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Centrifugal terms in the WKB approximation and semiclassical quantization of hydrogen

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A systematic semiclassical expansion of the hydrogen problem about the classical Kepler problem is shown to yield remarkably accurate results. *Ad hoc* changes of the centrifugal term, such as in the WKB approximation and semiclassical quantization of hydrogen, where the factor $l(l+1)$ is replaced by $(l+1/2)^2$, are avoided. Expanding systematically in powers of $\hbar$, the semiclassical energy levels are shown to be exact to first order in $\hbar$ with all higher-order contributions vanishing. The wave functions and dipole matrix elements are also discussed. [S1050-2947(99)10407-4]

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While the solution of the hydrogen problem was one of the early successes of quantum mechanics, it failed to be a showpiece for the WKB approximation, which proved to do rather poorly. Usually, this is attributed to the singularity of the Coulomb potential at $r=0$, where r is the distance between proton and electron. Clearly, near the origin the WKB expansion cannot be justified even in the semiclassical limit. Langer [1] showed that the correct behavior for $r\to 0$ can be enforced to the WKB wave function if the centrifugal term

$$V_C(r)=\hbar^2 l(l+1)/2mr^2 \tag{1}$$

in the radial Schrödinger equation is replaced by

$$V_L(r)=\hbar^2\left(l+\frac{1}{2}\right)^2/2mr^2 . \tag{2}$$

Quite remarkably, with the Langer modification (LM) [Eq. (2)] of the interaction potential, the WKB approximation gives exact energy eigenvalues for the hydrogen problem already to lowest order. As a consequence, the LM is now seen as a standard ingredient of WKB theory for the hydrogen problem and related systems with radial symmetry, such as the radial harmonic oscillator or the Morse potential in three dimensions. For recent applications and extensions we refer to the work of Refs. [2] and [3].

In the last years some attempts have been made to avoid the Langer modification. For the exactly solvable hydrogen problem, semiclassical theories based on nonlinear transformations [4] or supersymmetry [5] are powerful alternatives to conventional WKB methods. However, these approaches lead to exact results only for the strict $1/r$ potential, and do not constitute a general replacement for the standard semiclassical expansion. Within the conventional approach, Friedrich and Trost [6] avoided the LM, introducing instead an additional phase of the WKB wave function which is then optimized. For the repulsive $1/r^2$ potential their method gave results that are superior to those derived from conventional WKB theory with the LM. However, their approach also maintains that for Coulomb-type problems the textbook WKB expansion needs to be modified. In this paper we challenge this common belief.

We start from the obvious observation that in the classical limit the hydrogen problem should reduce to the Kepler problem. The form of the classical orbits depends on the energy E and the angular momentum L. Hence the leading-order WKB radial wave function should also be calculated for a given E and $L=\hbar l$. This implies that within the WKB expansion the centrifugal potential term (1) should be decomposed as

$$V_C(r)=L^2/2mr^2+\hbar L/2mr^2 , \tag{3}$$

where the first term is the classical centrifugal term and the second term is a quantum correction. Since the WKB expansion proceeds in powers of $\hbar$, this latter term has to be treated as a perturbation and expanded accordingly. Remarkably, the consequences of such a strictly systematic expansion in powers of $\hbar$ seem not to have been investigated previously.

We demonstrate that a systematic expansion about the Kepler problem yields WKB wave functions that are as accurate as for other potential problems despite the singularity at $r=0$. Notably, the semiclassical energy eigenvalues for the hydrogen problem become exact to first order in $\hbar$ with all higher-order corrections vanishing, while for the problem with the LM the exact semiclassical eigenvalues obtained in lowest order become worse when higher-order corrections are evaluated [7].

We start from the radial Schrödinger equation for the hydrogen atom,

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}-\frac{e^2}{r}+V_C(r)\right)\Psi(r)=E\Psi(r) \tag{4}$$

with $V_C(r)$ given by Eq. (3). Using the conventional WKB ansatz for the wave function,

$$\Psi(r)=\exp\left[\frac{i}{\hbar}\sum_{k=0}^{\infty}(-i\hbar)^k S_k(r)\right], \tag{5}$$

and expanding in powers of $\hbar$, for the quantities

$$y_k(r,E,L)=\partial S_k(r,E,L)/\partial r \tag{6}$$

we obtain the recursive set of equations

$$y_0=p(r,E,L)=\pm\sqrt{2m(E-V_{\rm eff}(r))}, \tag{7}$$

$$y_1=-\frac{1}{2y_0}\left(y_0'+i\frac{L}{r^2}\right), \tag{8}$$

$$y_{2m}=-\frac{1}{2y_0}\left[y_m^2+y_{2m-1}'+2\sum_{k=1}^{2m-2}y_{2m-k}y_k\right], \tag{9}$$

$$y_{2m+1}=-\frac{1}{2y_0}\left[y_{2m}'+2\sum_{k=1}^{2m-1}y_{2m+1-k}y_k\right], \tag{10}$$

where

$$V_{\rm eff}(r)=-\frac{e^2}{r}+\frac{L^2}{2mr^2}, \tag{11}$$

and where $p(r,E,L)=y_0(r,E,L)$ is the classical momentum. Further, the prime denotes differentiation with respect to r. These equations yield two functions $y^{(\pm)}(r,E,L)$ depending on the choice of the sign of the momentum $p(r,E,L)$, and the wave function is a linear combination of the form

$$\Psi(r,E,L)=\sum_{\sigma=\pm}c^{(\sigma)}\exp\left(\frac{i}{\hbar}\int_{r_0}^{r}dr\,y^{(\sigma)}(r,E,L)\right), \tag{12}$$

where

$$y(r,E,L)=\sum_{k=0}^{\infty}(-i\hbar)^k y_k(r,E,L). \tag{13}$$

The momentum $p(r,E,L)$ has a branch cut which is chosen conveniently between the classical turning points

$$r_{1,2}=a(1\mp\epsilon), \tag{14}$$

where a is the large axis and ϵ the eccentricity of the ellipse in the Kepler problem. Dunham [8] showed that by choosing the initial point of integration r_0 on the left side of the two classical turning points and a contour avoiding the turning points as indicated in Fig. 1(a), the wave function becomes

$$\Psi(r,E,L)=\begin{cases}c^{(-)}(\Psi^{(-)}+\Psi^{(+)}), & r_1<r<r_2\\ c^{(-)}\Psi^{(-)} & \text{elsewhere,}\end{cases} \tag{15}$$

with

$$\Psi^{(\pm)}(r,E,L)=\exp\left(\frac{i}{\hbar}\int_{r_0}^{r}dr\,y^{(\pm)}(r,E,L)\right). \tag{16}$$

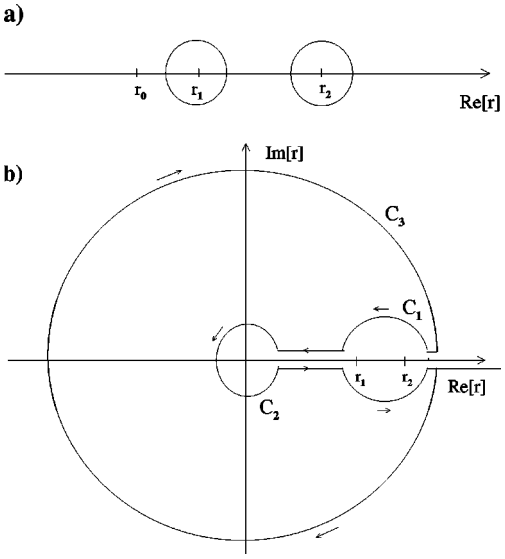

FIG. 1. (a) Complex r plane with the classical turning points $r_{1/2}$. Connecting points of the classical allowed and forbidden regions, one has to avoid the turning points by integrating along the circles. (b) Deformation of the integration contour in the complex plane.

Since we search for a unique solution, we have to require that the wave function is independent of whether one integrates above or below the branch cut. This leads to the condition

$$\frac{i}{\hbar}\oint dr\,y(r,E,L)=2\pi i(n_r+1), \tag{17}$$

where n_r is a positive integer and the integration contour encircles the branch cut. Using this equation one obtains a quantization of the energy which is related to the Bohr-Sommerfeld rule. To evaluate the contour integrals, we use a technique due to Sommerfeld which exploits the fact that the $y_k(r,E,L)$ have only poles on the positive real axis. As indicated in Fig. 1(b), one has to calculate integrals along the contours C_2 and C_3 instead of encircling the branch cut. To order $\hbar$ the integrals are readily evaluated, yielding

$$\frac{1}{2\pi\hbar}\oint dr\left(y_0+\frac{\hbar}{i}y_1\right)=-\frac{L}{\hbar}+\sqrt{-\frac{me^4}{2E\hbar^2}}=n_r+1,$$

which gives the exact energy eigenvalues for the bound states of the hydrogen atom,

$$E_n=-me^4/2\hbar^2n^2, \tag{18}$$

with the principal quantum number $n=n_r+l+1$. Corrections of higher order in $\hbar$ coming from the contour integrals over the functions y_k, $k\geq 2$ vanish exactly. To show this we first investigate the analytical structure of y_0 and y_1 at the origin. We find

$$y_0(r,E,L)=iLr^{-1}+O(r^0), \tag{19}$$

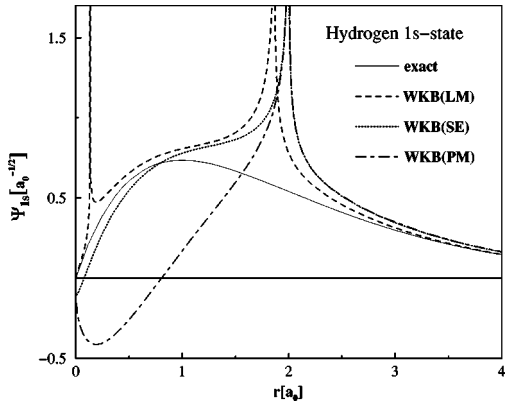

FIG. 2. WKB wave functions and exact wave functions for the 1*s* ground state. The WKB wave functions diverge at the turning points. r is measured in units of the Bohr radius a_0.

while the power series expansion of y_1 begins with a linear term. Consequently, the expansion of y_1' starts with a constant term. Now, using

$$y_2 = -(y_1^2 + y_1')/2y_0, \tag{20}$$

one immediately sees that the expansion of y_2 begins with a linear term, and therefore the residue of y_2 at the origin is zero. Since the recurrence relations (9) and (10) contain y_0 only in the denominator, it is easy to show by induction that the Taylor series of all y_k with $k \geqslant 2$ start with linear or higher-order terms. This implies that the integrals along the contour C_2 vanish for all y_k with $k \geqslant 2$. In an analogous way one can treat the integrals along the contour C_3 by replacing r by $1/u$ and remembering the additional factor $-1/u^2$ originating from the transformation of the integration measure. One finds that the integrals along the contour C_3 also vanish for all y_k with $k \geqslant 2$. Therefore, the semiclassical energy quantization (18) is exact to all orders in $\hbar$, while in the WKB approximation with Langer modification higher-order terms destroy the exactness of the energy eigenvalues.

Next we consider the wave functions. Disregarding quadratic and higher powers in $\hbar$ in Eqs. (15) and (16), we arrive at an expression for the lowest-order WKB wave functions for r on the positive real axis of the form

$$\Psi(r,E,L) = \tfrac{1}{2}\,\mathrm{Re}[\Psi^{(-)}(r,E,L) + \Psi^{(+)}(r,E,L)], \tag{21}$$

with

$$\Psi^{(\pm)}(r,E,L) = \frac{c(E,L)}{\sqrt{p(r,E,L)}} \times \exp\left[\pm\left(\frac{i}{\hbar}\int_{r_1}^{r} dr\, p - \frac{i}{2}\varphi - i\frac{\pi}{4}\right)\right], \tag{22}$$

where the additional phase $\varphi(r,E,L)$ arises from the part of the centrifugal term in Eq. (3) that is linear in $\hbar$. In fact,

$$\varphi(r,E,L) = -\partial S_0(r,E,L)/\partial L \tag{23}$$

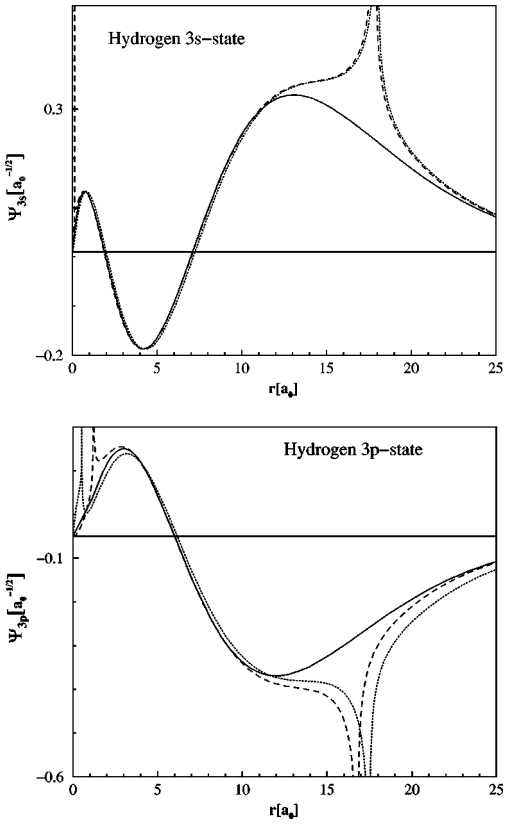

FIG. 3. WKB wave functions and exact wave functions for the excited 3*s* and 3*p* states. Again the solid, dashed, and dotted lines denote the exact, WKB(LM), and WKB(SE) wave functions, respectively.

is just the phase of the classical trajectory in the plane of motion of the Kepler problem in terms of which Eq. (8) can be written as

$$y_1 = -\frac{y_0'}{2y_0} - \frac{i}{2}\frac{\partial\varphi}{\partial r}. \tag{24}$$

A representation of the WKB wave function as the real part of the superposition of incoming and outgoing waves as in Eq. (21) was introduced previously by More and Warren [9] for the standard approach with the LM. Since the undesirable growing part of the wave function has a purely imaginary coefficient, it is removed when the real part is taken. The normalization $c(E,L)$ of the wave function is obtained from

$$\tfrac{1}{2}\mathrm{Re}\int_{r_1}^{r_2} dr\, \Psi^{(+)}\Psi^{(-)} = \tfrac{1}{4}\oint dr\, \Psi^{(+)}\Psi^{(-)} = 1. \tag{25}$$

which gives

$$c(E)^2 = (2m/\pi\hbar^2)\,dE/dn. \tag{26}$$

More and Warren referred to the omission of the terms $\Psi^{(+)}\Psi^{(+)} + \Psi^{(-)}\Psi^{(-)}$ in the normalization integral as the ''restricted interference approximation.'' Finally, for the WKB wave function of the hydrogen atom in the classical accessible region between the two turning points we obtain

TABLE I. WKB(SE) dipole matrix elements in units of Bohr's radius a_0 and exact quantum-mechanical values in parentheses.

n	2	3	4	5	6	7	8	9	10
$1s$-np	1.090(1.290)	0.512(0.517)	0.339(0.306)	0.257(0.209)	0.208(0.155)	0.177(0.121)	0.154(0.098)	0.137(0.082)	0.124(0.069)
$2p$-nd		4.542(4.748)	1.816(1.71)	1.104(0.975)	0.802(0.662)	0.641(0.492)	0.543(0.386)	0.478(0.314)	0.432(0.263)
$4p$-ns				4.673(4.600)	1.864(1.788)	1.120(1.044)	0.794(0.718)	0.614(0.539)	0.501(0.427)

$$\Psi(r,E,L)=\frac{c(E)}{\sqrt{p}}\cos\left(\frac{1}{\hbar}\int_{r_1}^{r}dr\,p-\frac{\varphi}{2}-\frac{\pi}{4}\right). \tag{27}$$

We now compare the WKB wave functions with the exact ones. A typical feature of WKB wave functions is the divergence at the classical turning points. As can be seen from Fig. 2, this behavior is qualitatively the same for the Langer modified expansion, our systematic $\hbar$ expansion WKB(SE), and ''poor man's'' WKB(PM) obtained when the full centrifugal term (1) is retained in the lowest order equation. While the WKB(PM) wave function for the ground state indeed does poorly, the main difference between the WKB(LM) and WKB(SE) wave functions comes from the fact that the distance between the turning points of the Langer modified wave functions is smaller. This is just a consequence of the shift of the turning points due to the LM. Therefore, between the turning points, our wave functions give a better approximation to the exact ones. For the s states, the Langer modified wave functions are constructed to vanish at $r=0$, and they have a divergence near the origin since the left turning point is moved away from $r=0$ by the artificial $\frac{1}{2}$ added to the angular momentum number l. Our wave function does not have the right power-law behavior near the origin, but there is only one divergence which is due to the right turning point. Hence we see that the wave functions obtained from a systematic expansion in powers of $\hbar$ without any *ad hoc* manipulation of the hydrogen problem are at least as accurate as those obtained from the problem with the LM (see Fig. 3).

Finally, we calculate radial dipole matrix elements between states with angular momentum l and $l\pm1$. Using the restricted interference approximation, we have

$$R^{\pm}_{\Delta n}(E,l)=\tfrac{1}{4}\oint dr\,\Psi^{(+)}(r,E,L)r\Psi^{(-)}(r,E+\Delta E,L\pm\hbar). \tag{28}$$

Expanding this in powers of $\hbar$, for the leading-order term one finds

$$R^{\pm\,(0)}_{\Delta n}(E,l)=a_0[n^2/\Delta n^2\;d/d\epsilon\;J_{\Delta n}(\Delta n\epsilon) \pm n/\Delta n\;\sqrt{1-\epsilon^2}/\epsilon\;J_{\Delta n}(\Delta n\epsilon)] \tag{29}$$

where a_0 is the Bohr radius, $\epsilon=[1-(l/n)^2]^{1/2}$ the eccentricity, and $J_n(z)$ a Bessel function. Naccache [10] obtained this leading-order term from the Heisenberg correspondence principle. The quantum correction of first order in $\hbar$ is found to read

$$R^{\pm\,(1)}_{\Delta n}(E,l)=\Delta n\omega(E)/2\;\partial/\partial E\;R^{\pm\,(0)}_{\Delta n}(E,l) +(1\pm1)/2\;\partial/\partial L\;R^{\pm\,(0)}_{\Delta n}(E,l), \tag{30}$$

with the angular frequency $\omega(E)=[-8E^3/(me^6)]^{1/2}$ of the Kepler problem. In Table I the semiclassical dipole elements are compared with the exact ones for some spectral series. We note that for large n and l and small Δn the WKB results give rather accurate estimates of the exact values. This is expected from a semiclassical approximation.

In summary, we have shown that a systematic semiclassical expansion of the hydrogen problem about the Kepler problem yields remarkably accurate results. In contrast to common belief, no modification of the WKB expansion is necessary when the centrifugal potential term is decomposed in the classical centrifugal potential and a quantum correction. The same method can be employed for other problems with radial symmetry.

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