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 $|\psi_n^0\rangle$ as follows.

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

1 Non-degenerate case

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 $|\psi_n\rangle$ which satisfy

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

can be Taylor-expanded as follows,

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

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

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

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

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

Therefore, we have:

$$\begin{aligned} H^0|\psi_n^0\rangle &= E_n^0|\psi_n^0\rangle && (7) \\ H^0|\psi_n^1\rangle + H'|\psi_n^0\rangle &= E_n^0|\psi_n^1\rangle + E_n^1|\psi_n^0\rangle && (8) \\ H^0|\psi_n^2\rangle + H'|\psi_n^1\rangle &= E_n^0|\psi_n^2\rangle + E_n^1|\psi_n^1\rangle + E_n^2|\psi_n^0\rangle && (9) \end{aligned}$$

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 $\langle\psi_n^0|$. We get:

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

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

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

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

$$E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle \tag{12}$$

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

Now, let's calculate the first order correction to the eigenvector of energy.

Problem 1. By multiplying (8) by $\langle\psi_m^0|$ on the left, where m is *not* equal to n, show the following:

$$\langle\psi_m^0|\psi_n^1\rangle = \frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0} \tag{13}$$

Given this, let's multiply this by $|\psi_m^0\rangle$ on the left, and sum over all m not equal to n.

$$\sum_{m\neq n}|\psi_m^0\rangle\langle\psi_m^0|\psi_n^1\rangle = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle \tag{14}$$

By using the following completeness relation,

$$1 = \left(\sum_{m\neq n}|\psi_m^0\rangle\langle\psi_m^0|\right) + |\psi_n^0\rangle\langle\psi_n^0| \tag{15}$$

we have

$$|\psi_n^1\rangle - \left(|\psi_n^0\rangle\langle\psi_n^0|\psi_n^1\rangle\right) = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle \tag{16}$$

Now, we will show that the term in the parenthesis can be set to be zero.

Problem 2. Let's say $|\psi_n^1\rangle$ satisfies (8). Then, show that another

$$|\tilde{\psi}_n^1\rangle = |\psi_n^1\rangle + \alpha|\psi_n^0\rangle \tag{17}$$

also satisfies (8) for arbitrary α.

Given this, let's say that the original solution $|\psi_n^1\rangle$ is given by

$$|\psi_n^1\rangle = \sum_m c_{nm}|\psi_m^0\rangle = \left(\sum_{m\neq n} c_{nm}|\psi_m^0\rangle\right) + c_{nn}|\psi_n^0\rangle \tag{18}$$

Now, if we set $\alpha = -c_{nn}$ in 917, the new $|\psi_n^1\rangle$ has no $|\psi_n^0\rangle$ component. Therefore, the new $|\psi_n^1\rangle$ satisfies $\langle\psi_n^0|\psi_n^1\rangle = 0$. Thus, (16) becomes

$$|\psi_n^1\rangle = \sum_{m\neq n} \frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle \tag{19}$$

This is the first order correction to the wave function.

Notice that, if there is a degeneracy in the eigenvalue of energy, we cannot use (19), as the denominator of (19) will be zero, for the degenerate eigenvalue. We will talk about this case in the next section.

Problem 3. By multiplying (9) by $\langle\psi_n^0|$ on the left, and using $\langle\psi_n^0|\psi_n^1\rangle = 0$, show the following.

$$\langle\psi_n^0|H'|\psi_n^1\rangle = E_n^2 \tag{20}$$

Problem 4. By plugging in (19) to this equation, show

$$E_n^2 = \sum_{m\neq n} \frac{|\langle\psi_n^0|H'|\psi_m^0\rangle|^2|}{E_n^0 - E_m^0} \tag{21}$$

This is the second order correction to the energy. We can go on and go on to calculate the higher order corrections, but more than often, the second order correction is enough.

Problem 5. 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]):

$$H' = -\frac{p^4}{8m^3c^2} \tag{22}$$

Problem 6. Use the above result to obtain the first order 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:

$$\psi(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0} \tag{23}$$

Use this.)

Problem 7. According to quantum electrodynamics, the corrected Coulomb potential for an electron in a hydrogen atom is given as follows (in natural units)

$$V(\vec{x}) = -\frac{\alpha}{r} - \frac{4\alpha^2}{15m^2}\delta^3(\vec{x}) - \frac{\alpha^2}{4\sqrt{\pi}r}\frac{e^{-2mr}}{(mr)^{3/2}} + \cdots \tag{24}$$

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

where α is the fine structure constant. Apart from the relativistic correction we considered in Problem 6, 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 (23))

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.

2 Degenerate case

If E_m^0 is equal to E_n^0 for some $m \neq n$, we have the degenerate case. As the denominator of (19) is zero, the numerator must be zero. In other words, we need to find $|\psi_{ni}^0\rangle$, the basis of the vector space of the degenerate eigenvector, that satisfies

$$\langle\psi_{ni}^0|H'|\psi_{nj}^0\rangle = 0, \quad \text{for } i \neq j \tag{25}$$

It is not difficult to see that the eigenvectors of H' satisfy such a condition. To see this, let's say the eigenvalues of H' are E_j', i.e.,

$$H'|\psi_{nj}^0\rangle = E_j'|\psi_{nj}^0\rangle \tag{26}$$

Now, recall that the eigenvectors of H' are orthogonal, as it is Hermitian. Therefore, the left-hand side of (25) becomes

$$\langle\psi_{ni}^0|E_j'|\psi_{nj}^0\rangle = E_j'\langle\psi_{ni}^0|\psi_{nj}^0\rangle = 0 \tag{27}$$

Given this, let's consider (8) again with this basis. We have,

$$H^0|\psi_{nj}^1\rangle + H'|\psi_{nj}^0\rangle = E_n^0|\psi_{nj}^1\rangle + E_{nj}^1|\psi_{nj}^0\rangle \tag{28}$$

If we multiply this by $\langle\psi_{ni}^0|$, for $i \neq j$, we have

$$\langle\psi_{ni}^0|H'|\psi_{nj}^0\rangle = \langle\psi_{ni}^0|E_{nj}^1|\psi_{nj}^0\rangle \tag{29}$$

The left-hand side is zero by (25). The right-hand side is zero, because the eigenvectors of H' are orthogonal. So, we are good.

Problem 8. Multiply (28) by $\langle\psi_{nj}^0|$ to get

$$E_{nj}^1 = E_j' \tag{30}$$

where E_j' is the eigenvalue of H', i.e., (26). In other words, the first order correction of energy eigenvalues in degenerate case is given by the eigenvalues of perturbed Hamiltonian.

Earlier, we saw that, in the lowest order, the eigenvectors of the new Hamiltonian is given by the eigenvector of H' in the degenerate case. Then, what is the first order correction to the eigenvector? The result of Problem 2 holds in the degenerate case as well. Thus, if we write

$$|\psi_n^1\rangle = \sum_m c_{nm}|\psi_m^0\rangle = \left(\sum_{E_m^0 \neq E_n^0} c_{nm}|\psi_m^0\rangle\right) + \left(\sum_{E_m^0 = E_n^0} c_{mn}|\psi_n^0\rangle\right) \tag{31}$$

the last term can be set to be zero. Thus,

$$|\psi_n^1\rangle = \sum_{E_m^0 \neq E_n^0} \frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle \tag{32}$$

In other words, in calculating the first order correction to the eigenvector, we can simply ignore the case that has the same eigenvalue in the sum.

In this article, we only considered the case that the perturbed Hamiltonian is independent of time. 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. 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.

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