Simple variational approaches to quantum wells

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Abstract

We discuss two simple variational approaches to quantum wells. The trial harmonic functions analyzed in an earlier paper give reasonable results for all well depths and are particularly suitable for deep wells. On the other hand, the exponential functions proposed here are preferable for shallow wells. We compare the shallow-well expansions for both kind of functions and show that they do not exhibit the cubic term appearing in the exact series. It is also shown that the deep-well expansion for the harmonic functions agree with the first terms of perturbation theory.

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I. INTRODUCTION

In a recent paper we discussed the application of the variational method to a Gaussian well. We showed that harmonic variational functions yield reasonably accurate results for all well depths despite the fact that the shallow-well expansion for the ground-state variational energy does not agree with the exact expansion beyond the leading term.

Students at introductory courses on quantum mechanics are commonly encouraged to solve the Schrödinger equation for a particle in a one-dimensional square box with finite walls. They thus learn that the exact solution decays exponentially as $|x| \to \infty$. After such an experience they would find it unreasonable the choice of harmonic variational functions that do not exhibit the behavior at infinity expected for the exact solutions to the Schrödinger equation for the Gaussian well. For this reason we think that it is interesting to show an alternative variational calculation based on trial functions with the expected exponential behavior at infinity.

In Sec. II we develop the variational method for a general single-well potential-energy function. In Sec. III we discuss the application of the harmonic and exponential trial functions to the Gaussian well, compare the approximate and exact energies for the ground and first-excited state as well as their shallow-well expansions. In Sec. IV we compare the variational and exact deep-well expansions that we did not consider in our previous paper. Finally, in Sec. V we discuss the main results and draw conclusions.

II. SIMPLE VARIATIONAL METHOD

We are interested in the solutions to the Schrödinger equation

$$\hat{H}\psi_n = \epsilon_n\psi_n, \quad n = 0, 1, \ldots$$

(1)

for the dimensionless Hamiltonian operator

$$\hat{H} = \hat{T} + v(x) = -\frac{1}{2}\frac{d^2}{dx^2} + v(x)$$

(2)

In our previous paper we showed how to convert the Schrödinger equation into a dimensionless eigenvalue equation and we do not repeat it here. For concreteness we choose the dimensionless potential-energy function to be of the form $v(x) = -v_0f(x)$, where $v_0 > 0$ and the function $f(x)$ exhibits a maximum at $x = 0$ and tends to zero when $|x| \to \infty$. Since
we restrict ourselves to single wells we also assume that $f'(x) > 0$ if $x < 0$ and $f'(x) < 0$ if $x > 0$ although we do not make use of this condition explicitly. We will discuss a particular example later on. The reader will find some references about quantum-mechanical wells in our earlier paper.

It is our purpose to obtain simple solutions for some states of the quantum well by means of the variational method. To this end we choose a variational function $\varphi(a, x)$ that depends on a variational parameter $a$. If we assume that $\epsilon_0 < \epsilon_1 < \epsilon_2 < \cdots$ then the variational principle gives us an upper bound to the smallest eigenvalue

$$W(a) = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} \geq \epsilon_0$$

and we realize that the optimum value of $a$ is given by the minimum of $W(a)$. If we write $W(a) = F(a) - v_0 G(a)$ where $F(a) = \langle \varphi | \hat{T} | \varphi \rangle / \langle \varphi | \varphi \rangle$ and $G(a) = \langle \varphi | f(x) | \varphi \rangle / \langle \varphi | \varphi \rangle$ then $W'(a) = 0$ becomes

$$F'(a) - v_0 G'(a) = 0$$

Commonly, solving this equation for $a$ may not be possible or may lead to cumbersome expressions. In that case we can resort to a simple parametric expression for the approximate energy in the form

$$v_0 = \frac{F'(a)}{G'(a)}$$

$$W(a) = \frac{F(a)G'(a) + F'(a)G(a)}{G'(a)}$$

If $f(-x) = f(x)$ then the states have definite parity $\psi_n(-x) = (-1)^n \psi_n(x)$ and the variational principle applies to $\epsilon_0$ or $\epsilon_1$ if the variational function is even or odd, respectively. Therefore, the variational equations apply to both the ground and first excited states.

III. THE GAUSSIAN WELL

In order to illustrate the performance of the variational method on quantum-mechanical wells we choose a particularly simple example that allows us to calculate the functions $F(a)$ and $G(a)$ analytically. As in our earlier paper we select the Gaussian well given by

$$f(x) = e^{-x^2}$$
and begin present discussion with the calculation based on Harmonic-oscillator-like variational functions. The simplest variational function for the ground state is

\[ \varphi_{0h}(a, x) = e^{-ax^2} \]  

and we easily obtain

\[ v_0 = \frac{\sqrt{2} \sqrt{a} (2a + 1)^{3/2}}{2}, \]

\[ W_{0h}(a) = -\frac{a (4a + 1)}{2} \]  

We showed that \( W_{0h} \rightarrow 0 \) as \( v_0 \rightarrow 0 \) according to

\[ W_{0h} = -v_0^2 + 4v_0^4 - 48v_0^6 + 832v_0^8 - 17408v_0^{10} + \ldots . \]  

(9)

while the exact expansion is

\[ \epsilon_0 = -\frac{\pi v_0^2}{2} + \sqrt{2} \pi v_0^3 - \frac{\pi (2\pi + 3\sqrt{3} + 3)}{3} v_0^4 + \frac{\sqrt{2} \pi (2\pi + 3\sqrt{3}) v_0^5}{3} - \ldots . \]  

(10)

Note that the cubic term is missing in the approximate expansion (9).

We have also shown that

\[ \varphi_{1h}(a, x) = xe^{-ax^2} \]  

is a suitable variational function for the first excited state, and in this case we have

\[ v_0 = \frac{\sqrt{2} \sqrt{2a + 1} (4a^2 + 4a + 1)}{4\sqrt{a}}, \]

\[ W_{1h}(a) = -\frac{a (8a^2 + 2a - 1)}{2 (2a + 1)} \]  

(12)

It is well known that \( \epsilon_1(v_0) \rightarrow 0^- \) as \( v_0 \) approaches a critical well strength \( v_{0,1} \approx 1.342 \) from above. We can estimate the critical strength by means of equations (12) in a quite simple way. We first obtain a positive root of \( W_{1h}(a_c) = 0 \) and then \( v_0(a_c) \); the result is \( a_c = 1/4 \) and \( v_0(1/4) = 9\sqrt{3}/8 \approx 1.95 \). Since the variational energy is an upper bound to the exact one for all \( v_0 \) then it is not surprising that \( v_0(a_c) \) > \( v_{0,1} \). The error for the critical strength obtained with this variational function is rather large: 45%.

We may try to improve those results by means of more convenient trial functions. Since \( v(x \rightarrow \pm \infty) = 0 \) we know that the eigenfunctions behave as \( \psi \sim e^{-a|x|} \) for sufficiently large
$|x|$, where $\alpha = \sqrt{-2\epsilon}$. In order to avoid the function $|x|$ in our calculations we work on the half positive line $x > 0$ and take into account the boundary conditions at origin: $\psi(0) \neq 0$, $\psi'(0) = 0$ for the even states and $\psi(0) = 0$, $\psi'(0) \neq 0$ for the odd ones. Thus, the simplest trial exponential function for the ground state appears to be

$$\varphi_{0e}(a,x) = (1 + ax)e^{-\alpha x}, \quad x > 0$$  \hspace{1cm} (13)

The calculation of the integrals is straightforward and we obtain

$$v_0 = -\frac{1}{\sqrt{\pi}}e^{a^2}(4a^6 + 4a^4 + 5a^2 - 2)\left[1 - \text{erf}(a)\right] - 2a(2a^4 + a^2 - 2)$$

$$W_{0e}(a) = \frac{a^2}{10}\left\{\sqrt{\pi}e^{a^2}(4a^6 + 4a^4 + 5a^2 - 2)\left[\text{erf}(a) - 1\right] + 2a(2a^4 - a^2 + 2)\right\}$$ \hspace{1cm} (14)

where $\text{erf}(z)$ is the error function.

In order to obtain the $v_0$-series for $W_{0e}$ we first expand $v_0(a)$ into an $a$-series:

$$v_0 = \frac{a}{2\sqrt{\pi}} + \frac{3a^3}{4\sqrt{\pi}} - \frac{4a^4}{3\pi} + \frac{9a^5}{8\sqrt{\pi}} + \ldots$$ \hspace{1cm} (15)

that we invert to obtain the $v_0$-series for $a$

$$a = 2\sqrt{\pi}v_0 - 12\pi^{3/2}v_0^3 + \frac{128\pi^{3/2}}{3}v_0^4 + 144\pi^{5/2}v_0^5 + \ldots$$ \hspace{1cm} (16)

Then, we expand $W_{0e}$ in a Taylor series about $a = 0$

$$W_{0e} = a^2 - \frac{a^4}{5} + \frac{2a^5}{5\sqrt{\pi}} + \ldots$$ \hspace{1cm} (17)

and substitute the series (16) to obtain the shallow-well expansion

$$W_{0e} = -\frac{2\pi v_0^2}{5} + \frac{8\pi^2 v_0^4}{5} - \frac{64\pi^2 v_0^5}{15} + \ldots$$ \hspace{1cm} (18)

The calculation is straightforward but extremely tedious if carried out by hand. For this reason it is a good exercise for showing the students the advantage and power of computer algebra. Such software even offer a command for obtaining the inverted series (16) in one step. For sufficiently small $v_0$ this expansion is slightly better than the one derived in our earlier paper, namely Eq. (9), as follows from comparing the leading terms of the variational and exact $v_0$-series: $W_{0h} \approx -v_0^2$, $W_{0e} \approx -1.26v_0^2$ and $\epsilon_0 \approx -1.57v_0^2$. However, the cubic term
that appears in the exact expansion (10) is also missing in the variational treatment based on the exponential function (13). From those results we conclude that \( \epsilon_0 < W_{0e} < W_{0h} \) for sufficiently small \( v_0 \). In other words, the trial function with the correct asymptotic behavior at infinity yields a more accurate variational energy for sufficiently shallow wells.

Fig. 1 shows \( W_{0h}, W_{0e} \) and \( \epsilon_0 \) (obtained by numerical integration\(^2\)) for some values of \( v_0 \). The variational curves are almost indistinguishable in the scale of the Figure. The numerical results show that they cross at \( v_0 = v_c \), where \( 2.4022 < v_c < 2.4023 \), so that \( W_{0e} < W_{0h} \) if \( v_0 < v_c \) and \( W_{0e} > W_{0h} \) if \( v_0 > v_c \). In other words: \( W_{0e} \) is more accurate for shallow wells as argued above and \( W_{0h} \) is more accurate for deep ones. The former inequality is consistent with the previous comparison of the leading terms of the \( v_0 \)-expansions. In the next section we discuss the deep-well limit.

For the first excited state we propose the simple trial function

\[
\varphi_{1e}(a, x) = xe^{-ax}, \ x > 0
\]

and obtain

\[
v_0 = \frac{1}{a \left[ \sqrt{\pi} e^{a^2} (4a^4 + 12a^2 + 3) \left[ 1 - \text{erf} \ (a) \right] - 2a (2a^2 + 5) \right]}
\]

\[
W_{1e}(a) = \frac{a^2 \left\{ \sqrt{\pi} e^{a^2} (4a^4 + 8a^2 + 1) \left[ \text{erf} \ (a) - 1 \right] + 2a (2a^2 + 3) \right\}}{2 \left\{ \sqrt{\pi} e^{a^2} (4a^4 + 12a^2 + 3) \left[ \text{erf} \ (a) - 1 \right] + 2a (2a^2 + 5) \right\}}
\]

The variational energy vanishes at \( a_c \approx 0.550 \) that leads to the approximate critical parameter \( v(a_c) \approx 1.56 \) with an error of 17\%, quite smaller than that for the harmonic function \((11)\). Once again we appreciate that the exponential function leads to more accurate results close to threshold (shallow well).

Fig. 2 shows \( W_{1h}, W_{1e} \) and \( \epsilon_1 \) (obtained by numerical integration\(^2\)) for a range of \( v_0 \) values. In this case the variational curves are not so close each other and the crossing takes place at \( 3.5154 < v_c < 3.51541 \). We realize that the exponential function is preferable for the description of shallow wells as suggested by the errors in the variational critical well strengths. On the other hand, the harmonic function leads to more accurate results for deep wells.
IV. THE DEEP-WELL CASE

The deep-well expansion for a general well can be easily derived by means of perturbation theory. It follows from those results that the first terms of the expansion for the Gaussian well are

\[ \epsilon_n = -v_0 + \left(n + \frac{1}{2}\right) \sqrt{2v_0} - \frac{3}{16} \left(1 + 2n + 2n^2\right) + O \left(v_0^{-1/2}\right) \]  

(21)

where \( n = 0, 1, \ldots \) is the harmonic-oscillator quantum number.

In order to obtain the deep-well expansion for \( W_{\text{oh}} \) first note that the expression for \( v_0 \) in equation (8) shows that \( a \to \infty \) as \( v_0 \to \infty \) and that the leading term is \( a \approx \frac{\sqrt{2v_0}}{2} \). Therefore, we substitute \( a = \frac{\sqrt{2v_0}}{2} + a_1 + \frac{a_2}{\sqrt{v_0}} \) into the expression for \( v_0 \) and set the unknown coefficients \( a_1 \) and \( a_2 \) in order to remove the leading powers of \( v_0 \). In this way we obtain

\[ a = \frac{\sqrt{2v_0}}{2} - \frac{3}{8} + \frac{3\sqrt{2}}{128 \sqrt{v_0}} + O \left(v_0^{-3/2}\right) \]  

(22)

Finally, we substitute this equation into the expression for \( W_{\text{oh}}(a) \), expand and keep the leading terms; the result is

\[ W_{\text{oh}} = -v_0 + \frac{\sqrt{2v_0}}{2} - \frac{3}{16} + O \left(v_0^{-1/2}\right) \]  

(23)

Note that this expression agrees with (21) for \( n = 0 \).

Proceeding exactly in the same way with equation (12) we obtain

\[ a = \frac{\sqrt{2v_0}}{2} - \frac{5}{8} - \frac{5\sqrt{2}}{128 \sqrt{v_0}} + O \left(v_0^{-3/2}\right) \]  

(24)

and

\[ W_{1\text{h}} = -v_0 + \frac{3\sqrt{2v_0}}{2} - \frac{15}{16} + O \left(v_0^{-1/2}\right) \]  

(25)

that agrees with (21) when \( n = 1 \). It is clear that the harmonic variational functions are suitable for the description of deep wells which is in agreement with the results in figures 1 and 2.

V. CONCLUSIONS

We have calculated the first two energy levels of the Gaussian well by means of two types of variational functions. The harmonic trial functions lead to simpler expressions and their
results are reasonable for all values of the well depth. The approximate energies exhibit a slightly accurate expansion for shallow wells and a more satisfactory one for deep wells. In the latter case they provide the first three dominant terms of perturbation theory.

On the other hand, the expressions for the energy obtained from exponential functions are rather complicated and their results are less accurate for deep wells. However, they are useful if one is interested in the behavior of the system near threshold (shallow wells).

Present results suggest that the appropriate behavior of the wavefunction at infinity does not always guarantee the greatest accuracy. In the case of a deep well the wavefunction is strongly localized and compressed about \( x = 0 \) and the description of the neighborhood of the origin is more important than what happens at larger \( |x| \).

A most intriguing result is that both variational approaches fail to yield the cubic term in the shallow-well expansion. We have carried out a similar calculation for the particle in the square box with finite walls and found that the expansion of the variational energy given by the trial function \([13]\) does not exhibit the cubic term that appears in the exact series. In this case one can obtain the exact \( v_0 \)-series for \( \epsilon_0 \) from the transcendental equation that determines the energy levels of that model. We do not have a satisfactory explanation for this failure of the variational method.

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FIG. 1: (Color online) Variational energies $W_{0e}$ (solid line, blue) and $W_{0h}$ (dashed line, red) and numerical ones (circles)

FIG. 2: (Color online) Variational energies $W_{1e}$ (solid line, blue) and $W_{1h}$ (dashed line, red) and numerical ones (circles)