

**NEW VERSION OF THE RAYLEIGH–SCHRÖDINGER  
PERTURBATION THEORY**Miloš KALHOUS<sup>a1</sup>, Lubomír SKÁLA<sup>a2,b,\*</sup>, Jaroslav ZAMASTIL<sup>a3,b</sup> and Jiří ČÍŽEK<sup>a4,b</sup><sup>a</sup> Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, 121 16 Prague 2,Czech Republic; e-mail: <sup>1</sup> kalhous@mff.cuni.cz, <sup>2</sup> lubomir.skala@mff.cuni.cz,<sup>3</sup> zamastil@mff.cuni.cz, <sup>4</sup> jiri.cizek@karlov.mff.cuni.cz<sup>b</sup> University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Received August 30, 2002

Accepted November 22, 2002

*Dedicated to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays.*

New version of the Rayleigh–Schrödinger perturbation theory based on the linear dependence of the perturbation wavefunctions on the perturbation energies is summarized. It is shown that this method is suitable also for multidimensional problems and the linear dependence can be used at an arbitrary point inside the integration region. The resulting perturbation theory is simple and can be used at large orders. As an example, the method is applied to the Barbanis hamiltonian.

**Keywords:** Quantum mechanics; Rayleigh–Schrödinger perturbation theory; Wavefunctions; Barbanis hamiltonian.

**THEORY**

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

$$H\psi(x) = E\psi(x) . \quad (1)$$

As usual, we assume the hamiltonian, wavefunction and energy in the form

$$H = H_0 + \lambda H_1 \quad (2)$$

$$\psi = \psi_0 + \lambda\psi_1 + \lambda^2\psi_2 + \dots \quad (3)$$

and

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \dots, \quad (4)$$

where  $\lambda$  is a perturbation parameter. Except for the simplest cases, these equations cannot be solved in analytical form and approximate methods have to be used. Using these assumptions in the Schrödinger equation (1) we get the well-known equations for  $E_n$  and  $\psi_n$

$$H_0\psi_0 = E_0\psi_0 \quad (5)$$

and

$$H_0\psi_n + H_1\psi_{n-1} = \sum_{i=0}^n E_i\psi_{n-i}, \quad n = 1, 2, \dots \quad (6)$$

We note the unperturbed wavefunction  $\psi_0$  can be the ground-state as well as an excited-state wavefunction.

There is one property of the perturbation theory which has been noticed<sup>1,2</sup> and used<sup>3-8</sup> only recently. It has been shown in the one-dimensional case<sup>1,2</sup> 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<sup>1,2</sup>. In this way, the functions  $\psi_n$  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  $\psi_n$ .

This method has a few advantages. First, the computation of  $\psi_n$  from Eq. (6) for a given energy  $E_n$  can easily be programmed for arbitrary large orders of the perturbation theory. For example, 200 perturbation energies  $E_n$  necessary for finding their large-order behaviour were calculated in ref.<sup>7</sup> Further, by solving Eq. (6) numerically both the discrete and continuous part of the energy spectrum is taken into account and the perturbation energies  $E_n$  can be calculated even in cases when 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 sub-

stantially. Finally, we note that only the wavefunctions are needed in this method and no integrals have to be calculated.

The aim of this paper can be formulated as follows. First, it is shown that this method can be extended to multidimensional problems. Further, the point  $x$  mentioned above need not be only a point sufficiently distant from the potential minimum as assumed in refs<sup>1,2</sup> but it can be an arbitrary point inside the integration region obeying conditions discussed below. This is advantageous from the viewpoint of numerical stability of the method. First we discuss a non-degenerate multidimensional case. We assume the perturbation functions  $\psi_i$  and perturbation energies  $E_i$  are already computed for  $i = 0, \dots, n - 1$ . Solution of Eq. (6) can be written as

$$\psi_n(E_n, \mathbf{x}) = E_n F(\mathbf{x}) - f_{n-1}(\mathbf{x}), \quad n = 1, 2, \dots, \quad (7)$$

where

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

and

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

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

Equations (7)–(9) show very simple structure of the perturbation functions. It follows from Eq. (7) that the function  $\psi_n(E_n, \mathbf{x})$  is a *linear function* of the energy  $E_n$ . Further, it is seen that  $F(\mathbf{x})$  is a function *independent* of  $n$ . We note also that, except for the exact perturbation energy  $E_n$ ,  $\psi_n(E_n, \mathbf{x})$  is not quadratically integrable and has not any physical meaning.

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

We note that the function  $F(\mathbf{x})$  diverges in the exact calculation; however, it has large but finite values in numerical calculations. The functions

$\psi_n(E_n, \mathbf{x})$  for the exact perturbation energy  $E_n$  are quadratically integrable. Therefore, we can assume they obey the condition

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

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

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

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

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

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.

After calculating the perturbation energy  $E_n$  from Eq. (12), the corresponding perturbation function  $\psi_n(E_n, \mathbf{x})$  can be found from Eqs (7)–(9).

Now we clarify the principle of our method for the case  $n = 1$ . In order to eliminate the divergence in calculating  $F(\mathbf{x})$  from Eq. (8) we replace the hamiltonian  $H_0$  by  $H_0 + i\delta$ , where  $\delta$  is a small real number. Then, the function  $F(\mathbf{x})$  can be written as

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

In the first order  $n = 1$ , we expand the function in the parantheses in Eq. (9) into the eigenfunctions of  $H_0$

$$H_1 \psi_0(\mathbf{x}) = b_0 \psi_0(\mathbf{x}) + \sum_j b_j \phi_j(\mathbf{x}). \quad (14)$$

Here,  $\phi_j$  are the eigenfunctions of  $H_0$  which obey the equation  $H_0 \phi_j = \varepsilon_j \phi_j$  and are different from  $\psi_0$ ,  $b_j$  are constants. Now, applying the operator  $(H_0 - E_0)^{-1}$  to Eq. (14) we obtain

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

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

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

In order to obtain quadratically integrable function  $\psi_1$ , the energy  $E_1$  must equal  $b_0$ . For  $\delta \rightarrow 0$ , the constant  $b_0$  can be calculated from Eqs (13) and (15)

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

This result is an independent proof of Eq. (12) for  $n = 1$ . In a similar way, the correctness of Eq. (12) can be proven at all higher orders.

In numerical calculations, the exact hamiltonian  $H_0$  is replaced by an approximate one and the functions  $F(x)$  and  $f_n(x)$  given by Eqs (8) and (9) do not diverge.

It can be shown that the function  $\psi_n$  calculated numerically from Eqs (7) for the energy (12) equals zero at the point  $x_0$

$$\psi_n(E_n, x_0) = 0. \quad (18)$$

Therefore, the usual orthogonality condition  $\langle \psi_0 | \psi_n \rangle = 0$  is not fulfilled in numerical calculations. Such functions can have in some cases a simpler form than the usual perturbation functions<sup>6</sup>. If necessary, the functions  $\psi_n$  can be made orthogonal to  $\psi_0$  by the usual orthogonalization procedure. It is shown in ref.<sup>9</sup> that Eq. (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 Eqs (8), (9) and (12) that

$$E_n (H_0 - E_0)^{-1} \psi_0 = (H_0 - E_0)^{-1} \left( H_1 \psi_{n-1} - \sum_{i=1}^{n-1} E_i \psi_{n-1} \right). \quad (19)$$

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

$$E_n = \langle \psi_0 | H_1 | \psi_{n-1} \rangle. \quad (20)$$

It confirms correctness of Eq. (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 only one point  $x$  are sufficient. To determine  $E_n$  for  $n = 2, 3, \dots$ , only the value of  $f_{n-1}(x)$  at the point  $x$  is to be computed.

We note that the zero-order function  $\psi_0$  has to be found only for the state for which the perturbation corrections are calculated. In contrast to the usual perturbation theory, other zero-order energies and wavefunctions are not needed in the calculation.

#### EXAMPLE

As an example of using our method, we calculated the perturbation energies for the ground state of the Barbanis hamiltonian with the unperturbed hamiltonian

$$H_0 = -\frac{\partial^2}{\partial x^2} + \omega_x^2 x^2 - \frac{\partial^2}{\partial y^2} + \omega_y^2 y^2 \quad (21)$$

and with the perturbation potential

$$H_1 = xy^2. \quad (22)$$

Here, we used the parameters  $\omega_x = 1$ ,  $\omega_y = 1$ . This hamiltonian has been often studied as a simple model for systems with the Fermi responses such as the CO<sub>2</sub> stretchbend resonance<sup>11</sup>.

The perturbation energies are calculated both numerically and analytically (see Table I). Analytical calculations are possible due to the polynomial form of the potential. The eigenfunctions of  $H_0$  are products of the corresponding eigenfunctions of the one-dimensional harmonic oscillators.

TABLE I

Perturbation energies  $E_n$  for the ground [0,0] state of the Barbanis hamiltonian (21)–(22).  $E_0^{\text{num}} = E_0^{\text{an}} = 2$  is the exact zero-order energy. The energies calculated numerically from Eq. (12) are denoted as  $E_n^{\text{num}}$ . The analytical energies denoted as  $E_n^{\text{an}}$  were calculated for  $n = 2, 4, \dots, 20$ . Odd-order perturbation energies equal zero

$n$	$E_n^{\text{num}}$	$E_n^{\text{an}}$
0	2	2
2	-0.1041666665	$-\frac{5}{48} = -0.10416666667\dots$
4	-0.0322627314	$-\frac{223}{6912} = -0.0322627314815\dots$
6	-0.02298880368	$-\frac{114\,407}{4\,976\,640} = -0.0229888036908\dots$
8	-0.024159131	$-\frac{346\,266\,143}{14\,332\,723\,200} = -0.0241591313924\dots$
10	-0.0326818070	$-\frac{2\,360\,833\,242\,959}{72\,236\,924\,928\,000} = -0.0326818070580\dots$
12	-0.05343610684	$-\frac{12\,969\,801\,730\,008\,377}{242\,716\,067\,758\,080\,000} = -0.0534361068462\dots$
14	-0.1019221649	$-\frac{124\,680\,261\,346\,275\,858\,491}{1\,223\,288\,981\,500\,723\,200\,000} = -0.101922164944\dots$
16	-0.2217101989	$-\frac{10\,935\,414\,749\,213\,048\,671\,720\,261}{49\,323\,011\,734\,109\,159\,424\,000\,000} = -0.221710199048\dots$
18	-0.541404172	$-\frac{4\,441\,356\,782\,637\,499\,756\,905\,980\,351\,899}{8\,203\,403\,311\,617\,035\,395\,399\,680\,000\,000} = -0.541404172625\dots$
20	-1.46666250	$-\frac{667\,033\,238\,517\,271\,928\,733\,626\,515\,967\,166\,703}{454\,796\,679\,596\,048\,442\,320\,958\,259\,200\,000\,000} = -1.46666250754\dots$
22	-4.366576807	
24	-14.17768870	
26	-49.8757770	
28	-189.0381799	
30	-768.15366	

Equation (6) for the Barbanis potential was integrated numerically in the region  $x \in [-11, 11]$ ,  $y \in [-11, 11]$ . To compute  $\psi_n$  in this region, we used a grid of points  $158 \times 158$ ,  $160 \times 160$ ,  $162 \times 162$ ,  $164 \times 164$ , assumed that the functions  $\psi_n$  equal zero at the border of this region and used the method of finite differences. The corresponding system of linear difference equations was solved in double precision arithmetics in Fortran. To eliminate the effect of a non-zero step of the grid, the perturbation energies were extrapolated to an infinitely dense grid by means of the Richardson extrapolation. This extrapolation is substantial for increasing the accuracy of the results.

The ground-state perturbation energies are shown in Table I. Only the digits which agree in the calculations for the points  $x = [0.2, 0.5]$  and  $x = [0.6, 0.8]$  are shown. It is seen that the results depend on the choice of the point  $x$  only slightly. The numerical results agree well with an independent analytical calculation made in Maple shown in Table I with the accuracy 6–9 digits.

Because of the antisymmetry of the potential  $H_1$  (Eq. (22)), the perturbation energies of the odd order equal zero,  $E_{2i+1} = 0$ ,  $i = 1, 2, \dots$ . In numerical calculations, the odd-order perturbation energies differ from zero within the accuracy 7–9 digits. The even perturbation energies  $E_{2i}$ ,  $i = 1, 2, \dots$  are negative and their absolute value increases rapidly with  $i$ . It is seen that the perturbation series for the Barbanis hamiltonian is a divergent series. Calculating the energy from Eq. (4) for small  $\lambda$ , the absolute values of the terms  $\lambda^n E_n$  go first down and then increase. This indicates the perturbation series (4) is the asymptotic series. It is obviously related to different asymptotic behaviour of the wavefunctions corresponding to the hamiltonians  $H = H_0$  and  $H = H_0 + \lambda H_1$  for  $x \rightarrow \pm\infty$ . Further investigation in this respect is necessary.

The perturbation functions following from the analytical calculations are given by the following expressions

$$\psi_0 = \frac{1}{\sqrt{\pi}} e^{-1/2 x^2 - 1/2 y^2},$$

$$\psi_1 = -\frac{x}{6\sqrt{\pi}} (1 + y^2) e^{-1/2 x^2 - 1/2 y^2},$$

$$\psi_2 = -\frac{1}{1152\sqrt{\pi}} (-51 + 36y^2 + 4y^4 + 24x^2 + 48x^2 y^2 + 16x^2 y^4) e^{-1/2 x^2 - 1/2 y^2},$$



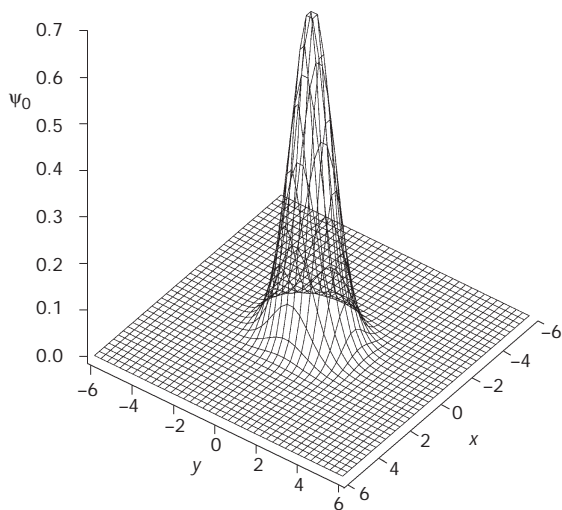


FIG. 1  
The ground-state zero-order wavefunction  $\psi_0$  for the Barbanis hamiltonian (21)–(22)

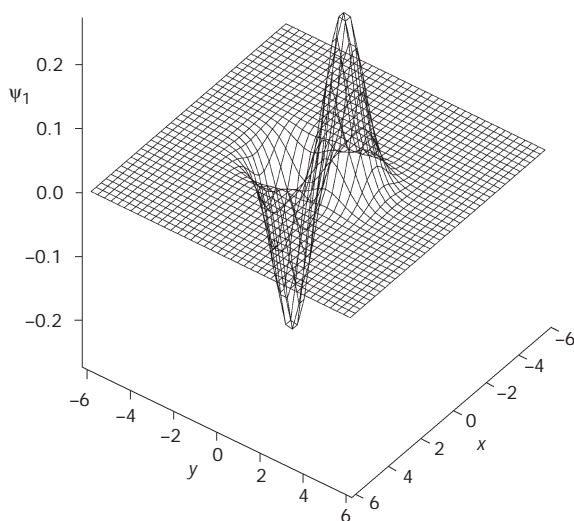


FIG. 2  
The first-order perturbation function  $\psi_1$  for the ground state of the Barbanis hamiltonian (21)–(22)

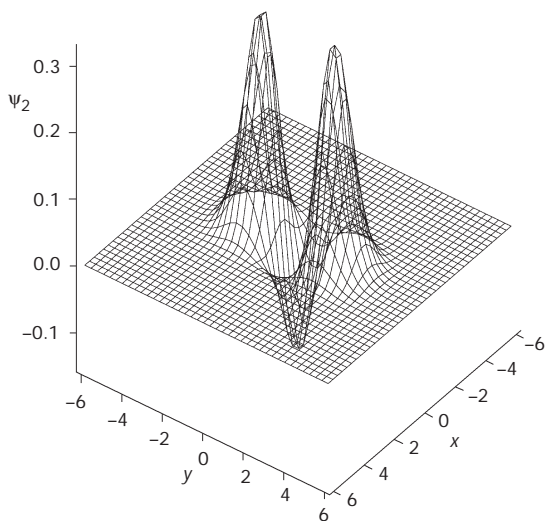


FIG. 3

The second-order perturbation function  $\psi_2$  for the ground state of the Barbanis hamiltonian (21)–(22)

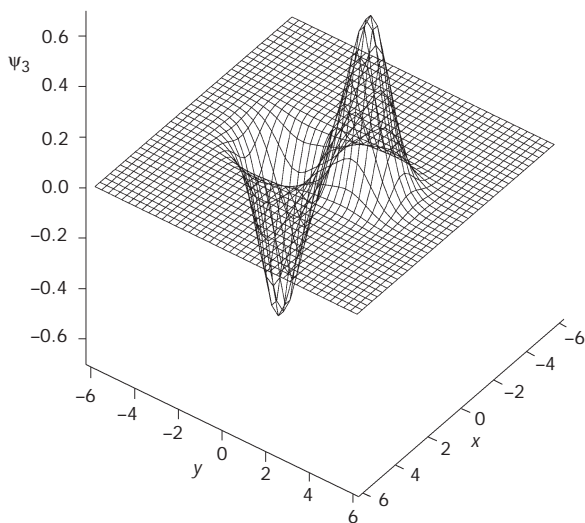


FIG. 4

The third-order perturbation function  $\psi_3$  for the ground state of the Barbanis hamiltonian (21)–(22)

$$\psi_3 = \frac{-x}{103\,680\sqrt{\pi}}(1203 + 1311y^2 + 792y^4 + 60y^6 + 264x^2 + 792x^2y^2 + 480x^2y^4 + 80x^2y^6)e^{-1/2x^2-1/2y^2},$$

$$\begin{aligned} \psi_4 = \frac{1}{39\,813\,120\sqrt{\pi}} & (-611\,433 + 350\,424y^2 + 66\,600y^4 + 7008y^6 + 240y^8 + \\ & + 200\,016x^2 + 366\,048x^2y^2 + 168\,480x^2y^4 + 35\,328x^2y^6 + \\ & + 1920x^2y^8 + 12\,864x^4 + 51\,456x^4y^2 + 43\,008x^4y^4 + 12\,800x^4y^6 + \\ & + 1280x^4y^8)e^{-1/2x^2-1/2y^2}. \end{aligned} \quad (23)$$

These functions agree well with the numerically calculated functions  $\psi_n$  shown in Figs 1–4.

## CONCLUSIONS

The version of the perturbation theory described in this paper is a simple and efficient alternative to the usual formulation of the perturbation theory. It can be used for one-dimensional as well as multidimensional problems and for non-degenerate as well as degenerate eigenvalues. Its main advantages are the easy calculation of the large-order perturbations and the possibility to find the perturbation corrections even in cases when only a few zero-order bound states exist. These properties are advantageous in calculating the electronic and vibrational spectra of atoms and molecules.

*This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (grants No. LN00A032 and No. 190-01/206053), the Grant Agency of the Charles University (grants No. 166/00 and No. 180/02) and the Grant Agency of the Czech Republic (grant No. 202/00/1026). J. Zamastil acknowledges the National Science and Engineering Research Council of Canada (NATO Science Fellowship).*

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