

## Exact perturbation theory for quantum-mechanical systems within boxes

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We apply perturbation theory to the Schrödinger equation for a system caged in a one-dimensional box with impenetrable walls and show how to obtain the perturbation corrections to both the energy eigenvalues and eigenfunctions in a systematic exact way when the potential function within the box is a polynomial. As an illustrative example we consider a linear potential obtaining analytic expressions for the perturbation corrections in terms of the quantum number.

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### I. INTRODUCTION

Quantum-mechanical systems surrounded by impenetrable or penetrable walls prove to be simple tractable models for many physical phenomena in which the walls simulate the effect of the neighboring atoms or molecules on the central particle. The dependence of the eigenvalues on the magnitude of the box allows a simple definition of the pressure exerted on the system. For instance, the caged harmonic oscillator has been extensively used in connection with the following phenomena: proton-deuteron transformation as a source of energy in dense stars [1], the state of an electron inside a cold stellar mass [2], the determination of the rate of escape of stars from galactic and globular clusters [3], the theory of the specific heats of solids [4,5], and the effect of finite boundaries on the magnetic properties of a solid [6]. The hydrogen atom within boxes of different shapes proves useful to draw theoretical conclusions about isotherm measurements and the Clausius-Mosotti function at high pressures [7], in understanding the shift of spectral lines under pressure [8], in the calculation of magnetic properties of metals in weak magnetic fields [9], as a model for partially ionized, partially dissociated plasmas [10], to study the thermodynamic properties of nonideal gases [11], to simulate pressure phase transitions in  $H_2$  and  $H$  to a metallic modification of hydrogen [12], and to calculate the hyperfine splitting of hydrogen trapped in a crystal [13,14]. The combination of a linear and a box potential models the effect of boundaries on the behavior of electrons in a crystal in the presence of a uniform electric field [15] and the emission and absorption in a quantum-well structure under the influence of a uniform electric field [16].

In addition to their varied physical applications these models constitute a useful benchmark for approximate schemes to solve the Schrödinger equation with boundary conditions at finite values of the coordinates. Therefore, there is a vast literature describing many alternative such methods, part of which is reviewed elsewhere [17]. Here we are interested in perturbation theory regarding the potential energy function other than the box effect as a perturbation; this approach applies to a box of small or moderate magnitude. For example, Kothari and Auluck

[18], Auluck [1], and Auluck and Kothari [19] obtained the first- and second-order corrections to the energy of a caged one-dimensional harmonic oscillator exactly. Dingle [6] derived the exact first-order correction to the eigenvalues of a harmonic oscillator within a cylinder. Aguilera-Navarro *et al.* [20,21] calculated perturbation corrections to the lowest-energy levels of several caged oscillators numerically. The application of perturbation theory to the bounded hydrogen atom is more difficult because of the Coulomb interaction. Dingle [9] overcame this difficulty by the transformation of the Coulomb potential into a harmonic one through an appropriate nonlinear change of variables and obtained the first-order perturbation correction to the energy. By direct application of perturbation theory treating the Coulomb potential as a perturbation, Aguilera-Navarro, Kloet, and Zimmerman [22] calculated perturbation corrections to the energy of the ground state numerically. Lukes, Ringwood, and Suprpto [23] derived the exact first- and second-order perturbation corrections to all the eigenvalues for the caged linear potential from the zeros of the Wronskian.

The main problem in the application of perturbation theory to caged quantum-mechanical systems is that the sums in the well-known textbook formulas that give the perturbation corrections of order larger than the first one have infinitely many terms and their exact summation is difficult although possible in some cases [23]. As far as we know the only efficient systematic method for the calculation of the perturbation corrections to the energy of such models is provided by an appropriate combination of the hypervirial and Hellmann-Feynman theorems [17]. This implementation of perturbation theory yields the perturbation corrections to all the energy levels and to the moments of the probability density simultaneously in terms of the zeroth-order energy. They are obtained from recurrence relations that are easily programmable. One disadvantage of this method is that it does not provide the eigenfunctions explicitly.

We have investigated the problem of the application of Rayleigh-Schrödinger perturbation theory to box models, finding that the calculation of exact perturbation corrections to both the energy and the wave function by the standard formulation of this approach is straightforward.

ward in certain cases of actual physical interest. We believe that this fact, which has been overlooked in previous applications of perturbation theory [1,6,9,15,18,19–23], may be useful and therefore we discuss it in this paper. In Sec. II we consider one-dimensional box models with polynomial potentials and show how to treat them by perturbation theory. As an illustrative example we obtain exact perturbation corrections in terms of the quantum number for a model for noninteracting electrons in a one-dimensional empty crystal in the presence of a uniform electric field [15,16,23]. Further comments and conclusions are found in Sec. III.

## II. PERTURBATION THEORY FOR BOX MODELS

For the sake of simplicity we only consider one-dimensional box models but the treatment can be surely extended to other problems. In fact, the results obtained below also apply to the  $s$  states of central-field systems in spherical boxes. The Schrödinger equation reads

$$-\frac{\hbar^2}{2m}\Psi''(x) + V(x)\Psi(x) = E\Psi(x), \quad (1)$$

and the cage effect results in the Dirichlet boundary conditions  $\Psi(0) = \Psi(L) = 0$ , where  $L$  is the box length. It is convenient to define a dimensionless coordinate  $q = x/L$ , energy  $\varepsilon = 2mL^2E/\hbar^2$ , and potential-energy function  $\lambda v(q) = 2mL^2V(Lq)/\hbar^2$ , where  $\lambda$  is the perturbation parameter, that lead to the reduced Schrödinger equation

$$-\Phi''(q) + \lambda v(q)\Phi(q) = \varepsilon\Phi(q), \quad (2)$$

with the boundary conditions  $\Phi(0) = \Phi(1) = 0$ . In other words,  $\Phi(q) \propto \Psi(Lq)$  and  $\varepsilon$  are, respectively, an eigenfunction and its corresponding eigenvalue of the differential operator  $H = -d^2/dq^2 + \lambda v$ . The solutions of its unperturbed part  $H_0 = -d^2/dq^2$  are

$$\Phi_{0,n}(q) = \sqrt{2}\sin(n\pi q), \quad \varepsilon_{0,n} = n^2\pi^2, \quad n = 1, 2, \dots \quad (3)$$

To simplify the notation from now on we omit the subscript  $n$  and write  $K = n\pi$  everywhere.

For  $\lambda \neq 0$  we seek a solution of the form

$$\Phi(q) = A(q)\sin(Kq) + B(q)\cos(Kq), \quad (4)$$

where  $B(0) = B(1) = 0$  to satisfy the boundary conditions. One easily verifies that if  $A(q)$  and  $B(q)$  satisfy

$$\begin{aligned} A''(q) - 2KB'(q) &= (\lambda v - \Delta\varepsilon)A(q), \\ B''(q) + 2KA'(q) &= (\lambda v - \Delta\varepsilon)B(q), \end{aligned} \quad (5)$$

$\Delta\varepsilon = \varepsilon - \varepsilon_0 = \varepsilon - K^2$  being the energy shift, then (4) is a solution of the eigenvalue equation (2). Other choices of  $A(q)$  and  $B(q)$  are possible but the condition (5) is simple enough for the present purposes.

When  $v$  is a polynomial function of the coordinate  $q$  the equations (5) are by far more tractable than the original eigenvalue equation (2) by means of perturbation theory because the trigonometric functions are completely factored out. To apply this approach we write

$$\begin{aligned} \varepsilon &= \sum_{j=0} \varepsilon_j \lambda^j, \\ A(q) &= \sum_{j=0} A_j(q) \lambda^j, \\ B(q) &= \sum_{j=0} B_j(q) \lambda^j, \end{aligned} \quad (6)$$

where  $\varepsilon_0 = K^2$ ,  $A_0(q) \equiv \sqrt{2}$ , and  $B_0(q) \equiv 0$ . The perturbation corrections are solutions of

$$\begin{aligned} A_k'' - 2KB_k' &= (v - \varepsilon_1)A_{k-1} - \sum_{j=2}^k \varepsilon_j A_{k-j}, \\ B_k'' + 2KA_k' &= (v - \varepsilon_1)B_{k-1} - \sum_{j=2}^k \varepsilon_j B_{k-j}. \end{aligned} \quad (7)$$

If the potential-energy function  $v(q)$  is a polynomial of degree  $\nu$ ,

$$v(q) = \sum_{m=0}^{\nu} v_m q^m, \quad (8)$$

then the functions  $A_k(q)$  and  $B_k(q)$  will be polynomials of degree  $k(\nu+1)$ ,

$$A_k(q) = \sum_{j=0}^{k(\nu+1)} a_{k,j} q^j, \quad B_k(q) = \sum_{j=0}^{k(\nu+1)} b_{k,j} q^j. \quad (9)$$

The boundary conditions lead to

$$b_{k,0} = 0, \quad b_{k,k(\nu+1)} = - \sum_{j=1}^{k(\nu+1)-1} b_{k,j}. \quad (10)$$

The systematic and hierarchical calculation of the coefficients  $a_{k,j}$  ( $j > 0$ ) and  $b_{k,j}$  from the differential equation (7) is straightforward. The perturbation corrections to the energy are completely determined by the boundary conditions (10) but it is more efficient to calculate them from the symmetrized perturbation equations given in the Appendix. The coefficients  $a_{k,0}$  which are not determined by the perturbation equations are obtained from the selected normalization condition. Here we choose  $\langle \Phi | \Phi \rangle = 1$ , which is convenient for further calculations of expectation values and matrix elements. To illustrate the process we consider the simple case  $V(x) = eFx$  which represents the interaction between a particle of charge  $e$  and a uniform electric field of intensity  $F$ . This model proves useful in the study of the behavior of electrons in a finite crystal in the presence of a uniform electric field [15,16,23]. In this case we choose  $\lambda = 2mL^3eF/\hbar^2$  so that  $v(q) = q$  ( $\nu = 1, v_m = \delta_{m1}$ ).

Although the coefficients  $a_{k,j}$  and  $b_{k,j}$  are easily obtained by hand, the integrals required in the application of the symmetrized perturbation equations given in the Appendix become increasingly cumbersome as the perturbation order increases; therefore, we carried out the calculation with the aid of a standard computer algebra package. The coefficients of the first three perturbation corrections to the wave function normalized to unity and the first six perturbation corrections to the energy in terms of  $K = n\pi$  are shown in Table I. Although  $\varepsilon_{2k+1} = 0$  if  $k > 0$  because of symmetry we have explicitly calculated these perturbation corrections to check our

equations. The present second-order correction to the energy agrees with previous results [17,23,24]. The fourth-order correction is in agreement with Eq. (43) of Ref. [24] but not with Eq. (45) of Ref. [24], which exhibits an obvious misprint. The sixth-order perturbation correction to the energy as well as the perturbation corrections to the wave function showed in Table I have not been published before as far as we know.

### III. FURTHER COMMENTS AND CONCLUSIONS

We have developed a simple and efficient implementation of perturbation theory for one-dimensional caged systems with polynomial potentials. It is clear that with a slight modification the method applies to boundary conditions other than the Dirichlet one considered above. The polynomial potential-energy function (8) includes the harmonic oscillator with an arbitrary center as a particular case. The method also applies to the  $s$  states of central-field systems in spherical boxes because their radial equations can be reduced to one-dimensional Schrödinger equations. In the case of the hydrogen atom it is necessary to carry out a previous transformation of

the Coulomb potential into a harmonic one [9]. The treatment of states with nonzero angular momentum is more complicated and is at present under investigation.

The strategy used above to factor out the trigonometric functions is reminiscent of that followed by Dalgarno and collaborators long ago (see for instance [25] and references therein). However, the present approach is more convenient for the examples discussed in this paper because the perturbation corrections to the wave function are not of the form  $\Phi_k = f_k \Phi_0$ .

As indicated above the perturbation parameter is proportional to the coefficients of the potential-energy function and to a power of the box length. For instance, in the particular case considered in the preceding section  $\lambda$  is proportional to  $L^3 F$  so that the perturbation expansion converges when this product is small enough. According to the Kato-Rellich theorem [26] the perturbation series for caged systems have finite convergence radii. Some of them have been calculated with sufficient accuracy [27]. The convergence radius determines the greatest magnitude of the potential parameters and box length for which the perturbation series converges. From a practical point of view the range of utility of the perturbation expansion

TABLE I. Perturbation corrections to the energy levels and eigenfunctions (coefficients  $a_{k,j}$  and  $b_{k,j}$ ) in terms of  $K = n\pi$  for the box model with potential  $v(q) = q$ . Notice that  $\varepsilon_3 = \varepsilon_5 = 0$ .

First order	
$a_{1,0} = -\frac{\sqrt{2}}{8K^2}$	$a_{1,1} = \frac{\sqrt{2}}{4K^2}$ , $a_{1,2} = 0$ , $b_{1,1} = \frac{\sqrt{2}}{4K}$ , $b_{1,2} = -\frac{\sqrt{2}}{4K}$ , $\varepsilon_1 = \frac{1}{2}$
Second order	
$a_{2,0} = \frac{\sqrt{2}(3K^2+40)}{128K^6}$	$a_{2,1} = -\frac{5\sqrt{2}}{32K^4}$ , $a_{2,2} = \frac{\sqrt{2}(5-K^2)}{32K^4}$ , $a_{2,3} = \frac{\sqrt{2}}{16K^2}$ ,
$a_{2,4} = -\frac{\sqrt{2}}{32K^2}$	$b_{2,1} = -\frac{5\sqrt{2}}{96K^3}$ , $b_{2,2} = \frac{5\sqrt{2}}{32K^3}$ , $b_{2,3} = -\frac{5\sqrt{2}}{48K^3}$ , $b_{2,4} = 0$ ,
$\varepsilon_2 = \frac{K^2-15}{48K^4}$	
Third order	
$a_{3,0} = \frac{\sqrt{2}(120-31K^2)}{3072K^8}$	$a_{3,1} = \frac{\sqrt{2}(121K^2-120)}{1536K^8}$ , $a_{3,2} = \frac{\sqrt{2}(7K^2-135)}{768K^6}$ ,
$a_{3,3} = \frac{\sqrt{2}(45-14K^2)}{384K^6}$	$a_{3,4} = \frac{35\sqrt{2}}{768K^4}$ , $a_{3,5} = -\frac{7\sqrt{2}}{384K^4}$ , $a_{3,6} = 0$ ,
$b_{3,1} = \frac{\sqrt{2}(7K^2-40)}{512K^7}$	$b_{3,2} = \frac{\sqrt{2}(120-121K^2)}{1536K^7}$ , $b_{3,3} = \frac{\sqrt{2}(50-K^2)}{384K^5}$ ,
$b_{3,4} = \frac{\sqrt{2}(3K^2-25)}{384K^5}$	$b_{3,5} = -\frac{\sqrt{2}}{128K^3}$ , $b_{3,6} = \frac{\sqrt{2}}{384K^3}$
Fourth order	
$\varepsilon_4 = \frac{K^4-210K^2+1980}{2304K^{10}}$	
Sixth order	
$\varepsilon_6 = \frac{K^6-825K^4+46800K^2-382500}{36864K^{16}}$	

is even smaller because it converges too slowly when  $\lambda$  is close to the convergence radius. The convergence radius of the perturbation series decreases with  $\nu$  because the larger the order of the polynomial representing the potential-energy function the stronger the perturbation [27].

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#### APPENDIX

Here we summarize the equations of perturbation theory used in the calculation of the corrections to the energy levels of the box model discussed in Sec. II. On substituting the perturbation expansions for the selected eigenvalue and eigenfunction into the Schrödinger equation one has

$$(H_0 - \varepsilon_0)\Phi_k = (\varepsilon_1 - \nu)\Phi_{k-1} + \sum_{j=2}^k \varepsilon_j \Phi_{k-j}. \quad (\text{A1})$$

If  $\Phi_0$  is normalized to unity we obtain the following expression for the energy:

$$\varepsilon_k = \langle \Phi_0 | \nu - \varepsilon_1 | \Phi_{k-1} \rangle - \sum_{j=2}^{k-1} \varepsilon_j \langle \Phi_0 | \Phi_{k-j} \rangle, \quad (\text{A2})$$

in which we do not specify the normalization of the perturbed eigenfunction. This equation is not the most convenient one because it requires  $\Phi_0, \Phi_1, \dots, \Phi_{k-1}$  in order to obtain  $\varepsilon_k$ . It is well known that with a more symmetric expression one can calculate up to  $\varepsilon_{2k+1}$  from the

corrections to the wave function up to  $\Phi_k$  [25]. For  $k=1$  and 2 we use (A2) directly but for the next orders it is convenient to write

$$\begin{aligned} \varepsilon_3 &= \langle \Phi_1 | \nu - \varepsilon_1 | \Phi_1 \rangle - \varepsilon_2 (\langle \Phi_0 | \Phi_1 \rangle + \langle \Phi_1 | \Phi_0 \rangle), \\ \varepsilon_4 &= \langle \Phi_2 | \nu - \varepsilon_1 | \Phi_1 \rangle - \varepsilon_2 (\langle \Phi_2 | \Phi_0 \rangle + \langle \Phi_1 | \Phi_1 \rangle) \\ &\quad - \varepsilon_3 (\langle \Phi_0 | \Phi_1 \rangle + \langle \Phi_1 | \Phi_0 \rangle), \\ \varepsilon_5 &= \langle \Phi_2 | \nu - \varepsilon_1 | \Phi_2 \rangle - \varepsilon_2 (\langle \Phi_1 | \Phi_2 \rangle + \langle \Phi_2 | \Phi_1 \rangle) \\ &\quad - \varepsilon_3 (\langle \Phi_1 | \Phi_1 \rangle + \langle \Phi_0 | \Phi_2 \rangle + \langle \Phi_2 | \Phi_0 \rangle) \\ &\quad - \varepsilon_4 (\langle \Phi_0 | \Phi_1 \rangle + \langle \Phi_1 | \Phi_0 \rangle), \\ \varepsilon_6 &= \langle \Phi_2 | \nu - \varepsilon_1 | \Phi_3 \rangle - \varepsilon_2 (\langle \Phi_2 | \Phi_2 \rangle + \langle \Phi_1 | \Phi_3 \rangle) \\ &\quad - \varepsilon_3 (\langle \Phi_1 | \Phi_2 \rangle + \langle \Phi_2 | \Phi_1 \rangle + \langle \Phi_0 | \Phi_3 \rangle) \\ &\quad - \varepsilon_4 (\langle \Phi_0 | \Phi_2 \rangle + \langle \Phi_2 | \Phi_0 \rangle + \langle \Phi_1 | \Phi_1 \rangle) \\ &\quad - \varepsilon_5 (\langle \Phi_0 | \Phi_1 \rangle + \langle \Phi_1 | \Phi_0 \rangle). \end{aligned} \quad (\text{A3})$$

If the perturbed eigenfunction is normalized to unity ( $\langle \Phi | \Phi \rangle = 1$ ) we have an additional equation

$$\sum_{j=0}^k \langle \Phi_j | \Phi_{k-j} \rangle = \delta_{k0}, \quad (\text{A4})$$

which enables us to obtain the coefficients  $a_{k,o}$ , defined in Sec. II, and also to reduce the number of integrals  $\langle \Phi_i | \Phi_j \rangle$  in (A3) [25]. However, we have not profited from the latter fact and have used Eqs. (A3) directly, keeping the coefficients  $a_{k,o}$  unevaluated because, as the results have to be independent of them, any mistake in the calculation is immediately detected.

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