Lecture 10

Perturbation theory

Nondegenerate perturbation theory: summary

The problem of the perturbation theory is to find eigenvalues and eigenfunctions of the perturbed potential, i.e. to solve approximately the following equation:

$$H\psi_n = E\psi_n\,, \quad H = H^0 + \underset{\uparrow\text{perturbation}}{H'}$$

using the known solutions of the problem

$$H^0\psi_n^0 = E_n^0\psi_n^0.$$

$$\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^2 + \dots$$

$$E_n = E_n^0 + E_n^1 + E_n^2 + \dots$$

The first-order energy is given by:

$$\boxed{E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle} \qquad (1)$$

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

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

The second-order correction to the energy is

$$\boxed{E_n^2 = \sum_{m\neq n}\frac{|\langle\psi_m^0|H'|\psi_n^0\rangle|^2}{E_n^0 - E_m^0}} \qquad (3)$$

Problem 1 (6.1)

Suppose we put a delta-function bump in the center of the infinite square well:

$$H' = \alpha\,\delta\left(x - \frac{a}{2}\right),$$

where α is a constant.

(a) Find the first-order correction to the allowed energies. Explain why energies are not perturbed for even n.

(b) Find the first three nonzero terms in the expansion (2) of the correction to the ground state, ψ_1^1.

Solution:

(a) Solutions of the $H^0 \psi_n^0 = E_n^0 \psi_n^0$ are:

$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right).$$

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \frac{2}{a}\alpha \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) \delta\left(x - \frac{a}{2}\right) dx$$

$$= \frac{2}{a}\alpha \sin^2\left(\frac{\pi n}{a}\frac{a}{2}\right) = \frac{2\alpha}{a} \sin^2\left(\frac{\pi n}{2}\right) =$$

$$= \begin{cases} 0, & \text{if } n \text{ is even} \\ 2\alpha/a, & \text{if } n \text{ is odd} \end{cases}$$

For even n, the wave function is zero at the location of the perturbation:

$$x = a/2 \Rightarrow \psi_n^0 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n}{a}x\right)\Big|_{x=a/2} = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n}{2}\right)$$

so it never "feels" H'.

(b) First-order correction to the wave function is given by

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

Here, n=1.

$$\boxed{\psi_1^1 = \sum_{m \neq 1} \frac{\langle \psi_m^0 | H' | \psi_1^0 \rangle}{E_1^0 - E_m^0} \psi_m^0}$$

$$\langle \psi_m^0 | H' | \psi_1^0 \rangle = \frac{2\alpha}{a} \int_0^a \sin\left(\frac{m\pi}{a} x\right) \delta\left(x - \frac{a}{2}\right) \sin\left(\frac{\pi}{x} a\right) dx$$

$$= \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{\pi}{2}\right) = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right)$$

$\sin\left(\frac{m\pi}{2}\right)$ is zero for even m, so the first three nonzero terms are m = 3, m = 5, and m = 7.

$$E_1^0 - E_m^0 = \frac{\pi^2 \hbar^2}{2 m a^2} (1 - m^2) \Rightarrow$$

$$\psi_1^1 = \sum_{m = 3, 5, 7, \ldots} \frac{(2\alpha / a) \sin(m\pi/2)}{E_1^0 - E_m^0} \psi_m^0$$

$$= \sum_{m = 3, 5, 7} \frac{(2\alpha / a) \sin(m\pi/2)}{\pi^2 \hbar^2 (1 - m^2)} 2 m a^2 \psi_m^0$$

$$= \frac{4 \alpha m a}{\pi^2 \hbar^2} \left\{ \frac{-1}{1 - 9} \psi_3^0 + \frac{1}{1 - 25} \psi_5^0 + \frac{-1}{1 - 49} \psi_7^0 + \ldots \right\}$$

$$= \frac{4 \alpha m a}{\pi^2 \hbar^2} \left\{ \frac{1}{8} \sin\left(\frac{3\pi}{a} x\right) - \frac{1}{24} \sin\left(\frac{5\pi}{a} x\right) + \frac{1}{48} \sin\left(\frac{7\pi}{a} x\right) + \ldots \right\}$$

Problem 2 [6.4 (a)]

Find the second-order correction to the energies for the same potential.

Solution: The second-order correction to the energy is

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \qquad (4)$$

$$\langle \psi_m^0 | H' | \psi_n^0 \rangle = \frac{2}{a} \alpha \int_0^a \sin\left(\frac{m\pi}{a} x\right) \delta\left(x - \frac{a}{2}\right) \sin\left(\frac{\pi n}{a} x\right) dx$$

$$= \frac{2\alpha}{a} \sin\left(\frac{m\pi}{a} \frac{a}{2}\right) \sin\left(\frac{\pi n}{a} \frac{a}{2}\right) = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{n\pi}{2}\right)$$

$$= \begin{cases} \frac{2\alpha}{a}, & \text{if both } m \text{ and } n \text{ are odd} \\ 0 & \text{otherwise} \end{cases}$$

Plugging in $\langle \psi_m^0 | H' | \psi_n^0 \rangle$ into (4), we get

$$E_n^2 = \sum_{\substack{m \neq n \\ \text{odd}}} \left(\frac{2\alpha}{a}\right)^2 \frac{1}{E_n^0 - E_m^0}, \text{ for odd } n, \; E_n^0 = \frac{\pi^2 \hbar^2}{2ma^2} \Rightarrow$$

$$E_n^2 = \begin{cases} 0 & \text{if } n \text{ is even} \\ 2m\left(\frac{2\alpha}{\pi\hbar}\right)^2 \sum_{\substack{m \neq n \\ \text{odd}}} \frac{1}{n^2 - m^2} & \text{if } n \text{ is odd} \end{cases}$$

In the homework, sum this series using $\frac{1}{n^2 - m^2} = \frac{1}{2n}\left(\frac{1}{m+n} - \frac{1}{m-n}\right)$.

Degenerate perturbation theory

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, i.e. when there are two states for each energy.

Two - fold degeneracy

We have two states ψ_a^0 and ψ_b^0 that are degenerate, i.e. they have the same energy E^0:

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

$$\langle \psi_a^0 | \psi_a^0 \rangle = \langle \psi_b^0 | \psi_b^0 \rangle = 1.$$

Linear combination of these states

$$\psi^0 = \psi_a^0 + \psi_b^0$$

is also an eigenstate of H^0 with eigenvalue E^0.

We want to solve

$$H\psi = E\psi, \qquad H = H^0 + H'.$$

$$E = E^0 + E^1 + \dots$$

$$\psi = \psi^0 + \psi^1 + \dots$$

$$\boxed{H^0\psi^1 + H'\psi^0 = E^0\psi^1 + E^1\psi^0} \qquad (5)$$

This time we multiply this equation from the left by ψ_a^0 and integrate, i.e. take inner product with ψ_a^0.

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

$$\downarrow$$

$$\langle H^0 \psi_a^0 | \psi^1 \rangle = \langle E^0 \psi_a^0 | \psi^1 \rangle$$

We now plug $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$

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

$$= \alpha E^1 \langle \psi_a^0 | \cancel{\psi_a^0} \rangle^{1} + \beta E^1 \langle \psi_a^0 | \cancel{\psi_b^0} \rangle^{0}$$

$$\alpha E^1 = \alpha \underbrace{\langle \psi_a^0 | H' \psi_a^0 \rangle}_{\equiv\, \alpha W_{aa}} + \beta \underbrace{\langle \psi_a^0 | H' \psi_b^0 \rangle}_{\equiv\, \beta W_{ab}}$$

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle, \quad (i, j = a, b)$$

$$\boxed{\alpha E^1 = \alpha W_{aa} + \beta W_{ab}} \qquad (6)$$

W_{ij} are known since we know $\psi_i^0 \Rightarrow$ we can calculate them.

If we take inner product of equation (5) with ψ_b^0 we get

$$\boxed{\beta E^1 = \alpha W_{ba} + \beta W_{bb}} \qquad (7)$$

We now solve this system of equations (6), (7) for E^1.

$$\alpha E^1 = \alpha W_{aa} + \beta W_{ab} \Rightarrow \boxed{\beta W_{ab}} = \alpha E^1 - \alpha W_{aa}$$

$$\left(\beta E^1 = \alpha W_{ba} + \beta W_{bb}\right) \times W_{ab}$$

$$E^1 \boxed{\beta W_{ab}} = \alpha W_{ab} W_{ba} + \boxed{\beta W_{ab}} W_{bb}$$

$$E^1 (\alpha E^1 - \alpha W_{aa}) = \alpha W_{ab} W_{ba} + W_{bb} (\alpha E^1 - \alpha W_{aa})$$

$$\alpha (E^1 - W_{aa})(E^1 - W_{bb}) = \alpha W_{ab} W_{ba}$$

If $\alpha \neq 0 \Rightarrow$

$$(E^1)^2 - E^1 (W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} W_{ba}) = 0$$

$W_{ba} = W_{ab}^*$ by definition $\Rightarrow$

$$\boxed{E^1_{\pm} = \frac{1}{2}\left[W_{aa} + W_{ab} \pm \sqrt{(W_{aa} - W_{ab})^2 + 4|W_{ab}|^2} \right]}$$

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

If $\alpha = 0 \Rightarrow \quad W_{ab} = 0$ and $E^1 = W_{bb}$

If $\beta = 0 \Rightarrow \quad E^1 = W_{aa}$ and

$$E^1_{\pm} = \begin{cases} W_{aa} = \langle \psi^0_a | H' | \psi^0_a \rangle \\ W_{bb} = \langle \psi^0_b | H' | \psi^0_b \rangle \end{cases}, \text{ i.e.}$$

if we could guess some good linear combinations ψ^0_a and ψ^0_b, then we can just use nondegenerate perturbation theory.

Theorem: let A be a hermitian operator that commutes with H^0 and H'. If ψ_a^0 and ψ_b^0 that are degenerate eigenfunctions of H^0, are also eigenfunctions of A with distinct eigenvalues,

$$A\psi_a^0 = \mu\psi_a^0, \quad A\psi_b^0 = \nu\psi_b^0, \quad \mu \neq \nu$$

then $W_{ab}=0$ and we can use degenerate perturbation theory.

Higher-order degeneracy: if we rewrite our equations

$$\left.\begin{aligned} \alpha E^1 &= \alpha W_{aa} + \beta W_{ab} \\ \beta E^1 &= \alpha W_{ba} + \beta W_{bb} \end{aligned}\right\} \Rightarrow \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

we see that E^1 are eigenvalues of the matrix

$$W = \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}.$$

In the case of n-fold degeneracy, E^1 are eigenvalues of n x n matrix

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle .$$

"Good" linear combinations of unperturbed states are eigenvectors of W.