Application of a Higher-Order WKB Approximation to Radial Problems

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The radial generalization of Dunham's one-dimensional WKB quantization condition, including second- and third-order corrections is derived using the Langer transformation. It is found that, although the first-order integral can be obtained from Dunham's results by substituting $(l+\frac{1}{2})^2$ for $l(l+1)$ in the effective potential, there is no choice of effective potential that leads to the correct second- and third-order integrals. It is suggested that all previous eigenvalue calculations using higher-order WKB approximations for the radial case should be reinvestigated. It is shown that the second- and third-order integrals identically vanish for the hydrogen atom and the three-dimensional harmonic oscillator, as expected.

I. INTRODUCTION

ONE of the earliest and simplest methods of obtaining approximate eigenvalues of the one-dimensional Schrödinger equation was originally proposed by Wentzel,[1] Kramers,[2] and Brillouin.[3] The method was further developed by Dunham,[4] who obtained the higher-order correction terms to the WKB quantization condition. The evaluation of these correction terms is very useful in improving the precision of the WKB calculated eigenvalues.[5,6]

When the Schrödinger equation is separated for a spherically symmetric potential the radial equation can be written in a form which is identical to the one-dimensional problem, with an effective potential given by the sum of the centrifugal potential and the original potential. This similarity to the one-dimensional problem led Dunham[7] to use the one-dimensional quantization condition on the effective potential to determine the eigenenergies of the rotating vibrator. This, however, cannot be a valid quantization rule because it is well known that, in order for the first-order WKB integral to give the exact eigenvalues for the hydrogen atom and the three-dimensional harmonic oscillator, the quantity $l(l+1)$ must be replaced by $(l+\frac{1}{2})^2$ in the quantization condition. It was observed by Langer[8] that the reason for this modification arose from the fact that the quantization condition for the one-dimensional problem was derived under the assumption that the wave function approached zero for $x\rightarrow\pm\infty$, whereas the radial part of the solution approached zero for $r\rightarrow 0$ and $r\rightarrow\infty$. He then introduced a transformation that mapped the point $r=0$ into $x=-\infty$ and $r=\infty$ into $x=\infty$, and as a result obtained an equation whose solutions satisfied Dunham's original boundary conditions. An immediate consequence was that the correct first-order quantization condition had $l(l+1)$ replaced by $(l+\frac{1}{2})^2$, the so-called Langer correction.

More recently,[9] an attempt has been made to obtain the higher-order corrections to the WKB quantization condition for spherically symmetric potentials. These workers have assumed that the Dunham[4] one-dimensional correction terms are applicable here provided one uses the appropriate effective potential. They find that, although the replacement of $l(l+1)$ by $(l+\frac{1}{2})^2$ is valid if only the first-order integral is considered, this replacement is no longer valid when the second-order integral is included, and instead they conclude that $l(l+1)$ should be replaced by K, with K satisfying $K+1/64K=l(l+1)$.

The purpose of this note is to derive the second- and third-order correction terms for the radial problem. We shall show that these terms are not given by the usual Dunham expression no matter how we choose the effective potential. We shall furthermore demonstrate that these higher-order correction terms are zero for the Coulomb potential and the harmonic oscillator.

II. WKB APPROXIMATION FOR ONE-DIMENSIONAL SYSTEMS

In this section we review Dunham's[4] method of obtaining the higher-order WKB integral corrections. Dunham takes the solution of the Schrödinger equation

$$-\frac{h^2}{2m}\frac{d^2}{dx^2}\psi(x)+V(x)\psi(x)=E\psi(x) \tag{1}$$

to be of the form

$$\psi(x)=A\exp\left[\frac{i}{h}\int^x y(x',E)dx'\right], \tag{2}$$

where A is an arbitrary constant. When Eq. (2) is substituted into Eq. (1), y obeys the equation

$$\frac{h}{i}\left(\frac{dy}{dx}\right)+y^2=2m(E-V). \tag{3}$$

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[7] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
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The WKB approximation assumes that y may be written as a series in $\hbar$, i.e.,

$$y=\sum_{n=0}(\hbar/i)^n y_n. \tag{4}$$

It can in fact be shown that such a series is really an asymptotic expansion,[10] with $\hbar$ the expansion parameter. Recursion formulas for the y_n are obtained by substituting Eq. (4) into Eq. (3) and equating coefficients of $\hbar^n$ to zero.

The requirement that $\psi(x)\to 0$ for $x\to\pm\infty$, ψ must be single valued and finite, and ψ can be chosen as real for it to be an acceptable solution, lead to the condition

$$\oint_c y\,dx=Nh, \tag{5}$$

where the integral is taken about a contour enclosing the classical turning points and no other singularities of y. When the expansion for y is substituted into Eq. (5) the quantization condition to third order in $\hbar^2$ is

$$\oint_c (E-V)^{1/2}dx-\frac{\hbar^2}{64m}\oint_c (V')^2(E-V)^{-5/2}dx$$
$$-\frac{\hbar^4}{8192m^2}\oint_c [49(V')^4(E-V)^{-11/2}-16V'V'''(E-V)^{-7/2}]dx=\frac{(N+\frac{1}{2})h}{(2m)^{1/2}}. \tag{6}$$

III. WKB APPROXIMATION FOR THE RADIAL EQUATION

If we substitute

$$\psi(\mathbf{r})=[U(r)/r]Y_{lm}(\theta,\phi) \tag{7}$$

into the Schrödinger equation for a spherically symmetric potential, the resulting equation for $U(r)$ is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}U+\left[V(r)+\frac{l(l+1)\hbar^2}{2mr^2}\right]U=EU, \tag{8}$$

and, from Eq. (7), the boundary conditions are $U=0$ for $r=0$ and $r\to\infty$, which are different from the boundary conditions under which Dunham derived the one-dimensional quantization rules. This can be remedied by using the Langer transformation, i.e.,

$$r=e^x,$$
$$U(r)=e^{x/2}X(x). \tag{9}$$

And since $e^{x/2}=r^{1/2}$ and $U(r)\to 0$ at least as fast as r, then $X(x)\to 0$ for $x\to-\infty$. Also since $U\to 0$ for $r\to\infty$, then $X\to 0$ for $x\to\infty$. Hence, X has the same boundary conditions as are implicit in Dunham's derivation. The equation obtained when Eq. (9) is substituted into Eq. (8) is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X+e^{2x}\left[V(e^x)-E+\frac{(l+\frac{1}{2})^2\hbar^2}{2m}e^{-2x}\right]X=0. \tag{10}$$

This equation is of the form

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X-q^2X=0, \tag{11}$$

which is of the same form as the ordinary one-dimensional equation provided we take

$$q^2(x,E)=\left[E-V(e^x)-\frac{(l+\frac{1}{2})^2}{2m}\hbar^2e^{-2x}\right]e^{2x}. \tag{12}$$

We can write Dunham's quantization rule for equations of the form of Eq. (11) as[7]

$$\oint q\,dx-\frac{\hbar^2}{64m}\oint\left[\frac{d}{dx}(q^2)\right]^2q^{-5}dx-\frac{\hbar^4}{8192m^2}\oint\left\{49\left[\frac{d}{dx}(q^2)\right]^4q^{-11}-16\left[\frac{d}{dx}(q^2)\right]\left[\frac{d^3}{dx^3}(q^2)\right]q^{-7}\right\}dx=\frac{(N+\frac{1}{2})h}{(2m)^{1/2}}. \tag{13}$$

Substituting Eq. (12) into Eq. (11) and transforming back to r as the integration variable we obtain

$$\oint\left[E-V(r)-\frac{(l+\frac{1}{2})^2\hbar^2}{2mr^2}\right]^{1/2}dr-\frac{\hbar^2}{64m}\oint\frac{\{(d/dr)[r^2(V-E)]\}^2}{\{E-V(r)-[(l+\frac{1}{2})^2\hbar^2/2mr^2]\}^{5/2}}\frac{dr}{r^4}-\frac{\hbar^4}{8192m^2}$$
$$\times\oint\left\{\frac{49\{(d/dr)[r^2(V-E)]\}^4}{\{E-V-[(l+\frac{1}{2})^2\hbar^2/2mr^2]\}^{11/2}}-\frac{-16r[(d/dr)\{r^2(V-E)\}]\times[r(d/dr)]^3[r^2(V-E)]}{\{E-V-[(l+\frac{1}{2})^2\hbar^2/2mr^2]\}^{7/2}}\right\}\frac{1}{r^8}dr=\frac{(N+\frac{1}{2})h}{(2m)^{1/2}}. \tag{14}$$

[10] A. Zwaan, Arch néerl Sci. 13, 33 (1929).

The first term[11] is just the usual first-order integral with an effective potential obtained by replacing $l(l+1)$ by $(l+\frac{1}{2})^2$ in the effective potential found in the radial equation. However, if we had merely substituted $V_{\text{eff}} \equiv V+[\hbar^2(l+\frac{1}{2})^2/2mr^2]$ into Dunham's second-order integral we would not have obtained the correct second-order integral as given in Eq. (14). The same is true concerning the third-order integral.

IV. EVALUATION OF HIGHER-ORDER INTEGRALS FOR THE COULOMB POTENTIAL AND HARMONIC OSCILLATOR

As is well known, the first-order integral leads to the exact eigenenergies for the Coulomb potential and harmonic oscillator. We shall now show that in both cases the second- and third-order integrals are identically zero.

A. Coulomb Potential $V(r)=-Ze^2/r$

From Eq. (14) we see that the second- and third-order integrals have singularities at the two classical turning points given by the solutions of

$$E-V-\frac{(l+\frac{1}{2})^2\hbar^2}{2mr^2}=0.$$

The integrands are not singular at $r=0$ since, as $r\to 0$ both the second-order integrand and the third-order integrand $\to r$. Since there are no other singularities, we can deform the contour to be a large circle with center at the origin. But for $r\to\infty$ the second-order integrand $\to 1/r^2$ and the third-order integrand $\to 1/r^4$, and hence evaluating the integral along a circle of radius R gives zero as $R\to\infty$.

B. Harmonic Oscillator $V=\frac{1}{2}kr^2$

From Eq. (14) we see again that the second- and third-order integrals have singularities at the two classical turning points given by the solution of

$$E-V-\frac{(l+\frac{1}{2})^2\hbar^2}{2mr^2}=0,$$

with $r>0$. There are also singularities at negative r but the contour of integration does not include them. However, since these singularities exist, it is not possible to simply deform the contour to a large circle as in the Coulomb-potential case. Instead, we note that the second-order integral can be written as a sum of terms of the form

$$I_n=\oint\frac{r^{2n}}{\{E-\frac{1}{2}kr^2-[(l+\frac{1}{2})^2\hbar^2/2mr^2]\}^{5/2}}dr,\quad n=-1,0,1.$$

These three integrals are separately zero. This follows from the fact that

$$J\equiv\oint\{E-\tfrac{1}{2}kr^2-[(l+\tfrac{1}{2})^2\hbar^2/2mr^2]\}^{1/2}dr$$

$$=\frac{1}{2(2m)^{1/2}}[E/\nu-h(l+\tfrac{1}{2})],\qquad(15)$$

where $\nu\equiv(1/2\pi)(k/m)^{1/2}$. Then I_1 is proportional to $(\partial/\partial k)(\partial^2/\partial E^2)J=0$, I_0 is proportional to $(\partial^3/\partial E^3)J=0$, and I_{-1} is proportional to $(\partial/\partial(\hbar^2))(\partial^2/\partial E^2)J=0$.

Thus, the entire second-order integral is zero. Similarly, all the contributions to the third-order integrals can be written in terms of integrals of the form

$$S_n=\oint\frac{r^{2n}}{\{E-\frac{1}{2}kr^2-[(l+\frac{1}{2})^2\hbar^2/2mr^2]\}^{11/2}}dr,$$

$$n=-2,-1,0,1,2$$

$$T_m=\oint\frac{r^{2m}}{\{E-\frac{1}{2}kr^2-[(l+\frac{1}{2})^2\hbar^2/2mr^2]\}^{7/2}}dr,$$

$$m=-2,-1,0.$$

For $n=-2,-1,0$,

$$S_n \text{ is proportional to } \frac{d^{|n|}}{d(\hbar^2)^{|n|}}\frac{d^{6+n}}{dE^{6+n}}J=0,$$

and for $m=-2,-1,0$,

$$T_m \text{ is proportional to } \frac{d^{|m|}}{d(\hbar^2)^{|m|}}\frac{d^{4+m}}{dE^{4+m}}J=0.$$

For $n=1,2$,

$$S_n \text{ is proportional to } \frac{d^n}{dk^n}\frac{d^{6-n}}{dE^{6-n}}J=0.$$

Hence the entire third-order integral is zero.

V. CONCLUSIONS

We have derived the radial generalization of the second- and third-order WKB correction terms to the energy quantization condition. In doing so we have seen that there is no effective potential that may be substituted into Dunham's expression which will give rise to the correct result for an arbitrary potential. The derived higher-order correction terms have been shown to be identically zero for the Coulomb potential and the harmonic oscillator, as expected.

Our results suggest that all earlier work in determining corrected WKB eigenvalues of the radial equation should be reinvestigated because previous workers have employed incorrect expressions for the higher-order correction terms.

[11] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1101.