Time-independent perturbation theory

Suppose we have a certain Hamiltonian H_0 and we know their nth eigenvalues E_n^0 and their normalized eigenvectors $|\psi_n^0>$ as follows.

$$H_0|\psi_n^0>= E_n^0|\psi_n^0>, \qquad <\psi_n^0|\psi_m^0>=\delta_{nm} \tag{1}$$

We further assume here that the eigenvalues are non-degenerate. In other words, no two normalized eigenvectors that cannot be related one another by global gauge transformation share the same eigenvalue.

Given this, let's say that we want to find the eigenvalues and eigenvectors of another Hamiltonian H which is very close to H_0 but is hard to find the exact answer. Then, is there a way in which we can obtain approximate answers by taking advantage of the fact that we already know the eigenvalues and eigenvectors to the Hamiltonian H_0? This is the question we will answer in this article.

If H (perturbed Hamiltonian) is close to H_0 (unperturbed Hamiltonian), we can write $H = H_0 + \lambda H'$ where λ is very small and H' is called perturbation. Furthermore, the new eigenvalues E_n and the new eigenvectors $|\psi_n>$ which satisfy

$$H|\psi_n>= E_n|\psi_n> \tag{2}$$

can be Taylor-expanded as follows,

$$\begin{aligned} |\psi_n> &= |\psi_n^0> + \lambda|\psi_n^1> + \lambda^2|\psi_n^2> + \cdots && (3)\\ E_n &= E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots && (4) \end{aligned}$$

as when $\lambda = 0$, we should have E_n^0 and $|\psi_n^0>$ as eigenvalues and eigenvectors. We call E_n^1 and $|\psi_n^1>$ the first-order corrections and E_n^2 and $|\psi_n^2>$ the second-order corrections and so on. Now, let's obtain them. Plugging (3) and (4) to (2), we get:

$$\begin{aligned} &\left(H^0 + \lambda H'\right)\left(|\psi_n^0> + \lambda|\psi_n^1> + \lambda^2|\psi_n^2> + \cdots\right)\\ &\quad = \left(E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots\right)\left(|\psi_n^0> + \lambda|\psi_n^1> + \lambda^2|\psi_n^2> + \cdots\right) \end{aligned} \tag{5}$$

Now, we have to compare order by order. We get:

$$\begin{aligned} &H^0|\psi_n^0> + \lambda\left(H^0|\psi_n^1> + H'|\psi_n^0>\right) + \lambda^2\left(H^0|\psi_n^2> + H'|\psi_n^1>\right)\cdots\\ &\quad = E_n^0|\psi_n^0> + \lambda\left(E_n^0|\psi_n^1> + E_n^1|\psi_n^0>\right) + \lambda^2\left(E_n^0|\psi_n^2> + E_n^1|\psi_n^1> + E_n^2|\psi_n^0>\right) + \cdots \end{aligned} \tag{6}$$

Therefore, we have:

$$H^0|\psi_n^0> = E_n^0|\psi_n^0> \tag{7}$$

$$H^0|\psi_n^1> + H'|\psi_n^0> = E_n^0|\psi_n^1> + E_n^1|\psi_n^0> \tag{8}$$
$$H^0|\psi_n^2> + H'|\psi_n^1> = E_n^0|\psi_n^2> + E_n^1|\psi_n^1> + E_n^2|\psi_n^0> \tag{9}$$

and so on.

Now notice that the λ to the zeroth order equation (7) is already satisfied by (1). Therefore, we get no new information from this. On the other hand, all the other orders equations give new information. Now, to obtain the first order corrections to the eigenvalues, let's multiply (8) by $<\psi_n^0|$. We get:

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

Now, as H^0 is hermitian, if we take the Hermitian conjugate of (7), we have:

$$<\psi_n^0|H^0 = E_n^0 <\psi_n^0| \tag{11}$$

Plugging this equation to (10), then using $<\psi_n^0|\psi_n^0> = 1$, we get:

$$E_n^1 = <\psi_n^0|H'|\psi_n^0> \tag{12}$$

In other words, the first order correction to the energy is given by the expectation value of the perturbation in the unperturbed wave function.

Let me conclude this article with some comments. Here, we have calculated up to the first order, but using the similar strategy one can easily calculate the higher order corrections. In reality, only up to the second order perturbation is used as it is accurate enough. Also in this article, we have assumed that the eigenvalues are nondegenerate. When they are degenerate the perturbation theory is more complicated as there are multiple eigenvectors $<\psi_n^0|$ that can be multiplied to (8). We also assumed that the Hamiltonian is time independent meaning that it doen't change as time goes on. However, if we consider the time dependent case such as when the electric field or magnetic field that enter into the Hamiltonian change, the analysis becomes more complicated. All these general cases are covered in details in the standard quantum mechanics textbooks which readers can refer to.

Problem 1. Show that the lowest order relativistic correction to the kinetic energy of particle with mass m and momentum p is given as follows (Hint[1]):

$$H' = -\frac{p^4}{8m^3c^2} \tag{13}$$

Problem 2. Use the above result to obtain the relativistic correction to the ground state energy of hydrogen atom. (Hint: If you solved the last problem in "Hydrogen atom" correctly, the wave function of the ground state is given as follows:

$$\psi(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \tag{14}$$

Use this.)

[1] Use $(K + mc^2)^2 = p^2c^2 + m^2c^4$ where K is kinetic energy

Problem 3. According to quantum electrodynamics, the corrected Coulomb potential for an electron in a hydrogen atom is given as follows (in natural unit)

$$V(\vec{x}) = -\frac{\alpha}{r} - \frac{4\alpha^2}{15m^2}\delta^3(\vec{x}) - \frac{\alpha^2}{4\sqrt{\pi}r}\frac{e^{-2mr}}{(mr)^{3/2}} + \cdots \tag{15}$$

where α is the fine structure constant. Apart from the relativistic correction we considered in Problem 2, how much of the ground state energy is shifted due to the second term (i.e. the delta function term) compared with the result we got in our earlier article "Hydrogen atom?" (Hint: Use (14))

Of course, the third term called "Uehling potential" also shifts the ground state energy, but the integration cannot be done analytically. (i.e. you need to use a computer to rely upon numerical calculation.) This is the reason why I am not asking you to calculate the shift due to Uehling potential.

In this article, we only considered the case that the perturbed Hamiltonian is independent of time. When it depends on time, the theory is more complicated. We will not deal with time-dependent perturbation theory in this article.

Summary

- If H (perturbed Hamiltonian) is close to H_0 (unperturbed Hamiltonian), we can write $H = H_0 + \lambda H'$ where λ is very small. Then, we want to find the eigenvectors and eigenvalues of the perturbed Hamiltonian as a Taylor expansion of λ as follows:

$$|\psi_n\rangle = |\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \lambda^2|\psi_n^2\rangle + \cdots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdot$$

  where $|\psi_n\rangle$ and E_n^0 are the eigenvectors and the eigenvalues of unperturbed Hamiltonian. Finding this Taylor series is known as "perturbation theory."

- The first order correction to the eigenvalue of the Hamiltonian is given by the expectation value of the perturbation in the unperturbed eigenfunction. i.e.

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