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LETTER TO THE EDITOR

Perturbation theory using functions that are not quadratically integrable

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Abstract

In previous work (Skála L and Čížek J 1996 *J. Phys. A: Math. Gen.* **29** L129, 6467), a new method of calculating perturbation energies for one-dimensional problems based on the linear dependence of the perturbation wavefunctions on the perturbation energies has been suggested. It is shown in this letter that this method can be extended to multi-dimensional problems and the linearity can be used not only at a boundary point but also at an arbitrary point inside the integration region. Degenerate eigenvalues are also discussed. The resulting perturbation theory is very simple and can be used at large orders.

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In this letter, we are interested in the perturbation theory for the bound states of the Schrödinger equation

$$H\psi(x) = E\psi(x). \tag{1}$$

As usual in the perturbation theory, we assume the Hamiltonian, wavefunction and energy in the form

$$H = H_0 + \lambda H_1, \tag{2}$$

$$\psi = \psi_0 + \lambda\psi_1 + \lambda^2\psi_2 + \cdots \tag{3}$$

and

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots, \tag{4}$$

where λ is a perturbation parameter. Using these assumptions in the Schrödinger equation (1), we get the well-known equations for E_n and ψ_n:

$$H_0\psi_0 = E_0\psi_0 \tag{5}$$

and

$$H_0\psi_n + H_1\psi_{n-1} = \sum_{i=0}^{n} E_i\psi_{n-i}, \qquad n = 1, 2, \ldots. \tag{6}$$

We note that ψ_0 denotes the unperturbed wavefunction of the Hamiltonian H_0. Depending on the problem in question, it can be the ground-state or the excited-state wavefunction.

Despite the well-known formulations that can be found in any textbook on quantum mechanics, there is one property of the perturbation theory which has been noticed [1, 2] and used [3–8] only recently. It has been shown in the one-dimensional case [1, 2] that the value of the perturbation wavefunction $\psi_n(x)$ at an arbitrarily chosen point x depends on the perturbation energy E_n linearly. This linear dependence makes it possible to determine the exact perturbation energies from the values of $\psi_n(x)$ for two arbitrarily chosen perturbation energies E_n by simple calculation [1, 2]. In this way, the functions ψ_n which are not quadratically integrable are used to calculate the exact perturbation energies E_n and, in the next step, the corresponding exact perturbation functions ψ_n.

This method has a few advantages. In contrast to the usual formulation of the perturbation theory, this method based on the computation of ψ_n from equation (6) for a given energy E_n can easily be programmed for arbitrarily large orders of the perturbation theory. For example, 200 perturbation energies necessary for finding the large-order behaviour of E_n were calculated in [7]. Further, by solving equation (6) numerically, both the discrete and continuous parts of the energy spectrum are taken into account and the perturbation energies E_n can be calculated even in cases where only a few bound states exist. The linear dependence of $\psi_n(x)$ on the energy E_n makes it possible to avoid the usual shooting method and reduce the computational time substantially. Finally, we note that only the wavefunctions are needed in this method and no integrals have to be calculated.

The aim of this letter can be formulated as follows. First, it is shown that this method can be extended to multi-dimensional problems. Further, it is shown that the point x mentioned above need not be just a point sufficiently distant from the potential minimum as assumed in [1, 2], but can be an arbitrary point inside the integration region obeying conditions discussed below. This is advantageous from the point of view of the numerical stability of the method. Finally, the method is extended to degenerate energies. As examples, the perturbation energies for two coupled harmonic oscillators and two coupled Morse oscillators are calculated.

First we discuss a non-degenerate multi-dimensional case. We assume that the perturbation functions ψ_i and perturbation energies E_i are already computed for $i = 0, \ldots, n-1$. The solution of equation (6) can be written as

$$\psi_n(E_n, x) = E_n F(x) - f_{n-1}(x), \qquad n = 1, 2, \ldots, \tag{7}$$

where

$$F(x) = (H_0 - E_0)^{-1}\psi_0(x) \tag{8}$$

and

$$f_{n-1}(x) = (H_0 - E_0)^{-1}\left(H_1\psi_{n-1}(x) - \sum_{i=1}^{n-1} E_i\psi_{n-i}(x)\right). \tag{9}$$

The general solution of equation (6) can contain also a term $c_n\psi_0(x)$ in the right-hand side of equation (7), where c_n is an arbitrary constant. For the sake of simplicity, we assume $c_n = 0$ here. As seen from equation (7), the perturbation function $\psi_n(E_n, x)$ depends on the energy E_n which is not yet known and the point $x = [x_1, \ldots, x_N]$ in N-dimensional space.

Equations (7)–(9) show that the structure of the perturbation functions is very simple. It follows from equation (7) that the function $\psi_n(E_n, x)$ is a *linear function* of the energy E_n. Further, it is seen that $F(x)$ is a function *independent* of n. We note also that, except for the case where E_n is the exact perturbation energy, $\psi_n(E_n, x)$ is not quadratically integrable and has no physical meaning.

The functions $F(x)$ and $f_{n-1}(x)$ are calculated from equations (8) and (9) numerically with the conditions $F(x_b) = 0$ and $f_{n-1}(x_b) = 0$, where x_b are points in the boundary region sufficiently distant from the potential minimum. The same boundary conditions are used for the function $\psi_0(x)$.

We note that the function $F(x)$ which would diverge in the exact calculation has large but finite values in numerical calculations. The functions $\psi_n(E_n, x)$ for the exact perturbation energy E_n are quadratically integrable. Therefore, we can assume that they obey the condition

$$|\psi_n(E_n, x)| \ll |F(x)|. \tag{10}$$

It follows from equations (7) and (10) that the functions $\psi_n(E_n, x)$ also satisfy the condition

$$|\psi_n(E_n, x)| \ll |f_{n-1}(x)|. \tag{11}$$

Therefore, we can neglect $\psi_n(E_n, x)$ in equation (7). The formula for the energy E_n then reads

$$E_n = \frac{f_{n-1}(x)}{F(x)}. \tag{12}$$

This equation can be used at an *arbitrarily chosen point* x inside the integration region—except for the points where the conditions (10) and (11) are not obeyed.

If the perturbation energy E_n is calculated from equation (12), the corresponding perturbation function $\psi_n(E_n, x)$ can be found from equations (7)–(9).

Now we clarify the principle of our method in more detail. In order to eliminate the divergence in calculating $F(x)$ from equation (8), we replace the Hamiltonian H_0 by $H_0 + \mathrm{i}\delta$, where δ is a small real number. Then, the function $F(x)$ can be written as

$$F(x) = \frac{1}{\mathrm{i}\delta}\psi_0(x). \tag{13}$$

In the first order $n = 1$, we expand the function in the parentheses in equation (9) into the eigenfunctions of H_0:

$$H_1\psi_0(x) = b_0\psi_0(x) + \sum_j{}' b_j\varphi_j(x). \tag{14}$$

Here, φ_j are the eigenfunctions of H_0 which obey the equation $H_0\varphi_j = \varepsilon_j\varphi_j$ and are different from ψ_0; the b_j are constants. Now, applying the operator $(H_0 - E_0)^{-1}$ to equation (14) we obtain

$$f_0(x) = \frac{1}{\mathrm{i}\delta}b_0\psi_0(x) + \sum_j{}' \frac{1}{\varepsilon_j + \mathrm{i}\delta - E_0}b_j\varphi_j(x), \tag{15}$$

where $\varepsilon_j \neq E_0$. By substituting equations (13) and (15) into (7) we get

$$\psi_1(E_1, x) = \frac{E_1 - b_0}{\mathrm{i}\delta}\psi_0(x) - \sum_j{}' \frac{1}{\varepsilon_j + \mathrm{i}\delta - E_0}b_j\varphi_j(x). \tag{16}$$

In order to obtain a quadratically integrable function ψ_1, the energy E_1 must equal b_0. For $\delta \to 0$, the constant b_0 can be calculated from equations (13) and (15):

$$E_1 = b_0 = \frac{f_0(x)}{F(x)}. \tag{17}$$

This result is an independent proof of equation (12) for $n = 1$. By substituting $E_1 = b_0$ into equation (16) it can also be shown that the function ψ_1 is orthogonal to ψ_0. In a similar way, the correctness of equation (12) and the orthogonality of the functions ψ_n to ψ_0 can be proven at all higher orders.

In numerical calculations, the sum in equation (15) is much smaller in absolute value than the first term but it cannot be neglected. Therefore, the energy E_1 computed from the equation

$$E_1(x_0) = \frac{f_0(x_0)}{F(x_0)} \tag{18}$$

depends slightly on the choice of the point x_0. Calculating ψ_1 from equation (7) for $n = 1$ we get the function

$$\psi_1(E_1, x) = \frac{f_0(x_0)F(x) - f_0(x)F(x_0)}{F(x_0)}. \tag{19}$$

This shows that the function ψ_1 calculated in this way equals zero at the point x_0:

$$\psi_1(E_1, x_0) = 0. \tag{20}$$

Therefore, the usual orthogonality condition $\langle\psi_0|\psi_1\rangle = 0$ is not fulfilled in numerical calculations. It can easily be shown that this result can be extended to all functions ψ_n. As shown in [6], such functions can have in some cases a simpler form than the usual perturbation functions. If necessary, the functions ψ_n can be made orthogonal to ψ_0 by the usual orthogonalization procedure.

It is seen from equation (13) that equation (10) is fulfilled everywhere inside the integration region except for the points where $\psi_0(x) = 0$. Therefore, the point x used in the calculation of the energy (12) should be sufficiently distant from the points where the function $\psi_0(x)$ equals zero.

The standard formula of the non-degenerate perturbation theory can be derived in the following way. It is seen from equations (8), (9) and (12) that

$$E_n(H_0 - E_0)^{-1}\psi_0 = (H_0 - E_0)^{-1}\left(H_1\psi_{n-1} - \sum_{i=1}^{n-1} E_i\psi_{n-i}\right). \tag{21}$$

Multiplying this equation by $(H_0 - E_0)$ and supposing that the functions ψ_n obey the conditions $\langle\psi_0|\psi_n\rangle = \delta_{0,n}$, $n = 0, 1, \ldots$, we get after simple calculation the well-known formula

$$E_n = \langle\psi_0|H_1|\psi_{n-1}\rangle. \tag{22}$$

This confirms the correctness of equation (12).

Our method is a remarkable example of calculating the perturbation energies E_n from the values of the functions $F(x)$ and $f_{n-1}(x)$, which are not quadratically integrable. Comparing with the standard formulation of the perturbation theory, large-order calculations are simple in our method. To determine E_1, the values of $F(x)$ and $f_0(x)$ at just one point x are sufficient. To determine E_n for $n = 2, 3, \ldots$, only the value of $f_{n-1}(x)$ at the point x is to be computed. Therefore, this method of calculating E_n is much faster than the usual shooting method.

We note that the zero-order function ψ_0 has to be found only for the state for which the perturbation corrections are calculated. In contrast to the case for usual perturbation theory, other zero-order energies and wavefunctions are not needed in the calculation.

Now we discuss the first-order perturbation correction to a degenerate eigenvalue E_0. Assuming that the energy E_0 is d_0-times degenerate and the corresponding zero-order function ψ_0 in equation (6) is replaced by the linear combination

$$\sum_{j=1}^{d_0} a_0^{(j)}\psi_0^{(j)} \tag{23}$$

it follows from equation (6) that equation (7) can be generalized as

$$\psi_1(E_1, x) = E_1 \sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x) - \sum_{j=1}^{d_0} a_0^{(j)} f_0^{(j)}(x), \tag{24}$$

where

$$F^{(j)}(x) = (H_0 - E_0)^{-1} \psi_0^{(j)}(x) \tag{25}$$

and

$$f_0^{(j)}(x) = (H_0 - E_0)^{-1} H_1 \psi_0^{(j)}(x). \tag{26}$$

It is seen from equation (24) that $\psi_1(E_1, x)$ depends on E_1 linearly as in the non-degenerate case. Therefore, by analogy with the non-degenerate case, we can derive the formula for the perturbation energy E_1:

$$E_1 = \frac{\sum_{j=1}^{d_0} a_0^{(j)} f_0^{(j)}(x)}{\sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x)}. \tag{27}$$

Here, $f_0^{(j)}(x)$ and $F^{(j)}(x)$ are known, E_1 and $a_0^{(j)}$ are to be found. To find E_1 and $a_0^{(j)}$ we exploit the fact that the energy E_1 is a constant and use equation (27) at d_0 different points $x = x_1, \ldots, x_{d_0}$ inside the integration region. Then, the solution of the equations

$$\frac{\sum_{j=1}^{d_0} a_0^{(j)} f_0^{(j)}(x_1)}{\sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x_1)} = \frac{\sum_{j=1}^{d_0} a_0^{(j)} f_0^{(j)}(x_2)}{\sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x_2)} = \cdots = \frac{\sum_{j=1}^{d_0} a_0^{(j)} f_0^{(j)}(x_{d_0})}{\sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x_{d_0})} \tag{28}$$

yields d_0 sets of the coefficients $a_0^{(j)}$. d_0 values of the energy E_1 are given by equation (27) and the corresponding perturbation functions equal

$$\psi_1 = \sum_{j=1}^{d_0} a_0^{(j)} \psi_0^{(j)}. \tag{29}$$

The usual formulation of the first-order degenerate perturbation theory can be derived from equation (27) as follows. We substitute equations (25) and (26) into (27) and get for a point x

$$E_1 = \frac{\sum_{j=1}^{d_0} a_0^{(j)} (H_0 - E_0)^{-1} H_1 \psi_0^{(j)}(x)}{\sum_{j=1}^{d_0} a_0^{(j)} (H_0 - E_0)^{-1} \psi_0^{(j)}(x)}. \tag{30}$$

Multiplying the numerator and denominator by $(H_0 - E_0)$ we get

$$E_1 = \frac{\sum_{j=1}^{d_0} a_0^{(j)} H_1 \psi_0^{(j)}(x)}{\sum_{j=1}^{d_0} a_0^{(j)} \psi_0^{(j)}(x)} \tag{31}$$

and

$$E_1 \sum_{j=1}^{d_0} a_0^{(j)} \psi_0^{(j)}(x) = \sum_{j=1}^{d_0} a_0^{(j)} H_1 \psi_0^{(j)}(x). \tag{32}$$

Further, multiplying this equation from the left side by the complex conjugate function $\psi_0^{(i)*}(x)$, integrating over x and assuming orthonormality of the functions $\psi_0^{(j)}(x)$, the standard secular problem is obtained:

$$\sum_{j=1}^{d_0} (W_{ij} - E_1 \delta_{ij}) a_0^{(j)} = 0, \qquad i = 1, \ldots, d_0, \tag{33}$$

where

$$W_{ij} = \langle \psi_0^{(i)} | H_1 | \psi_0^{(j)} \rangle. \tag{34}$$

Higher orders of the degenerate perturbation theory can be discussed in the following way. It is assumed that the energy E_0 is d_0-times degenerate. In the first-order calculation described above, d_0 functions ψ_1 corresponding to d_0 values of the energy E_1 are obtained. If the degeneracy is removed only partly, some of the energies E_1 may be equal. For each of these functions ψ_1, we make the second-order calculation and d_0 functions ψ_2 with the corresponding energies E_2 are obtained. In this way, we continue until the $(n-1)$th order is reached. Now we want to calculate the perturbation energy E_n and the corresponding perturbation functions $\psi_n(E_n, x)$. By analogy with the first-order calculation we assume

$$\psi_n(E_n, x) = E_n \sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x) - \sum_{i=1}^{n-1} \sum_{j=1}^{d_0} a_i^{(j)} f_i^{(j)}(x), \qquad n = 2, 3, \ldots, \tag{35}$$

where

$$F^{(j)}(x) = (H_0 - E_0)^{-1} \psi_0^{(j)}(x), \tag{36}$$

and

$$f_i^{(j)}(x) = (H_0 - E_0)^{-1} (\delta_{i,n-1} H_1 - E_{n-i}) \psi_i^{(j)}(x). \tag{37}$$

These equations yield

$$E_n = \frac{\sum_{i=1}^{n-1} \sum_{j=1}^{d_0} a_i^{(j)} f_i^{(j)}(x)}{\sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x)}, \qquad n = 2, 3, \ldots. \tag{38}$$

Here, $a_0^{(j)}$ is one set of the coefficients calculated from equation (28) and $a_i^{(j)}$ for $i = 1, \ldots, n-2$ are the corresponding coefficients. The coefficients $a_{n-1}^{(j)}$ are to be found. Then, the solution of the equations

$$\frac{\sum_{i=1}^{n-1} \sum_{j=1}^{d_0} a_i^{(j)} f_i^{(j)}(x_1)}{\sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x_1)} = \frac{\sum_{i=1}^{n-1} \sum_{j=1}^{d_0} a_i^{(j)} f_i^{(j)}(x_2)}{\sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x_2)} = \cdots = \frac{\sum_{i=1}^{n-1} \sum_{j=1}^{d_0} a_i^{(j)} f_i^{(j)}(x_{d_0})}{\sum_{j=1}^{d_0} a_0^{(j)} F^{(j)}(x_{d_0})} \tag{39}$$

at d_0 different points yields the coefficients $a_{n-1}^{(j)}$, $j = 1, \ldots, d_0$. The corresponding energy E_n is given by equation (38) and the perturbation function equals

$$\psi_n = \sum_{j=1}^{d_0} a_{n-1}^{(j)} \psi_{n-1}^{(j)}. \tag{40}$$

This calculation has to be performed for all the sets of the coefficients $a_0^{(j)}$ obtained from equation (28).

It is seen that our formulation of degenerate perturbation theory is simpler than the usual formulation [11] and can be used at large orders.

Assuming the normalization of the functions $\psi_0^{(i)}$ and the orthogonality of the functions $\psi_k^{(j)}$ to $\psi_0^{(i)}$, $k = 1, \ldots, n-1$, we obtain from equations (35)–(38)

$$\sum_{j=1}^{d_0} \langle \psi_0^{(i)} | H_1 | \psi_{n-1}^{(j)} \rangle a_{n-1}^{(j)} = E_n a_0^{(i)}, \qquad i = 1, \ldots, d_0. \tag{41}$$

This equation is a generalization of equation (22) to degenerate case.

Table 1. Perturbation energies E_n for the ground state of the Hamiltonian (42). E_0 is the exact zero-order energy.

n	E_n
0	2
1	−0.750 000 000
2	−0.937 500 00
3	−0.023 437 500 0
4	−0.013 305 664 0
5	−0.000 315 348 30
6	−0.013 279 491
7	0.024 044 310 6
8	−0.074 303 068 7
9	0.234 920 366
10	−0.845 542 55
11	3.345 687 31
12	−14.494 654 8
13	68.195 859
14	−346.325 41
15	1 888.182 52
16	−11 000.399 4
17	68 201.932
18	−448 367.10
19	3115 424.0
20	−22 813 412.6

As an example of using our method, we first calculated the perturbation energies for the ground state of two non-linearly coupled harmonic oscillators [9, 10]:

$$H = -\frac{\partial^2}{\partial x_1^2} - \frac{\partial^2}{\partial x_2^2} + x_1^2 + x_2^2 + \lambda(x_1^2 x_2^2 - x_1^2 - x_2^2). \tag{42}$$

To compute ψ_n from equation (6) in the region $x_1 \in [-11, 11]$, $x_2 \in [-11, 11]$, we used $158 \times 158, 160 \times 160, 162 \times 162, 164 \times 164$ grids of points, assumed that the functions ψ_n equal zero at the border of this region and solved the corresponding system of difference equations in double-precision accuracy in Fortran. To eliminate the effect of the non-zero steps of the grids, the perturbation energies were extrapolated to an infinitely dense grid by means of the Richardson extrapolation. The ground-state perturbation energies are shown in table 1. Only the digits which agree in the calculations for the points $x = [0, 0]$ and $[1, 1]$ are shown. These results agree also with an independent calculation made by means of the difference equation method suggested in [10]. The dependence of the results on the choice of the point x is small.

As a second test, we chose a more difficult problem with only one bound state of the Hamiltonian H_0 where the standard perturbation theory yields the first-order correction E_1 only. The perturbation energies were calculated for the ground state of two coupled Morse oscillators:

$$H = -\frac{\partial^2}{\partial x_1^2} - \frac{\partial^2}{\partial x_2^2} + (1 - \mathrm{e}^{-x_1})^2 + (1 - \mathrm{e}^{-x_2})^2 + \lambda(1 - \mathrm{e}^{-x_1})^2(1 - \mathrm{e}^{-x_2})^2. \tag{43}$$

The integration region $x_1 \in [-12, 20]$ and $x_2 \in [-12, 20]$ was used. The ground-state perturbation energies are shown in table 2. Only the digits which agree in the calculations for $x = [4, 4]$ and $[5, 6]$ are shown. The value of $E_1 = 0.25$ was verified by analytic calculation. The decrease in accuracy of the energies E_n with increasing n is due to the fact that the

Table 2. Perturbation energies E_n for the ground state of the Hamiltonian (43). E_0 is the exact zero-order energy.

n	E_n
0	3/2
1	0.250 0000
2	−0.069 635
3	0.039 03
4	−0.036 6
5	0.092 0
6	−0.611
7	6.43
8	−89.2
9	1550

functions ψ_n spread with increasing n rapidly, and get out of the integration region. These results show that, in contrast to the case for standard perturbation theory, our method can be used for calculating higher-order perturbations even in the case of only one zero-order bound state.

It is obvious from tables 1 and 2 that both perturbation series fail to converge and are asymptotic series only.

We verified that equations (27) and (28) yield correct numerical results for the Hamiltonian (42) and $d_0 = 2, 3$. Further results will be published elsewhere.

Summarizing, the method described in this letter is simple and efficient alternative to the usual formulation of the perturbation theory. It can be used for one-dimensional as well as multi-dimensional problems and for non-degenerate as well as degenerate eigenvalues. Its main advantages are easy calculation of the large-order perturbations and the possibility of finding the perturbation corrections even in cases where only a few zero-order bound states exist.

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