BRIEF COMMUNICATION

Fredholm integral equation for the perturbation theory in quantum mechanics

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Abstract A new approach for perturbation method, based on the Fredholm integral equation of the second kind has been introduced to theoretical physics and quantum chemistry. The method has been used in order to derive an analytical form of the υ-vibrational wavefunction in a form of a continuously convergent Liouville–Neumann perturbation series and to generate consecutive perturbation corrections to the wavefunction. The second-order correction to the energy levels has been obtained. Iterated kernels and a resolvent have been constructed and employed to the calculation of the wavefunction perturbation corrections. The method proposed can be used successfully in advanced calculations of quantum chemistry and theoretical spectroscopy because of a continuously convergence of the perturbation series.

Keywords Fredholm integral equation · Perturbation theory method · Vibrational problem · Molecular spectroscopy · Theoretical physics

1 Introduction

Perturbation theory method is one of the most widely used among the theoretical physicists and chemists, allowing them to obtain approximate analytical solutions of many physical problems and to describe the reality more properly than the so-called unperturbed model, which even though being exactly solvable, is purely mathematical. The method has been widely applied in almost every branch of physics, e.g.: nuclear

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physics [1], thermodynamics [2] and physics of diamagnetism [3], but it has the greatest impact on quantum mechanics and quantum chemistry computations (e.g. [4–6]), in which its application includes both analytical and numerical studies. Let us just mention a paper by Pople et al. [4]. In this remarkable research the authors proposed a new method that allowed study of physical properties of molecules with polarized or distorted electronic structure via, among the others, calculation of self-consistent molecular orbital wavefunctions based on the perturbation theory method.

Even though the perturbation theory method is so widespread that a person can easily acquire a book treating about it (e.g. [7]), physicists still face many problems connected with this way of solving physical problems. One of the most harsh of them and probably the most difficult to cope with is the problem of convergence of power series that can be obtained with the use of the approach.

The current work presents a novel attitude towards the perturbation theory method. An efficient and continuously convergent perturbation theory method, based on the Fredholm integral equation, is presented. On the basis of this approach a new form of perturbation series has been obtained.

2 Fredholm integral equation and the perturbation theory method

Let us the following Schrödinger equation for purely vibrational problem:

$$\frac{d^2 \Psi_\upsilon(r)}{dr^2} + \left[k^2 - V_{unpert}(r) - V_{pert}(r)\right] \Psi_\upsilon(r) = 0, \tag{1}$$

where

$$k^2 = -\frac{2\mu E_\upsilon}{\hbar^2}, \quad V_{unpert}(r) = \frac{2\mu V^0(r)}{\hbar^2}, \quad V_{pert}(r) = \frac{2\mu \lambda V(r)}{\hbar^2},$$

$V(r)$ denotes a perturbation energy function and $V^0(r)$ is an unperturbed potential energy function, the analytical solutions of which are known, μ is the reduced mass of a diatomic system, whereas λ is a perturbation parameter.

We can easily convert the Eq. (1) into a differential equation of the following form:

$$\frac{d^2 \Psi_\upsilon(r)}{dr^2} + \left[k^2 - V_{unpert}(r)\right] \Psi_\upsilon(r) = \frac{2\mu \lambda}{\hbar^2} V(r) \Psi_\upsilon(r). \tag{2}$$

That is obvious to notice that a solution of the Eq. (2) fulfills the following Fredholm integral equation:

$$\Psi_\upsilon(r) = \Phi_\upsilon(r) + \delta \int_0^\infty K\left(r, r'\right) \Psi_\upsilon\left(r'\right) dr', \tag{3}$$

where $\Phi_\upsilon(r)$ stands for an analytical solution of the unperturbed problem (2), $\delta = \frac{2\mu\lambda}{\hbar^2}$ and $K(r, r')$ is an integral kernel of the following form:

$$K\left(r, r'\right) = G\left(r, r'\right) V_{pert}\left(r'\right), \tag{4}$$

where $G(r, r')$ is a standard Green function, which fulfills the following differential equation:

$$\left[\frac{d^2}{dr^2} + k^2 - V_{unpert}(r)\right] G\left(r, r'\right) = \delta\left(r - r'\right). \tag{5}$$

We seek for a solution of the integral equation in a form of a power series of consecutive perturbation corrections to an unperturbed function.

$$\Psi_\upsilon(r) = \sum_{k=0}^{\infty} \delta^k \Psi_\upsilon^{(k)}(r). \tag{6}$$

We can notice that this series corresponds to a Liouville–Neumann series in the integral equations theory. Substituting the series (6) to the Eq. (3) and comparing the coefficients of the appropriate powers δ we obtain:

$$\Psi_\upsilon^{(0)}(r) = \Phi_\upsilon(r), \quad \Psi_\upsilon^{(1)}(r) = \int_o^\infty K\left(r, r'\right) \Phi_\upsilon(r) dr', \, \Psi_\upsilon^{(k)}(r) = \int_0^\infty K\left(r, r'\right) \Psi_\upsilon^{(k-1)} dr'. \tag{7}$$

On this point we can clearly see that the method allows to receive consecutive corrections to an unperturbated wave function in a strictly analytical way. These corrections can be used in quantum chemistry to compute vibrational energy levels of diatomic systems.

Let us define the following iterated kernels:

$$K_1\left(r, r'\right) = K\left(r, r'\right), \quad K_2\left(r, r'\right) = \int_0^\infty K(r, z) K\left(z, r'\right) dz,$$

$$K_n\left(r, r'\right) = \int_0^\infty \int_0^\infty \ldots \int_0^\infty K(r, z_1) K(z_1, z_2) \ldots K\left(z_{n-1}, r'\right) dz_1 dz_2 \ldots dz_{n-1} \tag{8}$$

After introducing these kernels to the Eq. (7) we get:

$$\Psi_\upsilon^{(k)}(r) = \int_0^\infty K_k\left(r, r'\right) \Phi_\upsilon\left(r'\right) dr'. \tag{9}$$

We are then able to construct the following resolvent:

$$K\left(r, r', \delta\right) = \sum_{k=0}^{\infty} \delta^k K_{k+1}\left(r, r'\right). \tag{10}$$

From the Eqs. (6) and (10) we find out that the solution of the integral Eq. (3) can be specified in a following manner:

$$\Psi_{\upsilon}\left(r\right) = \Phi_{\upsilon}\left(r\right) + \int_{0}^{\infty} K\left(r, r', \delta\right) \Phi_{\upsilon}\left(r'\right) dr'. \tag{11}$$

Basing on the standard perturbation theory and constructed the first-order correction to the wavefunction we can now analytically obtain the second-order correction to the energy levels:

$$E_{\upsilon}^{(2)} = \int_{0}^{\infty} \Phi_{\upsilon}^* \hat{V}_{pert} \Psi_{\upsilon}^{(1)} dr. \tag{12}$$

Other perturbation corrections to the energy level can be easily determined on the basis of the standard Rayleigh–Schrödinger perturbation theory method.

3 Perturbation series convergence problem

Let us present, according to the Fredholm's theory, the resolvent (10) as a quotient of two power series:

$$K\left(r, r', \delta\right) = \frac{D\left(r, r', \delta\right)}{D\left(\delta\right)}, \tag{13}$$

where

$$D\left(r, r', \delta\right) = K\left(r, r'\right) + \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} D_k\left(r, r'\right) \delta^k, \quad D\left(\delta\right) = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} C_k \delta^k. \tag{14}$$

We can find the coefficients C_k and functions $D_k\left(r, r'\right)$ with the use of the following recurrence relations [we presume that $K(r, r') = D_0(r, r')$]:

$$C_k = \int_{0}^{\infty} D_{k-1}\left(r, r'\right) dr', \tag{15}$$

$$D_k\left(r, r'\right) = K\left(r, r'\right) C_k - k \int_{0}^{\infty} K\left(r, z\right) D_{k-1}\left(z, r'\right) dz. \tag{16}$$

An outstanding advantage of the Fredholm method is that the resolvent (10) is continuously convergent for every δ, apart from those δ for which $D\left(\delta\right) = 0$. However, this

case can be omitted in perturbation problems of theoretical spectroscopy, because δ is usually not a solution of the equation $D(\delta) = 0$. Hence, we can see that employment of the Fredholm theory of integral equation allows to obtain a continuously convergent perturbation series.

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