

Comments on 'A new efficient method for calculating perturbation energies using functions which are not quadratically integrable'

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys. A: Math. Gen. 29 6461

(<http://iopscience.iop.org/0305-4470/29/19/030>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.70

The article was downloaded on 02/06/2010 at 04:01

Please note that [terms and conditions apply](#).

COMMENT

Comments on ‘A new efficient method for calculating perturbation energies using functions which are not quadratically integrable’

R Guardiola^{†§} and J Ros[‡]

[†] Departamento de Física Atómica y Nuclear, Universidad de Valencia, Avda. Dr. Moliner, 50, 46100 Burjassot, Valencia, Spain

[‡] Departamento de Física Teórica and IFIC, Universidad de Valencia, Avda. Dr. Moliner, 50, 46100 Burjassot, Valencia, Spain

Received 10 April 1996

Abstract. The recently proposed method of calculating perturbation energies using a non-normalizable wavefunction by Skála and Čížek is analysed and rigorously proved.

In a recent article, Skála and Čížek [1], hereafter referred to as SC, have described a new method for carrying out large-scale perturbation calculations specially adapted to numerical evaluations. The most appealing feature of their method is the use of non-quadratically integrable functions.

Large-scale perturbation calculations are commonly applied to problems, like the anharmonic oscillator $x^2 + \lambda x^4$, which permit very efficient evaluations by using hypervirial relations [2]. On the other hand, *numerically* perturbation expansions are not frequently to be carried out. Nevertheless, these expansions may be interesting in specific physical problems, like the Van der Waals perturbation theory applied to many-body systems [3], which do not permit an algebraic treatment.

However, the use of non-normalizable wavefunctions sounds abnormal in the field of quantum mechanics, always tied to a L^2 Hilbert space. Surprisingly, non-normalizable functions do appear in the bulk of the *exponential S* or coupled cluster theory, which is interesting for the description of many-particle quantum systems [4].

The subject of the mentioned work of SC is, then, quite appealing and of potential interest. A first consideration of their paper reveals, in our opinion, some weak mathematical points. However, some practice with the proposed algorithm convinced us of its correctness. The purpose of this comment is to give a general proof of the SC method.

The perturbation problem is stated in the usual way found in any quantum mechanics textbook: given a Hamiltonian $H = H_0 + \lambda H_1$, to find the energy E and wavefunction Ψ into which the unperturbed level E_0 and wavefunction Ψ_0 have changed. By assuming for E and Ψ a power expansion in the coupling parameter λ ,

$$\begin{aligned}\Psi &= \Psi_0 + \lambda \Psi_1 + \dots \\ E &= E_0 + \lambda E_1 + \dots\end{aligned}$$

[§] E-mail address: guardiola@kate.fisato.uv.es

one gets the hierarchy of equations

$$(H_0 - E_0)\Psi_0 = 0 \quad (1)$$

$$(H_0 - E_0)\Psi_n = E_n\Psi_0 + \sum_{i=1}^{n-1} E_i\Psi_{n-i} - H_1\Psi_{n-1}. \quad (2)$$

These equations are supplemented by a normalization condition, which is usually recast in the form

$$\langle \Psi_0 | \Psi_n \rangle = \delta_{n,0}. \quad (3)$$

The standard (academic) treatment of these equations proceeds by using the assumed completeness of the eigenfunctions of H_0 to determine E_n and Ψ_n just by calculating matrix elements. This is particularly useful in the case of low-order perturbation calculations or in problems (like the λx^4 perturbation) with a reduced number of non-null matrix elements. This requires, of course, the knowledge of the full spectrum of the unperturbed Hamiltonian.

One of the alleged advantages of the SC proposal is that one does not need to know the spectrum and eigenfunctions of H_0 . For the sake of comparison, we recall the usual *numerical* procedure to deal with the previous equations, which again does not require the knowledge of the H_0 spectrum. First of all, one must determine the unperturbed solution by solving the eigenvalue problem of equation (1), obtaining both E_0 and Ψ_0 . Then, assuming that the energies and wavefunctions up to order $n-1$ are known, i.e. up to E_{n-1} and Ψ_{n-1} , one gets the next correction to the energy as

$$E_n = \langle \Psi_0 | H_1 | \Psi_{n-1} \rangle \quad (4)$$

i.e. simply by means of a quadrature. Once E_n is known, Ψ_n is obtained by solving a second-order inhomogeneous differential equation, equation (2), which requires one to find two independent solutions and solve a 2×2 system of linear equations in order to fulfill the boundary conditions.

SC propose, instead, to use only equation (2) at order n to get both the energy and wavefunction corrections. To this end their key statement is that Ψ_n depends linearly on the parameter E_n

$$\Psi_n(E_n, x) = F(x)E_n + \Phi_n(x) \quad (5)$$

$F(x)$ being a *universal* function, independent of the order n of the perturbation.

This most remarkable fact turns out to be true, but the argument given by SC to prove it is not correct. They deduce it from their equation (10)

$$(H_0 - E_0) \frac{\partial \Psi_n(E_n, x)}{\partial E_n} = \Psi_0 \quad (6)$$

but from here one can only infer

$$\frac{\partial \Psi_n(E_n, x)}{\partial E_n} = F(x) + G(E_n)\Phi(x) \quad (7)$$

where $G(E_n)$ is an *arbitrary* function of E_n and $\Phi(x)$ is an eigenstate (not necessarily quadratically integrable) of H_0 with eigenvalue E_0 . Equation (7) is in contrast with the result of [1],

$$\frac{\partial \Psi_n(E_n, x)}{\partial E_n} = F(x). \quad (8)$$

Equation (5) may, in fact, be proved by directly integrating the perturbation equation (2). Let us note that the value of the energy E_n which has appeared so far is *not yet* the value

of the perturbation correction, but an arbitrary parameter, and, in consequence, the related solution $\Psi_n(E_n, x)$ will be, in general, non-normalizable.

In order to use a more compact notation, let us introduce

$$\mathcal{F}(x) = \sum_{i=1}^{n-1} E_i \Psi_{n-i} - H_1 \Psi_{n-1} \tag{9}$$

which at this step is already known, and concentrate on the equation

$$(-D^2 + V_0(x) - E_0)\Psi_n(x) = E_n \Psi_0(x) + \mathcal{F}(x) \tag{10}$$

where the unperturbed Hamiltonian has been explicitly written in terms of the second derivative operator D and the unperturbed potential V_0 . The perturbation is included in the inhomogeneous term $\mathcal{F}(x)$.

This equation may be easily integrated. After writing

$$\Psi_n(x) = \Psi_0(x) f_n(x) \tag{11}$$

the resulting equation for the new function f_n is

$$-f_n''(x) - 2 \frac{\Psi_0'(x)}{\Psi_0(x)} f_n'(x) = E_n + \frac{\mathcal{F}(x)}{\Psi_0(x)} \tag{12}$$

which is trivially recognized as a first-order linear differential equation for f_n' which is integrated with the result

$$f_n'(y) = -\frac{1}{\Psi_0^2(y)} \int_a^y \left[E_n + \frac{\mathcal{F}(z)}{\Psi_0(z)} \right] \Psi_0^2(z) dz. \tag{13}$$

The lower limit a of this integral represents the arbitrary constant in the integration process and will be used to accommodate the required boundary condition on the wavefunction.

The full solution is, obviously,

$$\Psi_n(x) = -\Psi_0(x) \int_b^x \frac{1}{\Psi_0^2(y)} \int_a^y \left[E_n + \frac{\mathcal{F}(z)}{\Psi_0(z)} \right] \Psi_0^2(z) dz \tag{14}$$

where again b accounts for the additive arbitrary constant introduced in getting f_n from f_n' . Notice that, as far as E_n is yet arbitrary, the resulting wavefunction will not be, in general, normalizable.

Equation (14) contains the main result of [1], i.e. it is a clear proof of the linear dependence on E_n of equation (5) and, even more, it gives the explicit form for $F(x)$

$$F(x) = -\Psi_0(x) \int_b^x dy \frac{1}{\Psi_0^2(y)} \int_a^y \Psi_0^2(z) dz. \tag{15}$$

Once the boundary conditions have been fixed, i.e. for specific values of a and b , this function is *universal*, i.e. independent of the perturbation order n .

For this equation to be useful, one would like to choose the boundary conditions in such a form that when E_n is the exact perturbation energy correction, the corresponding $\Psi_n(x)$ satisfies the physical boundary conditions, i.e. is square integrable. This means that the following limits should hold:

$$\lim_{x \rightarrow \pm\infty} \Psi_n(x) = 0. \tag{16}$$

The condition at $-\infty$ may be easily fulfilled by taking $b = -\infty$ for one of the lower limits. We have not found a simple way of ensuring the condition at $+\infty$. Alternatively, we have

assumed another condition for $f_n(x)$ at $-\infty$, namely, that its derivative also goes to zero. Then, the required value for a is again $-\infty$.

Concentrating on this specific function, explicitly given by

$$f_n(x) = - \int_{-\infty}^x dy \frac{1}{\Psi_0^2(y)} \int_{-\infty}^y \left[E_n + \frac{\mathcal{F}(z)}{\Psi_0(z)} \right] \Psi_0^2(z) dz \quad (17)$$

it is convenient to check its behaviour at large and positive values of x , to secure that it does not spoil the nice normalizability condition of $\Psi_0(x)$. So, let us analyse the limit

$$\lim_{x \rightarrow \infty} - \int_{-\infty}^x dy \frac{1}{\Psi_0^2(y)} \int_{-\infty}^y \left[E_n + \frac{\mathcal{F}(z)}{\Psi_0(z)} \right] \Psi_0^2(z) dz. \quad (18)$$

The integral over y refers to a function $1/\Psi_0^2(y)$ which grows unboundedly for large values of y , because $\Psi_0(y)$ is an eigenstate of the unperturbed Hamiltonian and consequently square integrable. To have a finite value, the other factor in this integral must go to zero at large y , i.e.

$$\int_{-\infty}^{\infty} \left[E_n + \frac{\mathcal{F}(z)}{\Psi_0(z)} \right] \Psi_0^2(z) dz = 0 \quad (19)$$

which gives exactly the value quoted in equation (4) for E_n . In conclusion, our specific way of selecting the boundary conditions guarantees the normalizability of the perturbation energy correction, once the appropriate value for the energy E_n has been used.

We may go one step further to obtain an operative method to get the value of the perturbed energy. If we consider two solutions for Ψ_n , one corresponding to E_n and the other to $E'_n = 0$, and both *with the same boundary conditions* as explained above, then there follows the relation

$$E_n = \frac{\Psi_n(E_n, x_0) - \Psi_n(0, x_0)}{F(x_0)} \quad (20)$$

in such a form that, for sufficiently large value of x_0 , it is converted into

$$E_n = \frac{-\Psi_n(0, x_0)}{F(x_0)} \quad (21)$$

which coincides with equation (14) of [1]. Our equation (21) is more precise than the equivalent equation of [1] because we have fixed the boundary conditions for the integration of the inhomogeneous equation.

Of course, given the universal character of the function $F(x)$, it needs to be determined only once, for example along the calculation of the first perturbation correction. Then, the determination of successive orders is done by integrating equation (2) for $E_n = 0$, starting at a large and negative x with starting values for $\Psi_n(x) = 0$ and $\Psi'_n(x) = 0$, up to some large and positive value of x , and dividing by $F(x)$ as in equation (21).

In conclusion, the main difference between the SC proposal and the usual numerical procedure consists in calculating E_n by solving the differential equation (10) instead of performing the quadrature (4). The SC method deals with growing functions and, consequently, is prone to numerical instabilities and overflows. So, one is tempted to conclude with the spanish proverb 'Para este viaje no hacían falta alforjas', which may be translated as 'too much luggage for such a short trip'. Nevertheless, the fact that when dealing with non-normalizable functions and, in consequence, exiting the usual Hilbert space of quantum mechanics, one may still get relevant results is very appealing.

Acknowledgments

This work is supported by DGICyT under contract No PB92-0820 and by the EEC network No ERBCHRXCT940456.

References

- [1] Skála L and Čížek J 1996 *J. Phys. A: Math. Gen.* **29** L129
- [2] Killingbeck J P 1983 *Microcomputer Quantum Mechanics* (Bristol: Adam Hilger)
- [3] Buendía E, Guardiola R and de Llano M 1989 *Atom. Data Nucl. Data Tables* **42** 293
- [4] Arponen J S and Bishop R F 1990 *Phys. Rev. Lett.* **64** 111