Perturbative examination of avoided crossings

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(Received 16 June 1980; accepted 26 September 1980)

Quantum perturbation theory is used to examine the eigenvalues of a nonseparable Hamiltonian system in the classically regular and irregular regimes. As a function of the perturbation parameter, the eigenvalues obtained by exact (matrix diagonalization) methods undergo an avoided crossing. In the present paper perturbation theory is used as an approximate method to predict the locations of such avoided crossings in energy-parameter space. The sparsity of such avoided crossings in the Hénon–Heiles system is seen to produce regular sequences in the eigenvalues even when the classical motion is predominantly chaotic.

I. INTRODUCTION

The behavior of isolated molecules, treated as anharmonic coupled oscillators in a rotating frame, is of considerable interest to the theory of unimolecular reactions,[1] infrared multiphoton dissociation,[2] and related topics. Several numerical studies have been made on the classical dynamics of anharmonic coupled oscillators.[3] They suggest regular (quasiperiodic) motion at low energies and stochastic (chaotic, but nevertheless deterministic) motion at high energies.[4] These results find an analytic basis in the Kolmogorov–Arnol'd–Moser theorem.[5]

The quantum mechanics corresponding to the *regular* (quasiperiodic) classical regime is now reasonably well understood with the aid of semiclassical ideas.[6,7] The quantum-mechanical counterpart of the classically *stochastic* regime is the subject of much current interest.[8] It has been suggested[9] that an eigenstate in the quantum stochastic regime would have a 'statistical' wave function, i.e., one in which the average of some dynamical quantity approximates a microcanonical average at that energy (e.g., either an average over quantum states in that neighborhood for high quantum numbers, or the classical microcanonical ensemble average at that energy).

A mechanism for forming a statistical wave function was recently proposed[9] in terms of multiple avoided crossings in plots of eigenvalues of Hamiltonian H versus a perturbation parameter λ.

$$\mathcal{H} = H_0 + \lambda H_1 \ . \tag{1.1}$$

Here H_0 is a (classically) integrable Hamiltonian and H_1 is a nonintegrable perturbation. The typical behavior[5(c)] of the eigenvalues as functions of a single parameter λ when they approach each other, is repulsion, or an "avoided crossing." When there were no avoided crossings of these eigenvalues in the vicinity of some value of λ, or if the avoided crossings were isolated, it was suggested that the corresponding quantum mechanical motion was "regular." But when a state was involved in a sufficient number of avoided crossings in some λ neighborhood together with an overlapping of these avoided crossings, it was proposed[9] that the state began to take on a statistical character. In the present paper we present a perturbation method for predicting these "avoided crossings."

An alternative approximate method has been used[10] to calculate eigenvalue versus perturbation parameter plots: For a pair of coupled oscillators the higher frequency mode was treated adiabatically during the motion of the lower frequency one. The resulting equation for the eigenvalue was solved numerically. We comment on it later.

II. THEORY

The basic idea is the following. In classical canonical perturbation theory,[11] the perturbed system H_0 is integrable, i.e., it has N well-defined action variables for an N-coordinate system. When the perturbation λH_1 is applied, the original action variables are no longer good, and better ones can be calculated using perturbation theory to some order. (A nonperturbative method for determing the good action variables has been given in Ref. 6.) Thus, though the perturbation λH_1 may sometimes destroy the invariant tori (a currently accepted belief, based on numerical experiments[3,4]), the tori (and thereby integrability) are assumed to still exist in perturbation theory.

Correspondingly, we assume that if one applies nondegenerate quantum perturbation theory,[12] one assumes the quantum analog of regular classical motion. Such perturbatively calculated eigenvalues will have crossings whenever the avoided crossings occur in the exact system. To calculate the splitting in the avoided crossings, one must supplement such a perturbation method by using a degenerate perturbation theory[12] in the vicinity of the crossing.

These ideas are tested in the following section for the Hénon–Heiles potential.[3(a),6(c)] In a recent study[13] for particular values of the parameters, only one avoided crossing was found in the 99 bound eigenstates. In that study, regular spacings of eigenvalues were also found that continued smoothly from the regular (quasiperiodic) into the classically stochastic regime. Such sequences are persumed to reflect the absence of quantum mechanical stochasticity (which is quite reasonably believed[7] to produce an "irregular spectrum"). Thus, classical stochasticity is not a sufficient condition for quantum stochasticity. [Some additional conditions are proposed in Ref. 9(c).] In the present paper we also calculate these sequences of eigenvalue differences and compare

[a]Contribution No. 6244.

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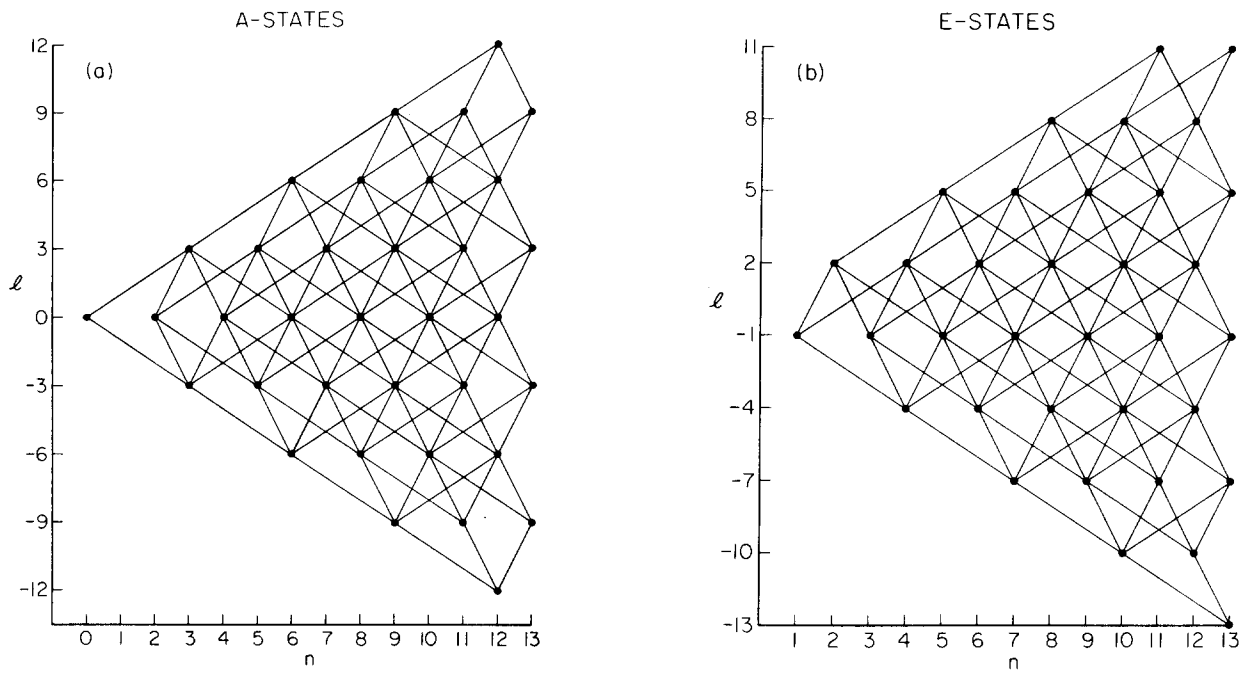

FIG. 1. Coupling scheme for the zeroth order states in the polar $(n\,l)$ basis.

with the results of Ref. 13.

The Hénon–Heiles Hamiltonian (in Cartesian x, y, p_x, p_y coordinates) is

$$\mathcal{H} = \tfrac{1}{2}(p_x^2 + p_y^2 + x^2 + y^2) + \lambda x(y^2 - x^2/3)\,, \tag{2.1}$$

and in polar coordinates[6(c),14] $(r,\ \theta,\ p_r,\ p_\theta)$,

$$\mathcal{H} = \tfrac{1}{2}(p_r^2 + p_\theta^2/r^2) - \lambda r^3/3\cos 3\theta \tag{2.2}$$
$$\equiv H_0 + \lambda H_1$$

It has been studied classically[3(a)] and quantum-mechanically.[6(c),13–15] In Ref. 6(c), the value of λ used was 0.1118 while in Ref. 14, it was 0.088. The perturbative eigenvalues are calculated below versus λ for both cases, to compare with results in the two systems. The eigenvectors of H_0 are denoted $|nl\rangle$ and satisfy

$$H_0|nl\rangle = E^0_{nl}|nl\rangle = (n+1)|n\,l\rangle\ ,$$
$$\langle r,\ \theta|nl\rangle = \psi^0_{nl}(r,\ \theta)\,, \tag{2.3}$$

where n is the principal quantum number $(E^0_{nl} \equiv E^0_n)$ and l is an orbital quantum number varying from $-n$ to $+n$ in steps of 2. Since the system (2.1) has C_3 symmetry, the eigenstates are either of A (singly degenerate: $l = 0$, ± 3, ± 6, etc.) or E (doubly degenerate; l is not a multiple of 3) symmetry. The perturbation H_1 couples states differing in the l-quantum number by 3 and in the n-quantum number by 1 or 3, and these matrix elements are well known.[16] Thus, the perturbation couples states of each symmetry species separately; a pictorial representation of the coupling scheme is given in Fig. 1.

The standard form of Rayleigh–Schrödinger perturbation theory[12] is employed. The matrix H_1 is purely off-diagonal in the $|nl\rangle$ basis, and thus first order perturbation terms vanish. The selection rules further ensure that all the odd-order perturbation terms vanish as well (this is apparent from Fig. 1; the nth order contribution to the perturbed eigenvalue comes from circuits of n sides beginning and ending at the same site. In these figures, no such odd-ordered circuits are possible). Thus, the energy of the nlth eigenstate is given by

$$E_{nl} = E^0_n + \lambda^2 E^{(2)}_{nl} + \lambda^4 E^{(4)}_{nl} + \cdots\ . \tag{2.3}$$

For compactness in presenting the expressions for the various $E^{(p)}_{nl}$, we use the notation

$$m \equiv (nl)$$
$$V_{ms} = \langle m|H_1|s\rangle \equiv \langle nl|H_1|n'l'\rangle\ ,$$

i.e., V_{ms} is a matrix element of H_1 in the basis of H_0, and

$$\Delta_{ms} = (E^0_m - E^0_s) \equiv (E^0_n - E^0_{n'})\,.$$

Thus,

$$E^{(2)}_m = \sum_s{}' |V_{ms}|^2/\Delta_{ms}\,, \tag{2.3a}$$

$$E^{(4)}_m = \sum_s{}' \sum_t{}' \sum_r{}' \frac{V_{ms} V_{st} V_{tr} V_{rm}}{\Delta_{ms}\Delta_{mt}\Delta_{mr}} - E^{(2)}_m \sum_s{}' \frac{|V_{ms}|^2}{\Delta^2_{ms}}\ . \tag{2.3b}$$

In the above Eqs. (2.3a, b), the prime on the summations indicate that the terms with m equal to the summation index are to be omitted.

All l states for a given principal quantum number n are degenerate in zeroth order. To higher order in the perturbation, the E states (l is not a multiple of 3) are always doubly degenerate; their $+l$ and $-l$ states are *not* coupled to each other through any circuits of any degree [see Fig. 1(b)]. The A states, on the other hand, are those for which l is a multiple of 3, and since $+l$ and $-l$ states are coupled by H_1, the perturbation lifts the degeneracy. As the results in the next section in-

TABLE I. Comparison of exact quantum results with 2nd and 4th order perturbation theory for $\lambda = 0.1118$.

n, l[a]	E_q[b]	E_p^2[c]	E_p^4[d]	Δ[e]
0, 0	0.9986	0.9986	0.9986	0.00
1, ±1	1.9901	1.9903	1.9901	0.01
2, 0	2.9562	2.9569	2.9563	0.00
2, ±2	2.9853	2.9861	2.9854	0.00
3, ±1	3.9260	3.9278	3.9262	0.01
3, ±3	3.9824	3.9861	3.9843	0.04[f]
	3.9858			
4, 0	4.8702	4.8736	4.8706	0.01
4, ±2	4.8987	4.9028	4.8996	0.02
4, ±4	4.9863	4.9903	4.9867	0.01
5, ±1	5.8170	5.8236	5.8184	0.02
5, ±3	5.8670	5.8819	5.8764	0.12[f]
	5.8815			
5, ±5	5.9913	5.9986	5.9923	0.02
6, 0	6.7379	6.7486	6.7404	0.04
6, ±2	6.7649	6.7778	6.7693	0.07
6, ±4	6.8354	6.8653	6.8562	0.30
6, ±6	6.9989	7.0111	7.0009	0.02[f]
	6.9994			
7, ±1	7.6595	7.6778	7.6654	0.08
7, ±3	7.6977	7.7361	7.7232	0.24[f]
	7.7369			
7, ±5	7.8327	7.8528	7.8389	0.08
7, ±7	8.0094	8.0278	8.0125	0.04
8, 0	8.5541	8.5819	8.5644	0.12
8, ±2	8.5764	8.6111	8.5932	0.20
8, ±4	8.6779	8.6986	8.6799	0.02
8, ±6	8.8113	8.8444	8.8244	0.12[f]
	8.8152			
8, ±8	9.0127	9.0486	9.0266	0.15
9, ±1	9.444	9.490	9.466	0.23
9, ±3	9.467	9.549	9.524	0.42[f]
	9.552			
9, ±5	9.629	9.665	9.639	0.10
9, ±7	9.794	9.840	9.812	0.18
9, ±9	10.0354	10.0736	10.0433	0.08[f]
	10.0356			
10, 0	10.3052	10.374	10.341	0.35
10, ±2	10.318	10.403	10.370	0.50
10, ±4	10.463	10.490	10.457	0.06
10, ±6	10.573	10.636	10.601	0.17[f]
	10.590			
10, ±8	10.774	10.840	10.803	0.27
10, ±10	11.050	11.103	11.062	0.11
11, ±1	11.152	11.261	11.219	0.60
11, ±3	11.160	11.319	11.277	0.67[f]
	11.325			
11, ±5	11.383	11.436	11.392	0.08
11, ±7	11.534	11.611	11.565	0.27
11, ±9	11.750	11.844	11.795	0.37[f]
	11.752			
11, ±11	12.065	12.136	12.083	0.15
12, 0	11.966	12.124	12.071	0.88
12, ±2	11.968	12.153	12.099	1.09
12, ±4	12.206	12.240	12.186	0.16
12, ±6	12.277	12.386	12.329	0.13[f]
	12.334			
12, ±8	12.480	12.590	12.531	0.41
12, ±10	12.712	12.852	12.790	0.61[g]
12, ±12	13.077	13.174	13.106	0.18[g,f]
	13.087			
13, ±1	12.762	12.990	12.924	1.3[g]
13, ±3	12.748	13.049	12.981	0.85[f]
	13.032			
13, ±5	13.081	13.165	13.096	0.11
13, ±7	13.233	13.340	13.269	0.27

[a] Quantum numbers nl in the polar basis.
[b] Exact quantum mechanical eigenvalues from Refs. 6(c) and 13.
[c] Second order nondegenerate perturbation theory result.
[d] Fourth order nondegenerate perturbation theory result.
[e] Δ is the absolute percentage error $= (|E_p^4 - E_q|/E_q) \times 100$.
[f] Geometric mean of the percentage error.
[g] Indicates that the state is involved in an avoided crossing near this value of λ.

dicate, nondegenerate perturbation theory is adequate (at least to the order we have studied) in the absence of avoided crossings. In order to estimate the approximate value for the splitting of the A states, a degenerate perturbation theory is used. From Fig. 1, it can be seen that for splitting the $l = \pm 3$ states, 4th order degenerate perturbation theory must be employed, for $l = \pm 6$, 6th order, and, for $\pm l$ states, $[2(l/3)+2]$th order theory. As a consequence, the energy difference between $+l$ and $-l$ states decreases sharply as l increases (see Table I). Since, for a given n, the different $\pm l$ pairs of states are not degenerate, one can, in a first approximation, treat only individual pairs n, $\pm l$ simultaneously. Thus, the 2×2 matrix to be diagonalized for the A states (the notation is $m \equiv nl$, $m' = n$, $-l$) is

$$\begin{bmatrix} E_m^{(p)} & V_{mm'}^{(p)} \\ V_{m'm}^{(p)} & E_{m'}^{(p)} \end{bmatrix} . \tag{2.4}$$

Here, $E_m^{(p)} = E_{m'}^{(p)}$, $p = 2(l/3)+2$, and $V_{mm'}^{(p)}$ is the matrix element connecting the $+l$ and $-l$ states. Thereby, for $l = 3$, we have

$$V_{m,m'}^{(4)} = \sum_s{}'' \sum_t{}'' \sum_r{}'' \frac{V_{ms} V_{st} V_{tr} V_{rm'}}{\Delta_{ms} \Delta_{mt} \Delta_{mr}} - E_m^{(2)} \sum_s{}'' \frac{V_{ms} V_{sm'}}{\Delta_{ms}^2} , \tag{2.5}$$

where now the double prime on the summations indicate the omission of terms with the summation index equal to either m or m'.

In order to treat the avoided crossings between any two levels, a locally degenerate perturbation theory can be used for these two levels, with m, m' in (2.4) now denoting the two states n, l and $n'l'$, and p, the order of the chain connecting the two levels. ($E_m^{(p)}$ equals $E_{m'}^{(p)}$ now only at the actual crossing point.)

III. RESULTS

Accurate eigenvalues for the Hénon–Heiles system with $\hbar = 1$ and $\lambda = 0.1118$ have been reported[6(c),13] up to state $nl = 13, \pm 7$. [These were computed by diagonalizing the Hamiltonian (2.2) with a large basis set.] The eigenvalues obtained by using the fourth-order perturbation theory are compared with the exact results in Table I. The splittings of the $l = \pm 3$ states are obtained by using Eqs. (2.4)–(2.5) and presented in Table II. Even in this low order perturbation theory, the agreement is seen to be good. In almost all the cases, the difference in Table I rarely exceeds 0.25%. The cases of large error correspond to either low l states or near degeneracies, i.e., at the avoided crossings. The percentage errors (Δ) of the eigenvalues in Table II are typically smaller than those in Table I. Even well into the (classically) stochastic regime, when semiclassical methods are inadequate due to the sparsity of invariant tori, the quantum perturbation theory is quite good. One reason for this behavior may be seen by examining the energy levels for $n \leq 13$ as a function of λ.

The dissociation energy E_d and the number of bound states,[17] N_λ, are given by

$$E_d^{(\lambda)} = 1/6\,\lambda^2 , \tag{3.1}$$

$$N_\lambda \simeq 1/4\lambda^2(1 + 1/18\lambda^2) . \tag{3.2}$$

In Fig. 2, the eigenvalues calculated by nondegenerate perturbation theory are shown as a function of λ in the interval (0, 0.20). In the neighborhood of $\lambda = 0.1118$, only a few of these states are involved in crossings or avoided crossings. (The dissociation energy is 13.33.) One of these pairs[18] involves $nl = 13, \pm 1$ and $nl = 12, \pm 10$. One anticipates that in order to treat these levels properly, a rediagonalization must be performed in this λ neighborhood. For smaller λ, the number of bound states increases the dissociation energy being much greater

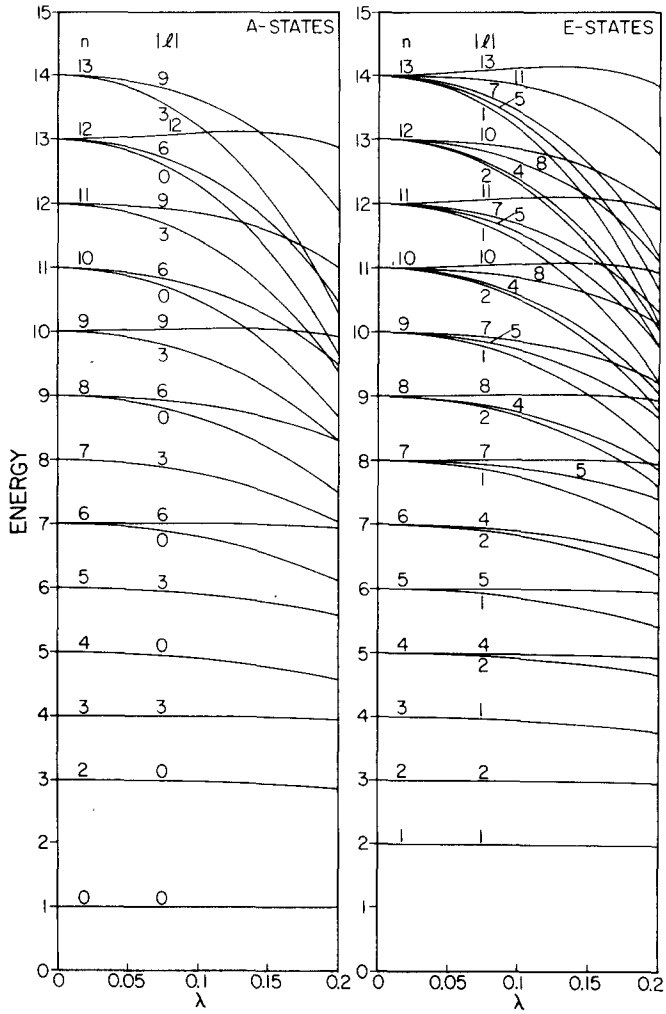

FIG. 2. Eigenvalue vs λ diagram for the states in the polar basis; the eigenvalues are computed via 4th order nondegenerate perturbation theory in the interval $0.0 \leq \lambda \leq 0.20$.

TABLE II. Degenerate perturbation eigenvalues and splittings for $l = \pm 3$ states.

nl[a]	E_q[b]	E_p[c]	S_q[d]	S_p[e]	Δ[f]
3, ±3	3.9824	3.9829	0.0034	0.0029	0.000
	3.9858	3.9858			
5, ±3	5.8670	5.8705	0.0145	0.0117	0.027
	5.8815	5.8822			
7, ±3	7.6977	7.7086	0.0392	0.0292	0.041
	7.7369	7.7378			
9, ±3	9.467	9.495	0.085	0.058	0.054
	9.552	9.553			
11, ±3	11.160	11.226	0.165	0.102	0.124
	11.325	11.328			
13, ±3	12.748	12.900	0.284	0.164	0.533
	13.032	13.063			

[a] Quantum numbers nl in the polar basis set.
[b] Exact quantum mechanical eigenvalues from Refs. 6(c) and 12.
[c] Fourth order *degenerate* perturbation theory result.
[d] Splitting between $\pm l$ states (exact).
[e] Splitting between $\pm l$ states (perturbation result).
[f] Geometric mean of percentage errors (cf. Table I, Footnote e).

and so, the system is, for any ratio E/E_d, more "classical." For example, at $\lambda = 0.088$, which was studied in Ref. 14, the dissociation energy is 21.52. In the vicinity of $\lambda = 0.088$, the number of predicted avoided crossings for the bound E symmetry states is large (see Fig. 3). It has been pointed out elsewhere[13] that an increased number of avoided crossings leads to a much stronger irregularity in the level spacings, and a larger number of large second differences $\Delta^2 E_i$,

$$\Delta^2 E_i = E_i(\lambda - \Delta\lambda) + 2E_i(\lambda) - E_i(\lambda + \Delta\lambda) , \tag{3.3}$$

at $\lambda = 0.088$ than at $\lambda = 0.1118$. Thereby, the larger number of large $\Delta^2 E_i$'s found in Ref. 14 compared with that found in Ref. 13 is explained.

We next consider certain regular sequences observed in the eigenvalue differences at $\lambda = 0.1118$.[13] Some of the energy differences computed were

$$\Delta E = E_{nl} - E_{n-1,\,l-1} \tag{3.4}$$

for different n, l's. Using the perturbation expression for the energy to order λ^2, one obtains the analytic expression,

$$\Delta E = 1 + \lambda^2/6\,[(n+l) - 6(n-l) - 6]\,. \quad (3.5)$$

Thus, for the low l case ($l=1$ in Table II of Ref. 12),

$$\Delta E = 1 + \lambda^2/6\,[1 - 5n]\,. \quad (3.6a)$$

In the intermediate l case, $n-l=4$, and thus

$$\Delta E = 1 + \lambda^2/6\,[n + l - 30]\,. \quad (3.6b)$$

In the high l case, $n-l=0$, giving

$$\Delta E = 1 + \lambda^2/6\,[n + l - 6]\,. \quad (3.6c)$$

One thus predicts differences $\Delta E > 1$ only for the high l cases with $n \geq 3$ (as observed), in contrast to all other sequences, where $\Delta E \leq 1$. The predicted values from the second order expression in Eq. (3.5) are compared in Table III with the results of Ref. 13 and the agreement is seen to be good overall.

Approximate eigenvalues versus perturbation parameter curves were obtained in Ref. 10 using an adiabatic method described there. The results for locating the avoided crossings were quite reasonable for the system studied (quartic potential). Interestingly enough, but still unexplained, the method gave a reasonable answer even when the assumed higher frequency mode was actually the lower frequency mode. The method of Ref. 10 is, however, not as simple as the present one, since it involves the numerical solution of a differential equation. (Incidentally, diagonalization of a local 2×2 Hamiltonian matrix was added in the vicinity of an "avoided" crossing, as in the present case also.)

TABLE III. Sequence of energy differences, $E_{nl} - E_{n-1,l-1}$.

nl[a]	Quantum[b]	Perturbation[c]	Eqs. (3.6)
	Low l case		
7, 1	0.92	0.93	0.93
9, 1	0.89	0.90	0.90
11, 1	0.84	0.88	0.89
13, 1	0.79	0.80	0.87
	Intermediate l case		
5, 1	0.95	0.95	0.95
6, 2	0.94	0.95	0.95
7, 3	0.95	0.95	0.96
8, 4	0.96	0.96	0.96
9, 5	0.95	0.96	0.97
10, 6	0.95	0.96	0.97
11, 7	0.95	0.96	0.98
12, 8	0.95	0.97	0.98
	High l case		
2, 2	1.00	1.00	1.00
3, 3	1.00	1.00	1.00
4, 4	1.00	1.00	1.00
5, 5	1.01	1.01	1.01
6, 6	1.01	1.01	1.01
7, 7	1.01	1.01	1.02
8, 8	1.01	1.01	1.02
9, 9	1.01	1.02	1.02
10, 10	1.01	1.02	1.03
11, 11	1.02	1.02	1.03
12, 12	1.01	1.02	1.04

[a] Quantum numbers nl in the polar basis.
[b] Exact differences from Ref. 13.
[c] Fourth order nondegenerate perturbation theory result.

IV. SUMMARY

In this paper the results of quantum perturbation theory for the eigenvalues of a nonseparable Hamiltonian system are described. The (nondegenerate) perturbation theory gives good agreement with exact results, both for the actual computation of eigenvalues, as well as in locating the "avoided" crossings; the crossings of the perturbatively computed eigenvalues are seen as the signature of avoided crossings in the true eigenvalues. Since it has been proposed that overlapping avoided crossings lead to a statistical character in the eigenfunctions, the knowledge of where such crossings occur, coupled with an estimate of the interaction in that region, may allow for a quantum-statistical treatment of such states. The semiclassical and classical extensions of this idea have interesting implications for the onset of chaotic behavior in such nonintegrable systems, and will be presented in a forthcoming publication.[19]

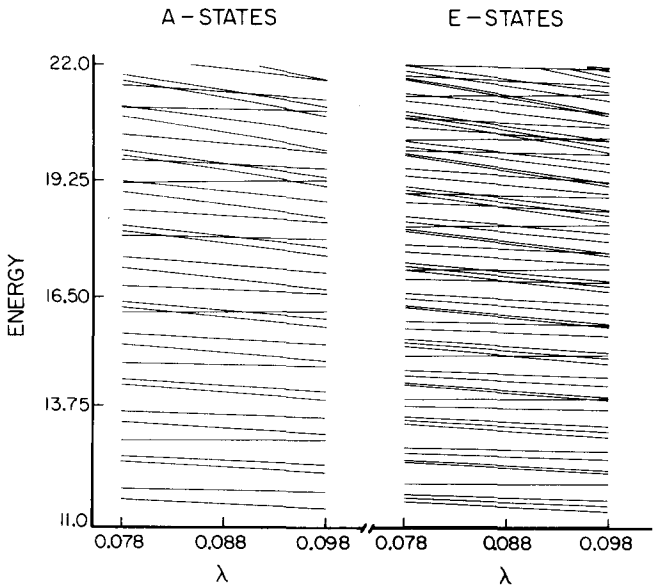

FIG. 3. Same as Fig. 2 in the interval $0.078 \leq \lambda \leq 0.098$. Only the higher energy states are shown here.

ACKNOWLEDGMENT

We are pleased to acknowledge the support of this research by a grant from the National Science Foundation.

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