Simple one-dimensional quantum-mechanical model for a particle attached to a surface

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Abstract
We present a simple one-dimensional quantum-mechanical model for a particle attached to a surface. It leads to the Schrödinger equation for a harmonic oscillator bounded on one side that we solve in terms of Weber functions and discuss the behaviour of the eigenvalues and eigenfunctions. We derive the virial theorem and other exact relationships as well as the asymptotic behaviour of the eigenvalues. We calculate the zero-point energy for model parameters corresponding to H adsorbed on Pd(1 0 0). The model is suitable for an advanced undergraduate or graduate course on quantum mechanics.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In an introductory course on quantum theory, one commonly discusses some of the simplest models, such as, for example, free particle, particle in a box, harmonic oscillator, tunnelling through a square barrier, etc with the purpose of making the students more familiar with the principles or postulates of quantum theory. Some time ago Gibbs [1] introduced the quantum bouncer as a model for the pedagogical discussion of some of the relevant features of quantum theory. He derived the solutions to the Schrödinger equation in terms of Airy functions and obtained the energy spectrum for two different model settings.

A closely related model, the harmonic oscillator with a hard wall on one side, had been discussed earlier by Dean [2] and later by Mei and Lee [3]. This model is as simple as the quantum bouncer and both can therefore be discussed in the same course. It is our purpose to show that this model may in principle be useful to simulate a particle attached to a wall-like surface, for example, an atom adsorbed on a solid surface [4, 5]. Although it
is an oversimplified one-dimensional model of the actual physical phenomenon, we deem it worthwhile to discuss some of its properties in this paper.

In section 2 we introduce the model, write the Schrödinger equation in dimensionless form and discuss some of the properties of its solutions. It is our purpose to provide an approach that is more suitable for pedagogical purposes than those given earlier [2, 3]. Besides, we discuss the effect of the boundary conditions on the form of the hypervirial theorems that were not studied in those earlier papers [2, 3]. In section 3, we obtain the eigenfunctions and eigenvalues explicitly in terms of the well-known Weber functions [7] and show the behaviour of the eigenvalues and excitation energies with respect to the distance between the particle and the wall. We also calculate the zero-point energy for values of the model parameters corresponding to the adsorption of H on Pd(1 0 0) [5]. Such physical application of the model was not considered in earlier discussion of the eigenvalue equation [2, 3]. Finally, in section 4 we give further reasons why this model may be useful in an advanced undergraduate or graduate course on quantum theory.

2. Simple model

We consider a simple one-dimensional model for a particle of mass \( m \) attached to a surface located at \( x = 0 \) that separates free space \( (x > 0) \) from the bulk of the material \( (x < 0) \). Therefore, we assume that the potential exhibits an attractive tail for \( x > 0 \) that keeps the particle in the neighbourhood of the surface and a repulsive one for \( x < 0 \) that prevents the particle from penetrating too deep into the material. Since we want to keep the model as simple as possible, we choose

\[
V(x) = \begin{cases} 
\infty & \text{if } x < 0 \\
\frac{k}{2} (x - d)^2 & \text{if } x \geq 0,
\end{cases}
\]

(1)

where \( k, d > 0 \). We note that the particle oscillates about \( x = d \) but the motion is not harmonic because of the effect of the hard wall.

The Schrödinger equation reads

\[
\frac{-\hbar^2}{2m} \psi''(x) + \frac{k}{2} (x - d)^2 \psi(x) = E \psi(x),
\]

\[
\psi(0) = 0, \quad \lim_{x \to \infty} \psi(x) = 0,
\]

(2)

where the boundary condition at \( x = 0 \) comes from the fact that in this simple model the particle cannot penetrate into the material and, consequently, \( \psi(x) = 0 \) for all \( x < 0 \). Since it is more convenient to work with a dimensionless equation, we define the length unit \( L = \left( \frac{\hbar^2 m}{k} \right)^{1/4} \) and the dimensionless coordinate \( q = (x - d)/L \). Thus, the dimensionless Schrödinger equation reads

\[
-\frac{1}{2} \varphi''(q) + \frac{1}{2} q^2 \varphi(q) = \epsilon \varphi(q),
\]

\[
\varphi(-q_0) = 0, \quad \lim_{q \to \infty} \varphi(q) = 0,
\]

(3)

where

\[
\epsilon = \frac{mL^2 E}{\hbar^2} = \frac{E}{\hbar \omega}, \quad \omega = \sqrt{\frac{k}{m}},
\]

\[
q_0 = \frac{d}{L} = \frac{d}{\left( \frac{km}{\hbar^2} \right)^{1/4}},
\]

\[
\varphi(q) = \psi(Lq + d).
\]

(4)
It is worth noting that $q_0$ increases with $d$, $m$ and $k$. It is precisely equation (3) that was discussed by Dean [2] and Mei and Lee [3].

When $q_0 \to \infty$, we have the well-known harmonic oscillator with the eigenvalues

$$\lim_{q_0 \to \infty} \epsilon_n = n + \frac{1}{2}, \quad n = 0, 1, \ldots.$$  \hspace{1cm} (5)

On the other hand, when $q_0 = 0$, we have the harmonic oscillator in the half-line and

$$\lim_{q_0 \to 0} \epsilon_n = 2n + \frac{3}{2}, \quad n = 0, 1, \ldots.$$  \hspace{1cm} (6)

Note that these are merely the harmonic-oscillator eigenvalues with odd quantum number (the corresponding eigenfunctions have a node at the origin). It follows from equation (A.6) in the appendix that

$$\frac{d\epsilon}{dq_0} < 0, \quad \lim_{q_0 \to \infty} \frac{d\epsilon}{dq_0} = 0,$$  \hspace{1cm} (7)

from which we conclude that the energy eigenvalues decrease monotonically between the following limits:

$$2n + \frac{1}{2} \geq \epsilon_n(q_0) > n + \frac{1}{2}, \quad n = 0, 1, \ldots,$$  \hspace{1cm} (8)

when $0 \leq q_0 < \infty$. In order to understand the connection between both limits, it should be kept in mind that the number of zeros $n$ of $\phi_n(q)$ should be the same for all $q_0$ from 0 to $\infty$.

Equation (A.6) is useful for obtaining the asymptotic behaviour of the energy as $q_0 \to \infty$. To this end, we simply integrate it from $-\infty$ to $-q_0$:

$$\epsilon(-q_0) = \epsilon(-\infty) + \frac{1}{2} \int_{-\infty}^{-q_0} \psi(b)^2 \frac{\psi'(b)}{\psi(q)} \frac{dq}{db} db.$$  \hspace{1cm} (9)

For the ground state, we expect that $\psi(q) \to N e^{-q^2/2}$ as $q_0 \to \infty$. The normalization factor is approximately given by

$$N^{-2}(q_0) = \int_{-q_0}^{\infty} e^{-q^2} dq = \frac{\sqrt{\pi}}{2} \left[ 1 + \text{erf}(q_0) \right],$$  \hspace{1cm} (10)

where erf($z$) is the error function. Since erf($z$) $\leq$ erf($\infty$) = 1, we write erf($q_0$) $= 1 - \xi$ and expand $N^2$ in a Taylor series about $\xi = 0$:

$$N(q_0)^2 \approx \frac{2 + \xi}{2\sqrt{\pi}} = \frac{3 - \text{erf}(q_0)}{2\sqrt{\pi}}.$$  \hspace{1cm} (11)

Finally, equation (9) yields

$$\epsilon_0(-q_0) \approx \frac{1}{2} + \frac{q_0 e^{-q_0^2}}{2\sqrt{\pi}}.$$  \hspace{1cm} (12)

In order to obtain this result, we substituted erf($q_0$) $\approx 1$ after the integration and neglected a term proportional to $e^{-2\xi^2}$ because it is much smaller than the exponential one retained in equation (12). This result agrees with the one derived by Mei and Lee [3] by means of perturbation theory (note that their parameter $R$ is $\sqrt{2q_0}$).

Proceeding in the same way for the first excited state, we obtain

$$\epsilon_1(-q_0) \approx \frac{3}{2} + \frac{q_0(2q_0^2 - 1)e^{-q_0^2}}{2\sqrt{\pi}},$$  \hspace{1cm} (13)

which is slightly different from the result of Mei and Lee [3]. However, they are equivalent for most purposes because the difference between them is smaller than their absolute errors.
Equation (A.10) gives us the virial theorem [6] for this model:

$$\langle \hat{D}^2 \rangle + \langle q^2 \rangle = q_0 \frac{\partial \epsilon}{\partial q_0},$$

(14)

where $\hat{D} = d/dq$. The right-hand side of this equation is the virial of the force exerted by the surface. Equation (A.13) provides us with another interesting relation

$$\langle q \rangle = -\frac{\partial \epsilon}{\partial q_0}$$

(15)

that clearly reveals the asymmetry of the interaction between the particle and the surface. In both cases we recover the well-known results for the harmonic oscillator $\langle \hat{D}^2 \rangle + \langle q^2 \rangle = 0$ and $\langle q \rangle = 0$, when $q_0 \rightarrow \infty$.

3. Results

If we define the new independent variable $z = \sqrt{2q}$ and write the energy as $\epsilon = m + 1/2$, then we realize that $D_m(z) = \psi(z/\sqrt{2})$ is a solution to the Weber equation [7]:

$$D_m''(z) + (m + 1/2 - z^2/4)D_m(z) = 0.$$  

(16)

The general solution is [7]

$$D_m(z) = 2^{m/2} \sqrt{\pi} e^{-z^2/4} \left[ \frac{1}{\Gamma\left(\frac{m+1}{2}\right)} F\left(\frac{m}{2}, \frac{1}{2}; \frac{z^2}{2}\right) - \frac{\sqrt{2}z}{\Gamma\left(-\frac{m}{2}\right)} F\left(\frac{1-m}{2}, \frac{3}{2}; \frac{z^2}{2}\right) \right],$$

(17)

where the confluent hypergeometric function $F(a | c | z)$ is a solution to

$$zF''(z) + (c - z)F(z) - aF(z) = 0$$

(18)

and can be expanded in a Taylor series about $z = 0$ as

$$F(a | c | z) = 1 + \frac{a}{c} z + \frac{a(a+1)}{2c(c+1)} z^2 + \cdots.$$  

(19)

The boundary condition $\psi(-q_0) = 0$ enables us to calculate the eigenvalues from the roots of $D_m(-\sqrt{2}q_0) = 0$. For each value of $q_0$, we solve

$$\frac{1}{\Gamma\left(\frac{m+1}{2}\right)} F\left(\frac{m}{2}, \frac{1}{2}; q_0^2\right) + \frac{2q_0}{\Gamma\left(-\frac{m}{2}\right)} F\left(\frac{1-m}{2}, \frac{3}{2}; q_0^2\right) = 0$$

(20)

for $m$ and then calculate the dimensionless energy $\epsilon = m + 1/2$. This approach has already been discussed by Dean [2] and Mei and Lee [3].

Figure 1 shows $\epsilon_n(q_0)$ for $n = 0, 1, 2, 3$ and a wide range of values of $q_0$. We note that the dimensionless energy decreases monotonically as predicted by equation (7) between the limits indicated in equation (8).

The gap between two consecutive energy levels of the harmonic oscillator is $\Delta \epsilon_n = \epsilon_{n+1} - \epsilon_n = 1$ ($\Delta E_n = \hbar \omega$). Figure 2 shows $\Delta \epsilon_n(q_0)$ for $n = 0, 1, 2$, where we note that the energy gap increases with $n$ revealing that the presence of the wall results in an anharmonic oscillation. It becomes more harmonic as $q_0$ increases (by increasing either $d$, $m$, or $k$).

In order to have a clearer physical idea of the kind of predictions of this simple model, we may choose the parameters for the adsorption of H on Pd(1 0 0). Gladys et al [5] estimated $d \approx 0.4$ Å and $k \approx 15$ N m$^{-1}$ for hydrogen that lead to $q_0 \approx 1.55$. The zero-point energy for such model parameters is approximately $0.57 \hbar \omega$ instead of the value $\hbar \omega/2$ chosen by those authors. Although they fitted the potential energy of the vertical displacement of the H atom from the Pd surface to a cubic polynomial, they simply chose the zero-point energy of the
harmonic oscillator. The present model predicts that the zero-point energy is slightly greater than the harmonic-oscillator one because of the repulsive effect of the surface. We agree that a hard wall may not be the most adequate representation of the short-range interaction between the H atom and the Pd surface, but we think that the model is a reasonably simple first approach to the physical phenomenon.

For deuterium we have \( d \approx 0.45 \text{ Å} \) which, together with the same force constant and about twice the mass, yields \( q_0 \approx 2 \) and \( \epsilon_0 \approx 0.52 \hbar \omega \) that is closer to the harmonic-oscillator zero-point energy [5]. We note the effect of the distance to the surface and the mass of the particle on the vibrational energies.

4. Further comments

The model discussed here is suitable for a course on quantum theory because it does not require much more mathematical background than is necessary for the discussion of the
well-known harmonic oscillator or the quantum bouncer [1]. It is useful for introducing a numerical calculation of the eigenvalues that the student does not find in the treatment of the harmonic oscillator. The student will also learn that it is necessary to modify the form of the well-known virial theorem and other mathematical expressions in order to take into account the effect of the wall. We believe that the present derivation of the analytical results in section 2 and in the appendix is simpler than those available in the scientific literature [2, 3].

In addition, the model enables us to simulate the adsorption of an atom on a surface and discuss anharmonic vibrations in quantum theory. In the study of molecular vibrations, one introduces nonlinear oscillations by means of cubic, quartic, and other terms of greater degree in the potential-energy function. In this case, it arises from the boundary condition forced by the hard wall.

Appendix. Some useful mathematical relations

In this appendix, we develop some useful analytical results for the eigenfunctions and eigenvalues of the constrained oscillator. Although similar expressions have already been shown elsewhere [6], we derive them here in a form that is more suitable for our needs.

Consider the dimensionless Schrödinger equation

\[ -\frac{1}{2} \phi''(x) + V(x) \phi(x) = \epsilon \phi(x), \]
\[ \phi(b) = 0, \quad \lim_{x \to \infty} \phi(x) = 0. \]  

(\text{A.1})

Both the eigenvalue \( \epsilon \) and the eigenfunction \( \phi(x) \) depend on the chosen value of \( b \) and we may consequently write \( \epsilon(b) \) and \( \phi(b,x) \) whenever necessary. If we differentiate equation (A.1) with respect to \( b \) and call \( \chi(x) = \partial \phi(x) / \partial b \), we have

\[ -\frac{1}{2} \chi''(x) + V(x) \chi(x) = \epsilon \chi(x) + \frac{d\epsilon}{db} \phi(x). \]

(\text{A.2})

If we multiply this equation by \( \phi(x) \) and integrate the result between \( b \) and \( \infty \), we easily obtain

\[ \frac{d\epsilon}{db} \int_b^\infty \phi(x)^2 \, dx = -\frac{1}{2} \chi(b) \phi'(b) \]

(\text{A.3})

because the integration by parts of the first term yields

\[ \int_b^\infty \chi''(x) \phi(x) \, dx = \chi(b) \phi'(b) + 2 \int_b^\infty [V(x) - \epsilon] \chi(x) \phi(x) \, dx. \]

(\text{A.4})

If we now differentiate the boundary condition \( \phi(b, x = b) = 0 \), we obtain

\[ \chi(b) + \phi'(b) = 0 \]

(\text{A.5})

so that equation (A.3) becomes

\[ \frac{d\epsilon}{db} \int_b^\infty \phi(x)^2 \, dx = \frac{1}{2} \phi'(b)^2. \]

(\text{A.6})

We define the operators

\[ \hat{H} = -\frac{1}{2} \hat{D}^2 + V(x) \]

(\text{A.7})

and \( \hat{v} = \hat{x} \hat{D}, \) where \( \hat{D} = d/dx \). The commutator between them reads

\[ [\hat{H}, \hat{v}] = \hat{H} \hat{v} - \hat{v} \hat{H} = -\hat{D}^2 - x V'. \]

(\text{A.8})
If \( \psi(x) \) is an eigenfunction of \( \hat{H} \) with the eigenvalue \( \epsilon \), then straightforward integration by parts leads to

\[
\int_{b}^{\infty} \psi [\hat{H}, \hat{v}] \psi \, dx = \frac{1}{2} b \psi'(b)^2
\]

which, by virtue of equation (A.6), becomes the virial theorem

\[
\langle \hat{D}^2 \rangle + \langle x V' \rangle = b \frac{\partial \epsilon}{\partial b}
\]

where

\[
\langle \hat{A} \rangle = \int_{b}^{\infty} \frac{\psi \hat{A} \psi \, dx}{\int_{b}^{\infty} \psi^2 \, dx}
\]

Analogously, from the commutator \([\hat{H}, \hat{D}] = -V'\), we obtain

\[
\int_{b}^{\infty} \psi(x)^2 V'(x) \, dx = \frac{1}{2} \psi'(b)^2
\]

or

\[
\langle V' \rangle = \frac{\partial \epsilon}{\partial b}
\]

We can test these equations quite easily by means of the well-known solutions to the free harmonic oscillator

\[
\psi_n = N_n H_n(x) e^{-x^2/2}
\]

where \( H_n(x) \) is a Hermite polynomial and \( N_n \) is the corresponding normalization factor [7]. If we choose \( b \) to be one of the zeroes \( x_{nj} \), \( j = 1, 2, \ldots, n \), of \( H_n(x) \), \( n = 1, 2, \ldots \), then we verify that \( \psi_n(x) \) satisfies equations (A.9) and (A.12) for \( V(x) = x^2/2 \). If, for example, \( b = 0 \) for \( n = 1 \) and \( b = \pm 1/\sqrt{2} \) for \( n = 2 \), then \( \epsilon = 3/2 \) is the energy of the ground state of the harmonic oscillator with the boundary condition at \( b = 0 \) and \( \epsilon = 5/2 \) is the energy of the ground state with \( b = 1/\sqrt{2} \) and of the first excited state with \( b = -1/\sqrt{2} \).

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