High-order Corrections of Time-independent Non-degenerate Perturbation Theory

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Abstract. Exactly solvable models in quantum mechanics are very rare. However, perturbation theory is a powerful tool to research the complex quantum systems and is widely used in theoretical physics and chemistry. For the particle weakly perturbed by the surrounding environment, its energy eigenstate and eigenvalue are separately calculated up to the first-order and second-order perturbation approximations in the undergraduate textbook of quantum mechanics. Whereas in reality, we have to calculate the high-order perturbation correction terms occasionally. Along the same lines of the low-order perturbation correction terms of energy eigenvalues and eigenstate for stationary state perturbation theory in the non-degenerate case, the third-order and fourth-order perturbation correction terms are strictly attained in this paper. Moreover, it points out the essence of perturbation theory and provides its derivation ideas. Students are no longer afraid of tedious derivation and can derive any-order perturbation correction. These results can serve as an extension and supplement for the quantum mechanics textbooks. Furthermore, it is very helpful for students to deeply understand quantum perturbation theory.

Keywords: Stationary state; Perturbation theory; Energy Eigenvalues; Eigenstate

1. Introduction

As an undergraduate course in physics, quantum mechanics has played an important role in various fields. With the advancement of technology, this subject has become increasingly closely related to the human life, such as with integrated circuits, microprocessors, lasers, high-precision medical imaging, etc. Even the theories behind the computers and mobile phones that we use every day cannot be separated from quantum mechanics. However, there are very few precisely solvable systems. Therefore, we have to resort to some common types of approximation methods in quantum mechanics, i.e., perturbation theory, variational method, semi-classical approximation and adiabatic approximation. Different approximation methods have different ranges of application. For theoretical physics and chemistry, the first approach is used frequently.

The Schrödinger equation cannot adequately explain the most quantum systems, because the Hamiltonian operator of the system is rather complicated in quantum mechanics. The perturbation theory, which can obtain the approximate solutions of the system by expanding the perturbation term step by step, is the most popular approximation method [1]. But only low-order perturbation correction terms for the energy and wave functions are presented in most textbooks [5]. Unfortunately, higher-order perturbation correction terms are often overlooked. Moreover, students with a solid foundation in mathematics and physics can keep up with the teacher's deduction in the teaching. However, most students have a weak background in mathematics and physics, and cannot catch up with the key points. Consequently, students often find the formulas to be complex and challenging to comprehend. The calculation and derivation processes can also appear daunting, leading to a lack of interest and motivation to learn. In fact, the higher order perturbation theory has received more attention recently. For instance, the higher orders of perturbation theory for the Stark Effect on an atomic multiplet are studied by Bolgova and coworkers [6]. Muller and Stace developed a theoretical technique by using Keldysh diagrammatic perturbation theory to derive a

Lindblad master equation that goes beyond the usual second-order perturbation theory [7]. Schröder and collaborators used the higher-order perturbation theory to research the reduced dynamics of coupled harmonic and anharmonic oscillators [8]. There is still a generation gap between the current textbooks of quantum mechanics and the scientific research. We still cannot find any formulas of the high-order perturbation theory in quantum mechanics textbooks.

In this paper, we take the inquiry-based teaching and adopt the idea of integrating science and education. Following the same path of low-order perturbation expansion terms in the non-degenerate case of time-independent perturbation theory, we will explicitly present how to derive the higher-order perturbation expansion terms. By studying non-degenerate high-order correction terms, students can deeply understand the perturbation theory and derive arbitrary order perturbation correction terms without any difficulty. This article is of great significance in both the teaching of quantum mechanics and the theoretical research of quantum physics and chemistry.

2. Non-degenerate Stationary State Perturbation Theory

Consider a system, the Hamiltonian operator of which does not explicitly depend on time. It should be divided into two parts: $\hat{H} = \hat{H}_0 + \hat{H}'$, where the unperturbed part referred as $\hat{H}_0$, which can be solved exactly, whereas the perturbation part indicated as $\hat{H}'$, which is a small quantity. In other words, the system is slightly influenced by the external perturbation.

For the total system, there is the stationary Schrödinger equation as follows:

$$\hat{H}\left|\Phi_n\right\rangle = \xi_n \left|\Phi_n\right\rangle, \tag{1}$$

where ξ_n and Φ_n are the eigenvalues and eigenfunction of the whole Hamiltonian $\hat{H}$.

The ordering parameter λ is introduced. Then the energy and wave functions are expanded as the power functions of λ,

$$\xi_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \tag{2}$$

$$\left|\Phi_n\right\rangle = \left|\Psi_n^{(0)}\right\rangle + \lambda \left|\Psi_n^{(1)}\right\rangle + \lambda^2 \left|\Psi_n^{(2)}\right\rangle + \cdots \tag{3}$$

Substituting Eq. 2 and Eq. 3 into Eq. 1, we obtain

$$\left(\hat{H}_0 + \lambda \hat{H}'\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda \left|\Psi_n^{(1)}\right\rangle + \cdots\right) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda \left|\Psi_n^{(1)}\right\rangle + \cdots\right). \tag{4}$$

Comparing the homogeneous power terms of λ in Eq. 4, we find the general formula,

$$\lambda^0\text{:}\quad \hat{H}_0 \left|\Psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\Psi_n^{(0)}\right\rangle, \tag{5}$$

$$\vdots$$

$$\lambda^l\text{:}\quad \hat{H}_0 \left|\Psi_n^{(l)}\right\rangle + \hat{H}' \left|\Psi_n^{(l-1)}\right\rangle = \sum_{k=0}^{l} E_n^{(k)} \left|\Psi_n^{(l-k)}\right\rangle. \tag{6}$$

Here l is a positive integer from one. Note that the eigenfunctions $\left\{\Psi_n^{(0)}\right\}$ of $\hat{H}_0$ is a complete set. However, any state vector can be expanded in terms of it. For this reason, the l th order perturbation correction of the wave function $\left|\Psi_n^{(l)}\right\rangle$ in the above equation can be expanded using this complete set $\left\{\Psi_n^{(0)}\right\}$. Moreover, we can always use any method to make the expansion coefficient of $\left|\Psi_n^{(0)}\right\rangle$ equal to zero. Therefore,

$$\left|\Psi_n^{(l)}\right\rangle = \sum_{m\neq n} a_m^{(l)} \left|\Psi_m^{(0)}\right\rangle. \tag{7}$$

Here m is not equal to n. That is, we can take the projection of $\left|\Psi_n^{(l)}\right\rangle$ on $\left|\Psi_n^{(0)}\right\rangle$ equal to zero. Furthermore, the inner product between them is given by

$$\left\langle \Psi_n^{(0)} \middle| \Psi_n^{(l)} \right\rangle = 0 \qquad (l \neq 0). \tag{8}$$

It is also called the intermediate normalization in the Re.[4].

When Eq. 7 is substituted into Eq. 6, we acquire the following equation,

$$\hat{H}_0 \sum_{m\neq n} a_m^{(l)} \left|\Psi_m^{(0)}\right\rangle + \hat{H}' \left|\Psi_n^{(l-1)}\right\rangle = E_n^{(0)} \sum_{m\neq n} a_m^{(l)} \left|\Psi_m^{(0)}\right\rangle + \sum_{k=1}^{l-1} \sum_{m\neq n} E_n^{(k)} a_m^{(l-k)} \left|\Psi_m^{(0)}\right\rangle + E_n^{(l)} \left|\Psi_n^{(0)}\right\rangle. \tag{9}$$

Multiplying $\left\langle \Psi_i^{(0)} \right|$ on the left of the above equation, we obtain

$$\sum_{m\neq n} \left(E_m^{(0)} - E_n^{(0)}\right) a_m^{(l)} \delta_{im} = -\left\langle \Psi_i^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(l-1)} \right\rangle + \sum_{k=1}^{l-1} \sum_{m\neq n} E_n^{(k)} a_m^{(l-k)} \delta_{im} + E_n^{(l)} \delta_{in}. \tag{10}$$

The characteristics of the Kronecker delta function, $\delta_{in} = 1 \text{for} i = n$, $\delta_{in} = 0 \text{for} i \neq n$, and the orthogonal normalization relationship of the wave function $\left\langle \Psi_i^{(0)} \middle| \Psi_n^{(0)} \right\rangle = \int \Psi_i^{(0)*}(r) \Psi_n^{(0)}(r) d\tau = \delta_{in}$ are used in the above derivation.

When $i = n$, we can find the expression of the l th perturbation correction to the eigenenergy value is as follows:

$$E_n^{(l)} = \left\langle \Psi_n^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(l-1)} \right\rangle. \tag{11}$$

When $i \neq n$, the recursive relationship for the coefficients of the perturbation correction terms of the wave function is given by

$$a_i^{(l)} = \frac{\left\langle \Psi_i^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(l-1)} \right\rangle - \sum_{k=1}^{l-1} E_n^{(k)} a_i^{(l-k)}}{E_n^{(0)} - E_i^{(0)}}. \tag{12}$$

Then the l th perturbation correction term of the wave function is obtained by inserting Eq. 12 into Eq.7,

$$\left|\Psi_n^{(l)}\right\rangle = \sum_{m\neq n} \frac{\left\langle \Psi_m^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(l-1)} \right\rangle - \sum_{k=1}^{l-1} E_n^{(k)} a_m^{(l-k)}}{E_n^{(0)} - E_m^{(0)}} \left|\Psi_m^{(0)}\right\rangle. \tag{13}$$

The above findings are consistent with those derived in the Refs.[10].

3. Results

According to Eq. 11-Eq. 13, we can obtain any order correction to the energy and wave function of the n th state.

3.1 First-order Perturbation Theory. For $l = 1$, there is

$$\hat{H}_0 \left|\psi_n^{(1)}\right\rangle + \hat{H}' \left|\psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\psi_n^{(1)}\right\rangle + E_n^{(1)} \left|\psi_n^{(0)}\right\rangle. \tag{14}$$

On the basis of Eq. 11, we can find

$$E_n^{(1)} = \left\langle \Psi_n^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle = \hat{H}'_{nn}. \tag{15}$$

Taking $\left|\psi_n^{(1)}\right\rangle = \sum_{m\neq n} a_m^{(1)} \left|\psi_m^{(0)}\right\rangle$ into Eq. 14 and multiplying $\left\langle \Psi_i^{(0)} \right|$ on the left with $i \neq n$, we derive the coefficient $a_m^{(1)}$. Consequently, the first-order perturbation correction term of the eigenstate is given by

$$\left|\Psi_n^{(1)}\right\rangle = \sum_{m\neq n} \frac{\hat{H}'_{mn}}{E_n^{(0)} - E_m^{(0)}} \left|\Psi_m^{(0)}\right\rangle. \tag{16}$$

In the unperturbed energy $\hat{H}_0$ representation, the eigenstates $\left\{\Psi_n^{(0)}\right\}$ of $\hat{H}_0$ are the basis vectors for the Hilbert space. $\hat{H}'_{nn}$ represents the diagonal elements of the perturbation Hamiltonian operator $\hat{H}'$, while $\hat{H}'_{mn}(m \neq n)$ stands for the non-diagonal elements of $\hat{H}'$ matrix. In the non-degenerate case, $E_n^{(0)} \neq E_m^{(0)}$ for $m \neq n$.

3.2 Second-order Perturbation Theory. When $l = 2$, there is

$$\hat{H}_0\left|\psi_n^{(2)}\right\rangle + \hat{H}'\left|\psi_n^{(1)}\right\rangle = E_n^{(0)}\left|\psi_n^{(2)}\right\rangle + E_n^{(1)}\left|\psi_n^{(1)}\right\rangle + E_n^{(2)}\left|\psi_n^{(0)}\right\rangle. \tag{17}$$

Based on Eq. 11, the second-order perturbation correction term of the energy eigenvalue is found,

$$E_n^{(2)} = \left\langle \Psi_n^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(1)} \right\rangle = \sum_{m\neq n} \frac{\left|\hat{H}'_{nm}\right|^2}{E_n^{(0)} - E_m^{(0)}}. \tag{18}$$

Where $\hat{H}'_{mn}$ is the complex conjugate of $\hat{H}'_{nm}$ due to the hermitian operators, $\hat{H}$, $\hat{H}_0$ and $\hat{H}'$. Putting $\left|\Psi_n^{(2)}\right\rangle = \sum_{k\neq n} a_k^{(2)} \left|\Psi_k^{(0)}\right\rangle$ into Eq. 17 and multiplying $\left\langle \Psi_i^{(0)} \right|$ on the left with $i \neq n$, then we get the second-order perturbation correction term for the wave function,

$$\left|\Psi_n^{(2)}\right\rangle = \sum_{k\neq n} \left(\frac{\sum_{m\neq n} \hat{H}'_{km}\hat{H}'_{mn}}{\left(E_n^{(0)} - E_k^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)} - \frac{\hat{H}'_{kn}\hat{H}'_{nn}}{\left(E_n^{(0)} - E_k^{(0)}\right)^2} \right) \left|\Psi_k^{(0)}\right\rangle. \tag{19}$$

In the traditional textbooks for quantum mechanics, only the above results are presented. These formulas are relatively simple and already have reflected the essence of perturbation theory. Before class, the teacher lets the students preview the course in advance, which is helpful for students to understand the teaching content. During class, the teacher writes on the blackboard and leads students step by step to derive the first-order and second-order perturbation theories. After class, the teacher leaves the homework for the students, which is to derive the third-order and the fourth-order perturbation theories and apply them to the multi-level quantum system by virtue of the scientific computing software. Breaking through the constraints of the textbooks, in the next section we will show how to derive the high-order perturbation corrections to the nth energy eigenvalues and the eigen wave function, which can be very useful to cultivate the scientific spirit and literacy of students.

3.3 Third-order Perturbation Theory. For $l = 3$, we have

$$\hat{H}_0\left|\psi_n^{(3)}\right\rangle + \hat{H}'\left|\psi_n^{(2)}\right\rangle = E_n^{(0)}\left|\psi_n^{(3)}\right\rangle + E_n^{(1)}\left|\psi_n^{(2)}\right\rangle + E_n^{(2)}\left|\psi_n^{(1)}\right\rangle + E_n^{(3)}\left|\psi_n^{(0)}\right\rangle. \tag{20}$$

By the aid of Eq. 11, we can easily attain

$$E_n^{(3)} = \left\langle \psi_n^{(0)} \middle| \hat{H}' \middle| \psi_n^{(2)} \right\rangle = \sum_{k\neq n}\sum_{m\neq n} \frac{\hat{H}'_{km}\hat{H}'_{mn}\hat{H}'_{nk}}{\left(E_n^{(0)} - E_k^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)} - \sum_{k\neq n} \frac{\hat{H}'_{nn}\left|\hat{H}'_{nk}\right|^2}{\left(E_n^{(0)} - E_k^{(0)}\right)^2}. \tag{21}$$

In terms of $\left|\Psi_n^{(3)}\right\rangle = \sum_{j\neq n} a_j^{(3)} \left|\Psi_j^{(0)}\right\rangle$, $\left\langle \Psi_i^{(0)} \right|$ with $i \neq n$ is multiplied on the left of Eq. 20. The third-order perturbation correction term of the wave function is given by

$$\begin{aligned} \left|\Psi_n^{(3)}\right\rangle = \sum_{j\neq n} \Bigg\{ & \sum_{m\neq n}\sum_{k\neq n} \frac{\hat{H}'_{kn}\hat{H}'_{mk}\hat{H}'_{jm}}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} - \sum_{m\neq n} \frac{\hat{H}'_{nn}\hat{H}'_{mn}\hat{H}'_{jm}}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)} \\ & \times \left(\frac{1}{E_n^{(0)} - E_m^{(0)}} + \frac{1}{E_n^{(0)} - E_j^{(0)}} \right) - \sum_{m\neq n} \frac{\hat{H}'_{jn}\left|\hat{H}'_{nm}\right|^2}{\left(E_n^{(0)} - E_j^{(0)}\right)^2\left(E_n^{(0)} - E_m^{(0)}\right)} + \frac{\left|\hat{H}'_{nn}\right|^2 \hat{H}'_{jn}}{\left(E_n^{(0)} - E_j^{(0)}\right)^3} \Bigg\} \left|\Psi_j^{(0)}\right\rangle. \end{aligned} \tag{22}$$

From these results, we can see the non-diagonal elements of $\hat{H}'$ matrix are very important in high-order perturbation theory, especially for the multi-level quantum systems.

3.4 Fourth Order Perturbation Theory. On the basis of the above results, the fourth-order perturbation correction term for the energy is found to be

$$\begin{aligned} E_n^{(4)} &= \left\langle \psi_n^{(0)} \middle| \hat{H}' \middle| \psi_n^{(3)} \right\rangle \\ &= \sum_{j\neq n} \Bigg\{ \sum_{m\neq n}\sum_{k\neq n} \frac{\hat{H}'_{kn}\hat{H}'_{mk}\hat{H}'_{jm}\hat{H}'_{nj}}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} - \sum_{m\neq n} \frac{\hat{H}'_{nn}\hat{H}'_{mn}\hat{H}'_{jm}\hat{H}'_{nj}}{\left(E_n^{(0)} - E_j^{(0)}\right)^2\left(E_n^{(0)} - E_m^{(0)}\right)} \\ &\quad - \sum_{m\neq n} \frac{\hat{H}'_{nn}\hat{H}'_{mn}\hat{H}'_{jm}\hat{H}'_{nj}}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)^2} - \sum_{m\neq n} \frac{\left|\hat{H}'_{nj}\right|^2\left|\hat{H}'_{nm}\right|^2}{\left(E_n^{(0)} - E_j^{(0)}\right)^2\left(E_n^{(0)} - E_m^{(0)}\right)} + \frac{\left|\hat{H}'_{nn}\right|^2\left|\hat{H}'_{nj}\right|^2}{\left(E_n^{(0)} - E_j^{(0)}\right)^3} \Bigg\}. \end{aligned} \tag{23}$$

By analogy, we can derive other high-order perturbation correction terms for energy eigenvalue and eigenstate. It is apparent that the high-order perturbation terms are rather complex. However, we can find that the multi-level system is more dependent on the high-order perturbation theory, which is connected with a series of the intermediate states.

With the assistance of computational software, we can visualize these abstract formulas. For a N-level system, the Hamiltonian operator $\hat{H}$ is a N-order square matrix. In the framework of perturbation theory, we first divide $\hat{H}$ into two parts, the exactly solvable part $\hat{H}_0$ and the perturbation part $\hat{H}'$, where $\hat{H}_0$ is a N-order diagonal matrix, the N diagonal elements of which are the energy eigenvalues $\left\{E_n^{(0)}\right\}$ of the exactly solvable part. In the non-degenerate case, these energy eigenvalues are completely different. The eigensates $\left\{\psi_n^{(0)}\right\}$ of $\hat{H}_0$ are the unit column matrices. As a consequence, we can obtain the modification results step by step in the first-order, second-order, third-order, and fourth-order perturbation theory using the computational software on the basis of the above formulas derived in this paper. Then we can also analytically attain the energy eigenvalues and eigenstates for the known matrix expression of $\hat{H}$. In the end, we can compare the approximate results of perturbation to the analytical solutions. By comparison, we can know what extent of perturbation is more suitable and how to approach the exact solution for this system. Meanwhile, we can see that the computational software is very helpful and has a positive auxiliary effect on quantum mechanics teaching and learning.

4. Summary

The perturbation theory is a rather powerful approximation method for researching the complex

systems in the quantum mechanics. Only the low-order perturbation expansions are presented in the traditional textbooks. With the progress of experimental technology, sometimes high-order perturbation terms are more desirable to obtain the relatively precise results. In this paper, it is shown how to derive the third-order and fourth-order correction terms of time-independent perturbation theory in the non-degenerate case step by step. It is very helpful for students to understand the perturbation theory deeply and enhances the interests from the students in studying quantum physics.

The theory of quantum mechanics in course is relatively abstract. Students are often lost in mathematical formulas and simply memories them without understanding. However, mathematics is only a tool used to express physical ideas and perform logical calculations on this basis. It cannot submerge physical content in complex mathematical forms. Beyond the content of the textbook, on the basis of the essence of perturbation theory, we present a detailed derivation process of high-order perturbation correction terms, which can eliminate students' fear of difficulties and help them establish confidence in learning. In fact, the learning method and the idea of derivation are the most important parts. The derivation of the high-order perturbation theory can be considered as the homework for students. Moreover, the science computation software can be used to assist students in checking the derivation process and applying the derived formulas to the specific systems as examples, which helps them deepen their theoretical learning and visualize these complex formulas.

Although, the homework for the derivation of the high-order perturbation theory is a challenge for students. Through this exercise, a significant improvement in the teaching effect of quantum mechanics can be achieved. Furthermore, it can cultivate the innovation abilities of college students.

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