

Energy and Wave-function correction for a quantum system after a small perturbation

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Abstract

This paper mainly focused on calculating the energy and the wave function of a new quantum system after the original quantum state is perturbed by a small perturbation or hamiltonian.

This paper also used perturbation theory to calculate the first and the second order of Energy and wave function correction for the new quantum state for both degenerate and non-degenerate quantum states.

Keywords

Time independent perturbation theory(TIPT), Degenerate and non- degenerate systems.

1 Introduction

Perturbation theory is an extremely important method of seeing how a Quantum System will be affected by a small change in the potential. And as such the Hamiltonian. Perturbation Theory revolves around expressing the Potential as multiple (generally two) separate Potentials, then seeing how the second affects the system. It allows us to get good approximations for systems where the Eigenstates are not all easily findable. In the real life not many hamiltonians are exactly solvable. Most of the real life situations requires some approximation methods to solve their hamiltonians. Perturbation theory is one

among them. Perturbation means small disturbance. Remember that the hamiltonian of a system is nothing but the total energy of that system. Some external factors can always affect the energy of the system and its behaviour. To analyse a system's energy, if we dont know the exact way of solution, then we can study the effects of external factors(perturbation) on the hamiltonian. Then we can approximately predict the properties of the concerned systems. Perturbation applied to a system of two types: time dependent and time independent theory. In this paper we calculated the approximation solution to a new quantum system after perturbation by using Time independent perturbation theory.

2 Time independent perturbation theory

2.1 Non-degenerate systems

We have been able to solve Schrodinger equation exactly for a variety of potential, such as the infinite square well, the finite square well and the harmonic oscillators, but there are many cases in nature, where it is not possible to solve the schrodinger equation exactly, such as hydrogen atom in external magnetic field.

We are going to develop some approximation method techniques for solving such schrodinger equation in special situations.

We solved the time-independent Schrodinger equation for some potential and obtained a complete set of orthonormal eigenfunctions ψ_n^0 and corresponding eigenvalues E_n^0 .

$$\hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0 \tag{1}$$

From this equation we obtained a complete set orthonormal eigenfunctions, ψ_n^0 .

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \tag{2}$$

From this equation we obtained a corresponding eigenvalues, E_n^0 .

Now, If a given quantum system is perturbed by a small potential, the new system would have a new energy and eigen function. so how to find the energy and the eigen function of a new quantum system after a small perturbation?

Perturbation theory is very important to answer this questions, since Perturbation theory is a systematic procedure for obtaining approximate solution for a perturbed system by building on the known exact solutions to the unperturbed case.

Therefore, to find eigenvalues and eigenfunctions of the perturbed system, we should solve the following equation by using the known solutions of the unperturbed system.

$$\hat{H} \psi_n = E_n \psi_n \tag{3}$$

To begin with, we write the new hamiltonian as the sum of the two terms:

$$\hat{H} = H^0 + H' \tag{4}$$

Where, H' is the perturbation and H^0 is Hamiltonian for the unperturbed system.

For now, we consider nondegenerate case, i.e. each eigenvalue corresponds to different eigenfunction.

Write ψ_n and E_n as power series:

$$\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^2 + \dots \tag{5}$$

$$E_n = E_n^0 + E_n^1 + E_n^2 + \dots \tag{6}$$

We plug our expansions into $\hat{H} \psi_n = E_n \psi_n$, We will have

$$(H^0 + H')(\psi_n^0 + \psi_n^1 + \psi_n^2 + \dots) = (E_n^0 + E_n^1 + E_n^2 + \dots)(\psi_n^0 + \psi_n^1 + \psi_n^2 + \dots)$$

When we multiply, we get

$$H^0 \psi_n^0 + H^0 \psi_n^1 + H^0 \psi_n^2 + H' \psi_n^0 + H' \psi_n^1 + H' \psi_n^2 + \dots = E_n^0 \psi_n^0 + E_n^0 \psi_n^1 + E_n^0 \psi_n^2 + \dots + E_n^1 \psi_n^0 + E_n^1 \psi_n^1 + E_n^1 \psi_n^2 + \dots + E_n^2 \psi_n^0 + E_n^2 \psi_n^1 + E_n^2 \psi_n^2 + \dots$$

We now separate this equation into a system of equations that are zeroth, first, second, and so on orders in perturbation potential H' :

Separating the equations for zeroth, first, and second orders we get:

$$\text{Zeroth order, } H^0 \psi_n^0 = E_n^0 \psi_n^0 \tag{7}$$

$$\text{First order, } H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \tag{8}$$

$$\text{Second order, } H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \tag{9}$$

If we consider more terms in the expansions for ψ_n and E_n we can write equations for third, fourth, and higher orders of perturbation theory.

The First term ψ_n^1 and E_n^1 are called the first order corrections to the wavefunction and energy respectively, The ψ_n^2 and E_n^2 are the second order corrections and so on. The task of perturbation theory is to approximate the energies and wavefunctions of the perturbed system by calculating corrections up to a given order.

2.2 First-order correction to the Energy

To derive an expression for calculating the first order correction to the energy E^1_n , we use the first order equation (use equation 8)

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

We are going to multiply this equation by $(\psi_n^0)^*$ and integrate:

$$\int (\psi_n^0)^* H^0 \psi_n^1 d^3r + \int (\psi_n^0)^* H' \psi_n^0 d^3r = E_n^0 \int (\psi_n^0)^* \psi_n^1 d^3r + E_n^1 \int (\psi_n^0)^* \psi_n^0 d^3r$$

Or by using Dirac notation We can write as follows:

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle \tag{10}$$

But, H^0 is a Hermitian operator so, $\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$

2.3 First-order correction to the Wave-function

To derive an expression for calculating the first order correction to the wavefunction, we use the first order equation (use equation 8)

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

$$H^0\psi_n^1 - E_n^0\psi_n^1 = -H'\psi_n^0 + E_n^1\psi_n^0$$

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0 \tag{12}$$

ψ_n^1 can be expanded as a linear combination of functions constitute a complete set as follows:

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^1 \tag{13}$$

Our mission now is to find coefficients $c_m^{(n)}$. To do so, we plug this expansion into the above first-order equation and we get:

$$(H^0 - E_n^0) \sum_{m \neq n} c_m^{(n)} \psi_m^1 = -(H' - E_n^1)\psi_n^0 \tag{14}$$

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^1 = -(H' - E_n^1)\psi_n^0 \tag{15}$$

We multiply this equation from the left side by ψ_ℓ^0 and integrate. I will not explicitly write integrals here, but use inner product notations right away. It is, of course, the same.

Therefore, the above equation become

$$\begin{aligned} E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle &= \\ E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle & \\ \cancel{[E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle - E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle]} + \langle \psi_n^0 | H' \psi_n^0 \rangle &= \\ E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle & \end{aligned}$$

Therefore, the first-order energy correction is given by:

$$E_n^1 = \langle \psi_n^0 | H' \psi_n^0 \rangle = H'_{nn} \tag{11}$$

Its says that the first order correction to the energy is the expectation values of the perturbation in the unperturbed state.

$$\begin{aligned} \sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_\ell^0 | \psi_m^1 \rangle &= -\langle \psi_\ell^0 | H' \psi_n^0 \rangle + \\ E_n^1 \langle \psi_\ell^0 | \psi_n^0 \rangle & \\ \sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \delta_{\ell m} &= -\langle \psi_\ell^0 | H' \psi_n^0 \rangle + E_n^1 \delta_{\ell n} \end{aligned} \tag{16}$$

If $\ell = n$, we get:

$$E_n^1 = \langle \psi_n^0 | H' \psi_n^0 \rangle \text{ again.}$$

If $\ell \neq n$, we get

$$(E_\ell^0 - E_n^0) c_\ell^{(n)} = -\langle \psi_\ell^0 | H' \psi_n^0 \rangle, \text{ this will give us}$$

$$c_\ell^{(n)} = \frac{\langle \psi_\ell^0 | H' \psi_n^0 \rangle}{E_n^0 - E_\ell^0} \tag{17}$$

when we insert this expression in the above expansion equation of ψ_n^1 , we will get.

First-order correction to the wave function is given by:

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0 \tag{18}$$

Note that as long as $m \neq n$, the denominator can not be zero as long as energy levels are nondegenerate. If the energy levels are degenerate, we need degenerate perturbation theory (We will consider later).

2.4 Second-order correction to the Energy

$H^0\psi_n^2 + H'\psi_n^1 = E^0\psi_n^2 + E^1\psi_n^1 + E^2\psi_n^0$
 again multiply this equation by $(\psi_n^0)^*$ and integrate:

$$\int (\psi_n^0)^* H^0 \psi_n^2 d^3r + \int (\psi_n^0)^* H' \psi_n^1 d^3r = E_n^0 \int (\psi_n^0)^* \psi_n^2 d^3r + E_n^1 \int (\psi_n^0)^* \psi_n^1 d^3r + E_n^2 \int (\psi_n^0)^* \psi_n^0 d^3r$$

Or by using Dirac notation we can write
 $\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$

But, H^0 is a hermitian operator so,
 $\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle$ Therefore, the above equation become

$$E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$$

By evaluating the inner product we will get

$$[E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle - E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle] + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$$

$$E_n^2 = \langle \psi_n^0 | H' \psi_n^1 \rangle \tag{19}$$

When we substitute the First-order correction to the wave function for ψ_n^0 in the above equation, we get the value of E_n^2 :

The second-order correction to the energy is

$$E_n^2 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' \psi_n^1 \rangle \langle \psi_n^0 | H' \psi_m^0 \rangle}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \tag{20}$$

This is a fundamental result of second-order perturbation theory. We can proceed to calculate the second order correction to the wave function and the third order correction to the energy.

3 Perturbation theory for degenerate states

The perturbation theory we have developed so far applies to non-degenerate states. For systems with degenerate states we need to modify our approach.

If the unperturbed states are degenerate, then the denominator $E_n^0 - E_m^0$ in the second order expression is zero, and, unless the numerator

($\langle \psi_n^0 | H' \psi_m^0 \rangle = 0$) is zero as well in this case, the perturbation theory in the way we formulated it fails.

First, we consider a case of a two-fold degeneracy, when there are two states for each energy.

3.1 Two-fold degeneracy

We have two states ψ_a^0 and ψ_b^0 are degenerate (they have the same energy E^0).

$$H^0 \psi_a^0 = E^0 \psi_a^0, \quad H^0 \psi_b^0 = E^0 \psi_b^0, \\ \langle \psi_a^0 | \psi_b^0 \rangle = 0, \quad \langle \psi_a^0 | \psi_a^0 \rangle = \langle \psi_b^0 | \psi_b^0 \rangle = 1$$

Linear combination of these states

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0 \tag{21}$$

is also an eigenstate of H^0 with eigenvalue E^0 .
We want to solve

$$H\psi = E\psi \tag{22}$$

with $H = H^0 + H'$

$$E = E^0 + E^1 + \dots \tag{23}$$

$$\psi = \psi^0 + \psi^1 + \dots \tag{24}$$

plugging these two equations in the equation ($H\psi = E\psi$), we get:

$$H^0 \psi^1 + H' \psi^0 = E^0 \psi^1 + E^1 \psi^0 \tag{25}$$

If we take inner product of this equation with ψ_a^0 and integrate, we get :

$$\langle \psi_a^0 | H^0 \psi^1 \rangle + \langle \psi_a^0 | H' \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle \tag{26}$$

Since H^0 is hermitian operator, we have $\langle \psi_a^0 | H^0 \psi^1 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle$ and the above equation become:

$$E^1 \langle \psi_a^0 | \psi^0 \rangle = \langle \psi_a^0 | H' \psi^0 \rangle \quad (27)$$

We now plug equation ($\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$) in the above equation

$$\alpha E^1 \langle \psi_a^0 | \psi_a^0 \rangle + \beta E^1 \langle \psi_a^0 | \psi_b^0 \rangle = \alpha \langle \psi_a^0 | H' \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' \psi_b^0 \rangle$$

$$\alpha E^1 = \alpha \langle \psi_a^0 | H' \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' \psi_b^0 \rangle, \text{ since } \langle \psi_a^0 | \psi_a^0 \rangle = 1 \text{ and } \langle \psi_a^0 | \psi_b^0 \rangle = 0$$

Therefore,

$$\alpha E^1 = \alpha \langle \psi_a^0 | H' \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' \psi_b^0 \rangle = \alpha H'_{aa} + \beta H'_{ab} \quad (28)$$

Similarly, If we take inner product of this equation with ψ_b^0 and integrate, we get:

$$\beta E^1 = \alpha \langle \psi_b^0 | H' \psi_a^0 \rangle + \beta \langle \psi_b^0 | H' \psi_b^0 \rangle = \alpha H'_{ba} + \beta H'_{bb} \quad (29)$$

Now, we can calculate E^1 by using the above two equations as follows:

From equation (28), we get

$$\alpha E^1 = \alpha H'_{aa} + \beta H'_{ab} \Rightarrow \beta H'_{ab} = \alpha E^1 - \alpha H'_{aa} \quad (30)$$

and If we multiply equation (29) both sides by H'_{ba} , we get

$$E^1 \beta H'_{ba} = \alpha H'_{ba} H'_{ba} + \beta H'_{ba} H'_{bb} \quad (31)$$

when we insert the values of $\beta H'_{ab}$ in this equation, we get:

$$E^1 [\alpha E^1 - \alpha H'_{aa}] = \alpha H'_{ab} H'_{ba} + H'_{bb} [\alpha E^1 - \alpha H'_{aa}] \\ \alpha (E^1 - H'_{aa})(E^1 - H'_{bb}) = \alpha H'_{ab} H'_{ab} \text{ If } \\ \alpha \neq 0, \text{ we get} \\ (E^1)^2 - E^1 (H'_{aa} + H'_{bb}) + (H'_{aa} H'_{bb} - H'_{ab} H'_{ba}) = 0$$

Therefore, the solution of this quadratic equation is given by:

$$E^1_{\pm} = \frac{1}{2} \left[H'_{aa} + H'_{bb} \pm \sqrt{(H'_{aa} - H'_{bb})^2 + 4|H'_{ab}|^2} \right] \quad (32)$$

This is the **first order energy correction to the degenerate states.**

Fundamental result of degenerate perturbation theory: two roots correspond to two perturbed energies (degeneracy is lifted).

$$\text{If } \alpha = 0 \Rightarrow H'_{ab} = 0 \text{ and } E^1 = H'_{bb}$$

$$\text{If } \beta = 0 \Rightarrow H'_{ba} = 0 \text{ and } E^1 = H'_{aa}$$

4 Results and Conclusions

In this paper, I derived first and second order energy and wavefunction correction to the new quantum system after the original quantum state is perturbed by small perturbation in a simple and short way.

By using perturbation theory approximation method, I calculated first and second order correction for both non-degenerate and degenerate states.

Therefore, the first-order energy correction for non-degenerate states are given by

$$E_n^1 = \langle \psi_n^0 | H' \psi_n^0 \rangle = H'_{nn} \quad (33)$$

First-order correction to the wave function for non-degenerate states are given by

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0 \quad (34)$$

The second-order correction to the energy for non-degenerate states are given by:

$$E_n^2 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' \psi_n^1 \rangle \langle \psi_n^0 | H' \psi_m^0 \rangle}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \quad (35)$$

The first order correction to the energy for degenerate states are given by:

$$E^1_{\pm} = \frac{1}{2} \left[H'_{aa} + H'_{bb} \pm \sqrt{(H'_{aa} - H'_{bb})^2 + 4|H'_{ab}|^2} \right] \quad (36)$$

Then by using the same methods, we can calculate third and fourth order correction to Energy

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