Approach to perturbation theory for box models

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We generalize a recently developed perturbation approach [F. M. Fernández and E. A. Castro, Phys. Rev. A **46**, 7288 (1992)], extending its applicability to a wider variety of separable quantum-mechanical problems. As an illustrative example, we consider a particle in a one-dimensional box with a finite potential wall perturbed by a linear potential and obtain the perturbation corrections to the wave function and energy of an arbitrary state in terms of the corresponding unperturbed quantities.

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I. INTRODUCTION

Particles within boxes prove to be useful models for the simulation of many quantum-mechanical physical phenomena. The confinement produced by the box walls is the simplest way of taking into account the effect of neighboring particles on a given atom or molecule. In a recent paper it was shown that perturbation theory is a convenient way of obtaining analytic expressions for the energy and other physical observables in the case of impenetrable walls [1].

It has been argued that boxes with finite walls are more realistic than boxes with impenetrable walls for the simulation of the environment of an atom or molecule because the former walls allow one to take into account long-range forces between particles [2]. The Schrödinger equation for such models has only been solved numerically. In spite of the vast literature on the subject there are no analytic perturbation calculations on box models except for the case of impenetrable walls [3].

The purpose of the present paper is the generalization of a recently developed perturbation method for box models to allow the treatment of a much larger variety of problems and the illustration of its application to a simple nontrivial box model with a finite wall. In this way we intend to extend the scope of calculation of analytic expressions by means of perturbation theory. One attractive feature of the example discussed is that the unperturbed eigenvalues are not given in closed form but determined by a transcendental equation.

In Sec. II we develop general perturbation equations for separable problems and in Sec. III we consider the illustrative example mentioned above. The application of the method to other problems is briefly discussed in Sec. IV.

II. THE METHOD

The Schrödinger equation for separable problems in N dimensions is reduced to a set of N equations of the form

$$P(x)\Phi''(x)+Q(x)\Phi'(x)+R(x)\Phi(x)=0 , \tag{1}$$

where the prime stands for differentiation with respect to the argument of the function. Typically the function $R(x)$ also depends on the energy eigenvalue and on the separation constants. If at least one of the resulting equations is not exactly solvable one resorts to an approximate method. Perturbation theory, for instance, constructs an approximate solution of (1) from the known solutions of a closely related problem, say

$$P(x)\Phi_0''(x)+Q(x)\Phi_0'(x)+R_0(x)\Phi_0(x)=0 . \tag{2}$$

We will prove that it is convenient to look for a solution of Eq. (1) of the form

$$\Phi(x)=A(x)\Phi_0(x)+P(x)B(x)\phi_0'(x) , \tag{3}$$

where $A(x)$ and $B(x)$ satisfy

$$PA''+QA'-2R_0PB'-(PR_0'+P'R_0)B +(R-R_0)A=0 , \tag{4a}$$

$$PB''+(2P'-Q)B'+2A'+(P''-Q')B+(R-R_0)B=0 . \tag{4b}$$

When $\Phi_0(x)=\sin Kx$ and $P=1$ the ansatz (3) reduces to the one used in the previous paper [1]. The ansatz (3) reminds one of the method of Dalgarno and Stewart [4] in which the perturbed solution is written $\Phi(x)=F(x)\Phi_0(x)$. The advantage of Eq. (3) is that the resulting equations (4) do not depend on Φ_0 explicitly. In the method of Dalgarno and Stewart [4], on the other hand, the equation for $F(x)$ contains a term of the form Φ_0'/Φ_0 which forces one to treat one state at a time. Therefore this approach becomes impractical for the treatment of highly excited states. The complication caused by the appearance of two coupled differential equations in the present approach is counterbalanced by a considerable gain in simplicity as shown below.

In order to apply perturbation theory one chooses an appropriate perturbation parameter λ and writes

$$R(x)-R_0(x)=\sum_{j=1}^{\infty} r_j(x)\lambda^j . \tag{5}$$

Substitution of this expansion and the corresponding ones for $A(x)$ and $B(x)$,

$$A(x)=\sum_{j=0}^{\infty} A_j(x)\lambda^j, \quad B(x)=\sum_{j=0}^{\infty} B_j(x)\lambda^j , \tag{6}$$

into (4) leads to the following differential equations for the perturbation corrections:

$$PA_k''+QA_k'-2PR_0B_k'-(PR_0'+P'R_0)B_k + \sum_{j=1}^{k} r_j A_{k-j}=0 , \tag{7a}$$

$$PB_k''+(2P'-Q)B_k'+2A_k'+(P''-Q')B_k + \sum_{j=1}^{k} r_j B_{k-j}=0 . \tag{7b}$$

One solves these equations hierarchically starting from $A_0=1$ and $B_0=0$. In many cases if the initial equation (1) is conveniently chosen, say by an appropriate selection of the independent and dependent variables, the perturbation corrections A_k and B_k are polynomials and the calculation is straightforward.

III. APPLICATION TO A SIMPLE MODEL

The time-independent dimensionless Schrödinger equation,

$$\Phi''(x)+[E-V(x)]\Phi(x)=0 , \tag{8}$$

is a particular case of (1) with $P=1$, $Q=0$, and $R(x)=E-V(x)$. In order to illustrate the application of the equations just developed to a quantum-mechanical box model with penetrable walls we choose the simple potential-energy function,

$$V(x)=\begin{cases}\infty & \text{if } x<0\\ \lambda f(x) & \text{if } 0\le x\le 1\\ W_0 & \text{if } x>1 ,\end{cases} \tag{9}$$

and consider only bound states: $E<W_0$. Any physically acceptable solution of (8) with the potential (9) vanishes at $x=0$ and is of the form $\Phi(x)=Ce^{-Kx}$ for $x>1$, where $K=\sqrt{W_0-E}$. Continuity of both Φ and Φ' at $x=1$ leads to the quantization condition

$$\frac{\Phi'(1)}{\Phi(1)}=-K . \tag{10}$$

For the unperturbed system ($\lambda=0$) we have

$$\Phi_0(x)=\begin{cases}C_1\sin q_0x & \text{if } 0\le x\le 1\\ C_2e^{-K_0x} & \text{if } 1<x ,\end{cases} \tag{11}$$

in which $q_0=\sqrt{E_0}$ and $K_0=\sqrt{W_0-E_0}$. The energy eigenvalues are given by the transcendental equation

$$\tan q_0=-q_0/K_0 . \tag{12}$$

In order to apply the perturbation method discussed above we write $\Phi(x)$ as in Eq. (3) for $0\le x\le 1$ and solve the perturbation equations (7) in this interval. For concreteness we specialize in $f(x)=x$. By inspection of Eqs. (7a) and (7b) for this particular case one concludes that the perturbation corrections $A_k(x)$ and $B_k(x)$ are polynomials of order $O(A_k)=2k+\frac{1}{2}[(-1)^k-1]$ and $O(B_k)=2k-\frac{1}{2}[(-1)^k+1]$, respectively, for which we write

$$A_k(x)=\sum_{j=0}^{O(A_k)} a_{kj}x^j, \quad B_k(x)=\sum_{j=1}^{O(B_k)} b_{kj}x^j . \tag{13}$$

Clearly, with these perturbation corrections, the wave function satisfies the boundary condition at $x=0$. The quantization condition (10) can be rewritten

$$A'(1)-k_0B'(1)-W_0B(1)+(K-K_0)A(1) +K_0(K_0-K)B(1)=0 . \tag{14}$$

Expansion of this equation in λ-power series leads to

$$A_k'(1)-k_0B_k'(1)-W_0B_k(1)+\sum_{j=1}^{k} K_jA_{k-j}(1) -K_0\sum_{j=1}^{k} K_jB_{k-j}(1)=0 , \tag{15}$$

TABLE I. Perturbation corrections to the wave function and energy of the particle in a one-dimensional box with a finite potential wall.

$$A_1(x)=a_{10}+\frac{x}{4E_0}$$

$$B_1(x)=\frac{(1+2K_0+W_0)K_0x}{4(K_0^2+W_0K_0+E_0)E_0}-\frac{x^2}{4E_0}$$

$$E_1=\frac{(1+2K_0+W_0)K_0}{2W_0(K_0+1)}$$

$$E_2=(6W_0E_0+E_0W_0^3K_0-E_0^2K_0W_0^2-36E_0^3W_0-54E_0^3+4E_0^2W_0^2+5E_0W_0^3-15W_0^3K_0 +27E_0^2K_0-15W_0^2-60E_0^3K_0-45K_0W_0^2+24E_0^4-45W_0^3+6E_0^2+60E_0W_0^2+33E_0^2W_0 +15E_0W_0K_0+30E_0^2W_0K_0+25K_0E_0W_0^2)/[48W_0^2E_0^2(1+3W_0+3K_0+W_0K_0-3E_0-E_0K_0)]$$

$$K_0=\sqrt{W_0-E_0}$$

which together with

$$K_i=-\frac{1}{2K_0}\left[E_i+\sum_{j=1}^{i-1}K_jK_{i-j}\right] \tag{16}$$

determines the perturbation corrections to the energy.

The procedure is straightforward and can be easily carried out by hand. However, the calculation of exact perturbation corrections of order larger than the second one is rather tedious and the use of a symbolic processor is advisable. For a given perturbation order (say k) one obtains the coefficients a_{kj} and b_{kj} from Eqs. (7a) and (7b) in terms of unevaluated E_k. To this end one solves a set of systems of two equations with two unknowns. The allowed value of E_k follows from Eqs. (15) and (16). An alternative strategy for the latter step is to make use of standard perturbation formulas which allow the calculation of the perturbation corrections $E_1,E_2,\ldots,E_{2k+1}$ from $\Phi_1,\Phi_2,\ldots,\Phi_k$ [1]. The undetermined coefficients a_{k0} are obtained from the normalization condition.

Because the length of the expressions increases rapidly with their order in Table I we only show the perturbation correction of first order to the wave function and the first two perturbation corrections to the energy. When $W_0\to\infty$, $q_0\to n\pi$, $n=1,2,\ldots$, and the results in Table I reduce to those obtained before for a box with impenetrable walls,

$$A_1(x)=a_{10}+\frac{x}{4E_0},\quad B_1(x)=-\frac{x(x-1)}{4E_0},$$
$$E_1=\tfrac{1}{2},\quad E_2=\frac{E_0-15}{48E_0^2}, \tag{17}$$

where $E_0=n^2\pi^2$.

For $W_0<\infty$ the results are given in terms of E_0 and the state is determined solely by the chosen root of Eq. (12). The fact that the unperturbed eigenvalues are obtained from a transcendental equation has no effect on the calculation of the perturbation corrections. The unperturbed model has at least one bound state provided $W_0>\pi^2/4$. If $f(x)$ is bounded in [0,1] the norm of the perturbation is finite and according to a theorem by Kato [5] the perturbation series has a nonzero radius of convergence r_c for any bound state with energy lower than W_0. Typically there will be a critical value of λ, say $\lambda_c=\lambda_c(W_0,n)$, for which $E(W_0,n,\lambda_c)=W_0$, n being the quantum number. In such a case $r_c\le|\lambda_c|$ provided that $E_0(W_0,n)<W_0$. According to a well-known variational theorem, if $E_0(W_0,n=0)+\lambda E_1(W_0,n=0)<W_0$, the perturbed potential supports at least one bound state.

From a practical point of view one expects the series to converge slowly if $|\lambda|$ is smaller than but close to r_c. This situation is likely to occur for large values of λ and small values of W_0. In Table II we compare the perturbation series including only the first two corrections to the energy with accurate numerical results obtained by expansion of the eigenfunction within the well in power series about $x=0$. Those results suggest that the analytic expression given by perturbation theory is accurate enough for most purposes for a wide range of values of W_0 and λ.

TABLE II. Dimensionless energy eigenvalues of the Schrödinger equation with the potential (9) and $f(x)=x$.

λ	$E_0+E_1\lambda$	$E_0+E_1\lambda+E_2\lambda^2$	Accurate numerical
	$W_0=20$, $E_0=6.441\,880\,0$		
0.01	6.447 457	6.447 456 4	6.447 456 4
0.1	6.497 646	6.497 630 7	6.497 630 7
1	6.999 54	6.998 034	6.998 026 9
	$W_0=50$, $E_0=7.525\,096\,2$, $29.285\,889\,0$		
0.01	7.530 648	7.530 647 7	7.530 647 7
	29.290 816 6	29.290 816 6	29.290 816 6
0.1	7.580 612 5	7.580 598 2	7.580 598 2
	29.335 164 7	29.335 166 7	29.335 166 7
1	8.080 258 5	8.078 828 64	8.078 826 0
	29.778 646 5	29.778 846	29.778 843 0

One easily finds cases in which the perturbation expansion fails. For instance, if $W_0=2.8$ the unperturbed problem has just one bound state with dimensionless energy $E_0=2.774\,816$. For $\lambda=1$ there are no bound states in agreement with the first-order result $E_0+\lambda E_1=2.875\,516$. However, $E_0+\lambda E_1+\lambda^2E_2=2.755\,458$ predicts a bound state. The study of larger orders will show that the series diverges in this case.

IV. FURTHER COMMENTS

Unlike the previous approach [1] the method presented here is not restricted to one-dimensional equations and s states of spherically symmetric potentials. It applies to a much wider variety of separable problems which can be reduced to a set of differential equations of the form (1). Here we have concentrated on a particle in a one-dimensional box with a finite wall because this problem was not treated before by perturbation theory in closed form. We believe that in this way we are helping to extend the applicability of perturbation theory to models commonly treated by alternative approximate methods which do not produce analytic expressions.

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