Quantization Rules for Bound States of
the Schrödinger Equation

Zhong-Qi Ma\(^1,2\)\(^\ast\) and Bo-Wei Xu\(^3\)\(^\dagger\)

1) CCAST (World Laboratory), P.O.Box 8730, Beijing 100080, China
2) Institute of High Energy Physics, Beijing 100039, China
3) Department of Physics, Shanghai Jiaotong University, Shanghai 200030, China

An exact quantization rule for the bound states of the one-dimensional Schrödinger equation is presented and is generalized to the three-dimensional Schrödinger equation with a spherically symmetric potential.

I. INTRODUCTION

In the development of quantum mechanics, the Bohr-Sommerfeld quantization rules of the old quantum theory [1] occupy a position intermediate between classical and quantum mechanics. The WKB approximation [2–4] is a method for the approximate treatment of the Schrödinger wave function with another quantization rule [1]:

\[ \int_{x_A}^{x_B} k \, dx = (n + 1/2)\pi, \quad k = \sqrt{2\mu (E - V(x)) / \hbar}, \quad n = 0, 1, 2, \ldots, \quad (1) \]

where \( x_A \) and \( x_B \) are two turning points

\[ E = V(x_A) = V(x_B), \quad EV(x), \quad x_A < x < x_B, \quad (2) \]

and \( n \) is the number of nodes of the WKB wave function between two turning points. The half-integer number is the quantum correction to the Bohr-Sommerfeld result, which comes from the fact that the wave function in WKB analysis may extend into the classically forbidden region. The WKB method is precise for the harmonic oscillator potential, and is expected to be most useful in the nearly classical limit of large

\(^\ast\)Electronic address: mazq@sun.ihep.ac.cn

\(^\dagger\)Electronic address: bwxu@sjtu.edu.cn
quantum numbers, namely, it is good when $n$ is large in comparison with unity. Various refinements have been developed to improve the accuracy of the WKB method [5–7] where the main modification was made on the phase loss at the turning points. Recently, Cao et al. presented a calculation method, called the analytic transfer matrix method (ATMM) [8,9], for the energy levels of bound states of the one-dimensional Schrödinger equation, where the phase contribution picked up by the scattered sub-waves was included in the new quantization rule. The accurate numerical calculation results for some examples were given there [8,9]. This is a prospective method for calculating the energy levels of bound states of the Schrödinger equation, but has to be developed and improved further. In this Letter we apply the matching condition of the logarithmic derivatives (which is a standard method in quantum mechanics) and the fundamental concept of the mathematical analysis to the problem of bound states of one-dimensional Schrödinger equation, and derive an exact quantization rule without any approximation. The quantization rule is rigorous and general for any Schrödinger equation with only one variable. It is a fundamental problem in quantum mechanics.

The plan of this Letter is as follows. In section 2 we will develop the method of the numerical calculation for the energy levels of bound states of the one-dimensional Schrödinger equation by the matching condition of the logarithm derivatives of the wave function. In section 3 we present an exact quantization rule for one-dimensional Schrödinger equation. The quantization rule is proved without any approximation. Its validity can also be confirmed with some solvable examples. In section 4 the quantization rule is generalized to the three-dimensional Schrödinger equation with a spherically symmetric potential. The conclusion is given in section 5.

II. MATCHING CONDITION OF LOGARITHM DERIVATIVES

Consider the one-dimensional Schrödinger equation

$$\frac{d^2}{dx^2} \psi(x) = -\frac{2\mu}{\hbar^2} [E - V(x)] \psi(x), \quad (3)$$

where $\mu$ is the mass of the particle, and the potential $V(x)$ is a piecewise continuous
real function of $x$. The logarithm derivative $\phi(x)$ of the wave function $\psi(x)$ is

$$
\phi(x) = \frac{1}{\psi(x)} \frac{d\psi(x)}{dx}.
$$

(4)

From the Schrödinger equation (3) we have

$$
\frac{d}{dx} \phi(x) = -k(x)^2 - \phi(x)^2, \quad E \geq V(x),
$$

(5)

$$
\frac{d}{dx} \phi(x) = \kappa(x)^2 - \phi(x)^2, \quad E \leq V(x),
$$

(6)

where

$$
k(x) = \sqrt{2\mu(E - V(x))}/\hbar, \quad E \geq V(x),
$$

$$
\kappa(x) = \sqrt{2\mu(V(x) - E)}/\hbar, \quad E \leq V(x),
$$

(7)

$$
k(x) = \kappa(x) = 0, \quad E = V(x).
$$

(7)

It is obvious that $\phi(x)$ decreases monotonically with respect to $x$ when $E \geq V(x)$, but not monotonically when $E \leq V(x)$. Note that near a node of the wave function $\psi(x)$ in the region where $E \geq V(x)$, $\phi(x)$ decreases to $-\infty$, jumps to $+\infty$, and then, decreases again.

Arbitrarily choosing an energy $E$ as a parameter, we assume for definiteness that the potential $V(x)$ satisfies

$$
V(x) = V_I E, \quad -\infty < x \leq x_I,
$$

$$
V(x)E, \quad x_I < x < x_A \text{ or } x_B < x < x_F,
$$

$$
V(x) = E, \quad x = x_A \text{ or } x = x_B,
$$

$$
V(x) < E, \quad x_A < x < x_B,
$$

$$
V(x) = V_F E \quad x_F \leq x < \infty.
$$

(8)

$x_A$ and $x_B$, $x_A < x_B$, are called two turning points where $V(x_A) = V(x_B) = E$. This potential can be easily generalized.

The Schrödinger equation (3) is a linear differential equation of the second order, for which there are two independent solutions. In the region $-\infty < x \leq x_I$, one solution is divergent exponentially, and the other is physically admissible:

$$
\psi(x) \sim e^{k_I x}, \quad \phi(x_I) = \kappa_I = \sqrt{2\mu(V_I - E)/\hbar} > 0.
$$

(9)

Similarly, in the region $x_F \leq x < \infty$, the physically admissible solution is

$$
\psi(x) \sim e^{-\kappa_F x}, \quad \phi(x_F) = -\kappa_F = -\sqrt{2\mu(V_F - E)/\hbar} < 0.
$$

(10)
For the general potential, if $E < V(\pm \infty)$, both $\phi(x_I)$ and $-\phi(x_F)$ are positive.

By making use of the fundamental concept of the mathematical analysis, we replace the continuous potential well with a stack of thin films each of which has a constant potential. We first divide the region $x_I \leq x \leq x_A$ into $n$ equal films with width $d_n$, where $E \leq V(x)$ and $x_A = x_I + n d_n$. In the $j$th film, $x_I + j d_n - d_n \leq x \leq x_I + j d_n$, $V(x)$ is replaced with a constant potential $V_j$

$$V_j = V(x_I + j d_n - d_n/2), \quad \kappa_j = \sqrt{2 \mu [V_j - E]/\hbar}. \quad (11)$$

Solving the Schrödinger equation at this film, we obtain

$$\psi_j(x) = A_j e^{\kappa_j x} + B_j e^{-\kappa_j x}. \quad (12)$$

On two ends of the film, the logarithm derivatives $\varphi_{j-1}$ and $\varphi_j$, which should match with the logarithm derivatives at the ends of the neighboring films, are

$$\varphi_j = \frac{1}{\psi_j(x)} \left. \frac{d\psi_j(x)}{dx} \right|_{x=x_I+j d_n} = \kappa_j \frac{A_j e^{\kappa_j (x_I+j d_n)} - B_j e^{-\kappa_j (x_I+j d_n)}}{A_j e^{\kappa_j (x_I+j d_n)} + B_j e^{-\kappa_j (x_I+j d_n)}},$$

$$\varphi_{j-1} = \frac{1}{\psi_j(x)} \left. \frac{d\psi_j(x)}{dx} \right|_{x=x_I+j d_n-d_n} = \kappa_j \frac{A_j e^{\kappa_j (x_I+j d_n-d_n)} - B_j e^{-\kappa_j (x_I+j d_n-d_n)}}{A_j e^{\kappa_j (x_I+j d_n-d_n)} + B_j e^{-\kappa_j (x_I+j d_n-d_n)}}. \quad (13)$$

From the second formula of Eq. (13) we obtain

$$A_j e^{\kappa_j (x_I+j d_n-d_n)} \{ \kappa_j - \varphi_{j-1} \} = B_j e^{-\kappa_j (x_I+j d_n-d_n)} \{ \kappa_j + \varphi_{j-1} \}. \quad \text{Substituting it into the first formula of Eq. (13) we have}$$

$$\varphi_j = \kappa_j \frac{\varphi_j - \kappa_j \tanh (\kappa_j d_n)}{\kappa_j + \varphi_{j-1} \tanh (\kappa_j d_n)}. \quad (14)$$

This is a recursive relation. If $\varphi_{j-1}$ is positive, $\varphi_j$ is positive, too. There is no zero both in the numerator and in the denominator of Eq. (14), so $\varphi_j$ is finite and non-vanishing. Since $\phi(x_I)$ is positive and known, one is able to calculate $\varphi_n = \phi(x_A)$ from $\varphi_0 = \phi(x_I) = \kappa_I$ with the recursive relation (14) as $j$ increases from 1 to $n$. $\phi(x_A)$ is positive, finite and non-vanishing (see Appendix A). The calculated precision depends on the number $n$ of the films. In principle, one may obtain a precise $\phi(x_A)$ if $n$ is large enough.

Similar calculation can be made in the region $x_F \leq x < \infty$. The recursive relation (14) becomes

$$\varphi_{j-1} = \kappa_j \frac{\varphi_j - \kappa_j \tanh (\kappa_j d_n)}{\kappa_j + \varphi_j \tanh (\kappa_j d_n)}. \quad (15)$$
If \( \varphi_j \) is negative, \( \varphi_{j-1} \) is negative, finite and non-vanishing. Since \( \phi(x_F) \) is negative and known, one is able to calculate \( \varphi_0 = \phi(x_B+) \) from \( \varphi_n = \phi(x_F) = -\kappa_F \) with the recursive relation (15) as \( j \) decreases from \( n \) to 1. \( \phi(x_B+) \) is negative, finite and non-vanishing. In principle, one may obtain a precise \( \phi(x_B+) \) if \( n \) is large enough. Physically, the fact that there is no zero of \( \phi(x) \) in the regions \(-\infty < x \leq x_A \) and \( x_B \leq x < \infty \) implies that in those two regions the wave function \( \psi(x) \) is exponential decay. However, there may be a zero of \( \phi(x) \) in the other classically forbidden regions (see the end of this section).

Now, we divide the region \( x_A \leq x \leq x_B \) into \( m \) equal films with width \( d_m \), where \( E \geq V(x) \) and \( x_B = x_A + md_m \). In the \( j \)th film, \( x_A + jd_m - d_m \leq x \leq x_A + jd_m, V(x) \) is replaced with a constant potential \( V_j \)

\[
V_j = V(x_A + jd_m - d_m/2), \quad k_j = \sqrt{2\mu [E - V_j]/\hbar}. \tag{16}
\]

Solving the Schrödinger equation at this film, we obtain

\[
\psi_j(x) = C_j \sin (k_jx + \delta_j). \tag{17}
\]

On two ends of the film, the logarithm derivatives \( \phi_{j-1} \) and \( \phi_j \), which should match with the logarithm derivatives at the ends of the neighboring films, are

\[
\begin{align*}
\phi_{j-1} &= \frac{1}{\psi_j(x)} \left. \frac{d\psi_j(x)}{dx} \right|_{x=x_A+jd_m-d_m} = k_j \cot \left[ k_j(x_A + jd_m - d_m) + \delta_j \right], \\
\phi_j &= \frac{1}{\psi_j(x)} \left. \frac{d\psi_j(x)}{dx} \right|_{x=x_A+jd_m} = k_j \cot \left[ k_j(x_A + jd_m) + \delta_j \right]. \tag{18}
\end{align*}
\]

From Eq. (18) we obtain

\[
\phi_j = k_j \cot \left\{ \arctan \left( \frac{k_j}{\phi_{j-1}} \right) + k_j d_m \right\}, \tag{19}
\]

and

\[
k_j d_m = -\arctan \left( \frac{k_j}{\phi_{j-1}} \right) + \arctan \left( \frac{k_j}{\phi_j} \right) + q\pi,
\]

\[
q = \begin{cases} 
0 & \text{no zero of } \phi(x) \text{ occurs in } x_A + jd_m - d_m \leq x \leq x_A + jd_m, \\
1 & \text{a zero of } \phi(x) \text{ occurs in } x_A + jd_m - d_m \leq x \leq x_A + jd_m.
\end{cases} \tag{20}
\]

where \( \arctan \beta \) denotes the principle value of the inverse tangent function:

\[
\arctan \beta = \alpha, \quad \beta = \tan \alpha, \quad -\pi/2 < \alpha \leq \pi/2. \tag{21}
\]
Note that \( \phi(x) \) decreases monotonically with respect to \( x \) when \( EV(x) \) [see Eq. (5)]. If no zero of \( \phi(x) \) occurs in the film \( x_A + jd_m - d_m \leq x < x_A + jd_m \),

\[
\arctan \left( \frac{k_j}{\phi_{j-1}} \right) < \arctan \left( \frac{k_j}{\phi_j} \right) \leq \frac{\pi}{2},
\]

Equation (20) holds with \( q = 0 \). If one zero of \( \phi(x) \) occurs in the film \( x_A + jd_m - d_m \leq x < x_A + jd_m \), \( \phi_{j-1} \geq 0 \), and \( \phi_j < 0 \). Thus,

\[
\arctan \left( \frac{k_j}{\phi_{j-1}} \right) \sim \frac{\pi}{2}, \quad \text{and} \quad \arctan \left( \frac{k_j}{\phi_j} \right) \sim -\frac{\pi}{2},
\]

we have to add an additional \( \pi \) on the right-hand side of Eq. (20) such that its right-hand side is positive and equal to \( k_j d_m \). Since the width \( d_m \) of the film is very small, we do not consider the case where more than one zeroes of \( \phi(x) \) occur in the film.

Equation (19) is a recursive relation, with which one is able to calculate \( \phi_m = \phi(x_B^-) \) from \( \phi_0 = \phi(x_A) \) as \( j \) increases from 1 to \( m \). The calculated precision depends on the number \( m \) of the films. In principle, one may obtain a precise \( \phi(x_B^-) \) if \( m \) is large enough.

From the Sturm-Liouville theorem (see Appendix B), as \( E \) increases, \( \phi(x_B^-) \) decreases monotonically and \( \phi(x_B^+) \) increases monotonically. Choosing the parameter \( E \) by dichotomy such that \( \phi(x_B^-) \) matches with \( \phi(x_B^+) \), we obtain a bound state with the energy \( E \).

Cao et al. [8] derived the recursive relations similar to Eqs. (14), (15) and (19), and calculated some examples with more precise results than those obtained with the nonintegral Maslov index and the standard WKB method. Zhou et al. [9] calculated a problem with a one-dimensional symmetric double-well potential. Since the potential is symmetric, \( V(-x) = V(x) \), the solution \( \psi(x) \) of the Schrödinger equation is even or odd in the spatial inversion, and then, its logarithm derivative \( \phi(x) \) is odd. If a nontrivial solution \( \psi(x) \) is odd, \( \psi(0) = 0 \) and \( \phi(x) \) has to be infinity, \( \phi(0+) = +\infty \). If a nontrivial solution \( \psi(x) \) is even, \( \psi(0) \neq 0 \) and \( \phi(x) \) has to be zero because \( \phi(x) \) is odd, namely, \( \phi(0+) = 0 \). One can calculate the energy levels of this system by the above method in the half space \( 0 < x < \infty \). The different boundary conditions of \( \phi(0+) \) will give different solutions with different energies, as calculated in [9].
III. QUANTIZATION RULE

In the preceding section, we divided the region $x_A \leq x \leq x_B$ into $m$ equal films, where $E \geq V(x)$, and obtained Eq. (20) for $k_jd_m$. Summing up Eq. (20) from $j = 1$ to $j = m$, we obtain

$$\sum_{j=1}^{m} k_jd_m = N\pi - \arctan \left( \frac{k_1}{\phi_0} \right) + \arctan \left( \frac{k_1}{\phi_1} \right) - \arctan \left( \frac{k_2}{\phi_1} \right) + \arctan \left( \frac{k_2}{\phi_2} \right) - \cdots - \arctan \left( \frac{k_{m-1}}{\phi_{m-2}} \right) + \arctan \left( \frac{k_{m-1}}{\phi_{m-1}} \right) - \arctan \left( \frac{k_m}{\phi_{m-1}} \right) + \arctan \left( \frac{k_m}{\phi_m} \right).$$

(22)

where $\phi_0 = \phi(x_A)$, $\phi_m = \phi(x_B)$, and $N$ is the number of zeroes of the logarithm derivative $\phi(x)$ in the region $x_A \leq x < x_B$. When $m$ goes to infinity, $d_m$ tends to zero, and the sum in Eq. (22) becomes an integral. Thus, we obtain a new quantization rule:

$$\int_{x_A}^{x_B} k(x)dx = N\pi + \lim_{m \to \infty} \left\{ -\arctan \left( \frac{k_1}{\phi(x_A)} \right) + \arctan \left( \frac{k_m}{\phi(x_B)} \right) + \sum_{j=1}^{m-1} \left[ \arctan \left( \frac{k_j}{\phi_j} \right) - \arctan \left( \frac{k_{j+1}}{\phi_j} \right) \right] \right\},$$

(23)

where $\phi_j$ is calculated recursively with Eq. (19). The first term of the right-hand side of Eq. (23) comes from the zeroes of the logarithm derivative $\phi(x)$ in the region $x_A \leq x < x_B$. Since $\phi(x_A)0$ and $\phi(x_B) < 0$, the second and the third terms are vanishing as $m$ goes to infinity if the potential is continuous at the turning points. The last sum denotes the phase contribution devoted by the scattered subwaves.

The formula (23) has another expression. If one changes $\delta_j = \delta_j' + \pi/2$ in Eq. (17), Eq. (18) becomes

$$\phi_{j-1} = -k_j \tan \left[ k_j(x_A + jd_m - d_m) + \delta_j' \right],$$

$$\phi_j = -k_j \tan \left[ k_j(x_A + jd_m) + \delta_j' \right].$$

Then, equations (20) and (23) become

$$k_jd_m = \arctan \left( \frac{\phi_{j-1}}{k_j} \right) - \arctan \left( \frac{\phi_j}{k_j} \right) + q'\pi,$$

$$q' = \begin{cases} 
0 & \text{no zero of } \psi(x) \text{ occurs in } x_A + jd_m - d_m < x \leq x_A + jd_m, \\
1 & \text{a zero of } \psi(x) \text{ occurs in } x_A + jd_m - d_m < x \leq x_A + jd_m, 
\end{cases}$$
\[ \int_{x_A}^{x_B} k(x)dx = N'\pi + \lim_{m \to \infty} \left\{ \arctan \left( \frac{\phi(x_A)}{k_1} \right) - \arctan \left( \frac{\phi(x_B)}{k_m} \right) \right\} \]
\[ + \sum_{j=1}^{m-1} \left[ \arctan \left( \frac{\phi_j}{k_{j+1}} \right) - \arctan \left( \frac{\phi_j}{k_j} \right) \right], \] (24)

where \(N'\) denotes the number of nodes of the wave function \(\psi(x)\) in the region \(x_A < x \leq x_B\). If the potential is continuous at the turning points, due to \(\phi(x_A) > 0\) and \(\phi(x_B) < 0\), the second and the third terms are

\[ \lim_{m \to \infty} \arctan \left( \frac{\phi(x_A)}{k_1} \right) - \lim_{m \to \infty} \arctan \left( \frac{\phi(x_B)}{k_m} \right) = \frac{\pi}{2} - (-\frac{\pi}{2}) = \pi. \] (25)

Since \(\phi(x)\) decreases monotonically in the region \(x_A < x < x_B\), \(N = N' + 1\).

The sum on the right-hand side of Eq. (23) can be transformed into an integral expression:

\[ \int_{x_A}^{x_B} k(x)dx = N'\pi + \lim_{m \to \infty} \left\{ -\arctan \left( \frac{k_1}{\phi(x_A)} \right) + \arctan \left( \frac{k_m}{\phi(x_B)} \right) \right\} \]
\[ - \int_{x_A}^{x_B} \frac{\phi(x)}{\phi(x)^2 + k(x)^2} (dk(x)/dx) \phi(x)^2 + k(x)^2 dx. \] (26)

Two terms in the curly brackets are vanishing as \(m\) goes to infinity if the potential is continuous at the turning points. The sum in Eq. (24) can also be transformed into an integral expression.

The quantization rule (26) is proved without any approximation, so that it is exact. Its validity can also be confirmed by comparing it with the following solvable examples. Both Eqs. (23) and (24) are the formulas of numerical calculation for Eq. (26). Cao et al. [8,9] presented an expression similar to Eq. (24) and demonstrated it to be very effective in numerical calculation through two examples: the one-dimensional Schrödinger equation with a power-law potential [8] and a symmetric double-well potential [9].

**Ex. 1.** The harmonic oscillator potential.

The WKB method is precise for the harmonic oscillator potential. Now, we are going to check our new quantization rule (26) for the harmonic oscillator potential \(V(x) = \mu \omega^2 x^2 / 2\). Let

\[ \alpha = \sqrt{\frac{\mu \omega}{\hbar}}, \quad \xi = \alpha x, \] (27)
we have
\[
\psi_n(x) = N_n e^{-\xi^2/2} H_n(\xi), \quad E_n = h\omega (n + 1/2),
\]
\[
\phi_n(x) = -\alpha \xi + 2n\alpha H_{n-1}(\xi)/H_n(\xi),
\]
where \(N_n\) is the normalization factor, \(H_n(\xi)\) denote the \(n\)th Hermitian polynomial. In the region \(x_A \leq x \leq x_B\), where \(-x_A = x_B = \sqrt{2n + 1}/\alpha\), we have
\[
k^{(n)}(x) = \alpha \sqrt{2n + 1 - \xi^2}, \quad \frac{dk^{(n)}(x)}{dx} = -\alpha x/k^{(n)}(x).
\]

After calculation for \(0 \leq n \leq 10\), we know that \(\phi_n(x_A) = -\phi_n(x_B)\), \(\phi_n(x)\) has \(n + 1\) zeroes in the region \(x_B \leq x < x_B\), and Eq. (26) becomes
\[
\int_{x_A}^{x_B} k^{(n)}(x)dx = (n + 1)\pi + \Phi_n,
\]
\[
\Phi_n = -\int_{x_A}^{x_B} \frac{\phi(x) [dk^{(n)}(x)/dx]}{\phi(x)^2 + k^{(n)}(x)^2}dx
\]
\[
= 2 \int_0^{\sqrt{2n+1}} \frac{2nH_{n-1}(\xi) - \xi H_n(\xi)}{[2n + 1 - \xi^2]H_n(\xi)^2 + [2nH_{n-1}(\xi) - \xi H_n(\xi)]^2} \frac{\xi H_n(\xi)d\xi}{\sqrt{2n + 1 - \xi^2}}
\]
\[
= 2 \int_0^{\sqrt{2n+1}} \frac{(2n - \xi^2) d\xi}{\sqrt{2n + 1 - \xi^2}} + F_n.
\]

At least for \(0 \leq n \leq 10\) we obtain \(\Phi_n = -\pi/2\) by Mathematica. In fact, the first term in \(\Phi_n\) is \((2n - 1)\pi/2\), and through a variable transformation:
\[
\sqrt{2n + 1 - \xi^2} = t(\xi + \sqrt{2n + 1}), \quad d\xi = -\frac{4\sqrt{2n + 1}dt}{(1 + t^2)^2},
\]
the second integral \(F_n\) is calculated to be \(-n\pi\):
\[
F_0 = 0,
\]
\[
F_1 = 2 \int_0^{\sqrt{3}} \frac{-2d\xi}{\sqrt{3 - \xi^2}(1 + \xi^2)} = -2 \int_0^1 \frac{(1 + t^2)dt}{1 - t^2 + t^4} = -\pi,
\]
\[
F_2 = 2 \int_0^{\sqrt{5}} \frac{-4(4\xi^2 + 5)d\xi}{\sqrt{5 - \xi^2(4\xi^4 + 4\xi^2 + 5)}}
\]
\[
= -16 \int_0^1 \frac{(1 + t^2)(5 - 6t^2 + 5t^4)dt}{25 - 76t^2 + 118t^4 - 76t^6 + 25t^8} = -2\pi,
\]
\[
F_3 = 2 \int_0^{\sqrt{7}} \frac{-6(4\xi^4 + 6\xi^2 + 9)d\xi}{\sqrt{7 - \xi^2(4\xi^6 + 9\xi^2 + 9)}}
\]
\[
= -24 \int_0^1 \frac{(1 + t^2)(247 - 748t^2 + 1146t^4 - 748t^6 + 247t^8)dt}{1444 - 8052t^2 + 20652t^4 - 27512t^6 + 20652t^8 - 8052t^{10} + 1444t^{12}}
\]
\[
= -3\pi.
\]
Thus, we demonstrate that the quantization rule (26) is the same as Eq. (1) for the harmonic oscillator potential.

Ex. 2. The square well potential.

Discuss a finite square well potential \( V(x) \)

\[
V(x) = \begin{cases} 
V_A & x \leq -\pi, \\
V_B & x \geq \pi, \\
0 & -\pi < x < \pi.
\end{cases}
\]  

(31)

The logarithm derivatives at the turning points \( x_A = -\pi \) and \( x_B = \pi \) are

\[
\phi(x_A) = \kappa_I = \sqrt{2\mu(V_A - E)/\hbar}, \quad \phi(x_B) = -\kappa_F = -\sqrt{2\mu(V_B - E)/\hbar},
\]

(32)

when \( E < V_A \) and \( E < V_B \). The solution to the Schrödinger equation is

\[
\psi_n(x) = \sin \left( k^{(n)} x + \delta^{(n)} \right),
\]

(33)

and its logarithm derivative \( \phi_n(x) \) is

\[
\phi_n(x) = k^{(n)} \cot \left( k^{(n)} x + \delta^{(n)} \right).
\]

(34)

\( k^{(n)} \) and \( \delta^{(n)} \) are determined by the matching conditions at the turning points \( x_A \) and \( x_B \),

\[
\tan \left( -k^{(n)} \pi + \delta^{(n)} \right) = k^{(n)}/\kappa_I, \quad \tan \left( k^{(n)} \pi + \delta^{(n)} \right) = -k^{(n)}/\kappa_F.
\]

Hence, we obtain

\[
k^{(n)} = - \left\{ \arctan \left( k^{(n)}/\kappa_I \right) + \arctan \left( k^{(n)}/\kappa_F \right) \right\} / (2\pi) + n/2.
\]

(35)

\( \phi_n(x) \) has \( n \) zeroes in the region \( -\pi \leq x \leq \pi \), and \( k(x) \) takes the constant value \( k^{(n)} \) in the region, \( dk(x)/dx = 0 \). The energy levels are \( E_n = \left( \hbar k^{(n)} \right)^2 / (2\mu) \). In terms of Eq. (35), the right-hand side of Eq. (26) is calculated to be

\[
n\pi - \arctan \left( \frac{k_1}{\phi(x_A)} \right) + \arctan \left( \frac{k_m}{\phi(x_B)} \right)
\]

\[
= n\pi - \left\{ \arctan \left( k^{(n)}/\kappa_I \right) + \arctan \left( k^{(n)}/\kappa_F \right) \right\} = 2\pi k^{(n)}.
\]

(36)

Due to the constant \( k(x) \), the left-hand side of Eq. (26) is equal to the same value:

\[
\int_{x_A}^{x_B} k(x) dx = 2\pi k^{(n)}.
\]

(37)
This quantization rule is different from both the Bohr-Sommerfeld one and that given by the WKB approximation. When \( V_A \) and \( V_B \) tend to infinity, due to Eqs. (32) and (35) \( k^{(n)} \) goes to \( n/2 \), and the quantization rule (37) coincides with the Bohr-Sommerfeld one.

IV. THREE-DIMENSIONAL SCHRÖDINGER EQUATION

Consider the three-dimensional Schrödinger equation with a spherically symmetric potential. After separation of the angular part of the wave function,

\[
\psi(r) = r^{-1} R(r) Y_{\ell m}(\theta, \varphi),
\]

the radial equation of the Schrödinger equation is

\[
\frac{d^2 R(r)}{dr^2} = -\frac{2\mu}{\hbar^2} \{E - U(r)\} R(r), \quad U(r) = \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} + V(r). \tag{39}
\]

Since Eq. (39) is similar to Eq. (3), its energy levels can be calculated by the matching conditions of the logarithm derivatives, where the logarithm derivative is defined as

\[
\phi(r) = R(r)^{-1} \frac{dR(r)}{dr}. \tag{40}
\]

As an example, we discuss the problem of the hydrogen atom, where the potential \( V(r) \) is

\[
V(r) = -\frac{e^2}{r}. \tag{41}
\]

When \( r \to \infty \), we have

\[
R(r) \sim \exp\{-r \sqrt{2\mu |E| / \hbar}\}, \quad \phi(r) \sim -\sqrt{2\mu |E| / \hbar}.
\]

When \( r \to 0 \), we have

\[
R(r) \sim r^{\ell + 1} \left[1 - \frac{\mu e^2}{\hbar^2 (\ell + 1)^2} r^2\right], \quad \phi(r) \sim (\ell + 1)/r.
\]

By the method of matching condition of logarithm derivatives, one is able to calculate the energy \( E \) with Eqs. (14), (15) and (19).

On the other hand, if the solution to Eq. (39) has known, we are able to check whether the quantization rule (26) holds. For the energy \( E_n \)

\[
E_n = -\frac{\mu e^4}{2\hbar^2 n^2}, \quad n = 1, 2, 3, \ldots, \tag{42}
\]
we have the solution [1]
\[ R_{n\ell}(r) = N_n e^{-\rho/2} \rho^{\ell+1} L^{2\ell+1}_{n+\ell}(\rho), \quad \rho = \frac{2\mu e^2}{nh^2} r, \]  
(43)
where \( N_n \) is the normalization factor and \( L^{2\ell+1}_{n+\ell}(\rho) \) is the associated Laguerre polynomials.

When \( \ell \geq 0 \), the turning points \( r_A \) and \( r_B \) satisfying \( U(r_A) = U(r_B) = E_n \) are
\[ r_A = \frac{nh^2}{2\mu e^2} \rho_A, \quad \rho_A = 2 \left\{ n - \left[ n^2 - \ell(\ell + 1) \right]^{1/2} \right\}, \]
\[ r_B = \frac{nh^2}{2\mu e^2} \rho_B, \quad \rho_B = 2 \left\{ n + \left[ n^2 - \ell(\ell + 1) \right]^{1/2} \right\}. \]  
(44)
When \( \ell = 0 \), we define \( r_A = 0 \) with \( U(r_A) = -e^2/r_A \sim -\infty \). \( r_B \) with \( U(r_B) = E_n \) still satisfies Eq. (37). The momentum \( k_{n\ell}(r) \) is
\[ k_{n\ell}(r) = \frac{1}{2r} \left\{ (\rho - \rho_A) (\rho_B - \rho) \right\}^{1/2}. \]  
(45)
In the Schrödinger equation for the hydrogen atom, the quantization rule (26) becomes
\[ \int_{r_A}^{r_B} k_{n\ell}(r) dr = N\pi + \lim_{m \to \infty} \left\{ -\text{Arctan} \left( \frac{k_1}{\phi_{n\ell}(r_A)} \right) + \text{Arctan} \left( \frac{k_m}{\phi_{n\ell}(r_B)} \right) \right\} \]
\[ - \int_{r_A}^{r_B} \frac{\phi_{n\ell}(r)}{\phi_{n\ell}(r)^2 + k_{n\ell}(r)^2} dk_{n\ell}(r) dr. \]  
(46)
Calculating the left-hand side of Eq. (51), we obtain with Eq. (50)
\[ \int_{r_A}^{r_B} k_{n\ell}(r) dr = \int_{r_A}^{r_B} \frac{d\rho}{\rho_A} \left\{ (\rho - \rho_A) (\rho_B - \rho) \right\}^{1/2} = \left[ n - \sqrt{\ell(\ell + 1)} \right] \pi. \]  
(47)
Now, we calculate the right-hand side of Eq. (51). The number \( N \) of zeroes of \( \phi_{n\ell}(r) \) in the region \( r_A \leq r < r_B \) is \( n - \ell \). The logarithm derivatives at the turning points \( r_A \) and \( r_B \) are non-vanishing. When \( \ell = 0 \), \( r_A \) is not the turning point, but \( \phi_{n0}(r_A) = 1/r \).

Thus, we have
\[ \lim_{m \to \infty} \text{Arctan} \left( \frac{k_m}{\phi_{n\ell}(r_B)} \right) = 0, \quad \ell \geq 0, \]
\[ \lim_{m \to \infty} \text{Arctan} \left( \frac{k_1}{\phi_{n\ell}(r_A)} \right) = 0, \quad \ell = 0, \]  
(48)
\[ \lim_{m \to \infty} \text{Arctan} \left( \frac{k_1}{\phi_{n0}(r_A)} \right) = \lim_{r \to 0} \text{Arctan} \left\{ r \sqrt{\frac{2\mu}{E_n + e^2/r}} / h \right\} = 0, \quad \ell = 0. \]
Calculating the integral in Eq. (51) by Mathematica, at least for \( n = 1, 2, 3 \), and \( \ell < n \), we obtain:
\[ - \int_{r_A}^{r_B} \frac{\phi_{n\ell}(r)}{\phi_{n\ell}(r)^2 + k_{n\ell}(r)^2} dk_{n\ell}(r) dr = \left[ \ell - \sqrt{\ell(\ell + 1)} \right] \pi. \]  
(49)
Therefore, the quantization rule (46) holds for the hydrogen atom.
V. CONCLUSIONS

In this Letter, with the matching condition of the logarithm derivatives and the fundamental concept of the mathematical analysis, we proposed a formula (23) for numerically calculating the energy levels of bound states of the Schrödinger equation in one dimension. Calculating the integral form of Eq. (23), we obtained an exact quantization rule (26) for the bound states of the one-dimensional Schrödinger equation. The exact quantization rule was generalized to bound states of the three-dimensional Schrödinger equation with a spherically symmetric potential. The quantization rule was confirmed by checking some examples where the solutions of the Schrödinger equation are known. Two examples of numerical calculation for the one-dimensional Schrödinger equation with a power-law potential [8] and with a symmetric double-well potential [9] demonstrated that the exact quantization rule is very effective in numerical calculation.

Cao et al. [8,9] derived a formula similar to Eq. (24). However, their formulation contained some unclear points. The integer N in Eq. (29) of Ref. [8] is unclarified. They introduced the “exponentially decaying coefficients” $P_j$, but the physical meaning of $P_j$ is rather ambiguous. In fact, $P_j$ are nothing but the logarithm derivatives of the wave function (in their region of $0 \leq x \leq x_C$) or that multiplied with $-1$ (in their region of $x_D \leq x \leq x_S$). This is the reason why the coefficients should be matched at the turning points, which was not explained clearly in Ref. [8]. Finally we would like to point out that the series form (23) is an approximate formula of the integral form (26) derived in the present Letter, which is the exact quantization rule.

ACKNOWLEDGMENTS. One of the authors (BWX) would like to thank Professor Z. Cao for drawing his attention to this problem. This work was supported by the National Natural Science Foundation of China.

[1] L. I. Schiff, Quantum Mechanics, Third Edition, (McGraw-Hill Book Co., New York, 1968).

[2] G. Wentzel, Z. Physik. 38, 518 (1926).
Appendix A  Property of $\phi(x_A)$

From the recursive relation (14) and $\phi(x_I)0$, we have proved that $\phi(x_A)$ is non-negative and finite. Now, we are going to prove that $\phi(x_A) \neq 0$ by reduction to absurdity. When $x \leq x_A$ and $x$ near $x_A$, consider the leading term in the power series in $(x_A - x)$. Due to $\kappa(x_A) = 0$, we have $\kappa(x) \simeq C(x_A - x)^\alpha$, where $C0$ and $\alpha0$. If $\phi(x_A) = 0$, from Eq. (6) we have $\phi(x_A) \simeq -C^2(x_A - x)^{2\alpha+1}/(2\alpha + 1) < 0$. It conflicts to the fact that $\phi(x_A)$ is non-negative.

Appendix B  The Sturm-Liouville Theorem

Denote by $\psi(E, x)$ the solution of the Schrödinger equation (3) with the energy $E$. Multiplying Eq. (3) with $\psi(E_1, x)$ we have

$$
\psi(E_1, x) \frac{\partial^2}{\partial x^2} \psi(E, x) = -\frac{2\mu}{\hbar^2} [E - V(x)] \psi(E, x)\psi(E_1, x) ,
$$

(B1)

Exchanging $E_1$ and $E$ and subtracting from it by Eq. (B1), we obtain

$$
\frac{\partial}{\partial x} \left\{ \psi(E, x) \frac{\partial \psi(E_1, x)}{\partial x} - \psi(E_1, x) \frac{\partial \psi(E, x)}{\partial x} \right\} = -\frac{2\mu}{\hbar^2} (E_1 - E) \psi(E, x)\psi(E_1, x).
$$

(B2)

When $E < V(-\infty)$, the boundary condition gives that both solutions $\psi(E, x)$ and $\psi(E_1, x)$ are vanishing at negative infinity. Integrating Eq. (B2) from $-\infty$ to $x_B-$, we obtain

$$
\frac{1}{E_1 - E} \left\{ \psi(E, x) \frac{\partial \psi(E_1, x)}{\partial x} - \psi(E_1, x) \frac{\partial \psi(E, x)}{\partial x} \right\}_{x=x_B^-} = -\frac{2\mu}{\hbar^2} \int_{-\infty}^{x_B} \psi(E, x)\psi(E_1, x) dx.
$$
Taking the limit as $E_1$ goes to $E$, we have

$$\left. \frac{\partial \phi(E, x)}{\partial E} \right|_{x=x_B^-} = \left. \frac{\partial}{\partial E} \left\{ \frac{1}{\psi(E, x)} \frac{\partial \psi(E, x)}{\partial x} \right\} \right|_{x=x_B^-}$$

$$= -\frac{2\mu}{\hbar^2 \psi(E, x_B)^2} \int_{-\infty}^{x_B} \psi(E, x)^2 dx < 0. \quad (B3)$$

Namely, at a given point $x_B^-$, the logarithm derivative $\phi(E, x)$ of the wave function $\psi(E, x)$ decreases monotonically as $E$ increases.

Similarly, when $E < V(\infty)$, the boundary condition gives that both solutions $\psi(E, x)$ and $\psi(E_1, x)$ are vanishing at positive infinity. Integrating Eq. (B2) from $x_B^+$ to $\infty$, we obtain

$$\frac{1}{E_1 - E} \left\{ \psi(E, x) \frac{\partial \psi(E_1, x)}{\partial x} - \psi(E_1, x) \frac{\partial \psi(E, x)}{\partial x} \right\} \bigg|_{x=x_B^+} = \frac{2\mu}{\hbar^2} \int_{x_B}^{\infty} \psi(E, x) \psi(E_1, x) dx.$$  

Taking the limit as $E_1$ goes to $E$, we have

$$\left. \frac{\partial \phi(E, x)}{\partial E} \right|_{x=x_B^+} = \frac{2\mu}{\hbar^2 \psi(E, x_B)^2} \int_{x_B}^{\infty} \psi(E, x)^2 dx < 0. \quad (B4)$$

Namely, at a given point $x_B^+$, the logarithm derivative $\phi(E, x)$ of the wave function $\psi(E, x)$ increases monotonically as $E$ increases.