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Semiclassical Interpretation of Eigenvectors for Excited Atoms in External Fields.

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Eigenvectors for an electron in an atom in parallel electric and magnetic fields are calculated, and a semiclassical interpretation of their behavior is obtained. Eigenvectors can in this case be regarded as "wave functions in angular momentum space." The matrix equation defining the eigenvectors is written as a difference equation, and then converted to a pseudodifferential equation; a systematic procedure is then used to construct a semiclassical approximation. It is found that the same classical Hamiltonian that has been previously used to calculate semiclassical eigenvalues provides a WKB-type representation of the eigenvectors. The development sheds new light on action-angle formulations of quantum mechanics and on semiclassical approximations in action-angle variables.

I. PURPOSE

In this paper we shall obtain a semiclassical approximation to eigenvectors representing excited states of a one-electron atom in collinear electric and magnetic fields.

II. PRELUDE

A standard method for calculating wave functions involves expansion in a basis set, evaluation of matrix elements of the Hamiltonian in that basis, and diagonalization of the resulting matrix. The eigenvalues and eigenvectors come out of this process as a collection of numbers. Confronted with the list of eigenvalues, with sufficient thought one can often discern patterns in the numbers, and thereby gain understanding of the physical system.

However, the numerical list of eigenvectors provides a more difficult challenge. As an example, the list of elements of an eigenvector that describes a wave function of an atomic electron in collinear electric and magnetic fields is given in Table I. At first glance it is a pretty formless collection of numbers. Lengthy perusal does not help; no pattern to the numbers becomes evident. Given a wave function in configuration space, we can often provide an intuitively satisfying interpretation of its structure. But given an eigenvector—which after all is just a wave function expressed in a different way—our abilities to give physical meaning to its elements are limited.

In this paper we show that eigenvectors can be understood in a much more complete and satisfying way. We will give a method for calculating semiclassical approximations to eigenvectors such that each element is given by a simple WKB form, or by an integral representation corresponding to a uniform WKB approximation.

This step forward in physical understanding arises at least partly from some relatively recent developments in mathematics: the study of "pseudodifferential equations" and especially the development of formal asymptotic series expansions of the solutions to these equations. While the words may seem a little intimidating at first, we hope to convince the reader that the essential ideas of the subject are easy to understand, and that they are a perfectly natural extension of familiar WKB theory. "Formal asymptotic expansions for pseudodifferential equations" is mathematicians' jargon meaning semiclassical approximations for unusual systems or unusual representations. Examples of pseudodifferential equations are the Schrödinger equation in momentum space (which is typically an infinite-order equation involving a continuous variable), or any matrix representation of the Schrödinger equation (in which the independent variable is discrete, and the equation could be regarded as a difference equation or recursion relation). We will discuss this in more detail later.

TABLE I. Elements of eigenvector number 17 for the system described in Sec. III.

l	$\tilde{\psi}_l^{17}$	l	$\tilde{\psi}_l^{17}$
1	0.156	16	−0.036
2	0.024	17	0.226
3	0.248	18	−0.298
4	−0.204	19	−0.099
5	0.049	20	0.060
6	−0.246	21	−0.026
7	0.013	22	0.414
8	0.118	23	−0.253
9	0.025	24	−0.301
10	0.253	25	0.289
11	−0.225	26	0.039
12	0.020	27	−0.096
13	−0.208	28	0.013
14	−0.007	29	0.008
15	0.236		

The recent mathematical advances are essential for a proper physical formulation. However, we should also mention some related earlier work in semiclassical theory, much of which was developed in an intuitive or heuristic fashion. Some of this work hinted at the existence of the general and systematic theory that is now available, and all of it can be more clearly understood now that a solid mathematical foundation has been built.

We already stated that the theory of formal asymptotic solutions to pseudodifferential equations is a natural outgrowth of WKB theory, which was originally set up for second-order ordinary differential equations.[1] Asymptotic approximations for difference equations also have been available for a long time.[2] After the fundamental work of the early 20th century, however, the theory of asymptotic approximations did not receive much attention from mathematicians for many years, and theoretical physicists and chemists were left to their own devices. A semiclassical approximation in momentum space seems to have first appeared in a book of problems.[3] More recently, a "discrete WKB approximation" was developed by Braun and by Kirkman, who used it to study excited states of a hydrogen atom in a magnetic field.[4] Also, the mathematically informal but physically suggestive "classical S-matrix theory" has been used to obtain semiclassical approximations for scattering amplitudes in discrete representations[5,6] and for Clebsch-Gordan coefficients.[7] Finally, there is a long history of attempts to formulate semiclassical mechanics or quantum mechanics in terms of action-angle variables. Some of these studies express semiclassical correspondences by using a variable (the action) which is continuous in classical mechanics but discrete in quantum mechanics.[6] Others attempt to formulate exact quantum-dynamical laws in a representation that goes in the classical limit to the action-angle picture.[8] If simple and general quantum analogues of classical angle variables exist, they have still eluded discovery; the formulation given here has some bearing on this problem. In recent years, mathematicians have found new reasons for interest in pseudodifferential equations and asymptotic expansions. Fundamental aspects of the theory, including theorems about existence and regularity of solutions, are discussed in recent work of Hörmander,[9(a)] Taylor,[9(b)] Treves,[9(c)] and Peterson.[9(d)] Maslov and Fedoriuk[10–12] have provided methods for calculating asymptotic solutions for a very wide class of pseudodifferential equations. This work has provided a mathematical imprimatur for some of the ideas that were already extant in the physics and chemistry communities; in addition, it has given important new insights and understanding of the great breadth of applicability of semiclassical ideas.

In this paper a semiclassical approximation provides an interpretation of the structure of the whole set of eigenvectors. This approximation is calculated by treating the matrix equation defining the eigenvector as a difference equation. This is rewritten as a pseudodifferential equation. Then we extend a procedure of Maslov and Fedoriuk and use it in a new way to calculate the semiclassical approximation.

III. SYSTEM: AN EXCITED ATOM IN COLLINEAR ELECTRIC AND MAGNETIC FIELDS

If the external fields lie along the z axis, then in a frame of reference that precesses at the Larmor frequency about this axis the Hamiltonian is[13,14]

$$H = H_0 + \lambda H_1 + \nu H_2 \ , \tag{3.1a}$$

where

$$\begin{aligned} &H_0 \equiv p^2/2\mu - Ze^2/r \ , \\ &\lambda \equiv e^2B^2/8\mu c^2, \quad \nu \equiv eF \ , \\ &H_1 \equiv (x^2+y^2), \quad H_2 \equiv z \ , \end{aligned} \tag{3.1b}$$

B and F being the magnetic and electric fields, respectively. We consider atoms in states of principal quantum number $n=30$, with $B=2$ T, and $F=-18.7$ V/cm. In this case the eigenfunctions of H can be calculated in first-order quantum-perturbation theory by using an expansion in Hydrogenic radial functions times spherical harmonics,

$$\Psi^{nmk}(r,\theta,\phi) = \sum_{l=|m|}^{n-1} \tilde{\psi}_l^{nmk} R_{nl}(r) Y_{lm}(\theta,\phi) \ . \tag{3.2}$$

This expansion involves only the degenerate l levels at the given n; m is an exact quantum number because of the cylindrical symmetry of the Hamiltonian, and n is a good quantum number because the external electric and diamagnetic fields are weak compared to the atomic Coulomb field. Henceforth, therefore, we drop the unnecessary labels n and m, and designate the coefficients in expansion (3.2),

$$\begin{aligned} \tilde{\Psi}_l^{nmk} \equiv \tilde{\psi}_l^k &\equiv \langle nlm \mid \Psi^{nmk} \rangle \\ &\equiv \int R_{nl}^*(r) Y_{lm}^*(\theta,\phi) \Psi^{nmk}(r,\theta,\phi) d\tau \ . \end{aligned} \tag{3.3}$$

By using the same letter for the coefficients, $\tilde{\psi}_l^k$, as for the wave function, $\Psi^{nmk}(r,\theta,\phi)$, we emphasize the fact that the coefficients are the representation of the abstract state vector $|\Psi^{nmk}\rangle$ in the $|nlm\rangle$ representation. We might say that the set of coefficients is "the wave function in $|nlm\rangle$ space."

Eigenvalues and eigenvectors can now be calculated by diagonalizing a matrix having $(n-|m|)^2$ elements,

$$\sum_{l=|m|}^{n-1} H_{jl} \tilde{\psi}_l^k - E_k \tilde{\psi}_l^k = 0 \ . \tag{3.4}$$

Within the set of states of fixed n, the zeroth-order Hamiltonian is a constant, $E^0 = -Z^2e^4/2n^2\hbar^2$, and it can be ignored.

Our basis functions $R_{nl}(r)$ and $Y_{lm}(\theta,\phi)$ have the phase conventions given by Condon and Shortley.[15] With these conventions, the matrix elements are (in atomic units, but with $\hbar$ kept explicit)

$$\langle nlm \mid z \mid nl'm \rangle = \begin{cases} \frac{3}{2}n[n^2-(l+1)^2]^{1/2}\left[\dfrac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2}\hbar^2 & \text{for } l'=l+1 \\ \frac{3}{2}n(n^2-l^2)^{1/2}\left[\dfrac{(l+m)(l-m)}{(2l-1)(2l+1)}\right]^{1/2}\hbar^2 & \text{for } l'=l-1, \end{cases}$$

$$\langle nlm \mid x^2+y^2 \mid nl'm \rangle = \begin{cases} -\frac{5}{2}[n^2-(l+2)^2]^{1/2}[n^2-(l+1)^2]^{1/2}n^2 \\ \times\left[\dfrac{(l+m+2)(l+m+1)(l-m+2)(l-m+1)}{(2l+5)(2l+3)^2(2l+1)}\right]^{1/2}\hbar^4 & \text{for } l'=l+2 \\ \dfrac{n^2[5n^2+1-3l(l+1)](l^2+l-1+m^2)}{(2l-1)(2l+3)}\hbar^4 & \text{for } l'=l, \\ -\frac{5}{2}(n^2-l^2)^{1/2}[n^2-(l-1)^2]^{1/2}n^2 \\ \times\left[\dfrac{(l+m)(l+m-1)(l-m)(l-m-1)}{(2l+1)(2l-1)^2(2l-3)}\right]^{1/2}\hbar^4 & \text{for } l'=l-2. \end{cases} \tag{3.5}$$

The result of this calculation for $n=30$, $m=1$ is shown in Fig. 1. Each of the 29 eigenvectors is represented by 29 coefficients $\tilde{\psi}_l^k$, which are plotted as spikes along the l axis at integer values of l from 1 to 29. The eigenvalues have already been discussed in a previous paper.[13] Here we seek a physical understanding of the eigenvectors.

Of course, the basic quantum-mechanical interpretation of the eigenvectors is well known. If the system is in a state represented by the wave function $\Psi^{nmk}(r,\theta,\phi)$, and if a measurement is made of L^2, the square of the electronic orbital angular momentum, then $|\tilde{\psi}_l^k|^2$ represents the probability that the value of L^2 will turn out to be $l(l+1)\hbar^2$. Another point of view is also well understood: according to (3.3), if we take an eigenfunction $\Psi^{nmk}(r,\theta,\phi)$ (a few are plotted in Ref. 13) and project it onto a $R_{nl}(r)Y_{lm}(\theta,\phi)$ basis function, then the result will be $\tilde{\psi}_l^k$.

However, we are seeking a different sort of understanding. We want to understand the patterns of behavior of the coefficients. For example, we want to know why some eigenvectors have elements that change smoothly with l while others have wildly varying elements—why some eigenvectors have elements that are significant in only a small region and others fill the whole range. We know that configuration-space representations of wave functions have oscillations in classically allowed regions, exponential behavior in forbidden regions, and Airy-function structure near turning points. The coefficients $\tilde{\psi}_l^k$ represent the wave function in angular momentum space. Are there similarly simple structures in this representation?

We can already see that the coefficients representing some of the eigenvectors show simple patterns, reminding us of wave functions of one-dimensional oscillators. But other sets of coefficients are much more disorderly.[16] Nevertheless, we shall show that all of these sets of coefficients can be well represented by combinations of simple WKB-like expressions

$$A_l^k \exp(iS_l^k/\hbar) \tag{3.6}$$

and by integral representations analogous to uniform WKB approximations. In this picture the coefficients are therefore discrete values of continuous functions of l. In various regions these functions represent either a superposition of traveling waves in l space, exponentially decaying waves in a forbidden region, or Airy-like diffraction near a classical turning point.

IV. CLASSICAL DESCRIPTION

Semiclassical approximations give a relationship between the quantum-mechanical description of a system and the classical description. In the present case, even the classical description is unusual enough to stretch our minds a bit.

Because the external fields are weak, classical perturbation theory can be used. The electron is said to move on a Kepler ellipse with slowly varying orbital parameters. These parameters are most conveniently chosen to be canonical action and angle variables $\{I_k,\phi_k\}$ defined in Table II.[13,14,17] In first order the average rate of change of each of these variables is obtained by averaging the perturbing Hamiltonian over a Kepler cycle,

$$\Delta I_j/\tau = \frac{1}{\tau}\int_0^\tau\left(-\frac{\partial H}{\partial\phi_j}\right)dt = -\frac{\partial}{\partial\phi_j}\left[\frac{1}{\tau}\int_0^\tau H\,dt\right] = -\partial h/\partial\phi_j\ . \tag{4.1}$$

The average Hamiltonian h was shown in an earlier paper[13] to be

$$\begin{aligned} h &\equiv \frac{1}{\tau}\int_0^\tau(\lambda H_1+\nu H_2)dt \\ &= \frac{\lambda I_3^2}{4I_2^2}[(I_1^2+I_2^2)(5I_3^2-3I_2^2) \\ &\quad +5(I_3^2-I_2^2)(I_2^2-I_1^2)\cos(2\phi_2)] \\ &\quad -\frac{3\nu I_3}{2I_2}[(I_3^2-I_2^2)(I_2^2-I_1^2)]^{1/2}\sin\phi_2\ . \end{aligned} \tag{4.2}$$

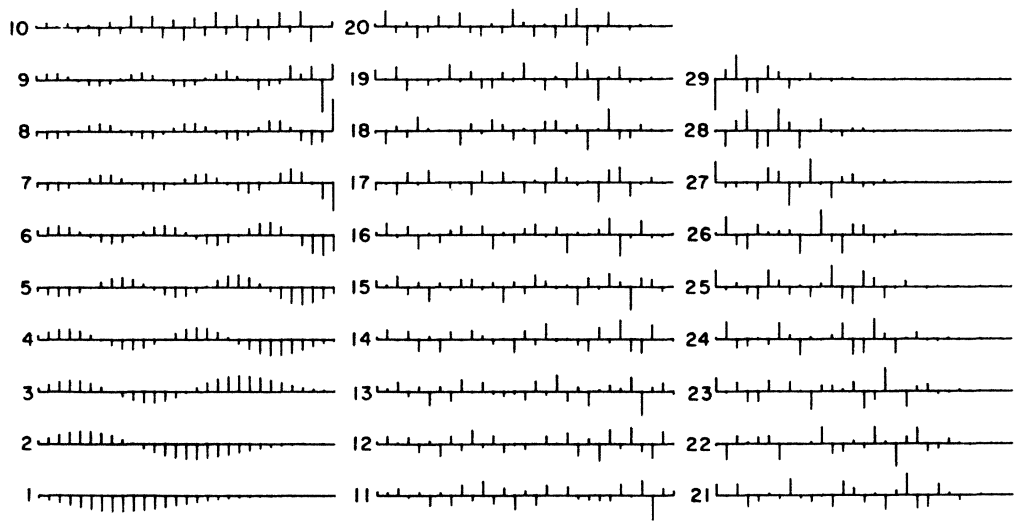

FIG. 1. Elements of the eigenvectors of the matrix defined in Eqs. (3.4) and (3.5). Each horizontal line is an l axis, with l going from 1 to 29. The vertical lines are the values of $\tilde{\psi}_l^k$, i.e., the lth element of the kth eigenvector. The first seven eigenvectors have simple patterns reminiscent of wave functions of a one-dimensional oscillator. The others have no obvious patterns. An interpretation of these structures is obtained in this paper.

The analysis given in this paper will be clearer if we use a minor change in notation. I_1 is the z component of angular momentum, which in quantum mechanics takes the value $m\hbar$; let us call it M. I_3 is the principal action, corresponding to $n\hbar$ in quantum mechanics, so we will call it N. I_2 is the magnitude of the orbital angular momentum, which in quantum mechanics is $[l(l+1)]^{1/2}\hbar$ or in semiclassical mechanics is $(l+1/2)\hbar$, so let us call it L. L, M, and N are therefore continuous classical variables related to the Hydrogenic quantum numbers l, m, and n. Finally, ϕ_2 is the only one of the three angle variables that occurs in (4.1), so let us drop the subscript and call it ϕ. With this change of notation, the effective Hamiltonian is

$$h=\lambda\frac{N^2}{4L^2}[(M^2+L^2)(5N^2-3L^2) +5(N^2-L^2)(L^2-M^2)\cos(2\phi)] -\nu\frac{3N}{2L}[(N^2-L^2)(L^2-M^2)]^{1/2}\sin\phi\ . \tag{4.3a}$$

For comparison with formulas that will appear later, let us write this in the form

$$h(L,\phi)=A^0(L)-\frac{1}{2i}[e^{i\phi/2}B^0(L)e^{i\phi/2}-e^{-i\phi/2}B^0(L)e^{-i\phi/2}]+\frac{1}{2}[e^{i\phi}C^0(L)e^{i\phi}+e^{-i\phi}C^0(L)e^{-i\phi}]\ , \tag{4.3b}$$

where

$$A^0(L)=\lambda\frac{N^2}{4L^2}(L^2+M^2)(5N^2-3L^2)\ ,$$
$$B^0(L)=\nu\frac{3N}{2L}[(N^2-L^2)(L^2-M^2)]^{1/2}\ , \tag{4.3c}$$
$$C^0(L)=\lambda\frac{N^2}{4L^2}5(N^2-L^2)(L^2-M^2)\ .$$

According to Eq. (4.1), this effective Hamiltonian gives equations of motion in canonical form. Since h is independent of ϕ_1 and ϕ_3, M and N are conserved quantities,

$$dM/dt=-\partial h/\partial\phi_1=0\ ,$$
$$dN/dt=-\partial h/\partial\phi_3=0\ . \tag{4.4}$$

The first of these holds exactly because the Hamiltonian (3.1) is cylindrically symmetric about the z axis. The second of these holds in first order because (4.1) involves an average over the Kepler orbit. Hence N and M are effectively fixed parameters in (4.3). Therefore, h can be regarded as a Hamiltonian for a system with a single degree of freedom, having coordinate ϕ and conjugate momentum L. [Compare the fact that in the quantum expansion (3.2) we may regard m and n as fixed parameters, and the single quantum number l as the variable.]

The equations of motion for L and ϕ are

$$d\phi/dt=\partial h/\partial L\ ,$$
$$dL/dt=-\partial h/\partial\phi\ . \tag{4.5}$$

Since h is a constant of the motion for these equations, the system evolves in its (L,ϕ) phase space on a contour of constant h. We saw that the formula for $h(L,\phi)$ was a little complicated, but its messiness is no problem; everything we need to know about the motion in (L,ϕ) space is contained in a contour plot of $h(L,\phi)$.

TABLE II. Action and angle variables of the Kepler Problem.

$I_1 \equiv L_z \equiv M$	Z component of the angular momentum vector I_1 corresponds to the magnetic quantum number m of the quantum mechanical Coulomb problem
$I_2 \equiv \vert \mathbf{L} \vert \equiv L$	Magnitude of the angular momentum vector I_2 corresponds to the total angular momentum quantum number 1 of the Coulomb problem $I_2 \geq \vert I_1 \vert$
$I_3 \equiv [\mu k^2/-2H_0]^{1/2} \equiv N$	The principal action, related to the Kepler energy H_0 and corresponding to the principal quantum number n of the Coulomb problem $k = Ze^2$ $I_3 \geq I_2$
ϕ_1	Longitude of the ascending node
$\phi_2 \equiv \phi$	Argument of the perihelion
ϕ_3	Mean anomaly

A contour plot of $h(L,\phi)$ is shown in Fig. 2. The arrows indicate the direction of motion of the trajectory on the contour. These contours fall into the following three groups, which were discussed in Ref. 13.

L_A, librators confined to the region $\pi < \phi < 2\pi$.

R_A, rotators having the property that L is large near $\phi = \pi/2$.

R_B, rotators having the property that L is small near $\phi = \pi/2$.

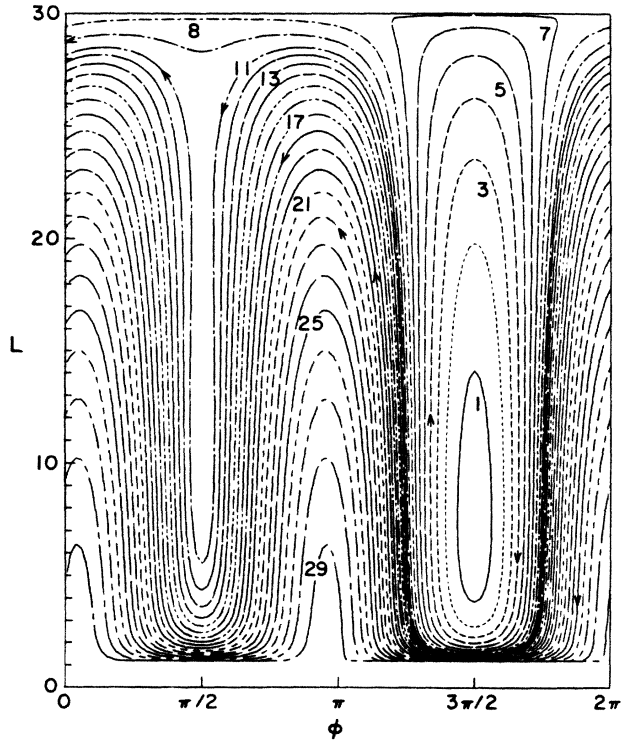

FIG. 2. Constant energy contours (or level curves) of the Hamiltonian $h(L,\phi)$. Librators are closed curves centered at $\phi = 3\pi/2$. Rotators are open curves extending from 2π to 0. The direction of motion on the curves is indicated by the arrows.

Of the 29 quantized energy levels, we shall show that 28 of them correspond to the contours shown in Fig. 2; states 1–7 are L_A librators, states 8 and 9 are R_A rotators, and states 11–29 are R_B rotators. (State number 10 will be discussed later.) In addition, if all of the contours were drawn,[13] the following two other classes of librators would appear.

L_B, librators confined to $0 < \phi < \pi$ and small L.

L_C, librators confined to $0 < \phi < \pi$ and L close to 12.

However, in the present case, the area in the (L,ϕ) plane occupied by these states is too small to support a quantum state. (At other field strengths these librators can be more important.)

We said that by means of a semiclassical approximation it should be possible to relate the Schrödinger equation, which in l representation is given by Eqs. (3.4) and (3.5), to the classical equations of motion, (4.5) and (4.3). At the moment, the relationship is not very obvious. One is a completely opaque matrix equation, and the other describes an alien form of one-dimensional motion. However, we shall show that there is a very simple relationship that makes both of them clearer. Upward- (or downward-) moving sections of classical paths in the (L,ϕ) phase space correlate through a WKB form such as (3.6) to traveling waves in l space which propagate in the direction of increasing (or decreasing) l.

V. PSEUDODIFFERENTIAL EQUATIONS AND FORMAL ASYMPTOTIC SOLUTIONS

A. Basic definitions

As a preliminary definition, a pseudodifferential equation is what one gets when one takes a general function of two variables $\mathcal{H}(p,q)$ and substitutes $(-i\hbar d/dq)$ for p,

$$\mathcal{H}\left[-i\hbar\frac{d}{dq},q\right]\Psi(q)=0\ . \tag{5.1}$$

In the cases of interest here, the equation contains an eigenvalue, and we write

$$\mathcal{H}(p,q)=H(p,q)-E \ . \tag{5.2}$$

We seek approximations to the solution $\Psi(q)$.

Any ordinary differential equation, such as the Schrödinger equation in one dimension, is a pseudodifferential equation. The Schrödinger equation in momentum space

$$\left[\frac{p^2}{2\mu}+V\left[i\hbar\frac{d}{dp}\right]-E\right]\tilde{\Psi}(p)=0 \tag{5.3}$$

is also a pseudodifferential equation. Difference equations, such as

$$\psi(q+\hbar a)=q\psi(q) \ , \tag{5.4a}$$

can be written as pseudodifferential equations using the exponential operator. For this example we define

$$\mathcal{H}(p,q)=\exp(ipa)-q \tag{5.4b}$$

so

$$\left[\exp\left[a\hbar\frac{d}{dq}\right]-q\right]\psi(q)=0 \ . \tag{5.4c}$$

Mathematical theories require a more precise definition and restrictions on the operator. Obviously, we must not be too capricious about the operators that are admitted: at least some sort of smoothness and boundedness properties are necessary. The restrictions chosen by Maslov and Fedoriuk (MF) are very mild.

(MF1). $\mathcal{H}(p,q)$ should be infinitely differentiable in p and q for all real values of p and q.

(MF2). At large real values of p and q, $\mathcal{H}$ and its derivatives should not increase faster than polynomials; for all k,l,

$$\left|\frac{\partial^k}{\partial q^k}\frac{\partial^l}{\partial p^l}\mathcal{H}(p,q)\right|\leq C_{kl}(1+|q|)^m(1+|p|)^n \ . \tag{5.5}$$

Furthermore, if $\mathcal{H}(p,q)$ has any explicit dependence on $\hbar$ (other than the implicit dependence arising from $p=-i\hbar d/dq$) then the following restrictions apply.

(MF3). $\mathcal{H}(p,q;\hbar)$ should be infinitely differentiable in p, q, and $\hbar$ for all real values of p and q, and for all strictly positive (nonzero) values of $\hbar$.

(MF4). $\mathcal{H}(p,q;\hbar)$ should have an expansion in powers of $\hbar$,

$$\mathcal{H}(p,q;\hbar)=\sum_{k=0}^{N}\hbar^k\mathcal{H}^{(k)}(p,q)+\hbar^{N+1}R_N(p,q;\hbar) \ , \tag{5.6}$$

such that the "expansion coefficients" $\mathcal{H}_k(p,q)$ satisfy conditions (MF1) and (MF2), and the remainder term can also be bounded; for all j,k,l,

$$\left|\frac{\partial^k}{\partial q^k}\frac{\partial^l}{\partial p^l}\frac{\partial^j}{\partial\hbar^j}R_N(p,q;\hbar)\right|\leq C_{klj}(1+|q|)^m(1+|p|)^n \ . \tag{5.5'}$$

In this type of theory, the WKB approximation is regarded as an expansion of $\Psi(q)$ in powers of $\hbar$; therefore, one should expect as a requirement of the theory that the operator $\mathcal{H}(p,q,;\hbar)$ must permit such an expansion. Of course it might also have no explicit dependence on $\hbar$.

Conditions such as (MF1)–(MF4) are *sufficient* to ensure the validity of the theorems developed by MF. To what extent these conditions are *necessary* is not presently known. Other mathematicians make use of different conditions on their operators, some more restrictive, some less so. In the case we shall examine, one of the conditions is violated in a minor way, so we are pushing the theory a little beyond its *proven* range of validity; the calculation shows that good results are obtained anyway.

Two additional conditions are required for the specific formulas we shall use.

(Sp5). If the operator $\mathcal{H}(p,q)$ involves products of noncommuting p's and q's, then the operator must be self-adjoint. For example, pq is not allowed by itself, but $(pq+qp)/2$ or $(pq-qp)/2i$ is allowed.

(Sp6). The expansion of the operator in powers of $\hbar$ [Eq. (5.6)] contains no term linear in $\hbar$.

These specific conditions are not required for the general theory. MF show that if an unsymmetrized operator is used, or if the operator contains a term linear in $\hbar$, then the formula for $\Psi(q)$ is slightly modified.

Now given the function $\mathcal{H}(p,q)$, we need a precise definition of the operator $\mathcal{H}(-i\hbar d/dq,q)$. Its Taylor expansion in powers of p is often useful, but this expansion raises difficult questions about convergence. A much better definition of the operator can be made by using the Fourier transform. MF define the Fourier transform operators $F_{q\to p}$ and $F_{p\to q}^{-1}$ as

$$[F_{q\to p}\Psi(q)]\equiv(2\pi i\hbar)^{-1/2}\int_{-\infty}^{\infty}\exp(-ipq/\hbar)\Psi(q)dq \ , \tag{5.7a}$$

$$[F_{p\to q}^{-1}\tilde{\Psi}(p)]\equiv(-2\pi i\hbar)^{-1/2}\int_{-\infty}^{\infty}\exp(ipq/\hbar)\tilde{\Psi}(p)dp \ . \tag{5.7b}$$

Then for any term $h(p)$ in $\mathcal{H}(p,q)$ that is independent of q the effect of $h(-i\hbar d/dq)$ on a wave function is defined by the following rule: take the Fourier transform of $\Psi(q)$, multiply by $h(p)$, then transform back to q space,

$$h\left[-i\hbar\frac{d}{dq}\right]\Psi(q)\equiv F_{p\to q}^{-1}\{h(p)[F_{q\to p}\Psi(q)]\} \ . \tag{5.8a}$$

If $h(-i\hbar d/dq)$ is an ordinary differential operator and $\Psi(q)$ is a smooth square-integrable function, one can easily show that this definition (5.8a) gives the same results as are obtained by differentiation.

More generally, $\mathcal{H}(p,q)$ may contain products, such as $g(q)h(p)$, or functions of such products, such as $\exp[h(p)g(q)]$. In such cases, the order of the operators is important, so the classical function $\mathcal{H}(p,q)$ by itself does not uniquely specify the quantum operator. We need a rule that will, in effect, tell which operator acts first.

A rule that says "differentiate first," or "put all p's to the right of all q's," is

$$\mathcal{H}\left[-i\hbar\frac{d}{dq},q\right]\Psi(q)=F_{p\to q}^{-1}\mathcal{H}(p,q)F_{q\to p}\Psi(q) \ , \tag{5.8b}$$

and a rule that says "differentiate last," or "put all p's to

the left of all q's," is

$$\mathcal{H}\left[-i\hbar\frac{d}{dq},q\right]\Psi(q)=F_{p\to q}^{-1}F_{q\to p}\mathcal{H}(p,q)\Psi(q)\ . \tag{5.8c}$$

The definition we shall use is the symmetric combination of these two, as required by condition (Sp5),

$$\mathcal{H}\left[-i\hbar\frac{d}{dq},q\right]\Psi(q)=\tfrac{1}{2}[F_{p\to q}^{-1}\mathcal{H}(p,q)F_{q\to p}+F_{p\to q}^{-1}F_{q\to p}\mathcal{H}(p,q)]\Psi(q)\ . \tag{5.8d}$$

The resulting operator is formally Hermitian if the function $\mathcal{H}(p,q)$ is real. As a example, if $\mathcal{H}(p,q)=pq$, it is easy to show that Eq. (5.8b) gives $\mathcal{H}(p,q)\Psi(q)=q(-i\hbar d/dq)\Psi(q)$, Eq. (5.8c) gives $\mathcal{H}(p,q)=(-i\hbar d/dq)q\Psi(q)$, and Eq. (5.8d) gives the symmetric combination.

The point of this definition (5.8d) is that it reduces to the Taylor expansion whenever that expansion makes sense, but the Fourier integrals converge under much more general conditions than does the Taylor expansion.

The Fourier transform of the pseudodifferential equation,

$$F_{q\to p}\left[\mathcal{H}\left[-i\hbar\frac{d}{dq},q\right]\Psi(q)\right]=0\ , \tag{5.9a}$$

can be written using the same definitions as

$$\mathcal{H}\left[p,i\hbar\frac{d}{dp}\right]\tilde{\Psi}(p)=0\ , \tag{5.9b}$$

and it is referred to as "the momentum-space representation" of the equation.

A formal asymptotic approximation to the solution $\Psi(q)$ is a function which satisfies the pseudodifferential equation with an error that is bounded by a constant times some power of $\hbar$. We write the function as $\Psi^{(N)}(q)$ if

$$\mathcal{H}\left[-i\hbar\frac{d}{dq},q\right]\Psi^{[N]}(q)\le C_N\hbar^{N+2}\ . \tag{5.10a}$$

These functions are usually constructed as power series in $\hbar$,

$$\Psi^{[N]}(q)=\sum_{j=0}^{N}\hbar^j\Psi^{(j)}(q)\ . \tag{5.10b}$$

Let us now describe the results. The major consequence of the theory is, that at least under conditions 1–6 above, a simple, so-called "primitive" semiclassical approximation to the solution $\Psi(q)$ can be obtained using the procedure stated in Sec. V B. A better, "uniform" semiclassical approximation can be obtained using the procedure in Sec. V C. This uniform semiclassical approximation is the leading term in a formal asymptotic expansion of the form (5.10b).

In the case considered in this paper, the operator depends explicitly upon $\hbar$, and its expansion in powers of $\hbar$ contains terms of order $\hbar^0$ and terms of order $\hbar^2$ and higher, but no terms linear in $\hbar$. We will describe only the procedure for calculation of $\Psi^{(0)}(q)$ and $\tilde{\Psi}^{(0)}(p)$. A more detailed study[10] shows that the term of order $N+1$ in the operator affects the term of order N in the solution. In particular, the quadratic-in-$\hbar$ term in $\mathcal{H}(q,p)$ affects the linear-in-$\hbar$ term $\Psi^{(1)}$ of the solution. Since we shall not include this term, we can replace the operator $\mathcal{H}(p,q;\hbar)$ by its leading term $\mathcal{H}(p,q;\hbar=0)$ and simply denote the resulting operator $\mathcal{H}(p,q)$.

B. Simple or primitive semiclassical approximation

We now give the procedure for constructing the primitive semiclassical approximation. If the procedure seems long, let us emphasize that it is a straightforward generalization of the procedure that one would follow in calculating a semiclassical wave function for a one-dimensional oscillator. A brief statement is that a primitive semiclassical wave function is a combination of terms of the form

$$\left|\frac{\partial\mathcal{H}(p,q)}{\partial p}\right|_{p=\not{p}(q)}^{-1/2}\exp\left[i\int^{q}\not{p}(q')dq'/\hbar\right]\ ,$$

where $\not{p}(q)$ is a level curve of $\mathcal{H}$, so that $\mathcal{H}(\not{p}(q),q)=0$. Care is required to combine terms with consistent phases. The precise procedure for this is described below. Once the procedure is clearly stated in this general way, the form of the Hamiltonian does not matter.

(1) Identify the appropriate eigenvalue E. The formula satisfied by E is a modified Bohr-Sommerfeld rule stated below.

(2) In the "phase space" (p,q), compute the level curve

$$\mathcal{H}(p,q)=0\ , \tag{5.11a}$$

i.e.,

$$H(p,q)=E\ . \tag{5.11b}$$

(The level curve is an elementary example of a "Lagrangian manifold."[10–13])

(3) Identify "q charts" on this curve. These are domains or sections of the curve in which it can be described by an infinitely differentiable function $p=\not{p}_j(q)$. The various q charts are separated from each other by singular points, where the level curve rises vertically, and the derivative $d\not{p}/dq$ would be infinite. The singular points are turning points of the q motion. Hence, each nonsingular point on the level curve is in one and only one q chart. Pick any one of the q charts as the initial chart and let it be described by the function $p=\not{p}_1(q)$. Pick an arbitrary nonsingular point (p^0q^0) in it as the initial point and choose an initial value S^0 arbitrarily at this point.

(4) Define for other points in the initial chart

$$S_1(q)=S^0+\int_{q^0}^{q}\not{p}_1(q')dq'\ . \tag{5.12}$$

Alternatively, $S(q)$ on any chart can be calculated by using an auxiliary variable t and solving the differential equations

$$\frac{dq}{dt}=\frac{\partial H}{\partial p}\ , \tag{5.13a}$$

$$\frac{dp}{dt}=-\frac{\partial H}{\partial q}\ , \tag{5.13b}$$

$$\frac{dS}{dt}=p\frac{dq}{dt}\ . \tag{5.13c}$$

The first two of these trace out the level curve of $H(p,q)$ in phase space and the third gives the rate of change of S on this curve.

(5) Extend $S(q)$ to other charts in the obvious way. From Eqs. (5.13), $q(t)$ and $S(t)$ are continuous functions of "time." Inverting the relationship between q and t gives $t=t_j(q)$ as a "multiply branched" function of q, and then

$$S_j(q)=S[t_j(q)]\ . \tag{5.14a}$$

S is therefore continuous on the level curve, and for every branch,

$$\frac{dS_j}{dq}=\not{p}_j(q)\ , \tag{5.14b}$$

$$S_j(q)=\int^q \not{p}_j(q')dq'+\text{const}\ , \tag{5.14c}$$

where the constant is chosen such that $S(t)$ is continuous.

Note that if the level curve closes on itself, $S_j(q)$ has another kind of multiple valuedness. If we start at p^0q^0, and follow (5.13) around the loop until we come back to the initial point, S will *not* return to its original value. Of the resulting values of $S_j(q)$, we can use any one we wish, provided that we put it together with the appropriate value of the Maslov index, defined below. The simplest choice is to integrate (5.13) from the initial point in the positive-t sense until the loop closes, then stop. On the level curve including the initial point but excluding the final point, S is then continuous.

(6) Calculate the Maslov index μ_j for each q chart. The index for the initial chart is taken to be zero, and it is found in the other charts by following the level curve in the direction implied by the equations of motion (5.13). The index changes when and only when the path goes through a singular point dividing two q charts. Upon passing through such a singular point from chart i to chart j, the change in the index is

$$\Delta\mu=\mu_j-\mu_i=\Theta^-\left[\frac{d\not{p}_i}{dq}\right]-\Theta^-\left[\frac{d\not{p}_j}{dq}\right]\ , \tag{5.15}$$

where $\Theta^-(x)$ is a step function such that

$$\Theta^-(x)=1 \quad \text{if } x<0\ ,$$
$$\Theta^-(x)=0 \quad \text{if } x>0\ . \tag{5.16}$$

The sign of $d\not{p}/dq$ is examined on either side of the singular point.

(7) Define in each chart

$$\mathcal{S}_j(q)=S_j(q)/\hbar-\frac{\pi}{2}\mu_j\ . \tag{5.17}$$

At last we can state the rule for the allowed eigenvalues—$\mathcal{S}(q)$ must be single valued, mod 2π. This leads to the quantization rule: for any cycle, the change in $\mathcal{S}$ must be 2π times an integer.

$$\Delta\mathcal{S}=\oint \not{p}(q')dq'/\hbar-\frac{\pi}{2}\Delta\mu=2\pi n\ . \tag{5.18}$$

(8) Define $\Psi_j(q)$ as

$$\Psi_j(q)\equiv\left|\frac{\partial H}{\partial p}\right|^{-1/2}_{p=\not{p}_j(q)}\exp[i\mathcal{S}_j(q)]\ . \tag{5.19}$$

Then the primitive semiclassical approximation to $\Psi(q)$ is

$$\Psi^{\text{prim}}(q)=\sum_j\Psi_j(q)\ . \tag{5.20}$$

The sum is over all charts that project to the point q. [If the level curve has no projection onto the point q, then $\Psi(q)$ is zero in this approximation.]

C. Uniform semiclassical approximation

To obtain a uniform semiclassical approximation, follow the steps above, but skip the last bit of step (8) [Eq. (5.20)]. Continue as below.

(9) Identify "p charts" of the level curve. These are domains in which the level curve can be described by a smooth function $q=\not{q}_k(p)$. These p charts are separated by "p-singular points," where the derivative $d\not{q}_k/dp$ becomes infinite. These are turning points in momentum space. Each point on the level curve that is not a p-singular point is in one and only one p chart. Use the same initial point as in step (3) (take the initial point to be nonsingular with respect to both q and p). Define

$$\tilde{S}^0=S^0-p^0q^0\ . \tag{5.21}$$

(10) Define for other points in the initial p chart

$$\tilde{S}_1(p)=\tilde{S}^0-\int_{p^0}^{p}\not{q}_1(p')dp'\ . \tag{5.22}$$

A differential equation for $\tilde{S}(p)$ analogous to (5.13c) is

$$\frac{d\tilde{S}}{dt}=-q\frac{dp}{dt}\ . \tag{5.23}$$

(11) Extend $\tilde{S}(p)$ to other p charts, again requiring that $\tilde{S}$ must vary continuously along the level curve. $\tilde{S}(p)$ is then multivalued in exactly the same way that $S(q)$ is.

(12) Compute the Maslov index ν_k for each p chart. For the initial p chart, the index is

$$\nu_1=\Theta^-\left[\frac{d\not{q}_1}{dp}\right]\ . \tag{5.24}$$

Then each time the level curve passes through a p-singular point from p chart i to p chart j, this index changes by

$$\Delta\nu=\nu_j-\nu_i=\Theta^-\left[\frac{d\not{q}_j}{dp}\right]-\Theta^-\left[\frac{d\not{q}_i}{dp}\right]\ . \tag{5.25}$$

Note that the order of terms in this equation is opposite to that in Eq. (5.15). Again the signs of the derivatives are examined on either side of the (p-)singular point.

(13) For each p chart, define

$$\tilde{\mathcal{S}}_k(p)=\frac{\tilde{S}_k(p)}{\hbar}-\nu_k\frac{\pi}{2}\ . \tag{5.26}$$

$\mathcal{S}_j(q)$, $\tilde{\mathcal{S}}_k(p)$ is single-valued mod (2π) for the quantized eigenvalues.

(14) (optional) A primitive semiclassical approximation in momentum space is given by

$$\tilde{\Psi}_k(p)=\left|\frac{\partial H}{\partial q}\right|^{-1/2}_{q=q_k(p)}\exp[i\tilde{\mathcal{S}}_k(p)] \tag{5.27}$$

and

$$\tilde{\Psi}^{\text{prim}}(p)=\sum_k\tilde{\Psi}_k(p)\ , \tag{5.28}$$

where the sum is over all charts that project to the point p.

(15) Define for each point on the level curve a pair of "switching functions" $e_j(q)$ and $\tilde{e}_k(p)$. The point (p,q) is in the jth q chart and the kth p chart. The switching functions have the following properties. (a) At every point on the level curve, the two switching functions sum to unity,

$$e_j+\tilde{e}_k=1\ , \tag{5.29}$$

i.e.,

$$e_j(q)+\tilde{e}_k(p_k(q))=1$$

or

$$e_j(q_j(p))+\tilde{e}_k(p)=1\ .$$

(b) Each is infinitely differentiable in its variable. (c) At any q-singular point (turning point in q space), $e_j(q)\to 0$, and at any p-singular point (turning point in p space), $\tilde{e}_k(p)\to 0$ in such a way that $e_j(q)\Psi_j(q)$ and $e_k(p)\Psi_k(p)$ are infinitely differentiable.

(16) The final formula for the uniform semiclassical approximation is

$$\Psi^{(0)}(q)=\sum_j e_j(q)\Psi_j(q)+\sum_k F^{-1}_{p\to q}[\tilde{e}_k(p)\tilde{\Psi}_k(p)]\ . \tag{5.30}$$

If desired, the uniform semiclassical approximation in momentum space is

$$\tilde{\Psi}^{(0)}(p)=\sum_k\tilde{e}_k(p)\tilde{\Psi}_k(p)+\sum_j F_{q\to p}[e_j(q)\Psi_j(q)]\ . \tag{5.31}$$

This procedure is easy to implement, as we shall show below. MF prove that the wave function so constructed is the first term of a formal asymptotic series solution to the pseudodifferential equation—i.e., it satisfies the pseudodifferential equation with an error that goes to zero as $\hbar\to 0$.

D. Modifications to the procedure

The procedures described above are most suitable if the range of the coordinate q is the entire real axis $(-\infty,+\infty)$. In the present case, our coordinate is an angle, so we will seek periodic solutions to a pseudodifferential equation. For this purpose, it is only necessary to redefine the Fourier transform operators, and then the rest of the theory is unchanged.

If the function $\Psi(q)$ has period Q, then let us redefine $F_q\to p$ as

$$\tilde{\Psi}(p)=F_{q\to p}\Psi(q)\equiv(iQ)^{-1/2}\int_0^Q\exp(-ipq/\hbar)\Psi(q)dq\ . \tag{5.32a}$$

This operation gives a continuous function of a continuous variable p. The inverse transform is defined as

$$\Psi(q)=F^{-1}_{p\to q}\tilde{\Psi}(p)\equiv(-iQ)^{-1/2}\sum_n\exp(ip_nq/\hbar)\tilde{\Psi}(p_n)\ . \tag{5.32b}$$

This formula makes use of the values of the function $\tilde{\Psi}(p)$ only at discrete points $p_n=2\pi n\hbar/Q$, so $\tilde{\Psi}(p)$ is of particular interest at those points. With these definitions, the rest of the theory goes through directly, and in particular, the stated procedures again lead to formal asymptotic approximations in q space and p space.[18]

The asymptotic approximations apply in the limit $\hbar\to 0$. For finite $\hbar$, a function which is accurate to order $\hbar$ is also nonunique to order $\hbar$. Given a function $\Psi_1(q)$ which satisfies the pseudodifferential equation to within a certain error, we can add to it a small smooth function $\Psi_2(q)$, and the sum will still satisfy the pseudodifferential equation to the same order of accuracy, provided only that $\Psi_2(q)$ is sufficiently small and sufficiently smooth. In this sense the approximations in each order are not unique. This also means that modifications to the stated procedures can be made to simplify the results. For example, the Fourier integrals appearing in (5.30) and (5.31) could be calculated exactly by numerical methods or they could be estimated by some approximation. The stationary-phase approximation leads back to the primitive semiclassical approximation. Extensions of the stationary-phase approximation, incorporating two coalescing stationary-phase points, lead to Airy-function formulas. In some cases, with finite $\hbar$, such approximate evaluation of the integrals could actually lead to a more accurate solution than is obtained by exact evaluation. We shall see an example of this later.

VI. THE MATRIX REPRESENTATION AS A PSEUDODIFFERENTIAL EQUATION

Now let us look again at the matrix representation of the Schrödinger equation (3.5). We would like to express this matrix equation as a pseudodifferential equation so that we can make a semiclassical approximation to the coefficients ψ^k_l. Since l represents the angular momentum, it is natural to set up the pseudodifferential equation in momentum space, as in Eq. (5.9b). (There is no fundamental distinction between coordinates and momenta in classical mechanics or in the theory of

pseudodifferential equations.)

Let us start with a phase change.[19] Consider any particular eigenvector $(\tilde{\psi}_l^k \mid l = \mid m \mid \cdots n-1)$, and set

$$\tilde{\psi}'_l = i^l \tilde{\psi}_l^k \ . \tag{6.1a}$$

(The label k in the elements $\tilde{\psi}'_l$ is dropped.) Then the matrix equation (3.4) retains its form

$$\sum_l (H'_{jl} - E\delta_{jl})\tilde{\psi}'_l = 0 \tag{6.1b}$$

if we define

$$H'_{jl} = i^{j-l} H_{jl} \ . \tag{6.1c}$$

The matrix elements H'_{jl} given in (3.5) connect state l to state $l \pm 1$ and $l \pm 2$, so $\underline{H}$ is a pentadiagonal matrix. (There is a way of reducing it to tridiagonal form, but we are content with the present representation, and the theory given in Sec. V is more than powerful enough to deal with it.) Let us define

$$\begin{aligned} c_l &= 2H'_{l-1,l+1} = 2H'_{l+1,l-1} = -2H_{l-1,l+1} \ , \\ b_l &= 2iH'_{l-1,l} = -2iH'_{l,l-1} = 2H_{l-1,l} \ , \\ a_l &= H'_{ll} = H_{ll} \ . \end{aligned} \tag{6.2}$$

The symmetry relations follow from (6.1c), together with the fact that H_{jl} is real and symmetric. With these definitions, and noting that $l \geq \mid m \mid$, the matrix equations for $\tilde{\psi}'_l$ can be written as

$$\begin{bmatrix} a_{\mid m \mid} - E & \frac{1}{2i} b_{\mid m \mid +1} & \frac{1}{2} c_{\mid m \mid +1} & & \\ \frac{-1}{2i} b_{\mid m \mid +1} & a_{\mid m \mid +1} - E & \frac{1}{2i} b_{\mid m \mid +2} & \frac{1}{2} c_{\mid m \mid +2} & \\ \frac{1}{2} c_{\mid m \mid +1} & -\frac{1}{2i} b_{\mid m \mid +2} & a_{\mid m \mid +2} - E & \frac{1}{2i} b_{\mid m \mid +3} & \frac{1}{2} c_{\mid m \mid +3} \\ & \frac{1}{2} c_{\mid m \mid +2} & -\frac{1}{2i} b_{\mid m \mid +3} & a_{\mid m \mid +3} - E & \frac{1}{2i} b_{\mid m \mid +4} \\ & & \ddots & \ddots & \ddots \end{bmatrix} \begin{bmatrix} \tilde{\psi}'_{\mid m \mid} \\ \tilde{\psi}'_{\mid m \mid +1} \\ \tilde{\psi}'_{\mid m \mid +2} \\ \tilde{\psi}'_{\mid m \mid +3} \\ \vdots \end{bmatrix} = 0 \tag{6.3a}$$

or

$$\begin{aligned} \tfrac{1}{2} c_{l-1} \tilde{\psi}'_{l-2} - \frac{1}{2i} b_l \tilde{\psi}'_{l-1} + (a_l - E)\tilde{\psi}'_l \\ + \frac{1}{2i} b_{l+1} \tilde{\psi}'_{l+1} + \tfrac{1}{2} c_{l+1} \tilde{\psi}'_{l+2} = 0 \ . \end{aligned} \tag{6.3b}$$

At this point we can start thinking of l as a continuous variable. The matrix elements c_l, b_l, and a_l are known functions of l; they are defined by Eqs. (6.2) and (3.4) for integer l and we can use these same formulas for all real values of l. The resulting continuous functions can naturally be denoted by $c(l)$, $b(l)$, and $a(l)$. The solution vector $(\tilde{\psi}'_l)$ is in principle specified by (6.3) only for integer values of l. Let us define $\tilde{\psi}'(l)$ to be any C^∞ function that reduces to $\tilde{\psi}'_l$ for integer l. Then Eq. (6.3) can be reexpressed as a pseudodifferential equation using the exponential operator as in Eq. (5.4),

$$\begin{aligned} \{ \tfrac{1}{2} c(l-1) e^{-2(d/dl)} - \frac{1}{2i} b(l) e^{-d/dl} + [a(l) - E] \\ + \frac{1}{2i} b(l+1) e^{d/dl} + \tfrac{1}{2} c(l+1) e^{2(d/dl)} \} \tilde{\psi}'(l) = 0 \ . \end{aligned} \tag{6.4}$$

To obtain a semiclassical approximation to $\tilde{\psi}'(l)$ we must define a classical variable related to l and obtain the expansion of the operator in powers of $\hbar$. It is desirable also to express the operator in a manifestly self-adjoint form.

This symmetrization is easy; we reexpress (6.4) as

$$\begin{aligned} \Big\{ \tfrac{1}{2} [e^{-d/dl} c(l) e^{-d/dl} + e^{d/dl} c(l) e^{d/dl}] \\ - \frac{1}{2i} [e^{-(1/2)d/dl} b(l+\tfrac{1}{2}) e^{-(1/2)d/dl} \\ - e^{(1/2)d/dl} b(l+\tfrac{1}{2}) e^{(1/2)d/dl}] \\ + [a(l) - E] \Big\} \tilde{\psi}'(l) = 0 \ . \end{aligned} \tag{6.5}$$

We *define* the classical variable to be[20]

$$L \equiv (l + \tfrac{1}{2})\hbar \ . \tag{6.6a}$$

The matrix elements also depend upon m and n, and it is convenient to express this dependence in terms of variables,

$$M \equiv m\hbar \ , \tag{6.6b}$$

$$N \equiv n\hbar \ , \tag{6.6c}$$

as was already suggested in our discussion of the classical Hamiltonian.

To write the pseudodifferential equation entirely in classical notation, let us define for the solution

$$\tilde{\Psi}(L) \equiv \tilde{\psi}' \left(\frac{L}{\hbar} - \frac{1}{2} \right) \equiv \tilde{\psi}'(l) \ . \tag{6.7}$$

When L is half an odd integer times $\hbar$, $\tilde{\Psi}(L)$ is equal to the element of the solution vector $\psi'(l)$ defined in (6.1). For the matrix elements we write

$$C(L)\equiv c(l)=c\left[\frac{L}{\hbar}-\frac{1}{2}\right], \tag{6.8a}$$

$$B(L)\equiv b(l+\tfrac{1}{2})=b\left[\frac{L}{\hbar}\right], \tag{6.8b}$$

$$A(L)\equiv a(l)=a\left[\frac{L}{\hbar}-\frac{1}{2}\right], \tag{6.8c}$$

and for the displacement operators we write

$$\hat{\phi}\equiv i\hbar\frac{d}{dL}, \qquad \exp\left[\mp\frac{d}{dl}\right]=\exp\left[\mp\hbar\frac{d}{dL}\right]=\exp(\pm i\hat{\phi}) . \tag{6.8d}$$

Then, using a little algebra, one can show that the pseudodifferential equation takes the form

$$[H(L,\hat{\phi};\hbar)-E]\tilde{\Psi}(L)=0 , \tag{6.9}$$

with

$$\begin{aligned}H(L,\hat{\phi};\hbar)=&\tfrac{1}{2}[e^{i\hat{\phi}}C(L;\hbar)e^{i\hat{\phi}}+e^{-i\hat{\phi}}C(L;\hbar)e^{-i\hat{\phi}}]\\&-\frac{1}{2i}[e^{i\hat{\phi}/2}B(L;\hbar)e^{i\phi\hat{\phi}/2}\\&\quad-e^{-i\hat{\phi}/2}B(L;\hbar)e^{-i\hat{\phi}/2}]+A(L;\hbar)-E\end{aligned} \tag{6.10}$$

and

$$\begin{aligned}A(L;\hbar)&=\lambda\left[\frac{N^2(5N^2-3L^2+\frac{7}{4}\hbar^2)(L^2+M^2-\frac{5}{4}\hbar^2)}{4(L^2-\hbar^2)}\right],\\B(L;\hbar)&=\nu\left[\frac{3}{2}\right]\left[\frac{N(N^2-L^2)^{1/2}(L^2-M^2)^{1/2}}{L^2-\hbar^2/4}\right],\\C(L;\hbar)&=\lambda 5N^2[(N^2-L^2)^2-\tfrac{1}{2}(N^2+L^2)\hbar^2+\tfrac{1}{16}\hbar^4]^{1/2}\\&\quad\times\frac{\left[(L+M)^2-\frac{\hbar^2}{4}\right]^{1/2}\left[(L-M)^2-\frac{\hbar^2}{4}\right]^{1/2}}{4[L^2(L^2-\hbar^2)]^{1/2}} .\end{aligned} \tag{6.11}$$

No approximations have been made in this section, and so the pseudodifferential equation (6.9) is exactly equivalent to the algebraic equations (3.4). Now, however, the equation is set up in a form appropriate for deriving a semiclassical approximation.

VII. SEMICLASSICAL APPROXIMATION TO THE EIGENVECTORS

The operator in (6.9) now looks very much like the classical Hamiltonian (4.3b). In fact we only have to take the limit as $\hbar\to 0$,

$$\begin{aligned}&A(L;\hbar)\to A^0(L) ,\\&B(L;\hbar)\to B^0(L) ,\\&C(L;\hbar)\to C^0(L) ,\\&H(L,\phi;\hbar)\to h(L,\phi) ,\end{aligned} \tag{7.1}$$

and we find that in this limit $H(L,\phi;0)$ is exactly the Hamiltonian obtained from classical perturbation theory.

Inspection shows that for most values of L and ϕ, $H(L,\phi;\hbar)$ satisfies the conditions mentioned in Sec. V A: it is infinitely differentiable, bounded as a function of ϕ, self-adjoint, and its expansion in powers of $\hbar$ contains no linear term [the difference between $H(L,\phi;\hbar)$ and $h(L,\phi)$ is proportional to $\hbar^2$]. MF recommended that these conditions should be satisfied for *all* L and ϕ, but in this regard, the operator violates the conditions in a minor way. Near the ends of the permissible range of L ($M\le L\le N$ in classical mechanics, or $m\le l<n$ in quantum mechanics) the operator has poles and branch points. Our calculations show that the semiclassical approximation remains accurate in these regions.

Let us now calculate the semiclassical approximation, following the procedures given in Sec. V. As stated earlier, since we are considering only the leading term $\tilde{\Psi}^{(0)}(L)$ of the formal asymptotic series for $\Psi(L)$, and since $H(L,\phi;\hbar)$ contains no term linear in $\hbar$, we can set $\hbar$ to zero in the operator, and thereby replace $H(L,\phi;\hbar)$ by $h(L,\phi)$. The semiclassical calculation involves examination of the level curves of $h(L,\phi)$. Two different types of states arise, depending on the structure of the level curves: librators and rotators. Each type can be treated by the methods given in Sec. V, but each introduces small surprises. We consider librators first, then rotators.

A. Librators

1. *Primitive semiclassical approximation*

Since we regard L as a "momentum," we first want a primitive semiclassical approximation in momentum space, so we follow steps (9)–(14) of Sec. V C. A typical librational level curve is shown in Fig. 3 (see also Fig. 2). We choose the initial point on the level curve to be just to the right of the uppermost point of the curve, at $\phi^0=3\pi/2+\delta$, $L^0=28.139-\varepsilon$, and there we set $S^0=0$, $\tilde{S}^0=-L^0\phi^0$. It is best to say that the level curve has three p charts, each corresponding to a smooth function $\phi=\varphi_k(L)$ such that $h(L,\varphi_k(L))=E$. The first chart has $\varphi_1(L)>3\pi/2$ and $L<L^0$, the second has $\varphi_2(L)<3\pi/2$, and the third has $\varphi_3(L)>3\pi/2$ and $L>L^0$. Starting at (L^0,ϕ^0), Eqs. (5.13a)–(5.13c) and (5.23) were integrated to obtain $L(t)$, $\phi(t)$, $S(t)$, and $\tilde{S}(t)$. The integrator paused at a grid of L points to tabulate $S_1(L)$ (while L was decreasing on the right-hand side of the curve) and $S_2(L)$ (while L was increasing on the left-hand side of the curve), and finally $S_3(L)$ (closing the loop). At the same time $dL/dt=-\partial h/\partial\phi$ was tabulated on this grid.

The Maslov indices for the three p charts are $\nu_1=1$, $\nu_2=2$, and $\nu_3=3$. The first of these comes from (5.24); at the initial point $d\varphi_1/dL$ is negative and $\Theta^-(d\varphi_1/dL)=1$. (Note that the sign of $d\varphi_1/dL$ changes in chart 1, but ν_1 is fixed for the entire chart at its initial value.) The level curve passes from chart 1 to chart 2 when $L(t)$ goes through a minimum. On either side of that point, $d\varphi_2/dL<0$ but $d\varphi_1/dL>0$. Therefore, according to Eq. (5.25), the index increases by 1.

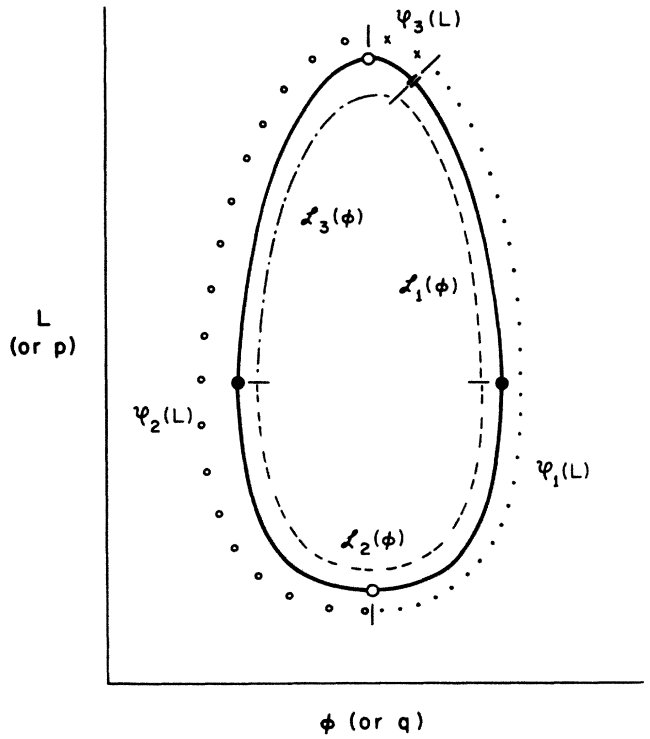

FIG. 3. Typical librational level curve and its charts. The solid line is the level curve, with turning points in q space and in p space marked with solid or hollow circles. The initial point is just to the right of the top of the curve. Charts correspond to sections of the level curve. P charts are sections defined by smooth functions $\varphi_k(p)$, $k=1,2,3$; they are marked ●, ○, and ×, respectively. Q charts are defined by smooth functions $\mathcal{L}_j(q)$, $j=1,2,3$; they are marked — — —, -- --, and —·—·—, respectively.

Then ν_2 retains its value of 2 all the way through the second chart (even though $d\varphi_2/dL$ changes sign). At the uppermost point of the curve, $d\varphi/dL$ again changes from positive to negative, and ν again increases by 1.

The quantization rule is obtained from the momentum-space version of (5.18). The total change of $\tilde{S}(L)$ on one cycle is equal to the area inside the loop,

$$\Delta\tilde{S}(L)=-\oint\varphi(L')dL' , \tag{7.2}$$

and the change of the index ν is 2, so the quantization rule for the librators is

$$-\oint\varphi(L')dL'/\hbar-\frac{\pi}{2}\Delta\nu=2\pi K \tag{7.3a}$$

or

$$\Delta\tilde{S}(L)=(K+\tfrac{1}{2})2\pi\hbar . \tag{7.3b}$$

This is the familiar rule that applies to any one-dimensional oscillator described by a Cartesian coordinate. The fact that it applies also to librators in these much more abstract action-angle coordinates is a lovely consequence of the theory.[21]

Now everything in the primitive semiclassical approximation is available, and

$$\tilde{\Psi}^{\text{prim}}(L)=\sum_{k=1}^{3}\left|\frac{\partial h(L,\phi)}{\partial\phi}\right|^{-1/2}_{\phi=\varphi_k(L)} \times\exp\left[-i\int^{L}\varphi_k(L')dL'/\hbar-i\frac{\pi}{2}\nu_k\right] . \tag{7.4}$$

Note that although we wrote this sum with three terms, for each L the second chart and either the first or the third chart contribute, so it is really a combination of two terms.

A graph of $\tilde{\Psi}^{\text{prim}}(L)$ is shown in Fig. 4, together with the discrete eigenvector elements already computed. Always the semiclassical results are multiplied by the appropriate phase factors for comparison with the exact real eigenvectors. From Eq. (6.1a) there is a factor $(-i)^{L/\hbar}=\exp(3iL\pi/2\hbar)$; in addition, there is a constant phase $e^{i\alpha}$ chosen such that the results are real at half-integer values of L. Also, the semiclassical results are normalized by dividing them by the square root of the period of motion around a cycle, T.

The semiclassical approximation reproduces the oscillations in $\tilde{\Psi}(L)$ beautifully. For most values of L, the difference between the exact values and the semiclassical values is less than the thickness of the line on the graph. Naturally, the primitive semiclassical approximation diverges at the turning points.

2. *Uniform semiclassical approximation*

To get the uniform approximation in L space we calculate also the primitive semiclassical approximation in ϕ space, attach switching functions, then transform using (5.31).

There are three q charts which are also shown in Fig. 3; they are represented by three functions $L=\mathcal{L}_j(\phi)$ such that $h(\mathcal{L}_j(\phi),\phi)=E$. The first is the part of the level curve on which $d\phi/dt>0$ and $\phi>\phi^0$, the second is where $d\phi/dt<0$, and the third is where $d\phi/dt>0$ and $\phi<\phi^0$. $S_j(\phi)$ is calculated for these charts concurrently with the calculation of $\tilde{S}(L)$.

From Eq. (5.15) the Maslov indices for these q charts are 0, 1, and 2, respectively. (At the right-hand turning point $d\mathcal{L}/d\phi$ changes from negative to positive, and the same thing happens at the left-hand turning point; the other places that $d\mathcal{L}/d\phi$ changes sign are irrelevant for the calculation of μ_j.)

Hence, the primitive semiclassical approximation to $\Psi(\phi)$ is

$$\Psi^{\text{prim}}(\phi)=\sum_{j=1}^{3}\left|\frac{\partial h(L,\phi)}{\partial L}\right|^{-1/2}_{L=\mathcal{L}_j(\phi)} \times\exp\left[i\int^{\phi}\mathcal{L}_j(\phi)d\phi/\hbar-i\frac{\pi}{2}\mu_j\right] . \tag{7.5}$$

Again at each ϕ only two terms contribute. These two terms are plotted in Fig. 5. One term is rapidly oscillating as a function of ϕ because $dS_j/d\phi=\mathcal{L}_j(\phi)$ is large near the top of the loop. The other is slowly varying—

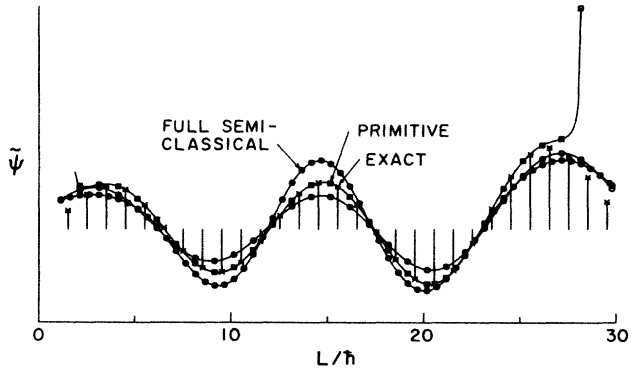

FIG. 4. Exact and approximate eigenvectors for a librator. Elements of the eigenvector of state No. 5 in Fig. 1 are plotted as *'s connected to the $L=(l+1/2)\hbar$ axis by lines. The curve with □ is the primitive semiclassical approximation. This curve passes right through most of the *'s, but it diverges at the L-space turning points. The curve with ○ is obtained by calculating the Fourier transform of the primitive semiclassical approximation in ϕ space $\Psi^{\text{prim}}(\phi)$. The curve with ● is the full semiclassical wave function (5.31).

in fact, almost constant—because $\mathcal{L}_2(\phi)$ is small near the bottom of the loop. Both terms have singularities near the turning points.

A smooth global wave function can be constructed by taking the Fourier transform of $\Psi^{\text{prim}}(\phi)$ in (7.5); the result is shown in Fig. 4 as the line marked with hollow circles. It is not at all as accurate as the primitive semiclassical wave function for most values of L, but it goes smoothly through the turning-point regions where the primitive semiclassical approximation diverges.

To construct the full wave function according to the prescription given by Maslov and Fedoriuk, we need an appropriate pair of switching functions. In principle, the results should not be very sensitive to the switching functions chosen. MF have proved that changing the switching functions changes the calculated $\tilde{\Psi}^{\text{prim}}(L)$ by an amount which is bounded by some constant times $\hbar$, so as $\hbar\to 0$ the results become independent of the switching functions. However, in any given physical system with $\hbar$ fixed, a poor choice of switching functions could lead to poor results. Since this aspect of the problem has not previously been explored computationally, we discuss it briefly in Appendix A.

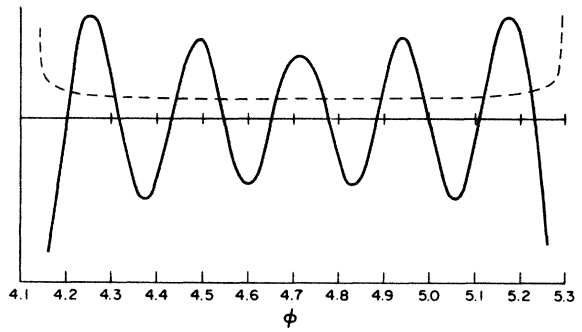

FIG. 5. Real part of semiclassical approximation in ϕ space $\Psi^{\text{prim}}(\phi)$ for eigenvector No. 5. The bold solid line is for the upper charts $\mathcal{L}_1(\phi)$ and $\mathcal{L}_3(\phi)$ and the dashed line is for the lower chart $\mathcal{L}_2(\phi)$.

The uniform approximation in L space, $\tilde{\Psi}^{(0)}(L)$, is calculated using (5.31), and the result is shown in Fig. 4 as the line of solid dots. This uniform approximation obtained from the prescription of Maslov and Fedoriuk is a reasonable approximation to the exact $\tilde{\Psi}(L)$ near the turning points, but near the center of the range it is not nearly as accurate as the primitive approximation. By varying parameters in the switching functions we found that we could improve the accuracy near the center, but at the price of lower accuracy near the ends. For many purposes (and certainly for ours) this residual error is not important—Fig. 4 clearly shows that this semiclassical approximation provides an interpretation of the structure of the eigenvector. However, if a more accurate result is desired, the major source of error is easily identified. The uniform approximation involves an integral over ϕ; this integral covers regions in which $\Psi^{\text{prim}}(\phi)$ is accurate as well as regions in which it is singular. The switching function inside the integral eliminates the singularity, but at the price of introducing some other form of distortion. If $\hbar$ is small enough (or L is large enough), then the factor $\exp(-iL\phi/\hbar)$ oscillates rapidly enough that such regions contribute negligibly to $\tilde{\Psi}^{(0)}(L)$. However, if $\hbar$ is not small enough, the errors are not necessarily negligible.

In Appendix B we describe a modification of the procedure that produces an improved uniform approximation, based upon an Airy-function representation. Using this improved approximation, $\tilde{\Psi}^{(0)}(L)$ has been calculated for all of the librator states. Representative results are shown in Fig. 6.

The four states shown correspond to eigenvalues numbered 1, 3, 5, and 7; their level curves are numbered the same way in Fig. 2. The values of the quantum number K for these states are 0, 2, 4, and 6, respectively. In Fig. 6 the values of the elements of the exact eigenvectors are again indicated by asterisks (they differ from those shown in Fig. 1 by the factor -1). The semiclassical approximation represents them all with acceptable accuracy, and it is best for states 3, 4, and 5. For states 1 and 2 the level curve is a small loop with turning points close together. For states 6 and 7 the turning points at the top and bottom of the loop are very close to the ends of the allowed region, and there the Hamiltonian (6.10) has poles and branch points. In either case we should expect semiclassical approximations to be less accurate than for the intermediate states 3—5.

Let us conclude our discussion of the librators by recalling our early observation that the first several eigenvectors show simple patterns similar to the wave functions of a one-dimensional oscillator. The same is seen in Figs. 4–6. The reason for this should now be clear. Such patterns do not require a Hamiltonian of the familiar form $p^2/2m+V(q)$; they emerge for very general Hamiltonians, including those as complicated as (4.3) or

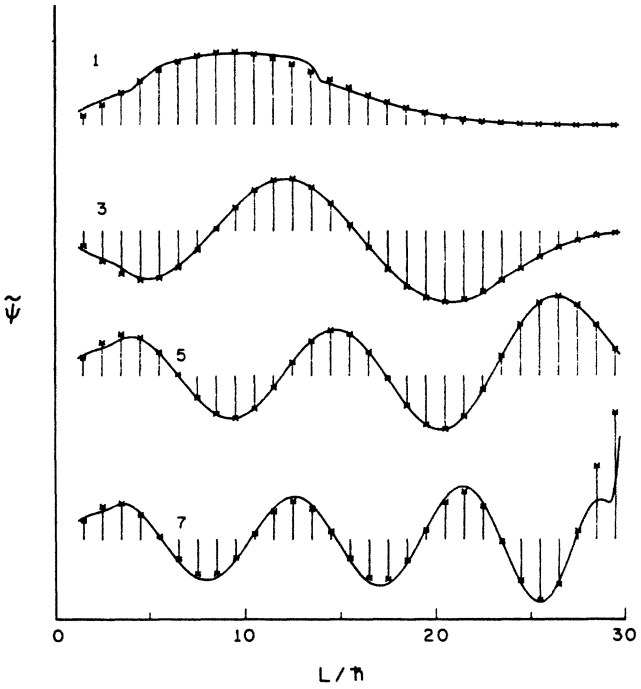

FIG. 6. Exact eigenvectors for states 1, 3, 5 and 7 compared with the uniform semiclassical approximation defined in Appendix B. Asterisks mark the values of the lth element of the eigenvector; they are placed on the axis at $L=(l+\frac{1}{2})\hbar$. The smooth curve is Eq. (B8).

(6.10). The characteristic functions $S(q)$ or $\tilde{S}(p)$ and the Maslov indices μ and ν, all of which determine the phase of the wave function in the semiclassical approximation, really do not depend upon the form of the Hamiltonian $H(p,q)$. Rather, they depend upon the structure of a level curve of $H(p,q)$. Independent of the detailed form of the Hamiltonian, whenever the level curves show closed loops the wave functions will have forms analogous to those of a one-dimensional oscillator.

B. Rotators

1. *Primitive semiclassical approximation*

Rotators are level curves in Fig. 2 that extend from 2π to 0. An example is shown in Fig. 7, with the range of ϕ changed to $(-\pi,\pi)$. The state considered is number 17.

For this level curve the primitive wave function (5.28) is a sum of four terms,

$$\tilde{\Psi}^{\text{prim}}(L)=\sum_{k=1}^{4}\left|\frac{\partial h(L,\phi)}{\partial\phi}\right|^{-1/2}_{\phi=\varphi_k(L)} \times\exp\left[i\tilde{S}_k(L)/\hbar-i\nu_k\frac{\pi}{2}\right], \tag{7.6}$$

having Maslov indices ν_k found from (5.24) and (5.25) to be 0, 1, 0, and 1 for $k=1$, 2, 3, and 4, respectively. Together, these four terms combine to give a rather complicated interference pattern, which is shown in Fig. 8, together with the exact values for this state. Again this primitive semiclassical approximation beautifully matches the exact results, except that it diverges near the turning points.

Additional interpretation can be gained by examining the terms two at a time. In particular, for charts 1 and 2, $\varphi_j(L)$ is close to $\pi/2$, and we can write each of these terms as

$$\exp\left[-i\int^{L}\varphi_k(L')dL'/\hbar\right] =\exp\left[-i\int^{L}\left[\varphi_k(L')-\frac{\pi}{2}\right]dL'/\hbar\right] \times\exp\left[-i\frac{\pi}{2\hbar}(L-L^0)\right]. \tag{7.7}$$

Since $\varphi_k(L)-\pi/2$ is small, the first factor is a slowly varying function of L. The combination of

$$\left|\frac{\partial h}{\partial\phi}\right|^{-1/2}\left\{\exp\left[-i\int^{L}\left[\varphi_1(L')-\frac{\pi}{2}\right]dL'/\hbar\right] +\exp\left[-i\int^{L}\left[\varphi_2(L')-\frac{\pi}{2}\right]dL'/\hbar\right]\exp\left[-i\frac{\pi}{2}\right]\right\} \tag{7.8}$$

is shown in the lower part of Fig. 8 as the dashed line. It is a smoothly oscillatory function (except for singularities near the turning points). Its wavelength is largest at small L, where $\varphi_k(L)$ is closest to $\pi/2$, and its wave-

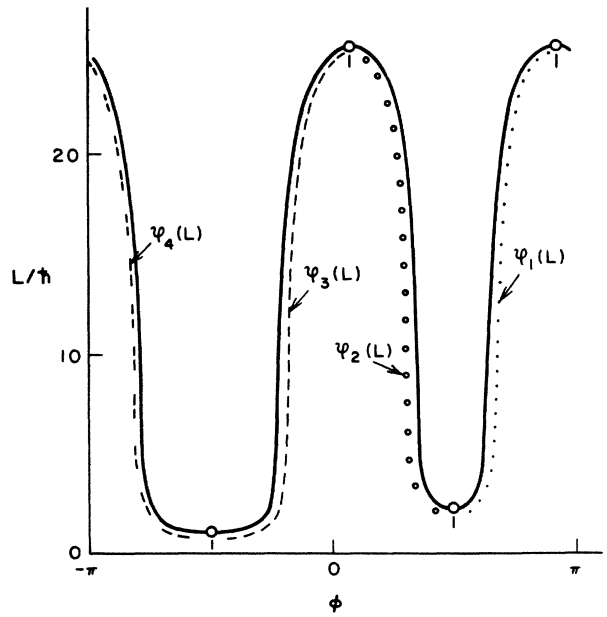

FIG. 7. Typical rotational level curve and its charts. ○ are turning points in L space, which separate the four p charts $\varphi_k(L)$ from each other. In ϕ space there is only one chart.

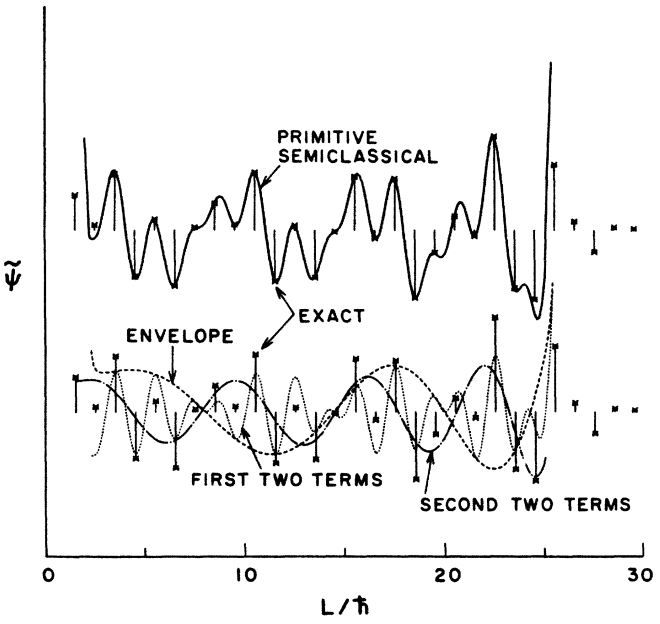

FIG. 8. Primitive semiclassical approximation for eigenvector number 17, a rotator. Asterisks mark the exact eigenvector elements $\tilde{\psi}_l$. The bold solid curve is the primitive semiclassical approximation. It is a sum of four terms shown pairwise below.

length gradually decreases as L increases.

When this quantity is multiplied by the last factor in (7.7), and also the phase factor in Eq. (6.1a) is incorporated, then the effect is to multiply (7.8) by $\exp(-i\pi(L-L_0)/\hbar)$. This is a rapidly oscillating function of L, changing sign each time L increases by $\hbar$. In Fig. 8 the dotted line is equal to the dashed line times the real part of this oscillating factor. The result is an amplitude-modulated cosine wave. Finally, for the other two terms in the primitive wave function, $\varphi_k(L)$ is close to $-\pi/2$, and we consider

$$\exp\left[-i\int^L\left[\varphi_k(L')+\frac{\pi}{2}\right]dL'/\hbar\right]\times\exp\left[-i\frac{\pi}{2\hbar}(L-L^0)\right]. \quad (7.9)$$

This time the last factor in (7.9) cancels the phase factor in (6.1a), so charts 3 and 4 combine to give a slowly varying contribution. This contribution is the dot-dashed line in Fig. 7. The sum of this dot-dashed line (charts 3 and 4) and the dotted line (charts 1 and 2) is equal to the primitive semiclassical approximation.

Let us now refer back to Fig. 1 and Table I (values shown in Fig. 1 differ from those plotted in Fig. 8 by the factor -1). We saw that the coefficients for this particular state showed no evident pattern. Now we recognize that these numbers are in no way random or chaotic; they are discrete values of a continuous function which is itself a superposition of four simple WKB terms.

2. *Uniform approximation*

For the level curve shown in Fig. 7, there are no turning points of the ϕ motion, and $\Psi^{\text{prim}}(\phi)$ consists of only one term, which is accurate over the whole range of ϕ. Before calculating it, however, let us look once more at the pseudodifferential equation for $\Psi(\phi)$. In ϕ space, the Schrödinger equation (6.9) is

$$\left[H\left[-i\hbar\frac{d}{d\phi},\phi;\hbar\right]-E\right]\Psi(\phi)=0\,, \quad (7.10)$$

with $H(L,\phi;\hbar)$ given by (6.10) and (6.11). For example, a term involving $B(L;\hbar)$ is

$$-\frac{1}{2i}\left[e^{i\phi/2(\frac{3}{2}\nu)}\left[\frac{N(N^2+\hbar^2d^2/d\phi^2)^{1/2}(-\hbar^2d^2/d\phi^2-M^2)^{1/2}}{(-\hbar^2d^2/d\phi^2-\hbar^2/4)}\right]e^{i\phi/2}\right]. \quad (7.11)$$

At first sight, this thing makes us ask if we should not find some other way to approach the problem [the terms involving $C(L;\hbar)$ are even worse]. However, their awful appearance only reemphasizes the great power of the methods discussed here. We obtain the semiclassical approximation to $\Psi(\phi)$ with only a few minutes of work.

Since there is only one ϕ chart, there is only one Maslov index μ, which is taken to be zero. At every point ϕ the level curve is described by a smooth, single-valued function $\mathcal{L}(\phi)$, and, therefore,

$$\Psi(\phi)=\left|\frac{\partial h(L,\phi)}{\partial L}\right|^{-1/2}_{L=\mathcal{L}(t)}\exp\left[i\int_\pi^\phi\mathcal{L}(\phi')d\phi'/\hbar\right]. \quad (7.12)$$

The only problem that remains is to identify the appropriately quantized level curves or eigentrajectories (actually we had to solve this problem before computing the primitive L-space approximation). Here we find a little surprise. One would first think that $\Psi^{(0)}(\phi)$ must be periodic with period 2π,

$$\Psi(\phi+2\pi)=\Psi(\phi)\,.$$

When this boundary condition is applied to Eq. (7.12), it leads to full-integer action quantization

$$\int_0^{2\pi}\mathcal{L}(\phi)d\phi/\hbar=2\pi K\,,$$

where K is any integer.

This quantization condition is known to give an incorrect spectrum of energy levels. In an earlier paper[13] we pointed out that the correct spectrum is obtained using half-integer quantization of action for all states, and we promised to give a new proof of that condition in the

action-angle formulation.

The proof is very simple. In the present case, the exact wave function in momentum space $\tilde{\Psi}(L)$ is defined in terms of the elements in the eigenvector $\tilde{\psi}'(l)=(-i)^l\tilde{\psi}_l$ through Eqs. (6.7) and (6.1a). The function $\Psi(\phi)$ is defined through the Fourier sum (5.32b). This sum involves only certain discrete values of L. Now according to Eq. (6.6a), the relevant discrete values of L are *half integers* times $\hbar$. It follows that the function $\Psi(\phi)$ obeys the unexpected condition

$$\Psi(\phi+2\pi)=-\Psi(\phi)\ . \tag{7.13}$$

[As a consequence, $\Psi(\phi)$ is periodic with period 4π.] When this boundary condition (7.13) is applied to the primitive semiclassical approximation (7.12), it leads to the half-integer quantization rule

$$\int_0^{2\pi}\mathcal{L}(\phi')d\phi'=(K+\tfrac{1}{2})2\pi\hbar\ . \tag{7.14}$$

Thus we obtain half-integer quantization of action for both librators and rotors. Further implications of this surprising condition are discussed in Sec. IX and in Appendix C.

Once the appropriate level curves are identified using (7.14), the calculation of wave functions using (7.12) is trivial. In Fig. 9 we show the real part of the primitive semiclassical wave function $\Psi^{\text{prim}}(\phi)$ for some of the rotator states. The curve marked 8 applies to one of the level curves for which $\mathcal{L}(\phi)$ is large ($\sim 29\hbar$) at $\phi=\pi/2$, and the one marked 21 refers to a more typical curve having $\mathcal{L}(\phi)$ small at $\phi=\pi/2$. These functions are rapidly oscillatory where $\mathcal{L}$ is large and slowly oscillatory where $\mathcal{L}$ is small; the amplitude of the oscillations is large where $d\phi/dt=\partial h/\partial L$ is small, and small where this is large. In particular, near $\phi=3\pi/2$, $\partial h/\partial L$ gets huge, and $\Psi^{(0)}(\phi)$ nearly vanishes. Generally, these wave functions look like a traveling wave in a system having a periodically varying potential energy. (There is one major difference: in more familiar systems the velocity $\partial H/\partial p$ is proportional to the momentum p, so the amplitude of the wave function is small where the wavelength is short; in the present case the opposite is true—the amplitude is large where the wavelength is short.)

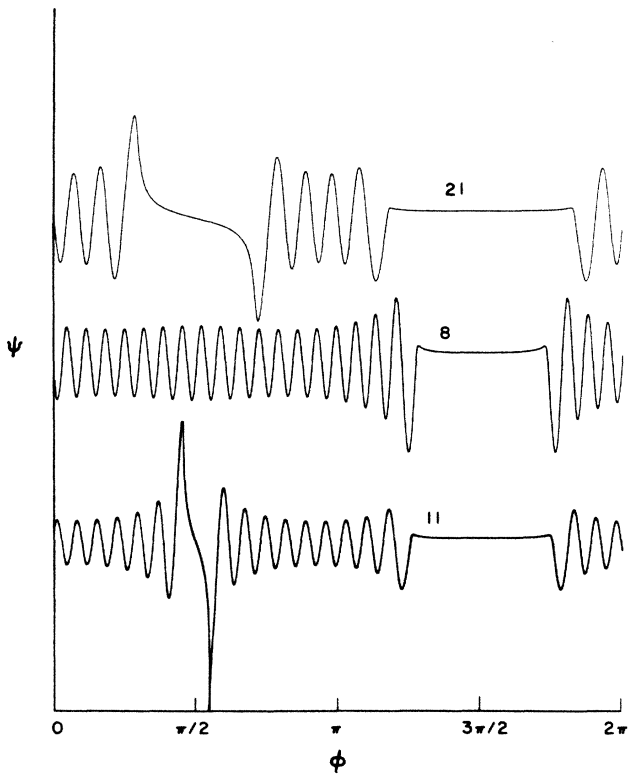

FIG. 9. Primitive semiclassical approximation in ϕ space for rotators 8, 21, and 11. Number 8 has a level curve in which $\mathcal{L}(\phi)$ is large when $\phi=\pi/2$. Number 21 has $\mathcal{L}(\phi)$ small at $\pi/2$, so it is more slowly varying. Number 11 has a level curve which folds back over itself as in Fig. 11, so it has turning points in ϕ space, and associated singularities.

The uniform semiclassical approximation in L-space $\tilde{\Psi}^{(0)}(L)$ was calculated by taking the Fourier transform between the limits $\pm\pi$. The result for several cases is shown in Fig. 10, along with the eigenvector elements $\tilde{\psi}_l$. Again the uniform semiclassical approximation gives a good representation of the overall structure of the eigenvectors, and it retains its accuracy at both large and small L. (As for the librators, however, the uniform approximation is somewhat less accurate than the primitive approximation near the center of the range of L.)

State 29 corresponds to the lowest [smallest $\mathcal{L}(\phi)$] curve in Fig. 2. Therefore, $\tilde{\Psi}(L)$ is significant only for small L, and for $L\geq 15$ it is wiggly but small, especially on the half-integers. States 25, 21, 17, and 13 have level curves that reach to successively higher values of L, and so $\tilde{\Psi}(L)$ is significant over more of the range.

As mentioned earlier, state 8 has a level curve that dips to small L only once, near $\phi=3\pi/2$, and $\mathcal{L}(\phi)$ is large near $\phi=\pi/2$. Therefore, the magnitude of $\tilde{\psi}_{29}$ for this state is very large, and the other elements show smooth oscillations as a function of L, consistent with a two-term interference pattern.

Finally, state 11 has a level curve that does not everywhere admit a good projection into ϕ space. An exaggerated picture of this level curve is shown in Fig. 11. This curve forces us to compute the Maslov index carefully. There is a misconception which asserts that the Maslov index μ increases by 1 each time a curve passes through a turning point. This level curve provides several counterexamples. Table III lists the Maslov indices of the various sections of the curve, together with the incorrect values that would be obtained if the indices were calculated according to the misconception.

The primitive wave function in ϕ space, $\Psi^{\text{prim}}(\phi)$, for this state is also shown in Fig. 9. Its singular behavior near the turning points is obvious. However, since the singularity is integrable, we computed an approximation to $\tilde{\Psi}^{(0)}(L)$ directly by Fourier transformation of $\Psi^{\text{prim}}(\phi)$ [omitting switching functions and $\tilde{\Psi}^{\text{prim}}(L)$]. The result for this is shown in Fig. 10 along with all the others; we see that $\tilde{\Psi}^{(0)}(L)$ for this state is somewhat less accurate than for the other states, but the presence of the singularities did not cause any serious problems.

C. The "missing" state

One quantum state is still missing from our semiclassical description. This is state number 10 in Fig. 1. Its energy places it somewhere in the large gap between level curves 9 and 11 in Fig. 2. In this gap there is a separatrix, and a small area near $\phi=\pi/2$, $L=12$, having closed level curves. Earlier we named these curves L_C librators, and they are shown in Fig. 2(c) of Ref. 13. For the present value of ν/λ the area in the (L,ϕ) space occupied by such L_C librators is less than $\pi\hbar$. Hence, there is no room for a quantum L_C librator here. On the other hand, the total area available for R_A rotators is only enough to support two states, and the area available for R_B rotators supports just 19 states. Together with the seven L_A librators, these 28 states occupy an area of less than $28\hbar$ in the (L,ϕ) plane. The total area in the gap between states 9 and 11 is large enough for the one additional state, but that state does not correspond to any single level curve of $h(L,\phi)$. It must therefore have a mixed character, partly R_A, partly R_B, and partly L_C. The eigenfunction for this state was shown in Fig. 10(h) of Ref. 13, and its mixed character is evident there. A semiclassical description of this exceptional eigenvector requires a more elaborate theory than that given here. We leave this for a future study.

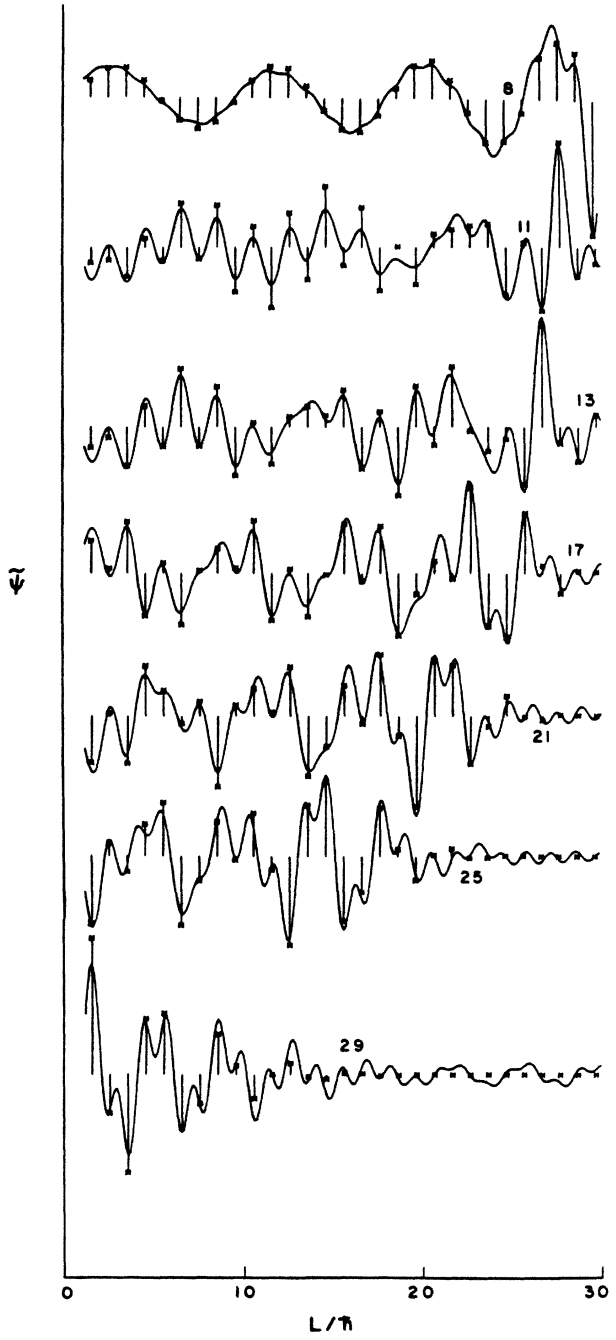

FIG. 10. Exact eigenvectors compared with the uniform semiclassical approximation for rotator states. Asterisks, exact; solid line, semiclassical, from Eq. (7.12).

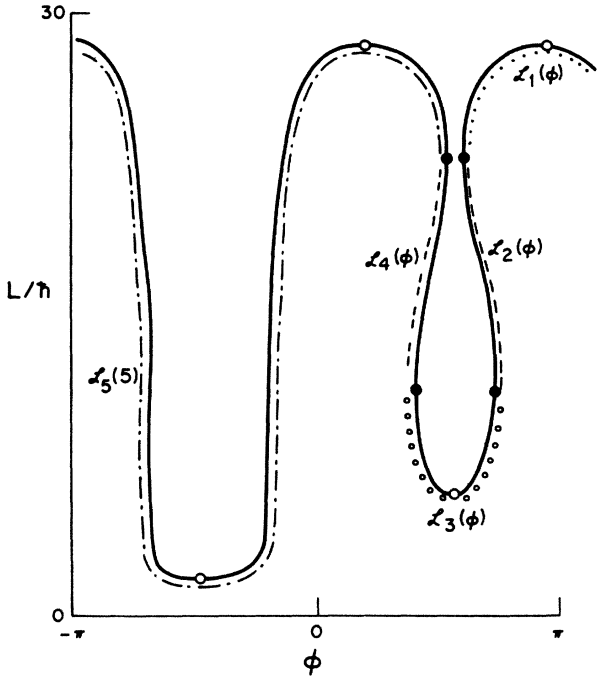

FIG. 11. Exaggerated picture of the level curve for state 11. ●, turning points in ϕ; ○, turning points in L. Labeling of charts is indicated.

VIII. SUMMARY

Eigenfunctions can be calculated by expansion in a basis, evaluation of matrix elements, and diagonalization of the resulting matrix. The sets of coefficients (the

TABLE III. Maslov index μ_k for charts indicated in Fig. 11. Note: If the Maslov index increased by 1 each time the path passed through a turning point, then the incorrect index would be obtained. Correct values are obtained from Eq. (5.15) (Ref. 27).

Chart	1	2	3	4	5
Incorrect index	0	1	2	3	4
Correct index	0	−1	0	1	0

eigenvectors) that result from this process are usually uninterpretable. We have calculated and plotted in Fig. 1 a set of eigenvectors obtained for a one-electron system in parallel electric and magnetic fields.

We have shown that a simple and systematic semiclassical approximation provides an understanding of these eigenvectors. The matrix equation was written as a difference equation, then as a "pseudodifferential" equation. The resulting operator $H(L,-i\hbar d/dL;\hbar)$ was given in Eq. (6.10). In the limit $\hbar\to 0$, this operator goes to the corresponding classical Hamiltonian $h(L,\phi)$ defined in Eq. (4.3b).

Eigenvectors were regarded as "wave functions in angular momentum space," and were denoted $\tilde{\Psi}(L)$. A primitive semiclassical approximation to $\tilde{\Psi}(L)$ was calculated using the formula

$$\tilde{\Psi}(L)=\sum_k \left|\frac{\partial h(L,\phi)}{\partial\phi}\right|^{-1/2}_{\phi=\varphi_k(L)} \times\exp\left[-i\int^L \varphi_k(L')dL'/\hbar-i\nu_k\pi/2\right], \tag{8.1}$$

where $\varphi_k(L)$ is a branch of the level curve $h(L,\varphi_k(L))=E$. This approximation is excellent over most of the range of L, but it fails near the L-space turning points, where $dL/dt=-\partial h/\phi$ vanishes. To obtain a uniform semiclassical approximation we calculated a primitive semiclassical approximation in ϕ space,

$$\Psi(\phi)=\sum_j \left|\frac{\partial h(L,\phi)}{\partial L}\right|^{-1/2}_{L=\mathcal{L}(\phi)} \times\exp\left[i\int^\phi \mathcal{L}(\phi')d\phi'/\hbar-i\mu_k\pi/2\right], \tag{8.2}$$

and computed its Fourier transform. The two types of forms were combined with switching functions, using Eqs. (5.30) and (5.31). An alternative form based on Airy functions was also used.

In this way, the structure of the eigenvectors shown in Fig. 1 was explained by examining the forms of the level curves of $h(L,\phi)$ in Fig. 2. Seven of the states are "librators," having closed level curves in Fig. 2. Their wave functions $\tilde{\Psi}(L)$ look like those of a one-dimensional oscillator. The remainder of the states are rotators, with open level curves. Two of these states have curves such that L is large near $\phi=\pi/2$. Those states have very large elements $\tilde{\Psi}(L)$ for large L, and for smaller L they have a simple oscillatory structure. The remaining states have more complicated wave functions, which are well represented as superpositions of four oscillatory terms.

IX. COMMENTARY ON ACTION AND ANGLE VARIABLES IN QUANTUM MECHANICS AND IN SEMICLASSICAL MECHANICS

The results obtained here shed new light on a very old problem—the formulation of quantum mechanics in action-angle variables. Classical mechanics permits change of phase-space variables from the original Cartesian coordinates $(\mathbf{p},\mathbf{q})$ to various types of action and angle variables $(\mathbf{I},\boldsymbol{\phi})$. For any given system, the "exact" action-angle variables are defined such that the actions are constants of the motion, the angles increase linearly with time, and the transformation $(\mathbf{p},\mathbf{q})\leftrightarrow(\mathbf{I},\boldsymbol{\phi})$ is periodic in the ϕ's, with period 2π. When they exist, such variables clearly provide the simplest possible description of the motion. Even systems that do not possess exact action-angle variables might admit "unperturbed" or "zeroth-order" action-angle variables, which are also useful for obtaining a quantitative description of the motion (cf., for example, the calculations in the present paper).

Hence, since the earliest days of quantum mechanics, a persistent question has arisen: Can quantum mechanics also be formulated in terms of action-angle variables? One would expect such a formulation to share many of the harmonious features of the classical formulation. However, the simple quantization prescription $p\to -i\hbar\partial/\partial q$ that applies in Cartesian coordinates certainly cannot be carried over into general coordinates. Is there a quantum analogue of the classical transformation to action-angle variables?

Dirac's early researches were particularly oriented toward formulating quantum laws in general variables, and he eventually arrived at the conclusion that "unitary transformations in the quantum theory are the analogue of [canonical] transformations in the classical theory."[22] Today, 60 years after the appearance of his papers, it still is not known exactly how far this analogy can be carried. Certainly the analogy is not an isomorphism: there exist classical canonical transformations for which no corresponding quantum unitary transformation exists, and vice versa. However, Dirac's seemingly successful early work using quantum action-angle variables for the hydrogen atom[8(a)] has suggested that a general quantum action-angle formulation might exist.[23,24]

Dirac's provocative remark could be restated a little more precisely as follows. Let classical variables be given by pq, and corresponding quantum operators by $\hat{p}\hat{q}$. *If* a certain classical canonical transformation $\mathbf{pq}\leftrightarrow\mathbf{PQ}$ exists, and is obtained by a generator such as $F_1(\mathbf{q},\mathbf{Q})$, as

$$p_i(\mathbf{q},\mathbf{Q})=\partial F_1/\partial q_i,\quad P_i(\mathbf{q},\mathbf{Q})=-\partial F_1/\partial Q_i\ , \tag{9.1}$$

and if a corresponding quantum unitary transformation $\hat{\mathbf{p}}\hat{\mathbf{q}}\leftrightarrow\hat{\mathbf{P}}\hat{\mathbf{Q}}$ exists having transformation matrix $\langle\mathbf{q}'\,|\,\mathbf{Q}''\rangle$, *then* the matrix elements are related to the generator $F_1(\mathbf{q},\mathbf{Q})$ by

$$\langle\mathbf{q}'\,|\,\mathbf{Q}''\rangle\leftrightarrow\left|\frac{\partial^2 F_1}{\partial\mathbf{q}'\partial\mathbf{Q}''}\right|^{-1/2}\exp[iF_1(\mathbf{q}',\mathbf{Q}'')/\hbar]\ . \tag{9.2}$$

The vagueness implicit in Dirac's "analogy" is here replaced by two existence conditions and a new vagueness in the meaning of the symbol $\leftrightarrow$ in (9.2). This symbol means that either the left-hand side is *equal to* the right-hand side, or else that the two approach each other over most of the range of the variables $\mathbf{q}$ and $\mathbf{Q}$ in a classical

limit. An obvious necessary condition for the existence of a unitary matrix $\langle \mathbf{q}' \mid \mathbf{Q}'' \rangle$ is the existence of a complete orthogonal set of kets $\mid \mathbf{Q}'' \rangle$ which are the eigenkets of the operator $\hat{\mathbf{Q}}$. Now in the case of the harmonic oscillator, the obvious definitions of action and angle operators are

$$\frac{1}{\sqrt{2}}(\hat{p}+im\omega\hat{q})=\hat{I}^{1/2}e^{i\hat{\phi}}\ ,$$
$$\frac{1}{\sqrt{2}}(\hat{p}-im\omega\hat{q})=\hat{I}^{1/2}e^{-i\hat{\phi}}\ . \tag{9.3}$$

However, calculation shows that the operators $\exp(i\hat{\phi})$ and $\exp(-i\hat{\phi})$ are not unitary, are not inverses of each other, and do not even commute with each other.[8(b)] This definition does not lead to a Hermitian angle operator, so it provides neither the required complete set of eigenkets $\mid \phi'' \rangle$ nor the unitary transformation matrix $\langle q' \mid \phi'' \rangle$.

It is puzzling, therefore, that many valuable results have been obtained in semiclassical mechanics by either ignoring this fact or by being unaware of it. For example, Miller[5(b)] bases his "classical S-matrix theory" on relationship (9.2), and he uses this relationship specifically with $\hat{Q}$ taken to be an angle operator $\hat{\phi}$, conjugate to an action operator $\hat{I}$. Many closely related formulas appear in the literature.[5,6] But since there is not any such set of kets $\mid \phi'' \rangle$, the right-hand side of (9.2) is somehow a semiclassical approximation to a unitary matrix that does not exist. We find this hard to understand.

Moshinsky and Seligman[8(d)] have closely examined the nature of the analogy between unitary transformations and canonical transformations. They pointed out again the impossibility of a quantum transformation from Cartesian coordinates and momenta to action-angle operators. But they showed by direct calculation that for certain systems, if the space of eigenstates is expanded in certain ways, then in the enlarged space a unitary transformation does exist, and its form closely corresponds to the form of the classical canonical transformation.

This issue was examined further by Newton.[8(e)] Considering one-dimensional oscillators, he defined a simple and general way of expanding the Hilbert space. In the case of the harmonic oscillator, if $\mid n \rangle$ is an eigenket of the Hamiltonian, $H \mid n \rangle = E_n \mid n \rangle$, then states in the expanded space are two-component "spinors" such as $\begin{pmatrix} \mid n \rangle \\ 0 \end{pmatrix}$ or $\begin{pmatrix} 0 \\ \mid n \rangle \end{pmatrix}$. He showed that in this doubled space it is possible to define a set of eigenkets $\| \phi' \rangle\rangle$ which are eigenkets of unitary operators with eigenvalues $\exp(\pm i\phi')$. These unitary operators could be denoted $\widehat{e^{\pm i\phi}}$, and they obey equations similar to (9.3). Hence, Dirac's analogy between unitary transformations and canonical transformations holds not in the Hilbert space of physical eigenstates, but in a more abstract, expanded Hilbert space. He suggested that calculations could be made in the expanded space, and then at the end a projection into the physical space could be made.

In the present paper we have arrived at a somewhat similar conclusion from a totally different starting point. We developed a semiclassical approximation: starting from quantum equations (3.5) we followed a systematic mathematical procedure to obtain approximations to eigenvectors. This procedure led us to the conclusion that when the wave function is expressed in angle space as $\Psi(\phi)$, then $\Psi(\phi+2\pi)=-\Psi(\phi)$. Specifically, if we want our quantum operators to have the same form as the classical operators, except for corrections of order $\hbar^2$ and higher, then we are forced to this conclusion. Then if we also decide that we want our wave functions to be periodic, the period must be 4π. The domain of definition of the semiclassical angle variable is therefore twice the domain of the classical angle variable. Eigenfunctions appearing in the "nonphysical" region $(2\pi \le \phi < 4\pi)$ are (except for a minus sign) the same as those in the "physical" region $(0 \le \phi < 2\pi)$. For Newton the doubling of the Hilbert space is a postulate or definition; for us it is a consequence of a systematic procedure. Although the doubling of the space takes two very different forms, the similarities between these two different conceptions is striking.

At present no final conclusion on the generality of Dirac's analogy or on the viability of theories based upon quantum action and angle operators is available. Semiclassical approximations starting from equations such as (9.2) have led to correct results, but the "derivations" of those results made more use of physical intuition and insight than of systematic mathematical analysis. Reexamination of such approaches in the light of these new developments may prove to be worthwhile.

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APPENDIX A: SWITCHING FUNCTIONS

Two principles guide the choice of switching functions. (i) The mathematical theory demands that the product of the switching function times the primitive semiclassical wave-function must be infinitely differentiable, even where the primitive wave function is singular. Functions like

$$e(w)=\begin{cases}0, & w<0\\ \exp(-1/w), & w>0\end{cases}$$

have the required property: they can be multiplied by a function with a pole or a branch point at $w=0$ and the product will still be C^∞. (From a numerical point of view, this property is not very important, because the uniform approximation is calculated by an integral, and the functions are never actually differentiated in the computation.) (ii) The switching functions should be slowly varying compared to the primitive semiclassical wave function. They must not introduce sharp edges, or additional oscillations, or any other significant structure

into the Fourier integrals (5.30) and (5.31).

Each point on the level curve lies in one ϕ chart and one L chart, so two switching functions are associated with each point, and $e+\bar{e}=1$. At the ϕ turning points $e=0$ and $\bar{e}=1$, while at the L turning points $e=1$ and $\bar{e}=0$. This suggests that the variable in the switching functions could be taken to be related to the slope of the level curve,

$$w(\phi)=\gamma[d\mathcal{L}(\phi)/d\phi]^d \ . \tag{A1}$$

With this choice of variable it makes sense to take the switching functions to be symmetric in w,

$$e(w)=e(-w) \ . \tag{A2}$$

Also, since wave functions in L or in ϕ space are treated on an equal footing, it is reasonable to incorporate a corresponding symmetry into the switching functions,

$$e(1/w)=\bar{e}(w)=1-e(w) \ . \tag{A3}$$

We chose switching functions of the form

$$\bar{e}=\tfrac{1}{2}(1+g) \ , \tag{A4a}$$

$$e=\tfrac{1}{2}(1-g) \ , \tag{A4b}$$

$$g=\frac{w\exp\left[2\left[w-\frac{1}{w}\right]\right]-1}{w\exp\left[2\left[w-\frac{1}{w}\right]\right]+1} \ . \tag{A4c}$$

It is easy to show that this function $e(w)$ goes to 1 when w goes to 0, to 0 when w goes to infinity, to $\frac{1}{2}$ when $w=1$, that it is infinitely differentiable as a function of w or as a function of ϕ, and that when it is multiplied by $\Psi^{\text{prim}}(\phi)$ the result is still infinitely differentiable. After a few trials, we chose $\gamma=0.05$, $d=0.5$ in our computations.

APPENDIX B: TWO WAYS TO IMPROVE THE ACCURACY OF THE UNIFORM APPROXIMATION

The uniform approximation computed from Eq. (5.31) was shown in Fig. 4. Compared to the exact result, this result is too large in the center of the range of L. We found two ways to improve the result.

(1) Take the switching functions outside the Fourier integral, so that (5.31) would be replaced by

$$\tilde{\Psi}^{(0)}(p)=\sum_k \bar{e}_k(p)\tilde{\Psi}_k(p)+\sum_j e_j[q_j(p)]F_{q\to p}[\Psi_j(q)] \ . \tag{B1}$$

The function $\Psi_j(q)$ is singular, but the singularity is integrable. The result is a smooth combination of the primitive semiclassical term and the transformed term, each of which was shown in Fig. 4. We have obtained good results this way.

(2) Use an Airy-function approximation near the turning-point regions. We label the two L-space turning points by the index α ($\alpha=$ upper or lower). Then the wave function $\tilde{\Psi}_\alpha(L)$ near turning point α is equal to

$$\tilde{\Psi}_\alpha=\left[\frac{2\pi}{|\dot{\phi}_\alpha|}\right]^{1/2}\left|\frac{z_\alpha}{L_\alpha-L}\right|\mathrm{Ai}(-z_\alpha)\times\exp\left[i\left[\frac{\tilde{S}_\alpha}{\hbar}-\frac{\pi}{4}+\eta_\alpha\right]\right] \ , \tag{B2}$$

where L_α is the value of L at turning point α,

$$\dot{\phi}_\alpha=\left[\frac{d\phi}{dt}\right]_\alpha=\left[\frac{\partial h}{\partial L}\right]_{L=L_\alpha,\ \phi=\frac{3\pi}{2}} \ , \tag{B3}$$

$$\tilde{S}_\alpha=\tilde{S}(L_\alpha)=-L_\alpha\frac{3\pi}{2} \ , \tag{B4}$$

$$z_\alpha=\mp\left|\tfrac{3}{2}\Delta_\alpha\right|^{2/3} \ , \tag{B5}$$

$$\Delta_\alpha=\tfrac{1}{2}\int_{L_\alpha}^{L}[\varphi_1(L')-\varphi_2(L')]dL'/\hbar \ . \tag{B6}$$

In Eq. (B5) the sign of z_α is taken to be positive in the classically allowed region and negative in the classically forbidden region. In Eq. (B6), $\varphi_1(L')$ and $\varphi_2(L')$ are the two branches (charts) of the level curve. In the classically forbidden regions, the equation $h(L,\varphi(L))=E$ admits two complex solutions $\varphi_i(L)$ such that $\varphi_i(L)$ goes to $3\pi/2$ as L goes to L_α. The phase η_α is

$$\eta_{\text{upper}}=-\frac{3\pi}{2}L \ , \tag{B7a}$$

$$\eta_{\text{lower}}=-\frac{3\pi}{2}L+k\pi \ , \tag{B7b}$$

where k is the librational quantum number.

A global wave function can be calculated by tying (B2) to the primitive approximation using switching functions

$$\Psi^{(0)}(p)=\bar{e}(p)\Psi^{\text{prim}}(p)+[1-\bar{e}(p)]\Psi^{\alpha}(p) \ . \tag{B8}$$

Justification of the formulas

We do not have a good mathematical justification of Eq. (B1). To establish this formula as the beginning of a formal asymptotic expansion, one would have to prove that the operator $\mathcal{H}(p,i\hbar d/dp)$ acting upon (B1) gives a result which is $O(\hbar^2)$ or less. Now when $\mathcal{H}$ acts upon the last terms, $\mathcal{H}[eF_{q\to p}\Psi(q)]$ gives among other things

$$e(q)\left[F_{q\to p}\mathcal{H}\left[-i\hbar\frac{d}{dq},q\right]\Psi(q)\right] \ .$$

The function $\Psi(q)$ contains turning-point singularities such as $|q-q_0|^{-1/2}$. These singularities are themselves integrable, but when d/dq acts upon them they become nonintegrable. Switching functions inside the Fourier integral annihilate the singularities, but outside they do not. Therefore, we have no proof that (B1) can give good results. Calculations in the present case show that it gives results more accurate than (5.31) but not as good as (B8).

Equation (B8) is on a somewhat more solid mathematical footing. It can be derived as an approximation to (5.31) by routine manipulations of the Fourier integral.[25] However, such a derivation does not make clear why

(B8) gives significantly better results than (5.31). Intuitively, we can understand (B8) as the beginning of another kind of locally valid formal asymptotic series, based upon Airy functions instead of exponential functions. Such series are well known as approximations for oscillatory integrals, but they have not yet been developed for solutions to pseudodifferential equations. Future work might address this problem.

APPENDIX C: A CONSISTENCY CHECK

In Eq. (5.32b) we defined the wave function in angle space as a Fourier sum, and in Eq. (6.6a) we took the angular momentum variable to have half-integer values times $\hbar$. Thus we may write Eq. (5.32b) in the form

$$\Psi(\phi)=(-2\pi i)^{-1/2}\sum_l \exp[i(l+\tfrac{1}{2})\phi]\tilde{\psi}'_l \ , \tag{C1}$$

where $\tilde{\psi}'_l=i^l\tilde{\psi}_l=\tilde{\Psi}(L)$ was given in (6.1a) and (6.7). We pointed out in Sec. VII B 2 that this wave function $\Psi(\phi)$ obeys the boundary condition

$$\Psi(\phi+2\pi)=-\Psi(\phi) \ , \tag{C2}$$

and we showed that this boundary condition leads to half-integral quantization of action for the rotator states.

The alert reader should be suspicious. Could we not drop the $\frac{1}{2}$ from $(l+\frac{1}{2})\phi$ in the exponential in (C1)? If this is done, the wave function

$$\bar{\Psi}(\phi)\equiv(-2\pi i)^{-1/2}\sum_l \exp(il\phi)\tilde{\psi}'_l \tag{C3}$$

would obey a "more reasonable" boundary condition

$$\bar{\Psi}(\phi+2\pi)=\bar{\Psi}(\phi) \ . \tag{C4}$$

Would this not lead to full-integral quantization of action?

In this appendix we show that (1) we *could* define the wave function in angle space as $\bar{\Psi}(\phi)$, given by (C3), instead of $\Psi(\phi)$, defined by (C1), and one consequence of such a definition is the boundary condition (C4). However, (2) another consequence of such a definition is that the pseudodifferential equation governing $\bar{\Psi}(\phi)$ contains terms linear in $\hbar$. Therefore, the semiclassical approximation to the wave function $\bar{\Psi}^{(0)}(\phi)$ is not determined by the classical limit of the operator $\mathcal{H}(L,\phi;\hbar=0)$; it contains also a correction factor coming from $\partial\mathcal{H}/\partial\hbar$. (3) As a consequence of the "classically reasonable" boundary condition (C4) and the "nonclassical" correction factor, the classical action variable must still be quantized in half integers, even for the rotators.

Statement (1) is trivial—one can define $\bar{\Psi}(\phi)$ any way one likes—and the boundary condition (C4) follows directly from (C3). Since $\Psi(\phi)$ satisfies exactly

$$\mathcal{H}\left[-i\hbar\frac{d}{d\phi},\phi;\hbar\right]\Psi(\phi) \equiv\left[\hat{H}\left[-i\hbar\frac{d}{d\phi},\phi;\hbar\right]-E\right]\Psi(\phi)=0 \ , \tag{C5}$$

with $\hat{H}(L,\phi;\hbar)$ defined in (6.10), it follows that

$$\bar{\Psi}(\phi)=\exp(-i\phi/2)\Psi(\phi) \tag{C6}$$

satisfies

$$\mathcal{H}\left[-i\hbar\frac{d}{d\phi},\phi;\hbar\right]e^{i\phi/2}\bar{\Psi}(\phi)=0 \tag{C7a}$$

or

$$\mathcal{H}\left[-i\hbar\frac{d}{d\phi}+\frac{\hbar}{2},\phi;\hbar\right]\bar{\Psi}(\phi)=0 \ . \tag{C7b}$$

As was mentioned at the end of Sec. V A, when the operator depends *explicitly* upon $\hbar$ (other than through $\hat{L}=-i\hbar d/d\phi$), then in calculating the semiclassical approximation $\bar{\Psi}^{(0)}(\phi)$ we may neglect terms in $\mathcal{H}$ that are quadratic or higher order in $\hbar$, but not those that are linear in $\hbar$; terms of nth degree in $\hbar$ in the operator affect terms of $(n-1)$th degree in the solution. From careful study of Ref. 10, pp. 54–59 and 78–85, we find that the semiclassical approximation to a pseudodifferential equation whose operator contains a term linear in $\hbar$ is

$$\bar{\Psi}^{(0)}[\phi(t)]=\left|\frac{d\phi}{dt}\right|^{-1/2}\exp i\int^t\left[\mathcal{L}[\phi(t)]\frac{d\phi}{dt}/\hbar-\frac{\partial\mathcal{H}}{\partial\hbar}\right]dt \ . \tag{C8}$$

Here $\mathcal{L}(\phi)$ is the function representing the level curve of the operator with $\hbar=0$,

$$\mathcal{H}^{(0)}(\mathcal{L}(\phi),\phi)\equiv\mathcal{H}\left[\mathcal{L}(\phi)+\frac{\hbar}{2},\phi;\hbar\right]\Big|_{\hbar=0}=0 \ , \tag{C9a}$$

and $d\phi/dt$ is, as always,

$$\frac{d\phi}{dt}=\frac{\partial\mathcal{H}^{(0)}(L,\phi)}{\partial L}\Big|_{L=\mathcal{L}(\phi)} \ . \tag{C9b}$$

Hence, the first parts of (C7) are the familiar form of the semiclassical approximation

$$\left|\partial\mathcal{H}^{(0)}(L,\phi)/\partial L\right|^{-1/2}_{L=\mathcal{L}(\phi)}\exp\left[i\int^\phi\mathcal{L}(\phi')d\phi'/\hbar\right] \ . \tag{C10}$$

The last term in the exponential in (C8) is a correction factor to the zeroth-order wave function arising from the first-order-in-$\hbar$ terms in the operator. Written out more explicitly, the correction factor is in our case

$$\exp\left[-i\int^t\partial\mathcal{H}\left[L+\frac{\hbar}{2},\phi;\hbar\right]\Big/\partial\hbar\Big|_{\hbar=0,\ L=\mathcal{L}(\phi),\ \phi=\phi(t)}dt\right] \ . \tag{C11}$$

To evaluate this correction factor we take the operator in (C7b) and recall its functional form, which was given in (6.10) and (6.11). The explicit dependence of $\mathcal{H}(L+(\hbar/2),\phi;\hbar)$ upon $\hbar$ arises in two ways: through the $\hbar/2$ in $L+\hbar/2$ and through the $\hbar$ after the sem-

icolon.[26] Through perusal of Eqs. (6.10)–(7.1), we find that the dependence on $\hbar$ after the semicolon involves only terms of order $\hbar^2$ and higher, so this dependence can be neglected. Hence to first degree in $\hbar$ the operator is

$$\mathcal{H}\left[L+\frac{\hbar}{2},\phi;\hbar\right]=h\left[L+\frac{\hbar}{2},\phi\right]-E+O(\hbar^2)\ . \tag{C12}$$

The correction factor (C11) is therefore

$$\exp\left[-i\int^t \frac{\partial h\left[L+\frac{\hbar}{2},\phi\right]}{\partial\hbar}dt\right]$$
$$=\exp\left[-i\int\left[\frac{\partial h(L,\phi)}{\partial L}\right]\left[\frac{1}{2}\right]\left[\frac{dt}{d\phi}\right]d\phi\right],$$

but from (C8b)

$$dt/d\phi=[\partial h(L,\phi)/\partial L]^{-1}\ ,$$

so the correction factor is

$$\exp\left[-\tfrac{1}{2}i\int^\phi d\phi\right]=\exp(-\tfrac{1}{2}i\phi)\ . \tag{C13}$$

Combining (C10) and (C13) we obtain the semiclassical approximation to $\bar{\Psi}(\phi)$,

$$\bar{\Psi}^{(0)}(\phi)=\left|\frac{\partial h(L,\phi)}{\partial L}\right|^{-1/2}_{L=\mathcal{L}(\phi)}\exp\left[i\int^\phi \mathcal{L}(\phi')d\phi'/\hbar\right]$$
$$\times\exp(-\tfrac{1}{2}i\phi)\ . \tag{C14}$$

The first two factors are $\Psi^{(0)}(\phi)$ and the last is the phase change as given in (C6).

Action quantization is obtained by applying the boundary condition (C4), from which it follows that

$$\int_0^{2\pi}\mathcal{L}(\phi)d\phi/\hbar-\pi=2\pi k$$

or

$$\int_0^{2\pi}\mathcal{L}(\phi)d\phi=(k+\tfrac{1}{2})2\pi\hbar\ .$$

We have therefore shown that consistent application of semiclassical formulas (including corrections coming from terms proportional to $\hbar$ in the pseudodifferential operator) leads to consistent results; consistent wave functions are obtained and half-integral quantization is an unambiguous consequence of the theory.

One is now free to select either of two formulations of the theory.

(A) As in the main text, the wave function in angle space is $\Psi(\phi)$ defined in (C1). It has a curious boundary condition (C2), but the semiclassical approximation to $\Psi(\phi)$ is completely determined by the classical Hamiltonian function $h(L,\phi)=\hat{H}(L,\phi;\hbar=0)$.

(B) As in this appendix, the wave function in angle space is $\bar{\Psi}(\phi)$ defined in (C3). It satisfies a more pleasing boundary condition (C4), but its semiclassical approximation cannot be determined solely from the form of the classical Hamiltonian function $h(L,\phi)$; it involves a correction arising from the explicit dependence of the quantum Hamiltonian $\hat{H}(L,\phi;\hbar)$ upon $\hbar$.

We prefer formulation (A).

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Adv. Chem. Phys. **36**, 1 (1977); M. V. Berry, in *Chaotic Behaviour of Deterministic Systems,* Proceedings of the Les Houches Summer School XXXVI, 1981, edited by G. Iooss (North-Holland, Amsterdam, 1983).

[13]R. L. Waterland, J. B. Delos, and M. L. Du, Phys. Rev. A **35**, 5064 (1987).

[14]J. B. Delos, S. K. Knudson, and D. W. Noid, Phys. Rev. Lett. **50**, 579 (1983); Phys. Rev. A **28**, 7 (1983); **30**, 1208 (1984); D. W. Noid, S. K. Knudson, and J. B. Delos, Chem. Phys. Lett. **100**, 367 (1983).

[15]E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1979), p. 48.

[16]Those who would like to find some evidence of quantum chaos here will be disappointed. In the present case, the trajectories are regular, and so are the eigenfunctions and eigenvectors.

[17]H. Goldstein, *Classical Mechanics,* 2nd ed. (Addison-Wesley, Reading, MA., 1980).

[18]One might ask what is the meaning of the "derivative" operator if p is discrete? The answer is simple: it is still defined as

$$i\hbar\frac{d}{dp}\tilde{\Psi}(p)=F_{q\to p}\{q[F^{-1}_{p\to q}\tilde{\Psi}(p)]\}$$

with the slightly revised definition of F's. In this theory, derivatives are *always* defined by Fourier integrals and $\lim([\tilde{\Psi}(p+\varepsilon)-\tilde{\Psi}(p)]/\varepsilon)$ never enters.

[19]This phase change amounts to adding a constant to the quantum analogue of the classical angle coordinate ϕ_2 so that the quantum coordinate and classical coordinate are consistent. The theory is entirely developed in terms of $\tilde{\psi}'_l$, but to compare our calculations to the quantum eigenvectors, we convert back to $\tilde{\psi}_l$ by multiplying by $i^{-l}=\exp(3il\pi/2)$.

[20]At this point in the analysis it is not obvious that this particular definition is better than other alternatives, such as $L=l\hbar$. In Appendix C it will be shown that (6.6a) leads to a pseudodifferential equation having no term linear in $\hbar$, so it is the choice having the property that the lowest-order approximation to the wave function can be calculated from the classical Hamiltonian.

[21]In fact, the characteristic functions $S_j(q),\tilde{S}_k(p)$ and the Maslov indices μ_j, ν_k are quantities that are fundamentally associated with a particular *level curve* rather than with a particular Hamiltonian. Two different Hamiltonians admitting the same level curve have for that curve identical characteristic functions and Maslov indices. It follows that complexities in the form of the Hamiltonian cause no problems in calculating semiclassical approximations.

[22]P. A. M. Dirac, *The Principles of Quantum Mechanics,* 2nd ed. (Oxford University Press, New York, 1935) (3rd ed., 1947, 4th ed., 1967). He used the work "contact" rather than "canonical."

[23]Marcus (Ref. 6) cited Ref. 8(a) as a partial justification of his own more recent work on semiclassical approximations based on action-angle variables. but actually Dirac's attempts to formulate quantum mechanics in action-angle variables were not completely successful, and they do not provide any justification of later work. The formulation given in those early papers is not consistent with the final form of quantum mechanics as Dirac developed it. For example, in his first paper Dirac described a planar hydrogen atom, and he did not obtain a correct description of the angular momentum of the electron. A clear account (focusing on the correct results obtained and deemphasizing the ideas that were later revised) is given by Mehra (see Ref. 24).

[24]J. Mehra and H. Rechenberg, *The Historical Development of Quantum Theory* (Springer, New York, 1982), Vol. 4, see especially p. 175 ff.

[25]C. Chester, B. Friedman, and F. Ursell, Proc. Cambridge Philos. Soc. **53**, 599 (1957).

[26]The partial derivative means that L and ϕ are held fixed.

[27]F. S. Henyey pointed this out in a different context in *The Physics of Phase Space,* edited by Y. S. Kim and W. W. Zachary (Springer, New York, 1987), p. 325. We thank him a helpful conversation.