus attention on the level shift  $\Delta$ ,

$$\Delta(N_1, N_2) \equiv E(N_1, N_2) - \omega_1(N_1 + \frac{1}{2}) - \omega_2(N_2 + \frac{1}{2}), \quad (3.7)$$

the displacement of the eigenvalue from its unperturbed harmonic

value. Figure 2 shows the percent error in the semiclassical level shift as a function of the non-separable strength parameter  $\lambda$ . The error is seen to be largest for the ground state, as expected, but even here it becomes sizeable only as the eigenvalue approaches the dissociation limit. The error is seen to drop substantially for the first two excited states, and one would expect it to be even less for higher states. In general, this level of accuracy--a few percent, except for the ground state--is typical of that given by the one-dimensional Bohr-Sommerfeld quantum condition [Eq. (1.1)], and one can hardly expect its multidimensional generalization to do better.

IV. GENERAL REFERENCE POTENTIAL.

The iteration procedure for finding the Fourier coefficients  $A_k$  will be most efficient if the reference Hamiltonian  $H_0$  is chosen to make the potential  $V$  as small as possible. To do this it may sometimes be advantageous to choose the one-dimensional potentials  $v_i(x_i)$  in Eq. (2.2) to be anharmonic; e.g., one might wish to take them to be Morse potentials

$$v_i(x_i) = D_i [e^{-(x_i - x_0)/a_i} - 1]^2 \quad (4.1)$$

In this case  $H_0(\tilde{n})$  is not given by Eq. (2.6), but by a more complicated function of the action variables  $\{n_i\}$ . For  $f$  Morse oscillators, for example,

$$H_0(\tilde{n}) = \sum_{i=1}^f \left[ \omega_i \left( n_i + \frac{1}{2} \right) - \frac{\omega_i^2}{4D_i} \left( n_i + \frac{1}{2} \right)^2 \right] \quad (4.2)$$

where

$$\omega_i = \left( \frac{2D_i}{\mu a_i} \right)^{1/2}$$

In this section we consider a general function  $H_0(\tilde{n})$  as the reference Hamiltonian.

The analysis in Section II up to Eq. (2.14) is exactly the same for the more general case now under consideration, and in Eq. (2.15) we add and subtract the first two terms in a Taylor's series expansion of  $H_0$ :

$$\begin{aligned}
 E(\underline{\tilde{N}}) = & [H_0(\underline{\tilde{N}}) + \underline{\omega}(\underline{\tilde{N}}) \cdot \frac{\partial G(\underline{q}, \underline{\tilde{N}})}{\partial \underline{q}} ] \\
 & + [V(\underline{q}, \underline{\tilde{N}} + \frac{\partial G(\underline{q}, \underline{\tilde{N}})}{\partial \underline{q}}) + H_0(\underline{\tilde{N}} + \frac{\partial G(\underline{q}, \underline{\tilde{N}})}{\partial \underline{q}}) - H_0(\underline{\tilde{N}}) \\
 & - \underline{\omega}(\underline{\tilde{N}}) \cdot \frac{\partial G(\underline{q}, \underline{\tilde{N}})}{\partial \underline{q}} ] \quad , \quad (4.3)
 \end{aligned}$$

where

$$\omega_i(\underline{\tilde{N}}) = \frac{\partial H_0(\underline{\tilde{N}})}{\partial N_i} \quad , \quad (4.4)$$

$$i = 1, 2, \dots, f.$$

Since the action variables  $\underline{\tilde{N}}$  only play the role of fixed parameters in Eq. (4.3), the frequency vector  $\underline{\omega}(\underline{\tilde{N}})$  is a constant vector just as in Section II; thus if the first term in square brackets in Eq. (4.3) is identified as a new "H<sub>0</sub>", and the second term in square brackets is identified as a new "V", then Eq. (4.3) has exactly the same form as Eq. (2.16) of Section II. With these identifications one can appeal directly to Eq. (2.25) and write down the answer for this more general situation: The Fourier coefficients  $A_{\underline{k}}$  are thus determined by the equation

$$\begin{aligned}
 A_{\underline{k}} = & (2\pi)^{-f} \int_0^{2\pi} d\underline{q} \quad e^{-i\underline{k} \cdot \underline{q}} \quad [H(\underline{q}, \underline{\tilde{N}} - \sum_{\underline{k}'} \frac{\underline{k}' e^{i\underline{k}' \cdot \underline{q}}}{\underline{\omega}(\underline{\tilde{N}}) \cdot \underline{k}'} A_{\underline{k}'}) \\
 & - H_0(\underline{\tilde{N}}) + \sum_{\underline{k}'} e^{i\underline{k}' \cdot \underline{q}} A_{\underline{k}'}] \quad ,
 \end{aligned}$$



which is equivalent to

$$A_{\tilde{k}} = A_{\tilde{k}} - [H_0(\tilde{N}) + A_0] \delta_{\tilde{k},0} + (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} e^{-i\tilde{k}\cdot\tilde{q}} H(\tilde{q}, \tilde{N} - \sum_{\tilde{k}'} \frac{\tilde{k}' e^{i\tilde{k}'\cdot\tilde{q}}}{\omega(\tilde{N})\cdot\tilde{k}'} A_{\tilde{k}'}) , \quad (4.5)$$

and the energy eigenvalue is then given by

$$E(\tilde{N}) = H_0(\tilde{N}) + A_0 . \quad (4.6)$$

The final expressions take on a simpler form if one makes the replacement  $A_{\tilde{k}} \rightarrow A_{\tilde{k}} - \delta_{\tilde{k},0} H_0(\tilde{N})$  in Eqs. (4.5) and (4.6), whereby Eqs. (4.5) and (4.6) become

$$A_{\tilde{k}} = (1 - \delta_{\tilde{k},0}) A_{\tilde{k}} + (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} e^{-i\tilde{k}\cdot\tilde{q}} H(\tilde{q}, \tilde{N} - \sum_{\tilde{k}'} \frac{\tilde{k}' e^{i\tilde{k}'\cdot\tilde{q}}}{\omega(\tilde{N})\cdot\tilde{k}'} A_{\tilde{k}'}) \quad (4.7a)$$

$$E(\tilde{N}) = A_0 . \quad (4.7b)$$

The meaning of Eq. (4.7) is the same as with Eq. (2.25) of Section II. For a given set of integers  $\tilde{N}$  one solves Eq. (4.7a) for the Fourier coefficients, and the eigenvalue corresponding to these quantum numbers is then given by Eq. (4.7b). As in Section II, the most direct way of solving Eq. (4.7a) is by successive substitution; i.e., Eq. (4.7a) is also in the form of Eq. (2.26), so that the iteration scheme defined by Eq. (2.27) and (2.28) is applicable. After one iteration, for example, one has

$$A_{\tilde{k}}^{(1)} = (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} e^{-i\tilde{k}\cdot\tilde{q}} H(\tilde{q}, N) \quad , \quad (4.8)$$

so that the result for the energy at this stage is

$$E(N) = (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} H(\tilde{q}, N) \quad , \quad (4.9)$$

the analogue of Eq. (2.30).

As noted at the end of Section II, iterating Eq. (4.7a) by successive substitution will not always be a convergent process. An iteration scheme with better convergence properties is described in the Appendix.

V. CONCLUDING REMARKS.

Eq. (2.25), or Eq. (4.7) for the case of a general reference Hamiltonian (or Eq. (A.11) in the Appendix), provides an efficient way of solving the Hamilton-Jacobi equation directly in action-angle variables and obtaining the Hamiltonian in terms of the "good" action variables  $N$ , and thus the semiclassical eigenvalues. Furthermore, the numerical results presented in Section II show that the semiclassical quantum condition for multidimensional systems can give good agreement with quantum mechanical eigenvalues even when the non-separability is quite large. To the extent that Keller's<sup>6</sup> formalism can be applied--and Marcus'<sup>7</sup> use of quasi-periodic trajectories is the only way now known for doing it--it and the present work give identical results for the semiclassical eigenvalues  $E(N)$ . This follows because they are both ways, albeit quite different, of constructing the energy in terms of the "good" action variables which are constants of the motion.

One of the important practical advantages of Born's<sup>5</sup> formulation, which has been followed in this paper, over Keller's<sup>6</sup> is that by dealing with the Hamilton-Jacobi equation in action-angle variables [Eq. (2.15)] one does not have to worry about the complicated structure of multivalued solutions, many-sheeted Riemann surfaces, caustics, turning surfaces, etc. This is because the unperturbed action-angle variables  $(\underline{n}, \underline{q})$  already have the topology of this structure built into them; i.e., the canonical transformation from  $(\underline{p}, \underline{x})$  to  $(\underline{n}, \underline{q})$  eliminates all of these complications. This resembles in spirit

Pechukas'<sup>9</sup> idea of using an underlying separable reference potential to carry the complicated multivalued structure of the action function. It appears, however, that solving the Hamilton-Jacobi equation in action-angle variables may be easier to accomplish than carrying out a generalized Miller-Good transformation.<sup>9</sup>

Finally, although we have discussed several ways of solving the equations for the Fourier coefficients  $A_k$  (or  $B_k$ ), the very existence of such solutions has not been proved. It seems intuitively clear that a solution will exist at least for potential functions and energy regimes that possess invariant manifolds of quasi-periodic trajectories--the KAM regime.<sup>18</sup> Whether solutions exist under more general conditions is not known. In certain cases, typically for highly excited states with many degrees of freedom, one actually expects that solutions will fail to exist, for here the eigenvalue spectrum is expected to become irregular,<sup>10,19</sup> unable to be characterized by a complete set of "good" quantum numbers. Keller's formalism must also fail in this case, too; e.g., Marcus'<sup>11</sup> approach is not possible because manifolds of quasi-periodic trajectories do not exist in the case of an irregular spectrum. Thus none of the existing approaches to semiclassical quantization seem capable of dealing with an irregular spectrum. For highly excited vibrational states of large molecules, however, one is usually less concerned about specific eigenvalues than with the density of quantum states as a function of energy. To the extent that this is true, then, the lack of a semiclassical condition for irregular spectra is not a serious shortcoming.

0 0 0 0 4 3 0 6 7 0 4

ACKNOWLEDGMENT

All calculations reported herein were performed on a  
Datacraft 6024/4 minicomputer funded by NSF grant GP-39317.

APPENDIX: A MORE EFFICIENT ITERATION PROCEDURE

Eqs. (2.25a) and (4.7a) for the Fourier coefficients  $A_k$  are of the form

$$x = f(x) \quad , \quad (A.1)$$

for the case of a single variable  $x$ , and the iteration procedure described for solving them corresponds to

$$x_{\ell+1} = f(x_{\ell}) \quad , \quad (A.2)$$

$\ell = 0, 1, 2, \dots$ , with  $x_0$  being some initial guess to begin the iteration. It is well known,<sup>20</sup> however, that the iteration defined by Eq. (A.2) converges to the root  $x_{\infty}$  only if

$$|f'(x_{\infty})| < 1 \quad . \quad (A.3)$$

One would like to have an iteration procedure that is more generally convergent.

This is easily accomplished by re-writing Eq. (A.1) as

$$F(x) \equiv f(x) - x = 0 \quad , \quad (A.4)$$

and applying Newton's iteration procedure to  $F(x)$ . This gives

$$x_{\ell+1} = x_{\ell} - F'(x_{\ell})^{-1} F(x_{\ell}) \quad , \quad (A.5)$$

$\ell = 0, 1, 2, \dots$ , which is guaranteed to converge if

$$F'(x) \neq 0 \quad (A.6)$$

for all  $x$ . In practice, too, this convergence criterion can often be relaxed.

Eq. (A.5) thus has much better convergence properties than Eq. (A.2); the price paid is that Eq. (A.5) requires evaluation of the derivative of the function whereas Eq. (A.2) does not. If Eq. (A.1) is generalized to  $N$  equations in  $N$  unknowns,

$$\underline{x} = \underline{f}(\underline{x}) \quad , \quad (\text{A.7})$$

then Eq. (A.2) is generalized in the obvious fashion,

$$\underline{x}_{l+1} = \underline{f}(\underline{x}_l) \quad . \quad (\text{A.2}')$$

Eq. (A.5) is generalized by the first factor in the second term becoming a matrix:

$$\underline{x}_{l+1} = \underline{x}_l - \left[ \frac{\partial \underline{F}(\underline{x}_l)}{\partial \underline{x}_l} \right]^{-1} \cdot \underline{F}(\underline{x}_l) \quad , \quad (\text{A.5}')$$

where  $\underline{F}(\underline{x}) \equiv \underline{f}(\underline{x}) - \underline{x}$  and where the matrix elements are defined by

$$\left[ \frac{\partial \underline{F}(\underline{x})}{\partial \underline{x}} \right]_{i,j} \equiv \frac{\partial F_i(\underline{x})}{\partial x_j} \quad . \quad (\text{A.8})$$

For the multidimensional case Eq. (A.5') is thus further complicated by requiring a matrix inversion.

We now give the explicit expressions for the multidimensional Newton iteration procedure applied to the problem of present interest. Since the harmonic reference potential of Section II is a special case of the more general situation treated in Section IV,

we consider only the latter case. The analog of Eq. (2.20)

for the general case is

$$E(\underline{N})\delta_{\underline{k},0} = (2\pi)^{-f} \int_0^{2\pi} d\underline{q} e^{-i\underline{k}\cdot\underline{q}} H(\underline{q}, \underline{N} - \sum_{\underline{k}'} \underline{k}' e^{i\underline{k}'\cdot\underline{q}} B_{\underline{k}'}) . \quad (\text{A.9})$$

For  $\underline{k} \neq 0$  this is a set of equations for the Fourier coefficients

$B_{\underline{k}}$ ,

$$0 = (2\pi)^{-f} \int_0^{2\pi} d\underline{q} e^{-i\underline{k}\cdot\underline{q}} H(\underline{q}, \underline{N} - \sum_{\underline{k}'} \underline{k}' e^{i\underline{k}'\cdot\underline{q}} B_{\underline{k}'}) , \quad (\text{A.10a})$$

and for  $\underline{k} = 0$  it gives the eigenvalue in terms of the coefficients

$B_{\underline{k}}$ :

$$E(\underline{N}) = (2\pi)^{-f} \int_0^{2\pi} d\underline{q} H(\underline{q}, \underline{N} - \sum_{\underline{k}'} \underline{k}' e^{i\underline{k}'\cdot\underline{q}} B_{\underline{k}'}) . \quad (\text{A.10b})$$

Applying the multidimensional Newton iteration [Eq. (A.5')] to

Eq. (A.10a) gives the following iteration procedure for the

coefficients  $B_{\underline{k}}$ :

$$B_{\underline{k}}^{(\ell+1)} = B_{\underline{k}}^{(\ell)} + \sum_{\underline{k}'} (M^{-1})_{\underline{k},\underline{k}'} W_{\underline{k}'} , \quad (\text{A.11a})$$

where the matrix elements  $M_{\underline{k},\underline{k}'}$  and vector  $W_{\underline{k}}$  involve  $B_{\underline{k}}^{(\ell)}$

and are defined by



$$M_{\tilde{k}, \tilde{k}'} = (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} e^{-i(\tilde{k}-\tilde{k}') \cdot \tilde{q}} \tilde{k}' \cdot \frac{\partial H(\tilde{q}, \tilde{n})}{\partial \tilde{n}} \Big|_{\tilde{n}=\tilde{n}(\tilde{q})} \quad (\text{A.11b})$$

$$W_{\tilde{k}} = (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} e^{-i\tilde{k} \cdot \tilde{q}} H(\tilde{q}, \tilde{n}) \Big|_{\tilde{n}=\tilde{n}(\tilde{q})} \quad , \quad (\text{A.11c})$$

with

$$\tilde{n}(\tilde{q}) = N - \sum_{\tilde{k}} \tilde{k} e^{i\tilde{k} \cdot \tilde{q}} B_{\tilde{k}} \quad (\ell) \quad (\text{A.11d})$$

Once the coefficients  $B_{\tilde{k}}$  are determined, the eigenvalue is the  $\tilde{k} = 0$  component of the vector  $W_{\tilde{k}}$ :

$$E(N) = W_0 \quad (\text{A.11e})$$

Eq. (A.11) is the desired result. Although it is more difficult to apply than the iteration procedures described in Sections II and IV--because it requires derivatives of the Hamiltonian and a matrix inversion--it has better convergence properties. If the simpler algorithms converge, then it is probably more convenient to use them (even if they are more slowly convergent than Eq. (A.11)). If convergence is a problem, however, Eq. (A.11) is preferable.

Finally, it is interesting to note that Eq. (A.11) involves the reference Hamiltonian  $H_0$  only implicitly, through the definition of the "unperturbed" action-angle variables  $(\tilde{n}, \tilde{q})$ . Making a specific choice for the unperturbed action-angle variables is the semiclassical

equivalent of choosing a specific basis set when carrying out a quantum mechanical calculation of the eigenvalues.

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TABLE I. Semiclassical Eigenvalues<sup>a</sup>

$\omega_1^2$	$\omega_2^2$	$\lambda$	$\eta$	$N_1$	$N_2$	Ref. 11a	Ref. 11b	Present	Exact Quantum
0.29375	2.12581	-.1116	.08414	0	0	.9920	.9922	.9920	0.9916
				1	0	1.5164	1.5164	1.5164	1.5159
				2	0	2.0313	2.0313	2.0313	2.0308
				0	1	2.4196	2.4198	2.4194	2.4188
0.36	1.96	-.1	0.1	0	0	0.9942	.9942	0.9941	0.9939
				1	0	1.5813	1.5812	1.5812	1.5809
				2	0	2.1615	2.1616	2.1615	2.1612
0.49	1.69	-.1	0.1	0	0	0.9955	0.9954	0.9955	0.9955
				1	0	1.6870	1.6870	1.6870	1.6870
				0	1	2.2780	2.2785	2.2782	2.2781
				2	0	2.3750	2.3751	2.3750	2.3750
				1	1	2.9584	2.9588	2.9584	2.9583
0.81	1.21	-.08	0.1	0	0	0.9978	0.9978	0.9978	0.9980
				1	0	1.8941	1.8944	1.8941	1.8944
				0	1	2.0897	2.0889	2.0890	2.0890
				2	0	2.7895	2.7900	2.7896	2.7899

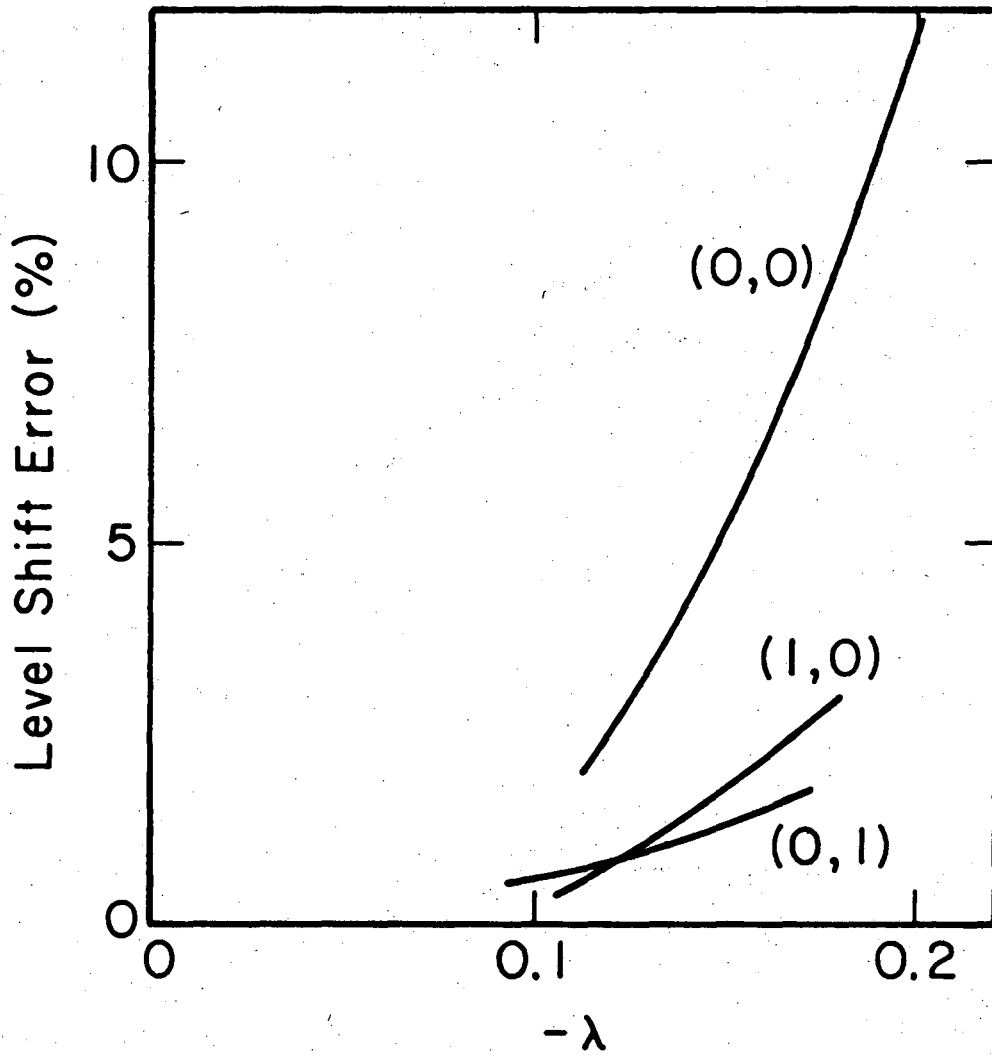
<sup>a</sup> These eigenvalues refer to the potential described in Section III.

TABLE II. Semiclassical Eigenvalues:  $\omega_1 = 0.7$  and  $\omega_2 = 1.3$

$\lambda$	$(N_1 = 0, N_2 = 0)$		$(N_1 = 1, N_2 = 0)$		$(N_1 = 0, N_2 = 1)$	
	Semiclassical	Quantum	Semiclassical	Quantum	Semiclassical	Quantum
0	1.	1.	1.7	1.7	2.3	2.3
-.06	.9987	.9988	1.6970	1.6970	2.2932	2.2932
-.08	.9975	.9975	1.6933	1.6933	2.2870	2.2870
-.10	.9955	.9955	1.6870	1.6870	2.2782	2.2781
-.12	.9927	.9926	1.6770	1.6769	2.2661	2.2658
-.14	.9889	.9884	1.6617	1.6612	2.2496	2.2490
-.16	.9836	.9826	1.6382	1.6370	2.2268	2.2257
-.18	.9764	.9743	1.6010	1.5980		
-.20	.9667	.9621				

FIGURE CAPTIONS

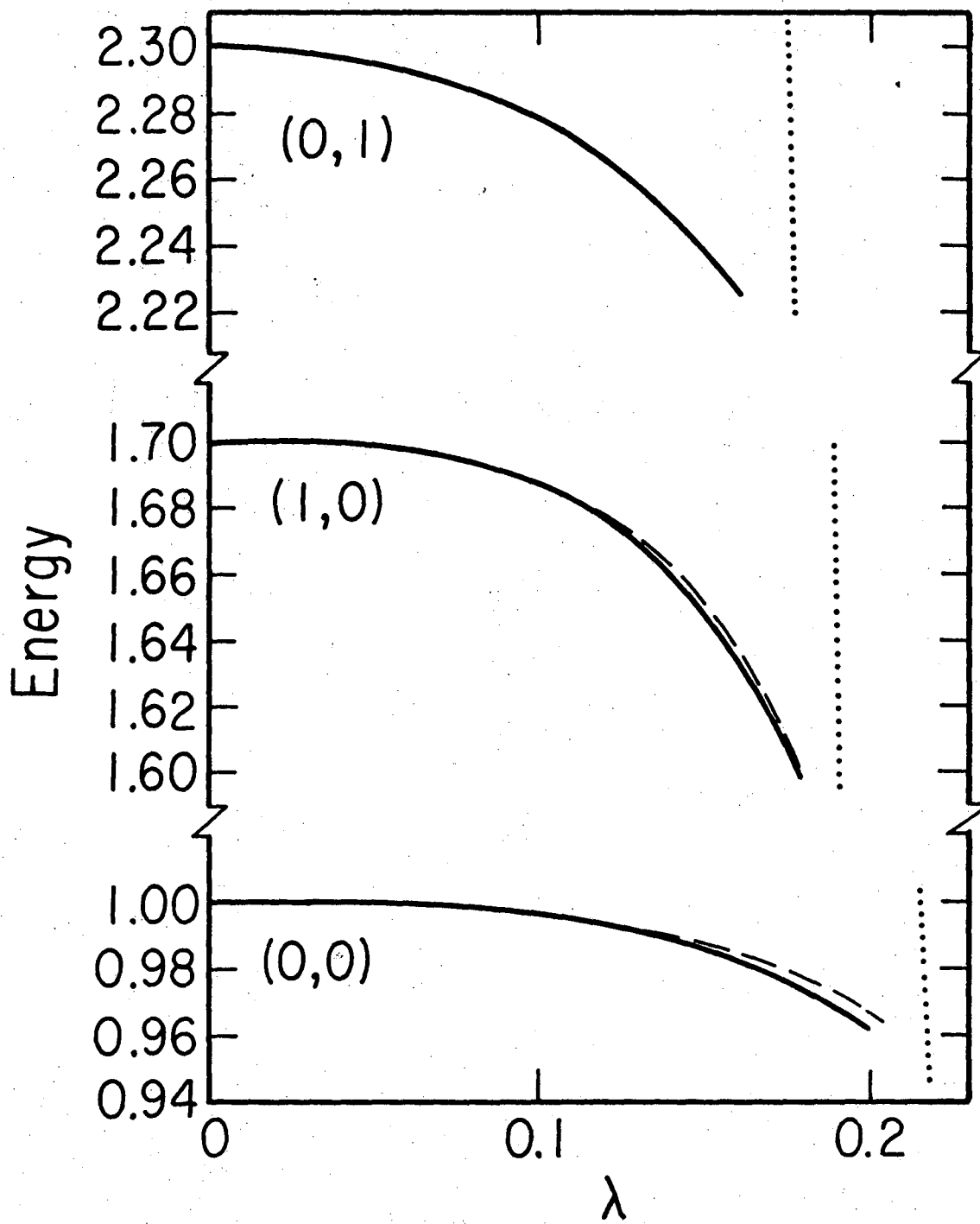
- Figure 1. Comparison of the exact quantum mechanical (solid line) and semiclassical (broken line) eigenvalues as a function of non-separable coupling. The lowest three eigenvalues-- $(N_1, N_2) = (0,0), (1,0),$  and  $(0,1)$ -- are shown for the system described in Section III, with  $\omega_1 = 0.7, \omega_2 = 1.3,$  and  $\eta = -\lambda.$  (For the top curve the solid and dashed lines are indistinguishable.) The dotted lines show the maximum in the potential energy surface as a function of  $\lambda,$  as given by Eq. (3.6).
- Figure 2. Percent error in the semiclassical level shift, as a function of the non-separable coupling. The results are those in Table II and Figure 1, and the quantity plotted is  $100X|(\Delta_{QM} - \Delta_{SC})/\Delta_{QM}|,$  where  $\Delta$  is defined in Eq. (3.7) and QM = quantum mechanical, SC = semiclassical.



NBL 758-1946

Fig. 1





XBL 757-6717

Fig. 2

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