

Quantum Mechanics: Time-Independent Perturbation Theory

Static weak disturbance of a system

By now it is very clear that we are able to calculate the eigenvalues and eigenfunctions of a very limited number of systems. For example, if a particle governed by a Harmonic potential, the Hamiltonian is given by $\hat{H} = \hat{p}^2/2m + 1/2m\omega^2x^2$, and can be solved easily. On the other hand, if the Hamiltonian is something like $\hat{H} = \hat{p}^2/2m + 1/2m\omega^2x^2 + \alpha x^4$, one cannot find the exact eigenfunctions and eigenvalues. However, if α is much smaller than $1/2m\omega^2$, we expect that the particle will broadly behave like a Harmonic oscillator, but with some small variations. The question is, can one get an approximate solution in such a situation? The answer is yes, and the *time-independent perturbation theory* provides a method for doing that.

Let us assume the system is governed by the Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}_1,$$

where the effect of \hat{H}_1 on the system is assumed to be very weak. The sense in which it is assumed to be weak, will be clear in the following discussion. For now it is sufficient to assume that the effect of \hat{H}_1^2 will be smaller than that of \hat{H}_1 . The parameter λ is not assumed to be small - it has been included just to keep track of the order to which the effect of \hat{H}_1 is being used. For example, the presence of λ^3 will indicate that one is using terms like \hat{H}_1^3 , or something equivalent. In the end we will put $\lambda = 1$. Let us assume that the eigenfunctions and eigenvalues of \hat{H}_0 are known:

$$\hat{H}_0|\phi_n\rangle = E_n^{(0)}|\phi_n\rangle, \quad (1)$$

where $|\phi_n\rangle, E_n^{(0)}$ are the eigenstates and eigenvalues of the unperturbed Hamiltonian \hat{H}_0 , respectively. Consequently, $\langle\phi_n|\phi_m\rangle = \delta_{nm}$. We are interested in the eigenstates and eigenvalues of the full Hamiltonian \hat{H} :

$$\hat{H}|\psi_n\rangle = (\hat{H}_0 + \lambda\hat{H}_1)|\psi_n\rangle = E_n|\psi_n\rangle. \quad (2)$$

The basic idea of perturbation theory is that the full eigenstates $|\psi\rangle$ and eigenvalues E_n can be expanded in the parameter λ :

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

where the superscripts (1), (2), (3) ... represent terms with progressively weaker effect of the perturbation. Inserting the series form in the time-independent Schrödinger equation for \hat{H} , i.e. (2), we get

$$(\hat{H}_0 + \lambda\hat{H}_1)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \dots)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \dots) \quad (4)$$

Next we equate same order terms in λ on both sides, and get

$$\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \quad (\text{zero'th order in } \lambda) \quad (5)$$

$$\hat{H}_0|\psi_n^{(1)}\rangle + \hat{H}_1|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle \quad (\text{1st order in } \lambda) \quad (6)$$

$$\hat{H}_0|\psi_n^{(2)}\rangle + \hat{H}_1|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle \quad (\text{2nd order in } \lambda) \quad (7)$$

Comparing (5) with (1), it is clear that $|\psi_n^{(0)}\rangle = |\phi_n\rangle$. Using this, and multiplying (6) by $\langle\phi_n|$, we get

$$\langle\phi_n|\hat{H}_0|\psi_n^{(1)}\rangle + \langle\phi_n|\hat{H}_1|\phi_n\rangle = E_n^{(0)}\langle\phi_n|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\phi_n|\phi_n\rangle.$$

It is easy to see that $\langle\phi_n|\hat{H}_0|\psi_n^{(1)}\rangle = \langle\phi_n|\hat{H}_0(\sum_m|\phi_m\rangle\langle\phi_m|)|\psi_n^{(1)}\rangle = E_n^{(0)}\langle\phi_n|\psi_n^{(1)}\rangle$, which simplifies the above equation to

$$E_n^{(1)} = \langle\phi_n|\hat{H}_1|\phi_n\rangle,$$

which tells us that the change in the energy of the n 'th energy level, due to the perturbing term, is just $\lambda\langle\phi_n|\hat{H}_1|\phi_n\rangle$. Assuming that $\lambda = 1$, we have a very simple result for the change in energy, namely, that the change in energy is just equal to the expectation value of the perturbation term \hat{H}_1 , calculated using the *unperturbed* eigenstate corresponding to that energy level.

If one considers the normalization of an eigenstate of the system including the perturbing term, $|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots$, it can be done in many ways. The most convenient way is to assume $\langle\phi_n|\psi_n\rangle = 1$, which leads to

$$\langle\phi_n|\psi_n^{(1)}\rangle = 0 = \langle\phi_n|\psi_n^{(2)}\rangle = \langle\phi_n|\psi_n^{(3)}\rangle = \dots$$

In order to obtain the first order change in the eigenstate of the system, we multiply (6) by $\langle\phi_m|$ (such that $m \neq n$), to get

$$\begin{aligned} \langle\phi_m|\hat{H}_0|\psi_n^{(1)}\rangle + \langle\phi_m|\hat{H}_1|\phi_n\rangle &= E_n^{(0)}\langle\phi_m|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\phi_m|\phi_n\rangle \\ E_m^{(0)}\langle\phi_m|\psi_n^{(1)}\rangle + \langle\phi_m|\hat{H}_1|\phi_n\rangle &= E_n^{(0)}\langle\phi_m|\psi_n^{(1)}\rangle \\ \langle\phi_m|\psi_n^{(1)}\rangle &= \frac{\langle\phi_m|\hat{H}_1|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}}. \end{aligned} \quad (8)$$

Since we know that any state can be expanded in terms of the complete set of eigenstates $\{|\phi_n\rangle\}$ as $|\chi\rangle = \sum_m\langle\phi_m|\chi\rangle|\phi_m\rangle$, the state $|\psi_n^{(1)}\rangle$ can be represented as

$$|\psi_n^{(1)}\rangle = \sum_m\langle\phi_m|\psi_n^{(1)}\rangle|\phi_m\rangle = \sum_{m(\neq n)} \frac{\langle\phi_m|\hat{H}_1|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}}|\phi_m\rangle. \quad (9)$$

The $m = n$ term is zero because $\langle\phi_n|\psi_n^{(1)}\rangle = 0$. One would notice that the term $E_n^{(0)} - E_m^{(0)}$ in the denominator has to be nonzero, which ruled out situations where two different states may have the same energy. Thus, this procedure applies only to *non-degenerate systems*. Thus, the first order correction to the n 'th eigenstate of the system can also be calculated. The approximate eigenstates and eigenvalues, to first order in perturbation, can then be written as (assuming $\lambda = 1$)

$$\begin{aligned} E_n &\approx E_n^{(0)} + \langle\phi_n|\hat{H}_1|\phi_n\rangle, \\ |\psi_n\rangle &\approx |\phi_n\rangle + \sum_{m(\neq n)} \frac{\langle\phi_m|\hat{H}_1|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}}|\phi_m\rangle. \end{aligned} \quad (10)$$

Second order effects

In the preceding analysis we discussed the effect of perturbation on the system up to first order. Sometimes one needs more accuracy than that, or more commonly, sometimes

the first order change in energy is zero. In such a situation one would like to calculate the effects of perturbation up to second order. The second order change in energy can be found by multiplying (7) by $\langle \phi_n |$. Doing that, and remembering that $\langle \phi_n | \psi_n^{(1)} \rangle = 0 = \langle \phi_n | \psi_n^{(2)} \rangle$, we get

$$E_n^{(2)} = \langle \phi_n | \hat{H}_1 | \psi_n^{(1)} \rangle$$

Using (9) we get

$$\begin{aligned} E_n^{(2)} &= \langle \phi_n | \hat{H}_1 \sum_{m(\neq n)} \frac{\langle \phi_m | \hat{H}_1 | \phi_n \rangle}{E_n^{(0)} - E_m^{(0)}} | \phi_m \rangle \\ &= \sum_{m(\neq n)} \frac{|\langle \phi_m | \hat{H}_1 | \phi_n \rangle|^2}{E_n^{(0)} - E_m^{(0)}}. \end{aligned} \quad (11)$$

Second order correction can be calculated if one can evaluate all the matrix elements $\langle \phi_m | \hat{H}_1 | \phi_n \rangle$. An interesting thing to notice is that if $E_n^{(0)}$ is the *ground* state energy, meaning n is the lowest energy level, all $E_m^{(0)}$ will be larger than it, making the second order correction necessarily *negative*.

Degenerate states

It is clear that the above procedure breaks down when there is degeneracy in the energy eigenstates of the unperturbed Hamiltonian \hat{H}_0 . Dealing with such a situation is not always easy. The general idea is that if two states $|\phi_{n_1}\rangle, |\phi_{n_2}\rangle$ are degenerate, with an energy $E_{n_1}^{(0)}$, any linear combination of these two is also an eigenstate of \hat{H}_0 , with the same eigenvalue. Thus, instead of $|\phi_{n_1}\rangle, |\phi_{n_2}\rangle$, one can choose two eigenstates $|\chi_{n_1}\rangle, |\chi_{n_2}\rangle$ which are linear combinations of $|\phi_{n_1}\rangle, |\phi_{n_2}\rangle$. These states are chosen such that \hat{H}_1 is *diagonal* in that sub-basis. If the eigenvalues of \hat{H}_1 in the basis $|\chi_{n_1}\rangle, |\chi_{n_2}\rangle$ are ϵ_1, ϵ_2 , inserting these states in (2), we get

$$\begin{aligned} (\hat{H}_0 + \hat{H}_1) |\chi_{n_i}\rangle &= E_{n_i} |\chi_{n_i}\rangle \\ E_{n_1}^{(0)} |\chi_{n_i}\rangle + \epsilon_i |\chi_{n_i}\rangle &= E_{n_i} |\chi_{n_i}\rangle \\ E_{n_i} &= E_{n_1}^{(0)} + \epsilon_i, \quad i = 1, 2. \end{aligned} \quad (12)$$

Thus the energy of the two levels, to first order in the perturbation, is given by $E_{n_1} \approx E_{n_1}^{(0)} + \epsilon_1$ and $E_{n_2} \approx E_{n_1}^{(0)} + \epsilon_2$. The two states which were initially degenerate, are no longer so due to the perturbation. The perturbation *lifts the degeneracy*.

One might wonder if \hat{H}_0 and \hat{H}_1 do not commute, how is it possible to find states which are eigenstates of both. It is true that in general this cannot be done, but in the subspace of a few degenerate eigenstates, the matrix for \hat{H}_0 is effectively a unit matrix. In this special situation, this can be done. For a detailed discussion, the reader is referred to *Quantum Mechanics* by N. Zettili.

