

SEMICLASSICAL EIGENVALUES FOR A NON-ADIABATIC SYSTEM

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We have performed a semiclassical quantization of the Meyer–Miller classical analog Hamiltonian for the Jahn–Teller $E \times e$ system, in the regime of small linear coupling. The primitive semiclassical energies are in good qualitative and reasonable quantitative agreement with the exact quantum-mechanical solution to this problem. These results demonstrate that such a classical model is able to accurately describe the behavior of non-adiabatic bound state systems, but that uniformization will be necessary to obtain more precise agreement with quantum mechanics.

1. Introduction

For problems that fall within the confines of the adiabatic Born–Oppenheimer approximation, the application of classical mechanics has long been of value in understanding molecular dynamics. With potential energy surfaces clearly defined, the classical (Ehrenfest) prescription for the time-evolution of nuclear coordinates provides a framework within which clear and intuitive pictures can be developed. Moreover, semiclassical methods provide an essential link between classical and quantal descriptions, enabling quantum properties such as energy level spectra to be calculated using classical dynamics. Comparison with exact quantum results shows that these methods generally work very well.

However, it is clear that situations in which the adiabatic hypothesis fails are not uncommon [1,2]. These are characterized by the non-adiabatic coupling of nuclear and electronic degrees of freedom. The application of classical mechanics is then no longer straightforward. The electronic subsystem is a few-level system, which is an inherently quantum-mechanical entity, and nuclear and electronic motions are no longer separable. One is thus required to treat the electrons and nuclei on the same footing. A unified method, explicitly including a classical description of the effective electronic dynamics, was recently developed to do this [3]. These classical analog models appear to give reasonable descriptions of the average dynamics and have been implemented to study several problems in non-adiabatic scattering [3] and ultra-fast radiationless transitions [4]. Both of these examples provide evidence for the validity and usefulness of the approach. To date, however, the classical analogs have not faced the rigorous test of semiclassical quantization. We have adapted the self-consistent Hamiltonian of the classical analog model to a non-adiabatic bound state problem, the two-state Jahn–Teller $E \times e$ conical intersection, and by making use of a key canonical transformation have succeeded in obtaining the semiclassical eigenvalue spectrum. It agrees well with the quantum-mechanical solution. This is an important validation of the classical analog model as a basis for a correct dynamical description of non-adiabatic systems.

2. Classical analog model

The quantum-mechanical $E \times e$ system is perhaps the simplest and best known non-adiabatic problem in molec-

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ular physics [5]. The electronic state is most conveniently described in terms of a two-dimensional diabatic basis $\{|+\rangle, |-\rangle\}$. In the linear coupling approximation, the Hamiltonian operator is

$$\hat{H} = \frac{1}{2} P_\rho^2 + (1/2\rho^2) P_\phi^2 + |+\rangle \frac{1}{2} \rho^2 \langle +| + |+\rangle k\rho \exp(-i\phi) \langle -| + |-\rangle k\rho \exp(i\phi) \langle +| + |-\rangle \frac{1}{2} \rho^2 \langle -|. \quad (1)$$

Here ρ is the magnitude of the internuclear (Jahn-Teller) distortion, ϕ its phase (or pseudo-rotation angle), and k the magnitude of the linear coupling.

A general electronic wavefunction in this diabatic basis takes the form

$$|\Psi\rangle = a_1 |+\rangle + a_2 |-\rangle. \quad (2)$$

The classical analog approach replaces the complex coefficients a_1 and a_2 with real variables $\{n_k, q_k\}$:

$$a_k(t) = n_k^{1/2}(t) \exp[-iq_k(t)], \quad (3)$$

while the electronic Hamiltonian operator is replaced with its expectation value:

$$\mathcal{H}_{e1} \equiv \langle \Psi | \hat{H}_{e1} | \Psi \rangle = n_1 H_{11} + n_2 H_{22} + 2(n_1 n_2)^{1/2} \text{Re}\{H_{12} \exp[i(q_1 - q_2)]\}, \quad (4)$$

and the heavy particle degrees of freedom are treated classically in the usual way. The self-consistently coupled time-evolution of the electronic (quantum) and nuclear (classical) degrees of freedom is then described by "Hamilton's equations":

$$\dot{n}_k = -\partial \mathcal{H} / \partial q_k, \quad \dot{q}_k = \partial \mathcal{H} / \partial n_k; \quad \dot{P}_i = -\partial \mathcal{H} / \partial Q_i, \quad \dot{Q}_i = \partial \mathcal{H} / \partial P_i. \quad (5)$$

Applying this formalism to the linear E X e Hamiltonian (1) we obtain the classical Hamiltonian function

$$\mathcal{H}(\rho, \phi, q_1, q_2, P_\rho, P_\phi, n_1, n_2) = \frac{1}{2} P_\rho^2 + (1/2\rho^2) P_\phi^2 + \frac{1}{2} \rho^2 (n_2 + n_1) + 2(n_1 n_2)^{1/2} k\rho \cos(q_1 - q_2 - \phi). \quad (6)$$

The electronic probability is conserved by time-evolution (5) so that n_1 and n_2 are not independent ($n_1 = 1 - n_2$). We take advantage of this by making a canonical transformation using the generating function [3]

$$F_2(q_1, q_2, \bar{n}_1, \bar{n}_2) = (q_1 - q_2) \bar{n}_1 + q_2 \bar{n}_2. \quad (7)$$

This allows the Hamiltonian to be rewritten:

$$\mathcal{H}(\rho, \phi, \bar{q}_1, P_\rho, P_\phi, \bar{n}_1) = \frac{1}{2} P_\rho^2 + (1/2\rho^2) P_\phi^2 + \frac{1}{2} \rho^2 + 2k\rho [\bar{n}_1 (1 - \bar{n}_1)]^{1/2} \cos(\bar{q}_1 - \phi). \quad (8)$$

Since \bar{q}_1 and ϕ appear only in the combination $\bar{q}_1 - \phi$ we can make a second canonical transformation [1], making use of the generating function (and dropping the bars and subscripts on n and q)

$$F_2(P_\rho, I_1, I_2, \rho, q, \phi) = (I_1, I_2) \begin{bmatrix} 1/2 & 1/2 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} q \\ \phi \end{bmatrix} + P_\rho \rho. \quad (9)$$

This leads to the important transformation equations

$$I_1 = n + P_\phi, \quad \phi_1 = \frac{1}{2}(q + \phi); \quad I_2 = \frac{1}{2}(P_\phi - n), \quad \phi_2 = -q + \phi, \quad (10)$$

of which use is made below. In these variables the Hamiltonian becomes

$$\mathcal{H}(\rho, \phi_2, P_\rho, I_2) = \frac{1}{2} P_\rho^2 + (1/2\rho^2) (\frac{1}{2} I_1 + I_2)^2 + \frac{1}{2} \rho^2 + k\rho [(\frac{1}{2} I_1 - I_2) (1 - \frac{1}{2} I_1 + I_2)]^{1/2} \cos \phi_2. \quad (11)$$

Note that ϕ_1 does not appear, and thus I_1 is conserved. We shall see that I_1 corresponds to the good quantum number j of the quantum-mechanical solution.

The semiclassical quantization methods we shall use are most efficient when the Hamiltonian is written in terms of zeroth-order action-angle variables. In our case the uncoupled problem is that of a two-dimensional isotropic harmonic oscillator and a degenerate two-level system. The zeroth-order Hamiltonian is then [6]

$$\mathcal{H}_0 = 2I_\rho + |\frac{1}{2}I_1 + I_2|, \quad I_\rho = \frac{1}{2\pi} \int P_\rho \, d\rho, \quad (12)$$

and the radial coordinate is

$$\rho^2 = 2I_\rho + |\frac{1}{2}I_1 + I_2| + 2(I_\rho^2 + I_\rho |\frac{1}{2}I_1 + I_2|)^{1/2} \sin \phi_\rho \quad (13)$$

The entire Hamiltonian then becomes

$$\begin{aligned} \mathcal{H} = & 2I_\rho + |\frac{1}{2}I_1 + I_2| + 2k [(\frac{1}{2}I_1 - I_2)(1 - \frac{1}{2}I_1 + I_2)]^{1/2} \\ & \times [2I_\rho + |\frac{1}{2}I_1 + I_2| + 2(I_\rho^2 + I_\rho |\frac{1}{2}I_1 + I_2|)^{1/2} \sin \phi_\rho]^{1/2} \cos \phi_2. \end{aligned} \quad (14)$$

This expression is valid for non-zero angular momentum P_ϕ . In the special case of zero initial angular momentum we take the zeroth-order problem to be a one-dimensional harmonic oscillator traversing the origin and a degenerate two-level system. Then the zeroth-order Hamiltonian is [6]

$$\mathcal{H}'_0 = I'_\rho \quad (12')$$

and the radial variable is

$$\rho = (2I'_\rho)^{1/2} \sin \phi'_\rho. \quad (13')$$

One final modification is required to make the Hamiltonian useful. This is the Langer correction [3,7], which increments the electronic action by 1/2. This modification does not change the electronic adiabatic eigenvalues, but avoids singularities in the equation of motion [7]. In final form our classical analog Hamiltonian is

$$\begin{aligned} \mathcal{H} = & 2I_\rho + |\frac{1}{2}I_1 + I_2| + 2k [(\frac{1}{2}I_1 - I_2 + \frac{1}{2})(\frac{3}{2} - \frac{1}{2}I_1 + I_2)]^{1/2} \\ & \times [2I_\rho + |\frac{1}{2}I_1 + I_2| + 2(I_\rho^2 + I_\rho |\frac{1}{2}I_1 + I_2|)^{1/2} \sin \phi_\rho]^{1/2} \cos \phi_2 \end{aligned} \quad (15)$$

for the case of non-zero angular momentum, and

$$\mathcal{H}' = I'_\rho + 2k [(\frac{1}{2}I_1 - I_2 + \frac{1}{2})(\frac{3}{2} - \frac{1}{2}I_1 + I_2)]^{1/2} (2I'_\rho)^{1/2} \sin \phi'_\rho \cos \phi_2 \quad (15')$$

for the case of initially zero angular momentum.

3. Semiclassical quantization

We have quantized the classical analog Hamiltonian (15) by applying a method proposed by Miller [8] (based on earlier work by Sorbie and Handy [9] and DeLeon and Heller [10]; see also ref. [11]). In brief this method proceeds as follows. To determine primitive semiclassical eigenvalues we must find trajectories for which the good action variables of the problem (assumed to exist, so that we are in the quasiperiodic or regular regime) have suitable quantized values. Finding such trajectories is in general difficult: for a system with F degrees of freedom, F good action variables must be calculated at each step of an F -dimensional search for quantizing initial conditions. Miller's approach avoids both the computation of individual action variables and the multi-dimensional search, by making use of a linear extrapolation approximation to the energy. Thus, the Hamiltonian, which is a function only of the good actions N , can be linearized about N :

$$\mathcal{H}(N_Q) \approx \mathcal{H}(N) + (\partial \mathcal{H} / \partial N) \cdot (N_Q - N). \quad (16)$$

Here N_Q represents the quantizing values of the good actions and N represents the good action variables for an arbitrary trajectory, which will in general have different values from the quantizing ones. The terms on the right-hand side in the above expression can be written in terms of a set of zeroth-order actions and angles, which are the variables that we can actually calculate at any point on a trajectory. Recognizing that the derivative is just the

frequency, we rewrite the linearized form as

$$\mathcal{H}(N_Q) \approx \mathcal{H}(N) + \omega(N) \cdot N_Q - \omega(N) \cdot N. \quad (17)$$

Now the strategy is to follow a trajectory, whose initial conditions are

$$n_0 = N_Q, \quad q_0 = \text{anything}. \quad (18)$$

until it closes arbitrarily well. For a closed trajectory the frequencies are related to the classical phase:

$$\omega(N) \cdot N = \frac{1}{T} \int_0^T dt \dot{q}(t) \cdot n(t). \quad (19)$$

Moreover, integration by parts of the linearized form with initial conditions (18) gives the expression (taking into account the closure of the trajectory):

$$\mathcal{H}(N_Q) = \mathcal{H}(n_0, q_0) + \frac{1}{T} \int_0^T dt q(t) \cdot \dot{n}(t). \quad (20)$$

Thus, by calculating a single closed trajectory (we close the trajectory by making the last step a linear interpolation to the initial conditions [12]) with initial conditions close to the quantum conditions, we obtain the semi-classical eigenvalue by formula (20) above. The success of this method rests on the existence of zeroth-order action angle variables that are close to the good variables. Examination of the surface of section as a function of k for system (15) indicates that ρ and ϕ_2 have the character of libration and rotation, respectively, for $k = 0$ to about $k = 0.2$. This is the same character they have in the uncoupled system, i.e. in the two-dimensional isotropic harmonic oscillator. Thus, Miller's method should apply in this range of k values.

The problem then becomes one of identifying the appropriate quantization conditions. For the radial motion we have two cases. For initially non-zero vibrational angular momentum the radial motion of the uncoupled system is a simple oscillation and the radial action takes on the usual values $m + \frac{1}{2}$, where m is a non-negative integer. For initially zero vibrational angular momentum, the motion of the uncoupled system consists of oscillations through the origin, with no angular motion. The quantizing condition for the radial motion is then $m + 1$ (extra phase is picked up upon traversing the origin [13]).

The variable I_1 is a constant of the motion, which can be identified with the good quantum number j . That comes about as follows. The operator with which the quantum-mechanical Hamiltonian operator commutes and which generates the good quantum number $2j$ is [14]

$$\hat{L} = 2\hat{P}_\phi + |+\rangle\langle +| - |-\rangle\langle -|. \quad (21)$$

Its electronic expectation value is

$$\langle \Psi | \hat{L} | \Psi \rangle = 2\hat{P}_\phi + |a_1|^2 - |a_2|^2. \quad (22)$$

Hence its classical analog transcription is

$$L(P_\phi, n) = 2P_\phi + 2n - 1. \quad (23)$$

Recalling the transformation equation $I_1 = P_\phi + n$ we have finally

$$I_1 = j + \frac{1}{2}. \quad (24)$$

The quantum number j must be half-integral to ensure single-valuedness of the total vibronic wavefunction, so I_1 is an integer. I_2 is chosen so that the system is initially in one or the other of the diabatic states. Thus, since $n = \frac{1}{2}I_1 - I_2$, then $I_2 = \frac{1}{2}I_1 - n$, and so $I_2 = \frac{1}{2}I_1$ or $\frac{1}{2}I_1 - 1$ in the uncoupled limit.

In the quantum-mechanical problem each eigenvalue is doubly degenerate because each depends only on the

magnitude of j , not its sign. This behavior is reproduced in the classical analog by freedom in the choice of I_1 . For example, the quantized actions for the $|j| = \frac{1}{2}$ manifold are picked as follows. Since $j = \frac{1}{2}$ or $-\frac{1}{2}$, we have $I_1 = 0$ or 1. For $I_1 = 0, I_2 = 0$ or -1 , while for $I_1 = 1, I_2 = \frac{1}{2}$ or $-\frac{1}{2}$. Choosing $I_\rho = \frac{1}{2}$ for definiteness and using formula (12) we see that the choices $I_1 = 0, I_2 = 0$, and $I_1 = 1, I_2 = -\frac{1}{2}$ are degenerate in zeroth order; they remain so in the coupled problem. These choices of I_ρ, I_1 , and I_2 correspond to the ground state of the $|j| = \frac{1}{2}$ manifold. The other possible choices, namely $I_1 = 0, I_2 = -1$, and $I_1 = 1, I_2 = \frac{1}{2}$ are also degenerate and correspond to the first excited states. Thus the zeroth-order level structure of a two-dimensional isotropic harmonic oscillator of doubled multiplicity is also retained.

4. Results

The semiclassical spectrum as a function of the linear coupling parameter, k , is compared with exact quantum results as a pair of correlation diagrams in fig. 1. Note that the qualitative trends in splitting patterns are repro-

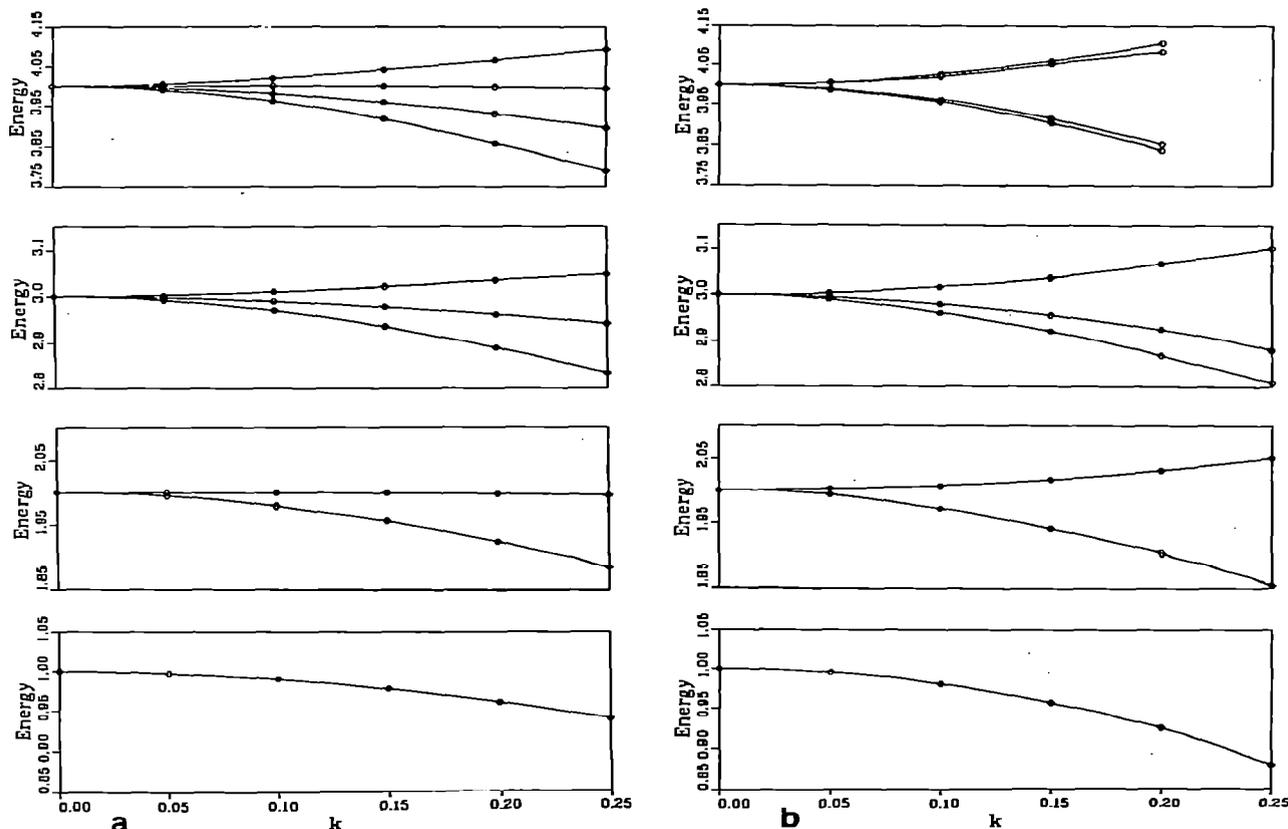


Fig. 1. (a) Exact quantum-mechanical eigenvalues as a function of the linear coupling parameter k . Each is doubly degenerate. The curves on these correlation diagrams are eigenvalues as a function of k for pairs of states that have the same value of $|j|$, the magnitude of the vibronic quantum number. Reading from the bottom the $|j|$ levels are: $1/2, 3/2, 1/2, 5/2, 1/2, 3/2, 7/2, 3/2, 1/2, 5/2$. (b) Eigenvalues computed semiclassically from the classical analog model, as a function of the linear coupling parameter. Each is doubly degenerate. The levels correlate correctly with the exact levels in that the semiclassical values of j for corresponding levels are the same as those of the exact quantum mechanical calculation.

duced. Moreover, quantitative agreement is to within a few percent on all values. Importantly, all semiclassical eigenvalues correlate correctly with their quantum-mechanical counterparts; the semiclassical J are in correspondence with quantum values, as are degeneracies.

The points where the qualitative agreement is worst, in the topmost quartet, were checked with a different semiclassical method. In this method the actions were calculated directly by numerical integration of the area in surface of section plots [12,15]. The energies calculated this way agree well with those calculated with Miller's method, demonstrating that the points shown are accurate primitive EBK eigenvalues.

5. Discussion and conclusions

Although the overall qualitative agreement of the two spectra is good, the discrepancy in the topmost quartet deserves further comment. The semiclassical eigenvalues calculated here are primitive, and thus contain no information about purely quantum-mechanical processes such as tunneling. Such processes can give rise to splittings of near-degenerate levels [16]. These splittings can be calculated by the procedure of uniformization [16,17]. Comparison of classical with exact quantum-mechanical results suggests that such a refinement is warranted here.

The overall results of this study show that semiclassical methods are useful, even for the study of what might be termed a strongly quantum-mechanical problem. We have seen that a classical analog model, which treats electronic and nuclear variables even-handedly, yields qualitative correct semiclassical results for a non-adiabatic system. We should be encouraged, then, that such an approach will be quite useful in studying the dynamics and eigenvalue spectra of complex non-adiabatic problems for which the quantum-mechanical solution is much more difficult or impossible to obtain.

The problem to be addressed next is the semiclassical quantization of the analog Hamiltonian for large values of k . In this regime the conjugate pair of variables ϕ_2 and I_2 exhibit oscillating rather than rotating behavior [1]. Moreover it appears that for low-energy states at least the system is more conveniently described in terms of an adiabatic rather than a diabatic basis. Investigation of the large- k problem using the approach of this paper is currently underway and will be described in a subsequent communication.

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