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Submitted on 1 Jan 1991

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Semiclassical matrix-mechanics.
II. Angular momentum operators

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(Received 27 June 1990, accepted in final form 29 October 1990)

Abstract. — Semiclassical angular momentum matrices are calculated using a new contour-integral formula for matrix-elements WKB spherical harmonic functions are found to be exactly orthonormal with the contour-integral inner-product Matrix-elements obtained from these wave-functions are accurate to about 2% and the matrices obey the commutation relations expected of quantum angular momentum operators The semiclassical wave-functions are related to a superposition of allowed classical orbits and this illustrates the connection to the Feynman path-summation formulation of quantum mechanics for electrons in a spherically symmetric potential.

1. Introduction.

A key step in the development of quantum mechanics was the introduction of matrices to represent dynamical variables such as position \(x\) or momentum \(p\) \([1]\) Matrices appeared as generalizations of Fourier components \(x(\omega), p(\omega)\) used in the classical calculation of radiation from atoms From a modern point of view the matrices \(X, P\) are given by quantum mechanics, and the connection with Fourier components is an approximate or limiting correspondence with quantities defined in the classical theory \([2]\) The correspondence is valid \textit{in the limit} of large quantum numbers for transitions with small changes in quantum number, i.e., for a small subset of matrix-elements near the diagonal One can ask how to interpret the rest of the matrix, or more exactly, how to relate the general matrix-element to a semiclassical quantity

Recently, More and Warren proposed an answer to this question, a semiclassical formula in which the matrix-element is determined by a contour integral over WKB wave-functions \([3]\). This formula has a simple physical interpretation for radiative transitions of atomic electrons, the transition is associated with a second-order orbit intersection which occurs at a uniquely defined radius for transitions having substantial matrix-elements, such as 1s-2p, 2s-3p, 2p-3d. The matrix-element calculated in this way is accurate to a few percent, quite generally, for large or small changes in the quantum numbers The method also works for radial integrals associated with quadrupole transitions and for the photoelectric effect

When applied to the harmonic oscillator, the contour-integral formula gives a surprising result for the first time a semiclassical theory agrees in almost every respect with the
quantum treatment [4]. The semiclassical matrices have the correct commutator $[P, X] = -i\hbar$, diagonalize the Hamiltonian and exactly obey the matrix equations of motion (e.g., $[H, P] \propto X$). However the matrices are not Hermitian and the excellent results described hold only for matrix-elements $F_{n,m}$ with $m > n$.

In this paper the contour integral method is applied to the angular momentum of a nonrelativistic electron in a spherically symmetric potential. The most interesting questions will be: How accurate are the semiclassical results? Do the semiclassical matrices obey the algebraic relations of the Heisenberg matrix mechanics? What is the physical interpretation of semiclassical spherical harmonic functions?

Section 2 outlines the contour-integral method. Semiclassical spherical harmonic functions are discussed in section 3.

Angular momentum matrices $L_x$, $L_y$, $L_z$ are calculated in section 4. They are within 2-3% of the quantum matrices and exactly satisfy the important algebraic relations:

$$[L_x, L_y] = iL_z$$

and cyclic permutations. (1)

The semiclassical matrices $L^2$ and $L_z$ are exactly correct; however $L_x$ and $L_y$ are slightly non-Hermitian. Thus the semiclassical theory agrees with quantum theory for all but one algebraic property of the angular momentum matrices.

These unexpected results are probably related to the fact that the WKB angular functions are exactly orthonormal when their inner product is defined by the contour-integral formula (Sect. 4).

Because the semiclassical matrix elements are analytic functions of the quantum numbers $\ell$, $m$ it is possible to evaluate them with half-integer values such as $\ell = 1/2$ (Sect. 5). Angular momentum matrices obtained this way are exactly the Pauli matrices.

Semiclassical angular functions $Y_{\ell m}(\theta, \phi)$ can be combined with WKB radial functions $R_{nl}(r)$ to make a three-dimensional wave-function $\psi_{n\ell m}(r)$. This function has a direct geometric interpretation related to Feynman’s quantum mechanics: for an electron moving in a spherically symmetric potential the semiclassical wavefunction is obtained by superposition of allowed classical orbits of a family such that one orbit passes through each point in space (Sect 6).

Orbits of this family are generated by rotating a single orbit through various angles; the phase assigned to each orbit is determined by the rotation angle. This construction gives a detailed connection between classical paths, rotational symmetry and the WKB wavefunction.

The overall goal of this work is to develop a complete semiclassical theory which will describe the entire range of phenomena encountered in quantum mechanics, as far as possible. Of course many aspects of the desired theory are already known [5, 6]. In searching for the rules of the semiclassical theory we are assisted by comparisons with the quantum theory. At the same time, the semiclassical theory also gives a better intuitive understanding of quantum theory.

2. Contour-integral formulation.

The usual semiclassical theory is based upon the Bohr-Sommerfeld quantization rule for one-dimensional motion,

$$\oint_{C_n} p_n(x) \, dx = 2\pi\hbar \left( n + \frac{1}{2} \right)$$

(2)
where \( p_n(x) \) = momentum \( \propto [E_n - U(x)]^{1/2} \) with \( E_n \) = energy eigenvalue, \( x \) is a coordinate, allowed to be a complex number, and \( U(x) \) is the potential, assumed to be an analytic function of \( x \). The positive and negative signs of \( p_n(x) \) correspond to the two directions of motion in the \( \pm x \)-direction; mathematically \( p_n(x) \) has a branch-cut along the real \( x \)-axis in the classically allowed range where \( E_n > U(x) \). Assuming this allowed range is a single interval, \( x_{\text{min}} \leq x \leq x_{\text{max}} \), \( p_n(x) \) will be positive and real just above the branch-cut and the contour \( C_n \) encircles the allowed range once in the clockwise sense. With these conventions, the Bohr-Sommerfeld rule is a contour integral.

The WKB travelling wave

\[
\psi_n^\pm(x) = \frac{a_n}{\sqrt{p_n(x)}} e^{\pm \frac{i}{\hbar} \int_{x_{\text{min}}}^x p_n(x') \, dx'}
\]

(3)

is typically an analytic function of \( x \) having a branch-cut along the allowed range \( x_{\text{min}} \leq x \leq x_{\text{max}} \). Both \( p_n(x) \), \( \psi_n^\pm(x) \) may be singular at the singularities of \( U(x) \). The prefactor \( 1/\sqrt{p_n(x)} \) and the action \( \int p(x') \, dx' \) have additional branch-cuts, but these cancel in the wave-function because of equation (2). Specific analytic properties of the WKB spherical harmonic functions are summarized in Appendix B.

One can construct a real wave-function \( \psi_n(x) \) defined for real \( x \) by the equation

\[
\psi_n(x) = \lim_{\epsilon \to 0^+} \text{Re} \left[ \psi_n^+(x + i \epsilon) + \psi_n^-(x + i \epsilon) \right]
\]

(4)

This function oscillates in the allowed range \( x_{\text{min}} \leq x \leq x_{\text{max}} \) and has the correct bounded behavior in the forbidden ranges. It gives a good approximation to the quantum wave-function aside from (weak) singularities at the turning points \( x_{\text{min}} \), \( x_{\text{max}} \). Equation (4) can be used in place of the usual connection formulas.

The matrix-element of a dynamical variable \( f(x, p) \) will be calculated by the contour-integral formula [3]

\[
F_{nm} = \int_C \psi_n^-(x) f(x, \hat{p}) \psi_m^+(x) \, dx
\]

(5)

where \( C \) encloses the allowed range for both states \( n, m \) in the clockwise sense. Here \( f(x, \hat{p}) \) is the quantum operator expression, but equation (5) is semiclassical because the WKB wave-functions are explicit combinations of classical momentum and action functions.

Although equation (5) is similar to the quantum formula for a matrix element there are also specific differences. The quantum formula is not a contour integral and contains additional terms associated with the integrals of \( \psi_n^+ f \psi_m^-, \psi_n^- f \psi_m^- \). The additional terms cause oscillatory (interference) modulation of the probability density and their omission can be called a restricted interference approximation. In Appendix A it is shown that equation (5) converges with the quantum expression in the semiclassical limit where the oscillatory integrals become small. The best agreement with the quantum theory is obtained when the \( \psi^- \) wave is taken for the state having the smaller allowed range of classical motion.

Equation (5) gives satisfactory results for matrix-elements of several systems [3,4] and in section 4 we will see that it succeeds again for the spherical harmonic functions. An extension to three-dimensional systems is indicated in section 6 (see especially Eq (78) below).

Temporarily adopting equation (5), one can ask whether it forms the basis for a consistent
semiclassical theory. For example, for the special case \( f = 1 \), equation (5) implies a contour-integral inner-product of semiclassical wave-functions,

\[
U_{n,m} = \oint \psi_n^-(x) \psi_m^+(x) \, dx . \tag{6}
\]

In part I of this paper, equation (6) was evaluated with WKB wave-functions for the harmonic oscillator with the unexpected result \( U_{n'n'} = \delta_{nn'} \) for all states \( n' \neq n \). For radial motion in the Coulomb potential and also in a screened Coulomb potential, it was found that integrals \( U_{n',\ell}^\ell \) were \( \delta_{nn'} + O(10^{-3}) \) [3].

With the usual inner product, WKB wave-functions are not even approximately orthonormal and therefore these results are evidence that equations (5), (6) can give a more satisfactory semiclassical theory. For the WKB spherical harmonic functions, the orthonormality relation is exact, \( U_{\ell\ell}^{\ell'} = \delta_{\ell \ell'} \) for all \( \ell' \neq \ell \) (see Eq (30) below).

\( U_{nn} = 1 \) corresponds to normalizing the wave-function in terms of the classical round-trip travel-time, this is a well-known normalization of WKB functions [6]. However this normalization agrees with the quantum normalization, \( \int |\psi_n|^2 \, dx = 1 \), only in the semiclassical limit.

Another special case of equation (5) is \( n = m \), the semiclassical expectation value

\[
\bar{f}_n = \oint \psi_n^- f \psi_n^+ \, dx \tag{7}
\]

When the quantity \( f \) is a function \( f(x) \), this is simply

\[
\bar{f}_n = |a_n|^2 \oint \frac{f(x)}{p_n(x)} \, dx . \tag{8}
\]

The right-hand side is the classical time-average of \( f \), which is usually a good approximation to the quantum expectation-value even for low quantum-numbers. For example, results from equation (8) are exactly correct for the expectation values \( \langle 1/r \rangle \), \( \langle 1/r^2 \rangle \) for electrons in a Coulomb potential [7].

We now compare equation (5) to the Heisenberg correspondence principle. In the limit of large and nearly-equal quantum numbers, equation (5) gives for the case \( f = f(x) \)

\[
F_{nm} = |a|^2 \oint \frac{dx}{p(x)} f(x) \, e^{-i(E_n - E_m) \int \frac{dp}{\hbar E} dx'/\hbar} = |a|^2 \oint \frac{dx}{p(x)} f(x) \, e^{-i\omega(t)} \propto \int f(x(t)) \, e^{-i\omega t} \, dt . \tag{9}
\]

Here quantities without a subscript are evaluated on an average orbit (e.g., \( p(x) \equiv p_n(x) \equiv p_m(x) \) for large and nearly-equal \( n, m \)). This is a well-known calculation [6]. In order to derive equation (9) it is necessary to omit the oscillatory terms \( \psi_n^- \, f \psi_n^+ \), \( \psi_n^- \, f \psi_m^+ \) and these are already omitted from equation (5) so \( F_{nm} \) automatically reduces to the Fourier component of \( f \) for the case \( |n - m| \ll n \). In general when \( |n - m| \) is not small, one cannot speak of Fourier components because the two orbits are too different to be approximated by a single space-time trajectory.
This is especially evident in calculations of the photoelectric matrix-element where one orbit is bound and the other extends out to infinite distance so there is no meaningful average trajectory. Equation (5) still gives good results for these matrix-elements [3].

Thus equation (5) does not disagree with the Heisenberg correspondence relation, but rather generalizes it by giving a semiclassical approximation to the entire matrix of $f$.

Equation (5) for the matrix-elements is a step toward a complete semiclassical theory, but many questions remain concerning the interpretation and the generalization to three-dimensional systems and/or time-dependent atomic dynamics. With some effort, one can employ equations (5)-(8) to derive solutions for certain specific three-dimensional and time-dependent systems. A fresh approach to the more general case is given by the orbit superposition method discussed in section 6.


Semiclassical spherical harmonic functions are easily constructed by the WKB method [6, 8, 9]. We sketch this calculation in order to draw attention to a few important technical points.

The associated Legendre equation may be written

$$\frac{d}{dx} \left[ (1 - x^2) \frac{d\Theta}{dx} \right] + \left( \Lambda - \frac{m^2}{1 - x^2} \right) \Theta = 0.$$  \hspace{1cm} (10)

In quantum mechanics, this equation arises by separation of variables and the eigenvalue $\Lambda$ is shared with the radial equation. The quantum eigenvalue is $\Lambda = \ell (\ell + 1)$, where $\ell$ is the (integer) angular momentum. However in the semiclassical theory it is normal to assume

$$\Lambda = \left( \ell + \frac{1}{2} \right)^2$$ \hspace{1cm} (11)

where $\ell$ is an integer. With this choice, the WKB wave-functions $\Theta_{\ell m}$ turn out to be single-valued analytic functions, a strict requirement for the method of this paper. The same separation constant, equation (11), is normally used in the WKB solution of the radial equation [3, 6-9]. Surprisingly, the semiclassical matrix $L^2$ has the quantum eigenvalues $\ell (\ell + 1)$ despite the use of equation (11) in the wave functions (Sect 4). For now we consider positive integer $m(0 < m \leq \ell)$. For a solution $\Theta$ of the form $\Theta = \exp[i \sigma(x)]$, equation (10) becomes

$$\left( 1 - x^2 \right) \left[ \frac{d\sigma}{dx} \right]^2 - \left( \left( \ell + \frac{1}{2} \right)^2 - \frac{m^2}{1 - x^2} \right) = i \frac{d}{dx} \left[ (1 - x^2) \frac{d\sigma}{dx} \right].$$ \hspace{1cm} (12)

For large quantum numbers the right-hand side is relatively small; when it is omitted one has the zero-order equation for $\sigma$:

$$\left( 1 - x^2 \right) \left[ \frac{d\sigma_0}{dx} \right]^2 = \left( \ell + \frac{1}{2} \right)^2 - \frac{m^2}{1 - x^2}.$$ \hspace{1cm} (13)

The right-hand side of equation (12) is equated to the first-order term on the left to give

$$\sigma_{(1)} = \frac{i}{2} \log \left( 1 - x^2 \right) \frac{d\sigma_0}{dx}.$$ \hspace{1cm} (14)

This is the usual WKB technique.

Planck's constant does not appear in equations (10)-(14). In physical terms the expansion parameter is $1/(\ell + 1/2)$ and therefore it is necessary to carefully inspect the results for small
Mathematically the expansion is not uniformly valid because of singular behavior at 
\( x = \pm 1 \) and at the zeroes of \( d\sigma_0/dx \).

The zeroes of \( d\sigma_0/dx \) are *turning points*, located at 
\[
x_0 = \sqrt{1 - \frac{m^2}{(\ell + \frac{1}{2})^2}}.
\]

The classical motion is confined to the region \(|x| = |\cos \theta| \leq x_0\), that is, excluded from a cone around the \( \pm z \)-axis. The physical significance of this restriction becomes clear in section 6.

It is useful to write
\[
q(x) = \sqrt{x_0^2 - x^2}
\]
(16)

With this notation equation (13) becomes
\[
\frac{d\sigma_0}{dx} = \left( \ell + \frac{1}{2} \right) \frac{q(x)}{1 - x^2}.
\]
(17)

Equation (17) is explicitly solved in terms of functions \( \xi(x) \), \( \eta(x) \) defined by
\[
\sin \xi = \frac{x}{x_0}, \quad \cos \xi = \frac{q(x)}{x_0} \quad \sin \eta = \frac{x}{x_0} \quad \cos \eta = \frac{q(x)}{x_0} \quad (19)
\]
The definitions are appropriate because the trigonometric relations \( \sin^2 \theta + \cos^2 \theta = 1 \) are obeyed for all \( x \). The boundary values of \( \xi \), \( \eta \) are
\[
\xi(\pm x_0) = \eta(\pm x_0) = \pm \frac{\pi}{2}.
\]
(20)

The derivatives are
\[
\frac{d\xi}{dx} = \frac{1}{q(x)}; \quad \frac{d\eta}{dx} = \frac{\sqrt{1 - x_0^2}}{(1 - x^2) q(x)} \quad (21)
\]
For either sign of \( m \) it follows that
\[
\sigma_0(x) = \left( \ell + \frac{1}{2} \right) \xi(x) - |m| \eta(x)
\]
(22)

At this point, equation (22) appears to be a mathematical relation having little intuitive content. In section 6 we will see that it has a simple geometric interpretation; in effect it is the transformation of a simple wave \( \exp(i(\ell + 1/2) y) \) defined in a rotated coordinate system.

We combine equations (14)-(22) to define the semiclassical travelling-wave for all \( m(-\ell \leq m \leq \ell) \) by
\[
\Theta_{\ell m}(x) = \frac{e^{i\ell m}}{\sqrt{q(x)}} \left( \frac{q(x) + i x}{x_0} \right)^{\pm \left( \ell + \frac{1}{2} \right)} \left( \frac{q(x) - i x \sqrt{1 - x_0^2}}{x_0 \sqrt{1 - x^2}} \right)^{\pm |m|}
\]
(23)
The right-hand side depends on the sign of $m$ only through the coefficient $c_{\ell m}$, which is taken to be

$$c_{\ell m} = \frac{1}{\sqrt{2 \pi}} e^{\pi i (\ell + m) \pi / 2}$$

(Equation 24)

Equations (23), (24) imply

$$\Theta_{\ell,-m}^f (x) = (-1)^m \Theta_{\ell,m}^f (x) .$$

The magnitude of $c_{\ell m}$ is chosen to normalize the functions with the inner product of equation (6). The phase agrees with a well-known definition of the spherical harmonic functions [10, 11].

The formulas simplify for $m = 0$. The appropriate special case of equation (23) may be written

$$P^f (\cos \theta) = \frac{1}{\sqrt{\ell + 1/2}} \Theta_{\ell,0}^f (\cos \theta) = \frac{\exp \pm i \left( \left( \ell + \frac{1}{2} \right) \theta - \frac{\pi}{4} \right)}{\sqrt{2 \pi \left( \ell + \frac{1}{2} \right) \sin \theta}}$$

(Equation 26)

These are travelling waves; to compare to the Legendre polynomial we form

$$P^f = \text{Re} \left[ P^f + P^\bar{f} \right].$$

(Equation 27)

Comparisons are given in figure 1, the agreement is good away from the turning points which occur at $x = \pm 1$. Equation (27) is a known asymptotic formula for the Legendre function [12].

The WKB approximation to the spherical harmonic function is obtained from

$$Y_{\ell m}^f (\theta, \phi) = \text{Re} \left[ \Theta_{\ell m}^f + \Theta_{\ell m}^{\bar{f}} \right] \Phi_m (\phi) = \text{Re} \left[ \Theta_{\ell m}^f + \Theta_{\ell m}^{\bar{f}} \right] \frac{e^{im\phi}}{\sqrt{2 \pi}}$$

(Equation 28)

Numerical comparisons show that equation (28) is a good approximation apart from the singularity at the turning points $\pm x_0$. A sample comparison is given in table I.

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$m$</th>
<th>WKB</th>
<th>Exact</th>
<th>Difference</th>
</tr>
</thead>
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<td>0.3184</td>
<td>0.2821</td>
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</tr>
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<td>0.0244</td>
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</tr>
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<td>-0.3451</td>
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</tr>
<tr>
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<td>1.0%</td>
</tr>
<tr>
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<td>1</td>
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<tr>
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<td>2</td>
<td>0.4105</td>
<td>0.3853</td>
<td>6.5%</td>
</tr>
</tbody>
</table>


In this section the contour-integral formula is used to calculate the inner product of WKB wave-functions and matrix-elements of $x = \cos \theta$. Angular momentum matrices $L_x$, $L_y$, $L_z$ are constructed and their algebraic properties examined.
The semiclassical functions $Y_{l}^{m}$ are obviously orthonormal with respect to the index $m$ because the $\phi$-dependence is a simple factor $\exp(im \phi)$ as in quantum mechanics. Thus it is only necessary to calculate the inner product of functions having the same $m$

$$U_{l}^{m} = \int \Theta_{l}^{m}(x) \Theta_{l}^{m+}(x) \, dx \quad \text{eq (29)}$$

From equation (23) we see that the factor $\sqrt{(1-x^2)}$ appears with powers $-|m|, +|m|$ in $\Theta^{+}, \Theta^{-}$ respectively and therefore cancels in equation (29). This means that the integrand is analytic except for branch-cuts along the allowed ranges $(-x_0, x_0)$ and
\((- \bar{x}_0, \bar{x}_0)\), where \(x_0, \bar{x}_0\) are turning points for quantum numbers \((\ell, m)\) and \((\ell', m)\). In particular the integrand of equation (29) has no branch-points at \(x = \pm 1\). Therefore the contour of integration may be displaced to large \(|x|\) and the integral is easily evaluated by residues, giving:

\[
U_{\ell m}^{\ell' m'} = \delta_{\ell \ell'} \quad \text{for all } \ell' \geq \ell
\]

The diagonal value \((U_{\ell m}^{\ell m})\) is unity because of the normalization chosen in equation (24). The surprise is the orthogonality for all pairs \(\ell, \ell'\) with \(\ell < \ell'\).

The calculation can be repeated for the special case \(m = 0\) where the simpler functional form of equation (26) gives an elementary trigonometric integral

\[
\int P_{\ell} (x) P_{\ell'} (x) \, dx = \frac{2}{2 \ell + 1} \delta_{\ell \ell'}.
\]

This is exactly the orthonormality relation for Legendre polynomials. It would be difficult to obtain anything like this result for WKB functions without use of the contour integral inner product.

Next we examine the matrix-element of \(x = \cos \theta\) between states \((\ell, m)\) and \((\ell', m)\). Contour integration shows this matrix-element is zero for \(\ell = \ell'\) and for all \(\ell' > \ell + 1\) This means the selection rules agree exactly with quantum mechanics. For \(\ell' = \ell + 1\) we find

\[
\langle \cos \theta \rangle_{\ell + 1, m}^{\ell + m} = \frac{1}{2} \bar{x}_0 \left( \frac{\bar{x}_0}{\bar{x}_0} \right)^{\frac{1}{2} - |m|} \left( \frac{1 + \sqrt{1 - \bar{x}_0^2}}{1 + \sqrt{1 - \bar{x}_0^2}} \right)^{|m|}
\]

Table II shows that this agrees closely with the quantum matrix-element even for small quantum numbers.

Next we form matrix-elements of the angular-momentum operators \(L_x, L_y, L_z\), using the usual representations

\[
\hat{L}_z = -i \frac{\partial}{\partial \phi}, \quad \hat{L}_z = \hat{L}_x \pm \hat{L}_y = e^{\pm i \phi} \left( \pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right)
\]

Table II — Test of equation (32) for the matrix-elements of \(x = \cos \theta\). QM and SC denote quantum and semiclassical matrix-elements.
Substituting \( x = \cos \theta \) and performing the integration over the angle \( \phi \), we have

\[
\langle \ell, m+1 \mid \hat{L}_+ \mid \ell, m \rangle = \int \Theta_{\ell,m+1}^2 \left( -\sqrt{1-x^2} \frac{d}{dx} \frac{mx}{\sqrt{1-x^2}} \right) \Theta_{\ell,m}^2 \, dx
\]  
(34)

For \( m \geq 0 \), we use the wave \( \Theta_{\ell,m+1} \) which has the smaller allowed range in agreement with the rule developed in Appendix A. For \( m < 0 \), \( \Theta_{\ell,m} \) has the smaller allowed range, so we take \( \Theta_{\ell,m} \) with \( \Theta_{\ell,m+1} \).

To calculate matrix-elements of \( \hat{L}_- \) we form the Hermitian adjoint of \( \hat{L}_+ \)

\[
\langle \ell, m \mid \hat{L}_- \mid \ell, m+1 \rangle = \int \Theta_{\ell,m}^2 \left( \sqrt{1-x^2} \frac{d}{dx} \frac{(m+1)x}{\sqrt{1-x^2}} \right) \Theta_{\ell,m+1}^2 \, dx
\]  
(35)

In equation (35) the waves chosen are \( \Theta_{\ell,m} \) and \( \Theta_{\ell,m+1} \) for \( m \geq 0 \) and vice versa for \( m' < 0 \). In this case the \((-\)) wave is not associated with the shorter branch-cut, this agrees with the procedure followed in part I of this paper and leads to interesting but non-Hermitian matrices.

Calculation of these matrix-elements is a straightforward contour integration. The contour may be displaced to large \( |x| \) because the factors \( \sqrt{1-x^2} \) cancel and one must simply extract the residue of the integrand at \( |x| \to \infty \).

The results are simplified by defining

\[
\Gamma = \frac{x_0^{\frac{1}{2}+\frac{1}{2} \pm m}}{(1+\sqrt{1-x_0^2})^{\frac{1}{2}+\frac{1}{2} \pm m+1}} \]  
(36)

Then we have

\[
(\hat{L}_+)_{\ell,m+1}^\ell = \begin{cases} \Gamma (\ell + m + 1) & m \geq 0 \\ (\ell - m) \Gamma & m < 0 \end{cases}
\]  
(37)

\[
(\hat{L}_-)_{\ell,m+1}^\ell = \begin{cases} (\ell - m) \Gamma & m \geq 0 \\ (\ell + m + 1) \Gamma & m < 0 \end{cases}
\]  
(38)

where \( x, x_0 \) are defined with respect to the pairs \( (\ell, m) \) and \( (\ell, m+1) \)

It is useful to write out these matrices for \( \ell = 1, 2 \) (Tabs III, IV)

| Table III — Semiclassical angular momentum matrices for \( \ell = 1 \) |
|------------------|------------------|------------------|
| \( L_x \)       | \[ \begin{pmatrix} 0.000 & 0.719 & 0.000 \\ 0.695 & 0.000 & 0.719 \\ 0.000 & 0.695 & 0.000 \end{pmatrix} \] |
| \( L_y \)       | \[ \begin{pmatrix} 0.000 & 0.719 & 0.000 \\ -0.695 & 0.000 & 0.719 \\ 0.000 & -0.695 & 0.000 \end{pmatrix} \] |
| \( L_z \)       | \[ \begin{pmatrix} -1.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 1.000 \\ 0.000 & 0.000 & 0.000 \end{pmatrix} \] |
Table IV. — *Semiclassical angular momentum matrices for L = 2*

<table>
<thead>
<tr>
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The most important feature of these matrices is their overall accuracy: each entry is within 2% of the corresponding quantum value. However the matrices $L_x$, $L_y$ are *non-Hermitian*, a typical result of calculations based on equation (5).

The matrices for $L_x$, $L_y$ have the property that if the product is formed between matrix-elements on opposite sides of the diagonal, the result is the square of the quantum matrix-element. This symmetry property holds also for the harmonic oscillator [4].

Given these semiclassical matrices $L_x$, $L_y$, $L_z$ an immediate question is whether they obey algebraic conditions which parallel the laws of the Heisenberg matrix mechanics.

The matrices given in tables III, IV exactly satisfy the following algebraic relations:

\[
[L_x, L_y] = iL_z, \quad [L_y, L_z] = iL_x, \quad [L_z, L_x] = iL_y
\]

\[L_z = m\delta_{nn},\]  \hspace{2cm} (39)

\[L^2 = L_x^2 + L_y^2 + L_z^2 = \ell (\ell + 1) \delta_{nn},\]  \hspace{2cm} (40)

These are the algebraic relations obeyed by the quantum angular momentum matrices. Equation (41) is especially surprising in view of equation (11).

Thus the contour-integral semiclassical theory reproduces the main results of the quantum treatment. The matrix-elements of $x = \cos \theta$ obey the quantum selection-rules. The semiclassical matrices $L$ have the correct eigenvalues, exactly obey the commutation relations but are non-Hermitian and inexact by a few percent.

Since the situation closely parallels that found for the harmonic oscillator one might suspect there is a general proof of these algebraic relations, perhaps based on the classical Poisson brackets. We have not found such a proof and in fact there is a sort of counter example provided by the radial matrix-elements for the Coulomb potential, which only approximately satisfy the desired algebraic relations. Perhaps the most general conclusion is that semiclassical results are good approximations containing most features of the quantum picture.

The wave-function defined by equation (23) is a single-valued function of $x$ when $\ell$ and $m$ are integers This may be tested by following the changes in $\Theta_{\ell m}^\pm$ when $x$ varies around a contour that just surrounds the allowed range ($-x_0, x_0$)

Surprisingly, $\Theta_{\ell m}^\pm$ is also single-valued when $\ell = 1/2, m = \pm 1/2$ This means that the functions $\Theta_{\ell m}^\pm$ can be used to calculate matrix-elements for a spin-1/2 system

For this calculation we substitute $x_0 = \bar{x}_0 = \sqrt{3}/4$ in equations (36)-(38). The results are

$$L_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$L_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$L_z = \frac{1}{2} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

Despite this nice result the calculation does not give an intuitive picture or mechanical model for spin phenomena That is more likely to be found by the method of section 6.


This section examines the meaning of WKB wave-functions and the connection between classical paths and quantum eigenstates The discussion assembles a number of elementary or known results [9, 13-15] and interprets them in terms of the superposition of classical paths [16]

The emphasis here is on the construction of semiclassical wave-functions rather than eigenvalue spectra or space-time Green's functions [17, 18, 19] The construction incorporates the EBK quantization rule [14, 15]

There are three ways to obtain the three-dimensional semiclassical wave-function first, it is a product of one-dimensional WKB functions for the separate coordinates $(r, \theta, \phi)$; second, it is the result of rotating a single classical orbit to generate a space-filling family of copies of the orbit, with each copy assigned a phase determined by the rotation angles; and third it is constructed by invariant vector-integration of the momentum field $\mathbf{p}(\mathbf{r})$ defined by the family of orbits.

For an electron moving in a spherically symmetric atomic potential $V(r)$ with energy $E_{n\ell}$, the product wave-function is

$$\psi_{n\ell m}(r) = \frac{1}{r} R_{n\ell}(r) \Theta_{\ell m}^\pm(\cos \theta) \Phi_m(\phi)$$

The radial wave-function $R_{n\ell}$ is

$$R_{n\ell}(r) = \frac{a_{n\ell}}{\sqrt{p_{n\ell}(r)}} e^{\pm i \int p_{n\ell}(r') \, dr'/\hbar + \pi/4}$$

The radial momentum $p_{n\ell}(r) = r \cdot \mathbf{p}/|\mathbf{r}|$ is

$$p_{n\ell}(r) = \sqrt{2m \left( E_{n\ell} + eV(r) - \frac{\hbar^2 L^2}{2mr^2} \right)}$$
The angular wave-function is taken from equation (28) of section 3. The angular momentum quantum numbers are

\[ L = \left( \ell + \frac{1}{2} \right) \]
\[ L_z = m \]  

(46)

(47)

The phase of the product wave-function in equation (43) is

\[ \frac{1}{\hbar} S = \frac{1}{\hbar} \int p_{nl}(r) \, dr + (L \xi - L_z \eta) + L_z \phi \]  

(48)

The two terms in parenthesis come from equation (22) for the phase of \( \Theta_{lm}^{\tau} \). Analysis of the classical orbits will now make clear the meaning of equation (48).

Until the work of Feynman [16] it was widely believed that one could not understand quantum states in terms of classical orbits, especially states of small quantum numbers such as the 1s, 2s, 2p states. Indeed, there are several important differences between classical motion along an orbit and the quantum state having the same energy and angular momentum. These differences include some of the more difficult or unique features of the quantum theory.

i) The classical motion is localized along a trajectory, \( r = r_0(t) \), leading to a time-averaged probability density of the form

\[ \rho(r) \propto \int \delta(r - r_0(t)) \, dt \]  

(49)

This function is nonzero along a curve or at most a planar surface. If \( \rho(r) \) were regarded as the square of some wave-function, in an effort to reconcile classical and quantum descriptions, that wave-function would have large (or infinite) derivatives perpendicular to the classical trajectory, and therefore a large (or infinite) kinetic energy computed by the quantum formula. This is quite unlike the quantum state, which gives a smoothly varying probability density and a kinetic energy close to the classical value.

ii) The classical electron is accelerated, especially when it passes close to the nucleus, and this leads to a fluctuating or time-dependent electric current. However the current vector calculated from a quantum energy eigenstate is time-independent.

iii) While the classical orbit has sharply defined values for all three components of the angular momentum vector \( L \), the quantum state does not. Typically only \( L_z \) and \( L_z \) have sharply defined values.

These important differences are reconciled if the quantum state is compared to a superposition of classical particles on a family of classical paths. The family \( F \) consists of allowed orbits such that one orbit traverses each point \( r \) in the region permitted by the conservation laws, and the superposition includes copies of the electron distributed along each orbit (see Fig 4).

i) Because orbits of the family pass through each point in the permitted volume, there is a probability for a copy of the electron to be at any position and hence a smooth probability density. As will be seen below, the quantum and classical kinetic energies are nearly equal.

ii) The current vector associated with the superposition of classical particles is time-independent because the copies of the electron flow in a smooth and laminar fashion around their orbits. As one copy moves away from the nucleus, another approaches and there is only a steady average current \( J(r) \).
Fig 2 — An allowed classical orbit located in the $x$-$y$ plane. The point of largest radius is located by the angle $\alpha$. The angle $\gamma(t)$ locates the current point on the orbit. The orbit is taken to be an ellipse (corresponding to the Coulomb potential) for simplicity but the results apply to any central-force motion.

Fig 3. — The orbit of figure 2 has been tilted through an angle $\theta_\circ$ and rotated (about $z$) by an additional angle $\beta$. 
iii) The family $F(E, L^2, L_z)$ fills space, i.e., one orbit of the family traverses each point $r$ in the permitted region. However one cannot not construct a space-filling superposition of paths without allowing two components of $L$ to vary (see below near Eq. (76)).

The possibility of constructing a precise picture of this type is best seen by working through some examples. We thereby obtain simple semiclassical pictures for various known solutions of Schroedinger’s equation, together with intuitive derivations of many formulas of quantum theory.

In this paper we consider the bound states of an electron in a spherically symmetric potential. First we construct a family $F(E, L^2, L_z)$ of classical orbits all having the same energy $E_m (< 0)$, total angular momentum $L = |L|$, and $z$-component $L_z$.

The family is not uniquely determined by the classical mechanics in this case, because of the degeneracy of the spherically symmetric system.

The discussion and figures refer to elliptic orbits in a Coulomb potential (Figs 2, 3) This case is chosen for simplicity of presentation but the method is not limited to that case. However, the Coulomb system has additional degeneracy (or symmetry) which plays no essential role in the following discussion.
We begin with an orbit in the $x$-$y$ plane, with angular momentum vector along $z$, and rotated in the $x$-$y$ plane so that the point of largest radius $r_{\text{max}}$ occurs at an angle $\alpha$ from the $x$-axis. The angle $\gamma(t)$ locates the current point on the orbit, relative to the $x$-axis. The orbit is given by (Fig. 2)

\begin{align*}
  x &= r(\gamma - \alpha) \cos \gamma \\
  y &= r(\gamma - \alpha) \sin \gamma \\
  z &= 0
\end{align*}

The function $r(\gamma - \alpha)$ is obtained by solution of the classical equations of motion, as is the time-dependence of $\gamma(t)$. For the Coulomb potential,

\begin{equation}
  r = \frac{r_n(1 - \varepsilon^2)}{1 - \varepsilon \cos (\gamma - \alpha)}
\end{equation}

\begin{equation}
  \frac{d\gamma}{dt} = \frac{hL}{mr^2}
\end{equation}

Here $r_n$ and $\varepsilon$ are constant for orbits of the family $F$. Equation (52) applies for any central-force potential.

We rotate the orbit by an angle $\theta_0$ around the $x$-axis, so that the angular momentum vector becomes

\begin{equation}
  \mathbf{L} = (0, -L \sin \theta_0, L \cos \theta_0)
\end{equation}

and then rotate by an angle $\beta$ around the $z$-axis, giving the final angular momentum vector

\begin{equation}
  \mathbf{L} = (L \sin \theta_0 \sin \beta, -L \sin \theta_0 \cos \beta, L \cos \theta_0)
\end{equation}

The angle $\theta_0$ is constant,

\begin{equation}
  \cos \theta_0 = \frac{L_z}{L}
\end{equation}

The rotations transform equation (50) into an orbit equation of the form

\begin{equation}
  r = r_0(E, L^2, L_z, \alpha, \beta, \gamma(t))\tag{56}
\end{equation}

The set of orbits defined by varying $\alpha$ and $\beta$ define a two parameter family of orbits, together with the time-dependence of $\gamma(t)$ this family covers the permitted region of three-dimensional space. This is verified by forming the Jacobian derivative,

\begin{equation}
  \frac{\partial (x, y, z)}{\partial (\alpha, \beta, \gamma)} = \frac{\partial x_0}{\partial \alpha} \times \frac{\partial y_0}{\partial \beta} = -r^2 \frac{dr}{d\gamma} \cos \gamma \sin \theta_0
\end{equation}

This Jacobian is nonzero except at isolated points. Equation (56) can be written in spherical polar coordinates $(r, \theta, \phi)$ with the result

\begin{equation}
  r = r(\gamma - \alpha)\tag{58}
\end{equation}

\begin{equation}
  \cos \theta = \sin \gamma \sin \theta_0\tag{59}
\end{equation}

\begin{equation}
  \sin \theta e^{\pm i\phi} = (\cos \gamma \pm i \sin \gamma \cos \theta_0) e^{\pm i\beta}\tag{60}
\end{equation}

The momentum $\mathbf{p}$ is

\begin{equation}
  \mathbf{p}(E, L^2, L_z, \alpha, \beta, \gamma(t)) = m \frac{dr_0}{dt}\tag{61}
\end{equation}
With these equations we can clarify the WKB spherical harmonic functions of section 3. Comparing equations (15) and (55) shows

$$x_0 = \sin \theta_0$$

Comparing equation (18) to equation (59) gives $\sin \theta = \sin \xi$, or

$$\xi = \gamma$$

There is also another solution, $\xi = \pi - \gamma$, used in analysis of $\Theta^-$. Equation (19) is compared to equation (60) to give $\sin \eta = \sin (\phi - \beta)$ or

$$\eta = \phi - \beta$$

Again there is a second solution which is used with the $-$ waves.

Now equation (48) for the phase of the wave-function can be simplified by returning to the original planar orbit and examining a line integral

$$S_{\text{int}} = \int \mathbf{p} \cdot d\mathbf{r} = \int p_{nf}(r) \, dr + \hbar L(\gamma - \alpha)$$

$S_{\text{int}}$ is a vector line integral taken along the orbit, which we simplify by using plane polar coordinates $(r, \theta)$ in which $p_r = p_{nf}$ and $p_\theta = \hbar |L|/r$. For simplicity we neglect constants in the phase. Comparing equations (48) and (65) we find that terms in $\gamma$ and $\phi$ cancel so the phase of the wave-function $\psi_{nfm}^+$ is

$$\frac{1}{\hbar} S = \frac{1}{\hbar} S_{\text{int}} + L\alpha + L_z\beta$$

From its geometric definition it is evident that $S_{\text{int}}$ is an intrinsic or invariant phase due to the time-dependent motion along the orbit. The other terms are constant for any one orbit and give the relative phase of the orbit in the superposition.

Evidently the rule generating these relative phases is that in turning the orbit through an angle $\Delta \theta$ about an axis $\mathbf{n}$, the phase changes by $\mathbf{n} \cdot \mathbf{L} \cdot \Delta \theta$.

Although this rule is simple, it applies only because we have chosen a set of configurations such that the rotations (by $\alpha$ and $\beta$) linking them form an Abelian group.

This method can be used when there is a continuous symmetry which generates new solutions of the classical equations of motion from a given one; the symmetry produces a family of orbits which fill space and the phase carried by the transformation determines a three-dimensional wave-function. The wave-function has a prefactor determined by the continuity equation for the flow of copies of the electron along their orbits (see Eq (73) below).

The procedure could be somewhat simplified in this case by using the fact that $\alpha$, $\beta$, $\gamma$ form angle variables conjugate to $L^2$, $L_z$ and $E$. In other, more degenerate systems, there are acceptable families (and semiclassical eigenfunctions) corresponding to more general choices of $\alpha$, $\beta$ and $\gamma$.

It is easy to eliminate the parameters $\alpha$, $\beta$, $\gamma$ and then $p$ is expressed directly in terms of $\mathbf{r}$ using the conserved quantities $E$, $L^1$, $L_z$

$$p_z(r) = \pm p_z(r, \theta) = \pm p_{nf}(r, \theta, \theta')$$

$$p_r = p_{nf} = \sqrt{2m} \sqrt{E_{nf} + eV(r) - \hbar^2 L^2/2mr^2}$$
\[ p_\theta = \frac{\hbar}{r \sin \theta} \sqrt{\sin^2 \theta_0 - \cos^2 \theta} \]  
\[ p_\phi = \frac{\hbar L_z}{r \sin \theta} \]  
\[ (69) \]
\[ (70) \]

In mathematical terms the family \( F \) of orbits is equivalent to the vector field(s) \( p_\pm (r) \); the orbits of the family can be obtained as integral curves of equations (67)-(70).

The semiclassical wave-function defined by the family \( F \) is now given by an invariant expression [13],
\[ \psi_{\pm} (r) = F(r) e^{i \int p_\pm (r) \, dr / \hbar} \]  
\[ (71) \]

where \( p_\pm (r) \) is defined with reference to the family \( F \). \( F(r) \) is a prefactor discussed below.

The line-integral \( \int p \cdot dr \) in the exponent is taken from an arbitrary fixed point \( r_0 \) to \( r \). In equation (71) the path chosen for the line integral does not matter because of the theorem
\[ \nabla \times p_\pm = 0 \]  
\[ (72) \]

which is easily proven from equations (67)-(70).

Because the exponential phase factor dominates in the derivative of equation (71) it is clear that the quantum kinetic energy is approximately equal to the classical value.

The prefactor \( F(r) \) can be determined in three equivalent ways, first by a formal WKB expansion technique, analogous to that used to obtain equation (14) in section 2, which gives
\[ 2 \, p_\pm \cdot \nabla F = - F \nabla \cdot p_\pm \]  
\[ (73) \]

Second, one can impose the continuity equation for the flow of copies of the electron, i.e.,
\[ \text{div } j = 0 \]
where \( j_\pm (r) \) is the probability current vector calculated from \( \psi_{\pm} \) by the quantum formula. This method also gives equation (73).

Third, there is a formula due to Van Vleck [13] which relates \( F \) to derivatives of the action function. For motion in the spherically symmetric potential this formula gives
\[ F(r) = \left[ 1 \left( \frac{\partial p_\theta}{\partial \theta} \cdot \frac{\partial p_\phi}{\partial \phi} \cdot \frac{\partial p_\phi}{\partial \phi} \right) \right]^{1/2} \]  
\[ (74) \]

This form is obviously just sufficient to establish the correspondence limit of the partition function for equilibrium statistical mechanics.

For motion in a spherically symmetric potential all three approaches give
\[ F(r) = \left( \frac{m}{(2 \pi)^3 \hbar^2 p_r(r)} \sqrt{\sin^2 \theta_0 - \cos^2 \theta} \frac{\partial E_{nl}}{\partial n} \right)^{1/2} \]  
\[ (75) \]

The formula falls into factors associated with the three coordinates, as does \( \exp \left( i \int p \cdot dr / \hbar \right) \). Then the invariant wave-function of equation (71) agrees completely with the product formula of equation (43).

More exactly there are four vector fields \( p_\pm (r) \) associated with the four choices of +, − signs in equation (67). These fields are connected along the turning-point (or caustic) surfaces where \( p_r = 0 \) or \( p_\theta = 0 \). The connected system of vector fields has the topology of a torus.
There are two invariant line-integrals
\[ \oint p \cdot dr \]
associated with this torus and these are just the quantization integrals for energy and \( L^2 \) This geometrical viewpoint is called EBK quantization [15]. The half-integers which appear in the quantization rules just cancel branch-cuts in the prefactor \( F(r) \) and make the resulting wave-function single-valued [14, 3, 4].

Analytic continuation to the classically forbidden range gives a complete wave-function numerically close to the quantum eigenfunction except near the turning-point (caustic) surfaces.

In order to construct a semiclassical wave-function by this method we require a family of solutions of the classical equations of motion,
\[ r = r_0(E, A, B, \alpha, \beta; \gamma(t)) \] 
(76)
where \( E (= \text{energy}) \), \( A \) and \( B \) are constants of the motion and constant on the family, and \( \alpha, \beta \) are parameters which identify a specific orbit in the family Two additional conditions are required the orbits must fill an allowed region of three-dimensional space, guaranteed if
\[ \frac{\partial r_0}{\partial \alpha} \times \frac{\partial r_0}{\partial \beta} \times \frac{\partial r_0}{\partial \gamma} \]
is nonvanishing, and the momentum field must obey equation (72). With these conditions the wave-function can be constructed by equation (71). The assumptions imply \( \{H, A\} = \{H, B\} = \{A, B\} = 0 \), where \( \{A, B\} \) is the classical Poisson bracket of \( A, B \).

Thus there exists a suitable family \( F(H, A, B) \) only if the quantities \( H, A, B \) have vanishing Poisson brackets, a classical or semiclassical equivalent of the well-known quantum condition for an eigenfunction of a set of (commuting) operators.

As an illustration of the orbit superposition picture we calculate the inner product of two states of the type constructed above. The first state has \( L_z = 0 \) (i.e., \( m = 0 \)) with respect to the usual \( z \)-axis. The second state will have \( m = 0 \) with respect to a tilted axis \( z' \) located in the original \( x-z \) plane, making an angle \( \mu \) to \( z \).

We calculate this inner product by contour-integration
\[ U(z, z') = \int_0^{2\pi} \frac{d\phi}{2\pi} \int dx \Theta_{k'0}(\cos \theta') \Theta_{k0}(\cos \theta) \]
\[ = \int_0^{2\pi} \frac{d\phi}{2\pi} (\cos \mu - i \sin \mu \cos \phi)^t = P_\ell(\cos \mu) \] 
(77)
This agrees exactly with the corresponding quantum inner product.

A physical picture emerges from the saddle-point evaluation of the integral In this approximation, there is a contribution from any point where an orbit of the family \( F(z) \) has the same momentum as one of the family \( F(z') \). Any such point leads by integration to an entire orbit belonging to both families \( F, F' \) and the inner product is dominated by these shared orbits. For the case shown in figure 5, these shared orbits lie in the \( x-z \) plane.

It can be shown that the saddle-point integral for the inner product of states \( \psi_L, \psi_R \) is
\[ U_{LR} = \int dA \psi_L^*(r) \psi_R(r) \frac{2\pi i\hbar}{(\text{div} p_L - \text{div} p_R)} \] 
(78)
Fig. 5a — Representation of a family of orbits having zero angular momentum along the z-axis. Orbits of the family fall in planes containing the z-axis.

Fig. 5b. — Representation of orbits for a state having zero angular momentum along a tilted axis labelled $z'$. These orbits lie in planes through the axis $z'$. However, a subset of these orbits (shaded plane) also have zero angular momentum with respect to the original z-axis. It is this subset which determines the inner product of the two states.

where the integral is an area integral over the surface $S$ on which $p_L(r) = p_R(r)$. In most cases, as for the example considered here, the integrand is a constant or an easy normalization integral on $S$. For the case considered here, this saddle-point evaluation of $U(z, z')$ gives the WKB result of equation (27) in place of equation (77). Figure 1 shows the accuracy of this approximation.

More generally the inner product of two (semiclassical) states is determined by classical paths which occur in both families defining the two states.

This method gives geometrical interpretations for many known mathematical results of quantum mechanics in the theory of the Stark effect, Landau levels and in collision theory.

7. Conclusions.

This paper has studied the angular momentum matrices calculated from semiclassical wave-functions by a new contour integral formula. The matrices prove to be accurate to about 2% and exactly obey algebraic laws identical to those of the quantum theory, except for the requirement that the matrices be Hermitian. The quantum selection rules are exactly satisfied by the semiclassical matrix of $x = \cos \theta$.

It was also shown that the semiclassical wave-functions result from a superposition of allowed classical paths, an explicit demonstration of the semiclassical limit of the Feynman quantum mechanics.
Acknowledgments.

The author is grateful to K. H. Warren for help with numerical calculations and computer graphics and grateful to J. Green for helpful discussion. This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Appendix A. Semiclassical and quantum formulas for $F_{n,m}$.

In this Appendix we compare the contour integral formula for the matrix-element, equation (5), to the usual formula used in quantum mechanics. We will see that equation (5) converges with the quantum formula in the *semiclassical limit* defined (loosely) as the limit in which wave-functions have many oscillations over the characteristic length for variation of the wavelength.

We require two analytic properties of the WKB travelling waves,

\[
[\psi_n^\pm(z^*)]^* = \mp \psi_n^\mp(z) \quad (A1)
\]

\[
[\psi_n^\pm(x - i\varepsilon)]^* = \mp \psi_n^\mp(x + i\varepsilon). \quad (A2)
\]

Equation (A1) applies for all complex $z$, equation (A2) applies for real $x$ in the allowed range and only in the limit $\varepsilon \rightarrow 0^+$. The formulas appear to be generally valid, they have been specifically confirmed for the WKB spherical harmonic functions (Appendix B). For the forbidden ranges $x < x_{mn}$ and $x > x_{\text{max}}$, one can use equation (A1) together with the Schwarz reflection principle to show

\[
\text{Re} \ [\psi_n^+(x)] = 0 \quad (A3)
\]

\[
\text{Im} \ [\psi_n^-(x)] = 0. \quad (A4)
\]

These equations justify the connection rule of equation (4) because the ill-behaved (growing) function $\psi_n^+$ is purely imaginary and its contribution is removed by taking the real part in equation (4). The minus wave $\psi_n^-$ is properly behaved (bounded) in the forbidden regions.

A matrix-element can be constructed from the WKB wave-function given in equation (4) by the usual quantum formula,

\[
F_{nm}^Q = \int \text{Re} \ [\psi_n^+ + \psi_n^-] f \text{Re} \ [\psi_m^+ + \psi_m^-] \ dx \quad (A5)
\]

For simplicity it will be assumed that $f = f(x)$ The integral is taken over the entire physical range of $x$, along a path just above the real axis. Equation (A5) is the quantum rule but not the quantum result, since the integral is evaluated with WKB wave-functions. In fact one does not know *a priori* whether equation (A5) will be more or less accurate than equation (5) when applied for finite (or small) quantum numbers. However in the semiclassical limit, where the wave-functions approach the quantum wave-functions, $F_{nm}^Q$ clearly approaches the quantum result.

We examine the relation between $F_{nm}$ and $F_{nm}^Q$. Equation (A5) consists of four combinations of $+$ and $-$ waves. The range of integration can be divided into three ranges. *region a* is allowed for both states $n$ and $m$, *region (s) b* allowed for $m$, but forbidden for state $n$, and *region c* is forbidden for both.

We assume that the allowed range for $m$ includes the allowed range for $n$, for motion in one-dimensional potentials this is true if $E_m > E_n$. 
Analysis of the resulting twelve terms in equation (A5) is given in Table AI. Five of the terms are exactly zero as a consequence of equation (A3) because they contain a vanishing factor $\text{Re} [\psi^+]$ on a forbidden range. The product $\text{Re} [\psi_n^+] \text{Re} [\psi_m^-]$ is very small in region c, when $n$ and $m$ are unequal, not only because $\psi_m^-$ decreases but because $\psi_n^+$ is already small at the beginning of the range.

Table AI. — Contributions to the Matrix-Element equation (A5) Five terms are exactly zero, one is exponentially small, four terms contribute to direct and return parts of semiclassical contour-integral, and two terms oscillate rapidly in the semiclassical limit

<table>
<thead>
<tr>
<th>form</th>
<th>region a</th>
<th>region b</th>
<th>region c</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_n^+ \psi_m^-$</td>
<td>oscillating</td>
<td>zero</td>
<td>zero</td>
</tr>
<tr>
<td>$\psi_n^- \psi_m^-$</td>
<td>Fsc return</td>
<td>zero</td>
<td>zero</td>
</tr>
<tr>
<td>$\psi_n^- \psi_m^+$</td>
<td>Fsc direct</td>
<td>Fsc direct</td>
<td>zero</td>
</tr>
<tr>
<td>$\psi_n^- \psi_m^+$</td>
<td>oscillating</td>
<td></td>
<td>small</td>
</tr>
</tbody>
</table>

In the range allowed for both states (range a) it is not necessary to take the real part as $(\psi^+ + \psi^-)$ is real. The integrals of $\psi_n^+ \psi_m^+$, $\psi_n^- \psi_m^-$ over this allowed range are oscillatory and therefore should become small in the semiclassical limit.

The remaining terms can be combined, using equation (A2), to give exactly equation (5) Table AI shows how this occurs, the notations direct and return refer to the contour $C$ used in equation (5), the direct portion being above the branch-cut. The ± signs in equation (A2) play an essential role in reconciling equations (5) and (A5).

Two conclusions emerge from this analysis: first, the agreement or disagreement of equations (5) and (A5) depends on integrals of the oscillating terms $\psi_n^+ \psi_m^+$, $\psi_n^- \psi_m^-$; and second, in order to have the closest agreement the minus wave $\psi^-$ should be taken for the state having the smaller allowed range of classical motion ($n$ in Tab. I) in equation (5).

In constructing the semiclassical matrix of a dynamical variable $f$, the following procedure is used for matrix-elements with $n > m$, $F_{nm}$ is evaluated by selecting ± waves so that the $(-)$ wave goes with the state having the smaller allowed range. For $F_{nm}$ we use the same assignment of $+$ and $-$ waves even though this does not associate the minus wave with the smaller branch-cut. This rule leads to interesting algebraic behavior of the matrix $F_{nm}$.

We have shown that in the semiclassical limit there is approximate equality of $F_{nm}$ defined by equation (5), $F_{nm}^Q$ defined by equation (A5) and the quantum matrix-element $F_{nm}^{QM}$. The empirical result for the systems studied in references [3, 4] is stronger, namely that $F_{nm} = F_{nm}^Q$ to an accuracy of 10% or better at almost all quantum numbers.

However the operators $f$ studied to date have been « smooth » operators involving only long-wavelength variation with $x$. There are physical reasons to expect that the good answers from equations (5) are limited to this class of operators.

Appendix B. Analytic properties of the wave-function.

To define the analytic properties of the functions $\Theta_{l,m}$ it is first necessary to define the branch-cuts of the functions $\varphi(x)$, $\sqrt{1 - x^2}$ which appear in equation (23). This will be done as follows.
Fig. 6a — Branch cut for the function \( q(x) = \sqrt{x_0^2 - x^2} \).

Fig. 6b — Branch cut chosen for the function \( \sqrt{1 - x^2} \) which appears explicitly in the wave-function.

Fig. 6c. — Branch-cuts for the semiclassical wave-function \( m \neq 0 \). In traversing the loop indicated by \( C \), the function returns to its original value. For the special case \( m = 0 \), the inner branch cut extends from \(-1\) to \(+1\) and the outer branch cut is not present.

Fig. 6 — Analytic configuration for semiclassical spherical harmonic functions.

1) The function \( q(x) = \sqrt{x_0^2 - x^2} \) is chosen to have a branch-cut linking \(-x_0\) to \(x_0\) along the real axis. \( q(x) \) is taken to be real just above the branch-cut. With this choice,

\[
q(x) \rightarrow -ix \left( 1 - \frac{1}{2} \left( \frac{x_0}{x} \right)^2 + \cdots \right)
\]

(B1)
as $|x| \to \infty$. For $m = 0$, we have $x_0 = 1$ but we retain his choice of branch-cut for $q(x)$ when it appears as such in equation (23) (see Fig. 6a).

11) For the function $\sqrt{1 - x^2}$ which appears explicitly in equation (23) the branch-cut is taken differently, running from $-1$ to infinity (along the negative real axis) and then from infinity to $+1$ along the positive real axis. $\sqrt{1 - x^2}$ is positive real and has no branch-cut on the range $(-1, 1)$ (see Fig. 6b).

Now it is possible to verify from equation (20) that the net variation of $(\sigma_0)$ around a contour enclosing $(-x_0, x_0)$ is just

$$2 \pi \left( \ell + \frac{1}{2} - |m| \right). \quad (B2)$$

The variation of $\exp(i\sigma_0)$ gives exactly the minus sign required to cancel the minus sign encountered in tracing $\sqrt{q}$ around the same contour. Thus although both $\sigma_0$ and $\sqrt{q}$ have extra branch-lines (starting at $x_0$), these cancel in $\Theta_{lm}^\pm$.

The resulting analytic properties are (see Fig. 6c)

a) $\Theta_{lm}^\pm$ has a branch-cut from $-x_0$ to $x_0$

b) $\Theta_{lm}^\pm$ has singularities at $\pm 1$, and a second branch-cut linking these which may be taken to run from $+1$ to infinity and back to $-1$ (For $m = 0$ this second branch-cut does not occur.)

c) Aside from these singularities, $\Theta_{lm}^\pm$ is analytic for all finite $x$.

d) For complex values of $x$,

$$[\Theta_{\lambda m}^\pm(x*)]^* = \mp \Theta_{\lambda m}^\pm(x). \quad (B3)$$

e) For real $x$ in the allowed range, $|x| < x_0$, and small $\varepsilon > 0$,

$$\Theta_{\lambda m}^\pm(x - i\varepsilon) = \mp \Theta_{\lambda m}^\pm(x + i\varepsilon). \quad (B4)$$

(This equation holds in the limit $\varepsilon \to 0$)

f) On the forbidden ranges of the classical motion, $(-1 < x < -x_0)$ and $(x_0 < x < 1)$,

$$\text{Re} \left[ \Theta_{\lambda m}^\pm(x) \right] = 0 \quad (B5)$$

$$\text{Im} \left[ \Theta_{\lambda m}^\pm(x) \right] = 0. \quad (B6)$$

These properties are established by analysis of the factors in equation (23). In order that equations (B3)-(B6) hold for the computer implementation of these functions it was necessary to change the branch-cuts of the complex square root in the way described above.

References


More R M in Physics of Highly-Ionized Atoms, Richard Marrus, Ed (Plenum Publishing Corp) 1989, p 419,