A semiclassical determination of the energy levels of a rigid asymmetric rotor

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(Received 9 September 1977)

Recent applications of semiclassical methods to vibrational energy levels have renewed interest in finding a semiclassical method for rotational levels. Here a simple semiclassical method is used to determine the $2J+1$ energy levels of an asymmetric rigid rotor.

INTRODUCTION

Recently, there has been a renewed interest in semiclassical methods for bound states of many-dimensional systems. Marcus led the way by applying classical trajectory methods to systems of the form

$$3\mathcal{C} = \frac{1}{2} \beta_{k}^{2} + \frac{1}{2} \omega_{k}^{2} \lambda_{k}^{2} + \frac{1}{2} \omega_{k}^{2} \nu_{k}^{2} + \epsilon V(x, y).$$

His original ideas are closely related to the old quantum theory ideas of "quantizing the action," and have been extended by many workers, in particular Marcus and collaborators, who have used Poisson surfaces of section; Chapman, Garrett, and Miller; who have used expansion techniques for solving the Hamilton Jacobi equation; Percival and Pumphrey, who have used perturbation techniques; and Sorbie and Handy, who have used a classical trajectory method.

Recently, Colwell and Handy have applied the latter method to the low-lying vibrational ($J=0$) states of SO$_2$ and H$_2$O, The results compared favorably with the accurate quantum mechanical energy levels calculated by workers at Cambridge (19) and Columbus. (8) In both cases the Hamiltonian was in normal coordinate form, as given by Watson. The semiclassical energy levels differed from the corresponding quantal energies by less than 0.5 cm$^{-1}$ for SO$_2$ and by less than 9 cm$^{-1}$ for H$_2$O.

Because of the success of the semiclassical methods in the $J=0$ case, and their comparative ease of operation, there is interest in applying them to the $J \neq 0$ case. The simplest problem that must be solved in order to do this is the asymmetric rigid rotor, for which the Hamiltonian is

$$\mathcal{C} = A_{k}^{2} + B_{k}^{2} + C_{k}^{2}, \quad A \geq B \geq C,$$

with

$$f_{k}^{2} = g_{k}^{2} + h_{k}^{2} + j_{k}^{2}.$$  

This may be reformulated into the problem

$$3\mathcal{C} = \frac{1}{2} (A + C)^{2} + \frac{1}{2} (A - C) E(\kappa),$$

where $\kappa$ is the asymmetry parameter

$$\kappa = (2B - A - C)/(A - C).$$

and $E(\kappa)$ is the energy for the hypothetical rotor with moments $1, \kappa, -1$:

$$3\mathcal{C}(\kappa) = f_{k}^{2} + \kappa f_{k}^{2} - f_{k}^{2}.$$  

Quantum mechanical values for $E(\kappa)$ are readily available in the literature, having been obtained from the diagonalization of $(2J+1) \times (2J+1)$ matrices. In the next section we introduce appropriate variables for the application of WKB type methods to this problem.

THE SEMICLASSICAL QUANTIZATION CONDITIONS

WKB methods were first applied to this problem by King. These methods were reformulated by Augustin and Miller, who give the $F_{j}$ generating function for the transformation from the Euler angles $\theta, \phi, \psi$ to $q_{m}, q_{n}$, the coordinates conjugate to the total angular momentum $j$, its component along the body fixed $z$ axis $k$, and its component along the space fixed $z$ axis $m$. In these coordinates

$$3\mathcal{C} = \int (\sin^{2} q_{m} + \kappa \cos^{2} q_{m}) + \int (\sin^{2} q_{m} - \kappa \cos^{2} q_{m}).$$  

Since neither $q_{m}$ or $q_{n}$ appears in the Hamiltonian, both $m$ and $j$ are constants of the motion, and the problem thus reduces to one of a single degree of freedom.

The usual Bohr-Sommerfeld, or WKB quantization condition (as used by King) determines the semiclassical eigenvalues by

$$2m = \oint dq_{m} k(q_{m}, E),$$

with $m$ an integer, where energy conservation $E = 3\mathcal{C}$ is used with Eq. (7) to define $k(q_{m}, E)$:

$$k(q_{m}, E) = \left( -E + \int \sin^{2} q_{m} + \kappa \cos^{2} q_{m} \right)^{1/2},$$

Alternatively, one may choose the $x$ axes as the quantization axes, and in this case the Hamiltonian is given by

$$3\mathcal{C} = \int (\sin^{2} q_{m} + \kappa \cos^{2} q_{m}) + \int (\sin^{2} q_{m} - \kappa \cos^{2} q_{m}),$$

where $k$ is now the projection of total angular momentum onto the body-fixed $x$ axis and $q_{m}$ its conjugate angle. Equation (8) is still the quantization condition, but now

$$k(q_{m}, E) = \left( -E + \int \sin^{2} q_{m} - \kappa \cos^{2} q_{m} \right)^{1/2}. $$
Note that Eqs. (9) and (11) transform into one another by the replacement

\[ \kappa \to -\kappa, \]
\[ E \to -E. \]

This is the semiclassical manifestation of the symmetry relation

\[ E(-\kappa) = -E(\kappa) \]  \hspace{1cm} (12)

obeyed by the quantum mechanical eigenvalues; it means that if \( E(\kappa) \) is an eigenvalue, so is \( -E(\kappa) \).

To apply this "primitive" WKB eigenvalue condition it is useful to consider \( k(q_\nu, E) \), in Eq. (11) say, to be of the form

\[ k(q_\nu, E) \to \sqrt{E - V(q_\nu)}, \]

so we define the "potential" \( V(q_\nu) \) by

\[
V(q_\nu) = \frac{\hbar^2}{\beta^2} \left( \kappa \cos^2 q_\nu - \sin^2 q_\nu \right) \\
= \frac{\hbar^2}{\beta^2} \left[ (\kappa - 1) \sin^2 q_\nu \right];
\]  \hspace{1cm} (13)

it is shown in Fig. 1. The WKB quantum condition (8) thus splits into two cases:

(a) \( E > \kappa \hbar^2 \). In this "above barrier" case there are no classical turning points (cf. Fig. 1), and Eq. (8) is given explicitly by

\[ 2\pi = \int_0^{\pi} dq_\nu k(q_\nu, E) \]

or because of the symmetry

\[ n\pi = \int_0^{\pi} dq_\nu k(q_\nu, E), \]  \hspace{1cm} (14)

with \( k(q_\nu, E) \) as in Eq. (11).

(b) \( E < \kappa \hbar^2 \). In this "below barrier" case there are four classical turning points (cf. Fig. 1), corresponding to two identical potential wells, so that Eq. (8) becomes (since \( \beta d\nu = 2\int_{q_0}^{q_\nu} dq_\nu \))

\[
(n + \frac{1}{2})\pi = \int_0^{\pi/2} dq_\nu k(q_\nu, E),
\]  \hspace{1cm} (15)

with \( k(q_\nu, E) \) given by Eq. (11); "\( n + \frac{1}{2} \)" has replaced "\( \kappa \)" because of the classical turning points. Also, since there are two identical potential wells, there are two eigenvalues for each value of \( n \).

In the symmetric top limits (\( \kappa = \pm 1 \)) it is not hard to show that Eqs. (14) and (15) give

\[ \kappa = -1, \quad E_n = -\frac{\hbar^2}{\beta^2} + 2n^2, \]  \hspace{1cm} (16a)
\[ \kappa = +1, \quad E_n = \frac{\hbar^2}{\beta^2} - 2(n + \frac{1}{2} - j)^2. \]  \hspace{1cm} (16b)

If one makes the usual semiclassical replacement \( j \to j + \frac{1}{2} \), then these become

\[ \kappa = -1, \quad E_n = -(j + \frac{1}{2})^2 + 2n^2, \]  \hspace{1cm} (17a)
\[ \kappa = +1, \quad E_n = -(j + \frac{1}{2})^2 - 2(n - j)^2, \]  \hspace{1cm} (17b)

which are the correct quantum mechanical results, except that \( (j + \frac{1}{2})^2 \) appears instead of \( j(j + 1) \). This, however, is also a shortcoming of semiclassical rotational eigenvalues even for the linear rotor, and although it means that the absolute eigenvalues are not given correctly, for a given value of \( \kappa \) (i.e., for a given molecule), differences between energy levels are correct [because \( (j + \frac{1}{2})^2 \) and \( j(j + 1) \) differ by a constant].

Although correct in both symmetric top limits, the primitive WKB eigenvalue relation in Eqs. (14) and (15) has severe shortcomings. Energy levels above, as well as below, the top of the barrier occur in degenerate pairs (see later), whereas the correct quantum mechanical eigenvalues have this degeneracy split by tunneling, except in the symmetric top limits (17). The primitive semiclassical eigenvalues are poorest for intermediate values of \( \kappa \) (i.e., not near \(+1\) or \(-1\)) and for energy levels close to the top of the barrier.

To remedy these defects of the primitive WKB eigenvalues it is necessary to use the uniform semiclassical
quantum condition for a hindered rotor in a double-well potential. The appropriate formula, which takes account of tunneling through the barrier in the case (a), and reflection by the barrier in case (a), is\textsuperscript{15,19}

\[ n\pi = \phi + \Delta \phi \pm \tan^{-1}(e^\phi), \]  

(18)

where \( \phi \) is the action integral across the well

\[ E > \kappa f^2, \quad \phi = \int_0^r dq_k k(q_k, E), \]  

(19a)

\[ E < \kappa f^2, \quad \phi = \int_0^r dq_k k(q_k, E); \]  

(19b)

\( \theta \) is the barrier penetration integral

\[ E > \kappa f^2, \quad \theta = -\int_{q_0}^{q} dq_k \left( \frac{E - j\sinh^2 q - \kappa f \cos^2 q}{1 - \sinh^2 q - \kappa \cos^2 q} \right)^{1/2}, \]  

(20a)

\[ E < \kappa f^2, \quad \theta = \int_{q_0}^{q} dq_k \left( \frac{-E + j\sinh^2 q + \kappa f \cos^2 q}{1 + \sinh^2 q - \kappa \cos^2 q} \right)^{1/2}; \]  

(20b)

and \( \Delta \phi \) is a "phase shift"

\[ \Delta \phi = \arg \Gamma\left(1 + \frac{i\theta}{\pi}\right) - \frac{\theta}{\pi} \log \left( \frac{1}{\tan \frac{\theta}{2}} \right). \]  

(21)

In Eq. (20a), \( \theta_0 \) is the zero of the numerator; \( \pm\theta_0 \) are the complex turning points for this over-barrier case. For each value of \( n \) in Eq. (18) there are two eigenvalues, corresponding to the \( \pm \) sign.

It is easy to see that the primitive WKB quantum conditions (14) and (15) are recovered by the following approximations in Eq. (18):

\[ E > \kappa f^2: \quad \theta = -\infty, \quad \Delta \phi = 0, \]  

(22a)

\[ E < \kappa f^2: \quad \theta = +\infty, \quad \Delta \phi = 0. \]  

(22b)

With these approximations Eq. (18) becomes for the case (a)

\[ n\pi = \phi \pm 0, \]  

which is Eq. (14) and which also indicates that there are two equal eigenvalues for each \( n \). For case (a) Eq. (18) becomes

\[ n\pi = \phi \pm \pi/2 \]

or

\[ (n \pm \frac{1}{2})\pi = \phi, \]

which is equivalent to Eq. (15); this also leads to doubly degenerate energy levels as noted above.

Equations (18)–(21) give the uniform semiclassical quantum condition which is valid for \( E \) above, below, or near the top of the barrier. The phase integrals \( \phi \) and \( \theta \) can be expressed in terms of elliptic integrals, and it can be shown, by using various transformation properties of these elliptic integrals, that the symmetry relation (12) is satisfied by the uniform semiclassical eigenvalues (and the primitive WKB eigenvalues) if (and only if) the correspondence relation \( j = J + 1/2 \) (\( J \) an integer) is used. This fact has been verified by direct numerical evaluation.

In the calculations reported below it is thus necessary to consider only the eigenvalues for the below barrier case (b), \( E < \kappa f^2 \), since the symmetry relation determines those for case (a), \( E > \kappa f^2 \).

**RESULTS**

Calculations have been carried out for \( \kappa = -1, 0 -1.0 \) in increments of 0.1, for \( j = 3 \), for \( E < \kappa f^2 \). Results for \( E > \kappa f^2 \) are obtained by \( E(\kappa) = -E(-\kappa) \), and the replacement \( j \to J+1/2 \) is always made in these semiclassical quantum conditions. Such a small value of \( j \) is a very severe test of semiclassical theory, which will in general be better the larger the value of \( j \). The integrals were numerically evaluated, and an iterative technique was used which adjusts \( E \) until \( n \) has an integral value.

Table I shows the primitive WKB eigenvalues and the uniform semiclassical eigenvalues (USC) compared to the exact quantum mechanical eigenvalues (QM) (taken from Allen and Cross\textsuperscript{20}) for \( \kappa \geq 0 \). For a given \( \kappa \) the table shows energies relative to the lowest eigenvalue, these being essentially the observed quantities. Several observations are possible:

(a) The uniform semiclassical eigenvalues, which take account of tunneling, are seen to be superior to the primitive WKB eigenvalues, and in general to be in good agreement with the quantum mechanical eigenvalues.

(b) The primitive WKB eigenvalues are seen to be poorer the smaller \( |\kappa| \) is, and for eigenvalues nearest to the top of the barrier.

(c) In the USC approach the correct number \( 2j+1 \) of energy levels are given, whereas the WKB method gives \( 2j-1 \) energy levels. In the table we have chosen the WKB levels which are closest to the QM levels.

**DISCUSSION**

In this paper we have shown how the energies of an asymmetric rigid rotor may be calculated by semiclassical methods. The methods give the correct number of rotational levels for a given \( j \), and furthermore are accurate, typical errors for frequencies being much less than 0.25 cm\(^{-1}\).

These calculations make it clear that tunneling effects must be taken into account in order to obtain the correct features of the spectrum. Therefore, semiclassical methods which depend upon purely classical trajectories are unlikely to be successful at determining the vibrational–rotational energy levels of molecules. This appears to make the semiclassical approach rather more difficult than for the \( J = 0 \) case.
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*Eigenvalues are given in each case relative to the lowest eigenvalue which is given in square brackets.

*Primitive WKB eigenvalues from Eq. (14) and (15).

*Uniform semiclassical eigenvalues from Eqs. (16)–(21).

*Exact quantum mechanical values from Ref. 20.
ACKNOWLEDGMENT

S. M. Colwell would like to thank the S.R.C. for financial support.

10S. M. Colwell and N. C. Handy (to be published).