Method of approximation for potentials in impenetrable boxes: Harmonic Oscillator and Coulomb potentials.

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Abstract

In this work we develop an approach to obtain analytical expressions for potentials in an impenetrable box. It is illustrated through the particular cases of the harmonic oscillator and the Coulomb potential. In this kind of system the energy expression respect the correct quantum limits, which is a very important quality. The similarity of this kind of problem with the quasi exactly solvable potentials is explored in order to accomplish our goals.

Quantum systems under non trivial boundary conditions, corresponding to penetrable and nonpenetrable walls, do simulate the effect of atoms or molecules in the neighbor of a central particle. The dependence of the eigenvalues on the box size, allows one to define the effect of the pressure over the system. Some examples would include that of the proton-deuteron transformation as a source of energy in dense stars [1], the determination of the escape rate from galactic and globular clusters [2], and the understanding

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of the spectral line shift under pressure \[3\]. One good list of phenomena
associated to this kind of physical system is presented in \[4\]. Recently, the
fabrication of the quantum dots in the semiconductor physics did brings a
renewed interested on this kind of problem \[5\]. Another example of application
of this type of system, would be that of the Casimir effect and even that
of Rydberg atoms between metallic plates \[6\].

These important systems are treated by imposing the vanishing of the
wave function in some finite point, once that the confined particle must
be found in a finite region of the space. On the other hand, a numerical
treatment of this problem has the natural drawback of becoming difficult
any qualitative analysis, and even estimation, due to the need of calculating
the energy for each new value of the potential parameter \[7\], \[8\]. Another
possibility of studying the system is to apply to the Rayleigh-Schroedinger
perturbation theory \[9\], \[10\], variational methods \[11\], \[12\], or some semi-
classical approximation \[13\]. Recently it was applied the strong-coupling
expansion approach to this kind of problem \[14\], and considering the case of
the pressure exerted by a stack of membranes upon enclosing walls \[15\], \[16\],
it has been treated particularly the case of a single membrane \[17\], \[18\].

Here we show that the imposition of the vanishing of the wave function
at the boundaries imply that the potential can be treated in a similar fashion
to that of the so called quasi exactly solvable potentials \[19\]–\[21\], which are
quantum potentials which have part of the energy spectrum exactly solvable,
provided that some relations between the potential parameters hold. In fact,
we use this feature in order to deal with the problem in the same way that it
was done in the case of an anharmonic oscillator \[22\], \[23\]. As an application
of the method, we present an analytically approximated expression for the
quantum problem of one particle under the action of a harmonic oscillator
bounded to a finite region of the space. Furthermore, our analytical expres-
sion does have all the correct physical limits as, for instance, that for large
values of the principal quantum number. On the other hand, in contrast with
other approaches, our result is valid for arbitrary values of the box size.

First of all, we illustrate the method by treating the harmonic oscillator
bounded in a “one-dimensional box” of length \(a\). Some similar problems were
treated previously in the literature \[7\], \[12\], but in general only solutions
valid for a specific value of the potential parameter are taken and, every
time one needs the energy spectra for another value of that parameter, the
numerical calculation must be repeated. This implies that one hardly can
visualize a qualitative behavior of the system, besides there is the obvious unpleasant need of repeated numerical calculations each time one needs to change the value of the potential parameter. By the other hand, methods like the perturbation theory are intrinsically limited due to the need of restricting the potential parameter or the length of the box.

1 Harmonic Oscillator in a one dimensional box

We start by treating the harmonic oscillator in a box, similarly to the treatment given to the quasi-exactly solvable potentials [19]-[21], which did lead us to obtain analytically approximated solutions for the eigenvalues of anharmonic oscillators under usual boundary conditions [22].

Remembering that the general solution for the harmonic oscillator is given by something like

\[
\Psi_n(x) = P_n(x) \exp \left( -\alpha x^2 \right), \tag{1}
\]

where \(P_n(x)\), in principle, is a polynomial of infinite degree (the parabolic cylindrical functions), which however is taken finite (Hermite polynomials) in the case of boundary conditions at the infinity, in order to get a convergent function. Here however, the exponential does not guarantees that the wavefunction vanishes at the walls of the interval, so that this condition determines the energy spectrum. Notwithstanding, when we do insist to using finite polynomials, which are nothing but the known Hermite ones, whose energy is well defined and given by \(E_n = \hbar \omega \left( n + \frac{1}{2} \right) \), we get an equation for the oscillator frequency which, once solved, give us those frequencies which generate polynomials whose zeroes are at the walls of the box. At this point it is important to stress the similarity of this problem with that of the so called quasi-exactly solvable potentials, in the sense that in this case only for some specific frequencies the eigenfunction will be elementary or, in other words, it is represented by a finite polynomial, the Hermite ones, times an usual exponentially decaying factor. Once one gets those frequencies, one must to substitute them on the above expression for the energy, so obtaining the corresponding exact energy for the harmonic oscillator in a box.
In order to obtain the frequency and the energy for an oscillator in a box whose walls are at \(-a/2\) and \(a/2\), by applying the idea which was outlined above, we use the condition

\[
H_n \left( \pm \frac{a}{2} \right) = 0,
\]

(2)

so that \(H_0(x) = 1\), does not give us any solution, the polynomial \(H_2 \left( \pm \frac{a}{2} \right)\) generates one solution, \(H_4 \left( \pm \frac{a}{2} \right)\) two solutions, so for and so on. To be more precise, let us exemplify with case of \(H_2 \left( \pm \frac{a}{2} \right)\). In this case the equation which implies that the wavefunction vanishes at the boundary is given by

\[
H_2 \left( \pm \frac{a}{2} \right) = a_0 \left( -2 + 4 \xi \right) = 0,
\]

(3)

where \(\xi = \sqrt{\frac{m \omega}{\hbar}}\). Remembering that in this case \(E_2 = \frac{5}{2} \hbar \omega\), one gets finally:

\[
\omega = \frac{2 \hbar}{m a^2}, \quad E = 5 \frac{\hbar^2}{m a^2}.
\]

(4)

As can be easily verified, the wavefunction of the harmonic oscillator for the above frequency and energy vanishes at the boundaries, not presenting any nodes between the walls. So it corresponds to the ground state of the oscillator in a box with impenetrable walls. Now, if one takes the following even case of \(H_4 \left( \pm \frac{a}{2} \right)\), it is straightforward to show that there are now two possible solutions of \(2\), respectively corresponding to the ground state and the second excited one, so for and so on. Analogously a similar structure appears in the odd cases. The first solution of each polynomial always corresponds to the first excited state, the second to the third excited state, etc...

However, before to do such a calculation, we take profit of a scaling symmetry of this kind of problem in order to simplify it. In doing so, we show that this problem has only one independent variable for the energy dependence. By choosing \(x = \frac{a}{2} \sqrt{\frac{\hbar}{m \omega_a}} y\), and redefining the frequency and the energy conveniently, one gets

\[
- \frac{1}{2} \frac{d^2 \psi}{dy^2} + \frac{1}{2} \omega_a^2 y^2 \psi = E_a \psi,
\]

(5)

where the new variables in terms of the old ones look like

\[
\omega_a = \frac{m a^2}{\hbar} \omega, \quad E_a = \frac{ma^2}{4 \hbar^2} E,
\]

(6)
and now we need to find the zeros of $\psi$ such that $\psi(\pm 1) = 0$. The resulting solution will be valid for arbitrary values of the box length and its frequency. In this way, by solving a sufficiently great number of polynomials, we can plot the energy as a function of the frequency for each one of the energy levels, and then try to get a functional relation between these several levels. So obtaining an approximate analytical expression for the dependence on the frequency, the length of the box and the quantum number.

At this point, in order to help our quest for a suitable analytical expression for the energy, we remember that in the limit of zero frequency one recalls the free particle in a box. On the other hand, when the length of the box goes to infinity, one should recover the well known harmonic oscillator spectra. Finally for great values of the principal quantum number, once again the energy becomes close to that of a free particle in a box. As a consequence of these physical constraints, we write the expression for the energy as

$$ E = \left(\frac{2ma^2}{\pi^2\hbar^2}\right)E = n^2 + k\omega_a + g(\omega_a), \quad (7) $$

where

$$ k = \frac{8}{\pi^2}\left(n - \frac{1}{2}\right), \quad n = 1, 2, 3, \ldots \quad (8) $$

and the function $g(\omega_a)$ should have the following appropriate limits

$$ g(\omega_a = 0) = 0, \quad g(\omega_a \to \infty) = 0. \quad (9) $$

Furthermore, one should also have this function going to zero when $n$ increases or at most growing more slowly than $n^2$. Using this hypothesis as a guide we try the following form for $g_n(\omega_a)$:

$$ g_n(\omega_a) = c_0(n) \omega_a e^{-\sum_{j=1}^{J} c_j(n)\omega_a^j}. \quad (10) $$

After performing the necessary calculations we verify that indeed, this function has the expected behavior supposed above. Besides, by obtaining the roots of Hermite polynomials up to two hundred degree, we did find an approximated expression for the coefficients $c_j(n)$, taking $J = 3$, whose expressions are given below:

$$ c_0(n) = \frac{1}{(0.405231 + 0.810579n)}. \quad (11) $$
\[ c_1(n) = \frac{0.0104832}{n} - \frac{0.00588616}{n^2} - \frac{0.00187449}{n^3}, \quad (12) \]

\[ c_2(n) = 10^{-6} \left[ -1.24 + 1.35 \cosh (0.1762 n - 0.12) \right]^{-1}, \quad n > 1, \quad (13) \]

\[ c_3(n) = 10^{-8} \left[ -2.5 + 2.6 \cosh (0.086 n - 0.278) \right]^{-1}, \quad n > 3, \quad (14) \]

Note that for the last two coefficients, the first elements were separated in order to getting better fittings. In these cases one have

\[ c_2(1) = 3.70973 \times 10^{-6}, \]

\[ c_3(1) = -1.54146 \times 10^{-6}, \quad c_3(2) = -8.78283 \times 10^{-7}, \quad c_3(3) = 4.56951 \times 10^{-8}. \]

Note that, in fact, the coefficients really approaches to zero for larger values of \( n \). These calculations were performed for \( n \leq 20 \), so that for higher values of \( n \), one must extrapolate it, but it should be expected good results due to the behavior of \( g_n(\omega_a) \) when \( n \) becomes greater and greater.

The comparison of the energy coming from the above analytical approximation with pure numerical values, in the case of the range of frequencies considered, shows that the error was always less than 0.07\% along the range of the parameters verified which due to technique reasons, depend of the energy level studied and grows for higher quantum numbers, below we present a Table with the corresponding ranges and their respective maximum per- centual errors for the first twenty levels.

| \( n \) | \( \omega_{a_{\text{max}}} \) | \( \delta\%_{\text{max}} \) | \( n \) | \( \omega_{a_{\text{max}}} \) | \( \delta\%_{\text{max}} \) |
|---|---|---|---|---|---|
| 1 | 2.0 | 9.0 \times 10^{-5} | 11 | 60.5 | 0.018 |
| 2 | 6.0 | 0.072 | 12 | 67.3 | 0.018 |
| 3 | 10.9 | 9.1 \times 10^{-3} | 13 | 74.1 | 0.017 |
| 4 | 16.3 | 0.02 | 14 | 81 | 0.017 |
| 5 | 22.1 | 0.016 | 15 | 87.9 | 0.016 |
| 6 | 28.1 | 9.3 \times 10^{-5} | 16 | 94.9 | 0.016 |
| 7 | 34.4 | 0.012 | 17 | 101.9 | 0.015 |
| 8 | 40.8 | 0.017 | 18 | 109 | 0.013 |
| 9 | 47.2 | 0.019 | 19 | 116.1 | 0.016 |
| 10 | 53.8 | 0.019 | 20 | 123.2 | 8.9 \times 10^{-3} |

It is interesting to stress that the type of energy expression obtained here, can be used to study the appearing of quantum chaos in the cases of
anharmonic systems \cite{24}, \cite{25}. This happens because one can use the energy expressions coming from this approach in order to get the number of levels for a given range of energy and the corresponding related parameters, used to discuss the appearing of the quantum chaos.

2 Coulomb Potential in a sphere

In this section we work with the more mathematically involved case of the Coulomb potential in a sphere of radius \( a \). Notwithstanding, the basic program to be followed is the same of the previous section. Once again the general solution for the radial wavefunction of this problem is of the kind

\[
R(x) = R_n^*(x) \exp \left( \frac{-\mu \alpha x}{\hbar^2 n} \right)
\]

where \( V(r) = -\frac{\alpha}{r} \), and \( n \) is the principal quantum number. This polynomial will be of infinity degree, unless that we impose that the wavefunction vanishes at the infinity, in which case the polynomial degree is finite, one gets the generalized Laguerre polynomials. However, as in the previous section, despite we are treating a case with finite boundary conditions for which it has in general an infinity number of terms, we will insist in using a finite polynomial in order to generate simple exact solutions, remembering that the price to be paid is that consequently, the energy is established and given by \( E_n = -\frac{\mu \alpha}{2 \hbar n} \). As a consequence the constant \( \alpha \) will be chosen in a manner to guarantee the vanishing of the wavefunction at the sphere surface. After that we substitute the so obtained constant in the above expression for the energy, getting the corresponding energy for the system.

Starting from the radial Schroedinger equation, once that the angular part of it is unchanged due to the fact that the boundary condition preserves the spherical symmetry \cite{29}:

\[
-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{d^2}{dr^2} \left( r (R(r)) \right) + \left[ \frac{l(l+1)}{2\mu r^2} \hbar^2 + V(r) \right] R(r) = E R(r)
\]

with \( V(r) = -\frac{e^2}{r} \). Defining \( R(r) = \frac{u(r)}{r} \), we have
Redefining the radial variable as $\rho = \frac{\mu e^2}{\hbar^2} r$ and then substituting it in the previous equation one gets

$$\left[ -\hbar^2 \frac{d^2}{dr^2} + \frac{l(l+1)}{2\mu r^2} \hbar^2 + V(r) \right] u(r) = E u(r). \quad (18)$$

By choosing the ansatz $u(\rho) = v(\rho) \exp(-ar)$ one obtains

$$\left[ C \left[ -\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} - \frac{2}{\rho} \right] - E \right] v(\rho) = 0 \quad (19)$$

By choosing $v(\rho) = \rho^{l+1} \sum_n b_n \rho^n$ and performing the identification $E = -Ca^2$, we get the following recurrence relation

$$b_{n+1} = \frac{2(1-a(n+l+1))}{l(l+1) - (n+l+2)(n+l+1)} b_n. \quad (21)$$

Taking into account the boundary conditions at the infinity, we can truncate the series at $b_N$ ($N$, integer), getting $b_{N+1} = 0$, so obtaining

$$a = \frac{1}{N+l+1},$$

and as $E = -Ca^2$, one gets the usual expression for the eigenenergies in such boundary conditions

$$E_N = -\frac{C}{(N+l+1)^2} = -\frac{\mu e^2}{2\hbar^2} \frac{1}{n^2}. \quad (22)$$

We can still use the recurrence relation in order to obtain an expression for the generic coefficient $b_n$ in terms of $b_0$. In doing so we get

$$\frac{b_n}{b_0} = \prod_{j=l}^{n} \left\{ \frac{2[a(j+l)-1]}{j(j+2l+1)} \right\}. \quad (23)$$

As in the case of boundary condition at a finite radius, the series does not truncate and so we must to work with the infinite polynomial generated from
the above coefficients. This polynomial will be analogous to the Parabolic Cylinder function which appeared in the case of the harmonic oscillator, as treated in the last section.

On the other hand the equation for $R(r)$, can be written in terms of the Laguerre polynomial

$$R(r) = r^l \exp(-kr) L_{n-l-1}^{2l+1}(2kr),$$

where $k = \sqrt{\frac{2\mu E}{\hbar^2}}$. Imposing that $R(r = r_0) = 0$, we get

$$L_{n-l-1}^{2l+1}\left(\frac{2\mu e^2 r_0}{\hbar^2 n}\right) = L_{n-l-1}^{2l+1}\left(\frac{g}{n}\right) = 0,$$

with $g = \frac{2\mu e^2 r_0}{\hbar^2}$. In absolute analogy with the case of the harmonic oscillator, in this case we must to substitute the values of $g$ coming from the above equation in that of the energy of the Coulomb potential,

$$E_{n,l} = -\frac{\mu e^4}{2\hbar^2 n^2} = -\frac{g^2}{8n^2 \mu r_0^2}.$$ (26)

Now, by using the recurrence relation and imposing that the polynomial be finite, one obtains as expected the usual generalized Laguerre polynomials. In this case, the first solution coming from the equation (25) for each polynomial will give us the ground state energy, each second solution generates the first excited state, so for so on. Consequently we used the Mathematica software in order to perform this calculation in a systematic way. This was done for the first nine energy levels, using one hundred degree polynomials. For each energy level, we plotted the exact energies coming from the solutions described above as a function of the parameter $g$, and fitted it with a polynomial of the third degree given by

$$E_{n,l} = \sum_{m=0}^{3} C_{m}^{(n,l)} g^m$$

where the coefficients $C_{m}^{(n,l)}$ are presented in the Table 1.
The energy expression coming from the use of the above parameters is in good accordance with the exact numerical data and, as happened in the harmonic oscillator case, does have an increasing range of validity with the increasing of the principal quantum number, as can be seen in the Table below. In these ranges, the error is quite small, about $10^{-2}\%$.

| n,l | $g_{\text{max}}$ | $g_{\text{min}}$ | $\delta \%_{\text{max}}$ |
|-----|-----------------|-----------------|---------------------|
| 1,0 | 2.0             | 1.8             | $4.7 \times 10^{-5}$ |
| 2,0 | 7.1             | 6.15            | $4.3 \times 10^{-3}$ |
| 2,1 | 6.0             | 5.0             | $6.2 \times 10^{-4}$ |
| 3,0 | 15.5            | 12.9            | $9.4 \times 10^{-3}$ |

By analyzing the data, one can verify that the range was limited by the maximum polynomial used (in this case we used polynomials of degree 100). So, in order to increase the precision and the range of validity, one should use higher degrees for the Laguerre polynomials.

One interesting feature observed was that, in this case the energy is no more degenerate in the angular momentum quantum number, in contrast with the usual boundary condition at the infinite. So indicating the broke of some symmetry of the system. As the spherical symmetry was preserved by the boundary condition used, we must to look for another broken symmetry to be responsible for this behavior. In fact, the symmetry related to the conservation of the Runge-Lenz vector is that one. This can be argued by remembering that classically is associated to fact that the eccentricity of the elliptical orbits does not alter their energy. However in a finite sphere some of those will not be allowed. From the point of view of a geometric transformation, one can use the fact that the commutator of the Runge-Lenz vector with the radial coordinate, will generate a change in this coordinate such as

$$r' = r + \{ r, \alpha.E \}, \quad \{ r, \alpha.E \} = \frac{1}{km} \frac{(r \times L)}{r} \alpha,$$

(28)
where $E$ and $\alpha$ are respectively the Runge-Lenz vector and the infinitesimal vectorial parameter of this symmetry transformation. From above one can conclude that when one is close to the frontier, the transformation could led it to beyond it, and this is not allowed by the boundary condition. Consequently this symmetry is now broken at the quantum level. It is interesting to observe that technically the Runge-Lenz operator and the Hamiltonian of the system is still commuting but, now due to the boundary conditions, the eigenfunctions of the Hamiltonian of this complete set of commuting operators is not shared with those of the Runge-Lenz operator. It is interesting to note that this is a generic property of this kind of system.

On the other hand it is not difficult to extend this approach in order to take care of other situations like, for instance, the case of finite walls, symmetric and antisymmetric boundary conditions, which can represent other kind of physical systems. Finally it should be interesting to study the applicability of this approach to systems with time-dependent boundary conditions [26]-[28].

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