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Miller, William H.

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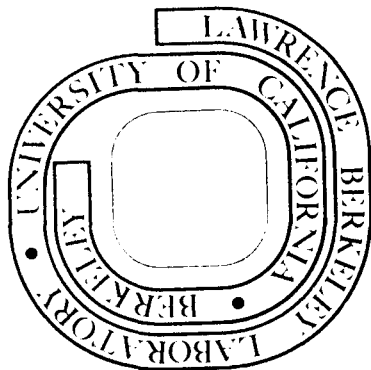
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ON THE EXISTENCE OF

SEMICLASSICAL EIGENVALUES FOR IRREGULAR SPECTRA[*]

William H. Miller[†]

University Chemical Laboratory
Lensfield Road
Cambridge CB2 1EW
England

ABSTRACT

It is shown that the semiclassical limit of eigenvalues for
a multi-dimensional system can exist even when a complete set of
"good" action variables (i.e., quantum numbers) do not.

I. INTRODUCTION.

There has recently been considerable interest and progress in generalizing the one-dimensional Bohr-Sommerfeld quantum condition to dynamical systems with several degrees of freedom.[1-13] The one-dimensional semiclassical quantum condition

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

$n = 0, 1, 2, \ldots$, provides an accurate description of vibrational eigenvalues of diatomic molecules, and it is anticipated that its multi-dimensional extension would be of considerable utility in describing vibrational spectra of simple polyatomic molecules.

Essentially all of the work to date (except that in ref. 6 and 10) on the multi-dimensional eigenvalue problem has dealt with the case of regular[8] spectra, i.e., the case that the eigenvalues of the system are characterizable by f "good" quantum numbers, f being the number of degrees of freedom. In Born's formulation[3,11] of the problem, for example, one considers the classical Hamiltonian first in terms of some "unperturbed" action-angle variables[14] $(\underset{\sim}{n},\underset{\sim}{q}) \equiv (n_i, q_i)$, $i = 1, \ldots, f$:

$$H(\underset{\sim}{n},\underset{\sim}{q}) = H_0(\underset{\sim}{n}) + V(\underset{\sim}{q},\underset{\sim}{n}) \quad , \tag{1.2}$$

where $H_0(\underset{\sim}{n})$ is a separable reference Hamiltonian that is introduced for the purpose of defining the unperturbed action-angle variables, and V is the non-separable coupling which precludes the action

variables $\underset{\sim}{n}$ from being constants of the motion. The task is then to carry out a canonical transformation[15] from the unperturbed action-angle variables $(\underset{\sim}{n},\underset{\sim}{q})$ to the "good" action-angle variables $(\underset{\sim}{N},\underset{\sim}{Q})$ such that the total Hamiltonian, when expressed in terms of $\underset{\sim}{N}$ and $\underset{\sim}{Q}$, is a function only of the action variables $\underset{\sim}{N}$,

$$H(\underset{\sim}{N},\underset{\sim}{Q}) = E(\underset{\sim}{N}) \qquad . \tag{1.3}$$

The "good" action variables $\{N_i\}$, $i = 1, \ldots, f$ are therefore constants of the motion, and the semiclassical eigenvalues are obtained simply by requiring that the $\{N_i\}$ be integers (or perhaps half-integers). The recent paper by Chapman et al.[11] has shown how this canonical transformation can actually be carried out non-perturbatively (i.e., numerically).

One does not expect, however, there always to exist a complete set of f "good" action variables; i.e., it may not always be possible to carry out Born's canonical transformation. In practice, too, one would not expect to be able to characterize highly excited vibrational states with a complete set of f quantum numbers. Numerical experiments[16,17] have also suggested that the spectrum of eigenvalues becomes irregular[8] at sufficiently high energy or strong non-separable coupling.

In such cases of an irregular spectrum none of the recent approaches to semiclassical quantization appear to be applicable; since the f "good" action variables $\{N_i\}$ do not exist, Born's formulation[3,11] is clearly meaningless, and other approaches similarly fail because the requisite "invariant toroids" fail to

exist. It has been conjectured that the semiclassical limit of eigenvalues in this irregular region may even fail to exist.

This paper presents an analysis which shows that the semi-classical limit of eigenvalues in the irregular region of the spectrum can indeed exist. The formulation completely by-passes the intermediary of f "good" action variables $\{N_i\}$ which must be set to integers in order to obtain the eigenvalues; rather it produces semiclassical eigenvalues directly without any reference to "good" action variables or "invariant toroids". This is the important feature, of course, since "good" action variables are thus not required to exist in this formulation. Unfortunately, the computational procedure which results from this approach does not appear to be particularly useful in practice since it involves as much computational effort as a fully quantum mechanical calcula-tion. The analysis is nevertheless interesting in showing that the semiclassical limit of eigenvalues can exist for the case of an irregular spectrum.

II.   FORMULATION.

Recall first some specifics of Born's approach.[3,11] The generating function[15] for the $(\underset{\sim}{n},\underset{\sim}{q}) \to (\underset{\sim}{N},\underset{\sim}{Q})$ transformation is $F(\underset{\sim}{q},\underset{\sim}{N})$, and the transformation is specified by the two differential equations which give $\underset{\sim}{n}$ and $\underset{\sim}{Q}$ in terms of $\underset{\sim}{q}$ and $\underset{\sim}{N}$:

$$\underset{\sim}{n}(\underset{\sim}{q},\underset{\sim}{N}) = \frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{q}} \tag{2.1}$$

$$\underset{\sim}{Q}(\underset{\sim}{q},\underset{\sim}{N}) = \frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{N}} \quad . \tag{2.2}$$

Using Eq. (2.1) to eliminate $\underset{\sim}{n}$ from the Hamiltonian $H(\underset{\sim}{q},\underset{\sim}{n})$, and imposing Eq. (1.3), gives the Hamilton-Jacobi equation for F:

$$E(\underset{\sim}{N}) = H\left(\underset{\sim}{q}, \frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{q}}\right) \quad . \tag{2.3}$$

For simplicity the reference Hamiltonian H_0 will be taken to be harmonic (but this is not essential),

$$H_0(\underset{\sim}{n}) = \underset{\sim}{\omega} \cdot \underset{\sim}{n} = \sum_{i=1}^{f} \omega_i n_i \quad , \tag{2.4}$$

so that Eq. (2.3) becomes

$$E(\underset{\sim}{N}) = \underset{\sim}{\omega} \cdot \frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{q}} + V\left(\underset{\sim}{q}, \frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{q}}\right) \quad . \tag{2.5}$$

To solve Eq. (2.5) the generator is expanded as

$$F(\underset{\sim}{q},\underset{\sim}{N}) = \underset{\sim}{q} \cdot \underset{\sim}{N} + \sum_{\underset{\sim}{k}} B_{\underset{\sim}{k}} \, e^{i\underset{\sim}{k} \cdot \underset{\sim}{q}} \quad , \tag{2.6}$$

and the Fourier coefficients $B_{\underset{\sim}{k}}$ are determined by substituting this expansion into Eq. (2.5)

The first term in the expansion of the generator in Eq. (2.6) is determined by the result desired for F in the limit that the non-separable interaction V is "switched off". In this limit one wants the "new" variables $(\underset{\sim}{N},\underset{\sim}{Q})$ to be the same as the "old" ones $(\underset{\sim}{n},\underset{\sim}{q})$, and one can readily verify that the generator F_0,

$$F_0(\underset{\sim}{q},\underset{\sim}{N}) \equiv \lim_{V \to 0} F(\underset{\sim}{q},\underset{\sim}{N}) = \underset{\sim}{q} \cdot \underset{\sim}{N} \quad , \tag{2.7}$$

accomplishes this. This is more clear intuitively if one recognizes that the generator $F(\underset{\sim}{q},\underset{\sim}{N})$ is related to the semiclassical wave function in q-space by

$$\psi_{\underset{\sim}{N}}(\underset{\sim}{q}) \sim e^{iF(\underset{\sim}{q},\underset{\sim}{N})} \quad , \tag{2.8}$$

units being used so that $\hbar = 1$. If $V \to 0$, then one has the obvious limit

$$\lim_{V \to 0} \psi_{\underset{\sim}{N}}(\underset{\sim}{q}) \equiv \psi_{\underset{\sim}{N}}^{(0)}(\underset{\sim}{q}) \sim e^{i\underset{\sim}{q} \cdot \underset{\sim}{N}} \quad ; \tag{2.9}$$

Eqs. (2.8) and (2.9) thus also lead to Eq. (2.7).

By invoking the identification in Eq. (2.8) it is also easy to see physically why the "good" action variables $\{N_i\}$ are required to be integers: The expansion of $F(\underset{\sim}{q},\underset{\sim}{N})$ in Eq. (2.6) corresponds to the

following expansion for ψ:

$$\psi_{\underset{\sim}{N}}(\underset{\sim}{q}) \sim \exp(i\underset{\sim}{q}\cdot\underset{\sim}{N} + \sum_{\underset{\sim}{k}} B_{\underset{\sim}{k}}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{q}}) \quad . \tag{2.10}$$

Singlevaluedness of ψ in the space of physical (i.e., cartesian) coordinates requires that ψ be a periodic function of $\underset{\sim}{q}$, and this then requires that the $\{N_i\}$ be integers; i.e., <u>quantization results because the generator F is required to be the logarithm of a periodic function.</u>

One other feature which is crucial in motivating the approach taken below, and that has to do with <u>degeneracy</u>. Suppose the frequencies $\underset{\sim}{\omega} \equiv \{\omega_i\}$, $i = 1$, ..., f of H_0 are such that the unperturbed energies of two different sets of quantum numbers, $\underset{\sim}{N}_1$ and $\underset{\sim}{N}_2$ say, are equal,

$$\underset{\sim}{\omega}\cdot\underset{\sim}{N}_1 = \underset{\sim}{\omega}\cdot\underset{\sim}{N}_2 \quad . \tag{2.11}$$

Born's formulation, and the other equivalent approaches, has great difficulty in dealing with this because the zero$\underline{th}$ order term in $F(\underset{\sim}{q},\underset{\sim}{N})$ is no longer obvious; it is not $\underset{\sim}{q}\cdot\underset{\sim}{N}_1$ or $\underset{\sim}{q}\cdot\underset{\sim}{N}_2$ but should in some sense be a combination of the two.

The situation is much simpler quantum mechanically, for in this case one knows that the zero$\underline{th}$ order wave function is a simple linear superposition of the two degenerate zero$\underline{th}$ order functions:

$$\psi^{(0)}(\underset{\sim}{q}) \sim c_1\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{N}_1} + c_2\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{N}_2} \quad . \tag{2.12}$$

Eq. (2.8) then shows that

$$F_0(\underset{\sim}{q}) \sim -i\ell n \left[c_1 e^{i\underset{\sim}{q}\cdot\underset{\sim}{N}_1} + c_2 e^{i\underset{\sim}{q}\cdot\underset{\sim}{N}_2} \right] \quad . \tag{2.13}$$

If c_1 or $c_2 \to 0$, then the simple form for F_0 in Eq. (2.7) is recovered, but the logarithmic structure in general is considerably more difficult to represent by the Fourier series expansion in Eq. (2.6).

In the case of degeneracy, therefore, the generating function $F(\underset{\sim}{q})$ is not at all well-represented by the Fourier series in Eq. (2.6), but the exponential function of the generator is well-represented by a Fourier series in the degenerate as well as the non-degenerate case. This suggests, therefore, that one would do better to write the generator $F(\underset{\sim}{q})$ (dropping the label $\underset{\sim}{N}$ since it is "passive") in terms of a function $\psi(\underset{\sim}{q})$,

$$F(\underset{\sim}{q}) \equiv -i\ell n \, \psi(\underset{\sim}{q}) \quad , \tag{2.14}$$

and expand $\psi(\underset{\sim}{q})$ in a Fourier series

$$\psi(\underset{\sim}{q}) = \sum_{\underset{\sim}{k}} C_{\underset{\sim}{k}} \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{q}} \quad . \tag{2.15}$$

Since $F(\underset{\sim}{q})$ is now manifestly the logarithm of a periodic function of $\underset{\sim}{q}$, it must happen that semiclassical eigenvalues appear "automatically" since there is now no additional condition to impose in order to produce quantization.

Although the form of the generating function $F(\underset{\sim}{q})$ given by Eqs. (2.14) and (2.15) is certainly motivated by quantum mechanics, it is simply a special form of the generator of a canonical transformation

in classical mechanics. Once this form is chosen for the generator, the rest is purely classical mechanics. With Eq. (2.14) one has

$$\frac{\partial F(\underset{\sim}{q})}{\partial \underset{\sim}{q}} = \frac{\partial \psi(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \bigg/ i\psi(\underset{\sim}{q}) \quad , \qquad (2.16)$$

so that Eq. (2.5) gives the following equation for $\psi(\underset{\sim}{q})$:

$$E\psi(\underset{\sim}{q}) = -i\underset{\sim}{\omega} \cdot \frac{\partial \psi(\underset{\sim}{q})}{\partial \underset{\sim}{q}} + V(\underset{\sim}{q}, \underset{\sim}{n}(\underset{\sim}{q})) \, \psi(\underset{\sim}{q}) \qquad (2.17a)$$

with

$$\underset{\sim}{n}(\underset{\sim}{q}) \equiv \frac{\partial \psi(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \bigg/ i\psi(\underset{\sim}{q}) \quad . \qquad (2.17b)$$

(The resemblance of Eq. (2.17) to a Schrödinger equation in action-angle variables is striking, but this is all strictly <u>classical</u> mechanics.) If the Fourier expansion of $\psi(\underset{\sim}{q})$, Eq. (2.15), is substituted into Eq. (2.17), and one multiplies by a specific plane wave $e^{-i\underset{\sim}{k} \cdot \underset{\sim}{q}}$ and integrates over $\underset{\sim}{q}$, then one obtains the following set of equations for the Fourier coefficients $C_{\underset{\sim}{k}}$:

$$E \, C_{\underset{\sim}{k}} = \underset{\sim}{\omega} \cdot \underset{\sim}{k} \, C_{\underset{\sim}{k}} + \sum_{\underset{\sim}{k}'} V_{\underset{\sim}{k}, \underset{\sim}{k}'} \, C_{\underset{\sim}{k}'} \quad , \qquad (2.18a)$$

for all $\underset{\sim}{k}$, where

$$V_{\underset{\sim}{k}, \underset{\sim}{k}'} = (2\pi)^{-f} \int_0^{2\pi} d\underset{\sim}{q} \; e^{-i(\underset{\sim}{k} - \underset{\sim}{k}') \cdot \underset{\sim}{q}} \, V(\underset{\sim}{q}, \underset{\sim}{n}(\underset{\sim}{q})) \qquad (2.18b)$$

with

$$\underset{\sim}{n}(q) = \left(\sum_{\underset{\sim}{k}} \underset{\sim}{k} \; C_{\underset{\sim}{k}} \; e^{i\underset{\sim}{k}\cdot\underset{\sim}{q}}\right) \Big/ \left(\sum_{\underset{\sim}{k}} C_{\underset{\sim}{k}} \; e^{i\underset{\sim}{k}\cdot\underset{\sim}{q}}\right) \quad . \tag{2.18c}$$

Eq. (2.18) is a set of non-linear (because $C_{\underset{\sim}{k}}$ occurs in $\underset{\sim}{n}(q)$)

equations for the Fourier coefficients $C_{\underset{\sim}{k}}$.

If for the moment one ignores the fact that $\underset{\sim}{n}(q)$ depends on

$\{C_{\underset{\sim}{k}}\}$, then Eq. (2.18a) is recognized as a set of linear homogenous

equations which has a non-trivial solution for $\{C_{\underset{\sim}{k}}\}$ only if

$$\det \left| \underset{\sim}{\omega}\cdot\underset{\sim}{k} \; \delta_{\underset{\sim}{k},\underset{\sim}{k}'} \; + \; V_{\underset{\sim}{k},\underset{\sim}{k}'} \; - \; E \; \delta_{\underset{\sim}{k},\underset{\sim}{k}'} \right| = 0 \quad . \tag{2.19}$$

Eq. (2.19) is a secular equation for the energy E, and its

solutions are the eigenvalues of the matrix

$$\underset{\sim}{\omega}\cdot\underset{\sim}{k} \; \delta_{\underset{\sim}{k},\underset{\sim}{k}'} + V_{\underset{\sim}{k},\underset{\sim}{k}'} \quad . \tag{2.20}$$

(One will note the strong resemblance between Eq. (2.20) and the

quantum mechanical matrix of the Hamiltonian operator in the basis

set of eigenstates of H_0.) As expected, therefore, discrete values

for E have emerged "automatically", completely within the realm of

classical mechanics, once the generator is taken to be the logarithm

of a periodic function of q, Eq. (2.14) and (2.15).

$\underset{\sim}{n}(q)$, however, _does_ depend on the coefficients $\{C_{\underset{\sim}{k}}\}$, as given

by Eq. (2.18c), so that Eq. (2.18) must be solved iteratively, like

the Hartree-Fock self-consistent field problem[18] in quantum chemistry.

Thus one first assumes an initial eigenvector $C_{\underset{\sim}{k}}^{(0)}$ for the particular

eigenvalue being sought, and uses it to calculate $n(q)$ via Eq. (2.18c)

and then the matrix $V_{\underset{\sim}{k},\underset{\sim}{k}'}$ via Eq. (2.18b). The matrix in Eq. (2.20)

is then diagonalized (or the eigenvalue extracted by some other

procedure), and one identifies one of its eigenvalues as an

approximation to the particular semiclassical eigenvalue being

sought. The corresponding eigenvector, call it $C_k^{(1)}$, is now

used to re-compute $\underset{\sim}{n}(q)$ via Eq. (2.18c) and then $V_{\underset{\sim}{k},\underset{\sim}{k}'}$ via Eq.

(2.18b). The matrix is then diagonalized again, one of its

eigenvalues identified as the desired one, and its corresponding

eigenvector as $C_k^{(2)}$, etc., until the desired eigenvalue converges.

In the simple case of a non-degenerate regular spectrum one

can easily see what the initial guess for the eigenvector should

be. If the desired eigenvalue is characterized by the complete

set of quantum numbers $\underset{\sim}{N}$, then the zero$\underline{^{th}}$ order approximation for

$\psi(\underset{\sim}{q})$ is

$$\psi(\underset{\sim}{q}) = e^{i\underset{\sim}{N}\cdot\underset{\sim}{q}} \quad ,$$

and from Eq. (2.15) this is seen to correspond to the coefficients

$C_{\underset{\sim}{k}}$ being

$$C_{\underset{\sim}{k}}^{(0)} = \delta_{\underset{\sim}{k},\underset{\sim}{N}} \quad . \tag{2.21a}$$

With this initial choice for $C_{\underset{\sim}{k}}$ the "old quantum number function"

$\underset{\sim}{n}(q)$ of Eq. (2.18c) is seen to be

$$\underset{\sim}{n}(\underset{\sim}{q}) = \underset{\sim}{N} \quad ; \tag{2.21b}$$

i.e., for the first iteration $\underset{\sim}{n}(q)$ is constant and equal to the

"good" quantum numbers $\underset{\sim}{N}$. This will not be true, of course, for

later iterations.

In the case of degeneracy, the zero$^{\text{th}}$ order approximation

to $\psi(q)$ is that in Eq. (2.12), and this corresponds to an

initial choice for $C_{\underset{\sim}{k}}^{(0)}$ as

$$C_{\underset{\sim}{k}}^{(0)} = c_1 \delta_{\underset{\sim}{k},\underset{\sim}{N}_1} + c_2 \delta_{\underset{\sim}{k},\underset{\sim}{N}_2} \quad . \qquad\qquad (2.22)$$

III. CONCLUDING REMARKS.

The interesting and important features of the formulation carried out above is that semiclassical eigenvalues emerge "automatically" from Eq. (2.18)-(2.19) without any auxiliary criteria such as requiring "good" action variables to be integers. "Good" action variables do not even appear in Eqs. (2.18)-(2.19), and this is the important fact, for it means that the semiclassical eigenvalues determined by Eqs. (2.18)-(2.19) may exist even when a complete set of "good" action variables do not, i.e., in the irregular portion of the spectrum.

Although Eqs. (2.18)-(2.20) look remarkably like quantum mechanics--with secular equations, Hamiltonian matrices, eigen-values, etc.--it should be remembered that they are strictly classical mechanics with the requirement that the generator be the logarithm of a function periodic in the old angle variables q. In Born's formulation, too, it is the condition that $e^{iF(q)}$ be periodic that produces quantization, only in the present formulation this requirement is injected at the very beginning rather than at the end. To the extent that both approaches are applicable it is clear that they must yield precisely the same semiclassical eigenvalues.

A disappointing practical aspect of the present approach is that the computational procedure suggested by Eqs. (2.18)-(2.19) is probably as difficult to carry out as a purely quantum mechanical one (or even more so). The calculation of the matrix elements $V_{k,k'}$ is perhaps easier via Eq. (2.18b) than quantum mechanically,

but the eigenvalue problem must be solved <u>iteratively</u> rather than

just once as in quantum mechanics. Also, one matrix diagonalization

produces <u>all</u> the eigenvalues quantum mechanically, but Eqs. (2.18)-

(2.19) must be solved for each semiclassical eigenvalue one at a

time.

There is one trivial modification of Eqs. (2.18)-(2.19) that

should be made which for simplicity of presentation has not been

mentioned above, and this is the replacement $\underset{\sim}{k} \to \underset{\sim}{k} + \frac{1}{2}$. The

modified equations which replace Eqs. (2.18)-(2.19) are

$$\det \left| \underset{\sim}{\omega} \cdot (\underset{\sim}{k} + \frac{1}{2}) \; \delta_{\underset{\sim}{k},\underset{\sim}{k}'} + V_{\underset{\sim}{k},\underset{\sim}{k}'} - E \; \delta_{\underset{\sim}{k},\underset{\sim}{k}'} \right| = 0 \tag{3.1a}$$

where

$$V_{\underset{\sim}{k},\underset{\sim}{k}'} = (2\pi)^{-f} \int_0^{2\pi} d\underset{\sim}{q} \; e^{-i(\underset{\sim}{k}-\underset{\sim}{k}') \cdot \underset{\sim}{q}} \; V(\underset{\sim}{q}, \underset{\sim}{n}(\underset{\sim}{q})) \tag{3.1b}$$

with

$$\underset{\sim}{n}(\underset{\sim}{q}) = \frac{1}{2} + \left(\sum_{\underset{\sim}{k}} \underset{\sim}{k} \; C_{\underset{\sim}{k}} \; e^{i\underset{\sim}{k} \cdot \underset{\sim}{q}} \right) \Big/ \left(\sum_{\underset{\sim}{k}} C_{\underset{\sim}{k}} \; e^{i\underset{\sim}{k} \cdot \underset{\sim}{q}} \right) \quad . \tag{3.1c}$$

This modification results when one takes into account that $\psi(\underset{\sim}{q})$

should actually change sign when any of the angles $\{q_i\}$ is

increased by 2π; this comes from the phase contribution to ψ

from the two classical turning points for each of the (oscillatory)

degrees of freedom.

Finally, one should note that mathematical rigor is totally

absent from the presentation in Section II. It has not been

proved, for example, that the "self consistent field" procedure described at the end of Section II converges or even that solutions to Eqs. (2.18)-(2.19) exist. These are very thorny questions that must be left to those more mathematically competent than the author.

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