Degenerate Perturbation theory

Note Title 11/23/2009

It is easiest to understand the perturbation theories using matrix notation.

Unperturbed Hamiltonian H° is diagonalized w.r.t. its eigenfunctions such that with $\psi_1^\circ \equiv \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$ $\psi_2^\circ = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$

$\psi_3^\circ = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \end{pmatrix}$ ----

$$H^\circ \equiv \begin{pmatrix} E_1^\circ & & & \\ & E_2^\circ & & \\ & & E_3^\circ & \\ & & & \ddots \end{pmatrix}$$

, where $E_n^\circ \equiv \langle \psi_n^\circ | H^\circ | \psi_n^\circ \rangle$.

If a perturbation H' is added, in general H' is not diagonalized with the basis $\{ \psi_1^\circ, \psi_2^\circ, \psi_3^\circ, \ldots \}$.

In other words, with the original basis

$$H' \equiv \begin{pmatrix} H'_{11} & H'_{12} & H'_{13} & \cdots \\ H'_{21} & H'_{22} & H'_{23} & \\ H'_{31} & H'_{32} & H'_{33} & \\ \vdots & & & \ddots \end{pmatrix}$$

solving the new Schrödinger equation exactly is equivalent to finding new eigen functions (new basis) that diagonalize

$$H = H^\circ + H'.$$

Then with the new exact eigenfunctions

$$\psi_n = \psi_n^\circ + \psi_n^1 + \psi_n^2 + \cdots$$

(ψ_n^1: first order; ψ_n^2: 2nd order ...)

the total Hamiltonian is exactly diagonalized such that

$$H = H^\circ + H' = \begin{pmatrix} E_1 & & 0 \\ & E_2 & \\ & & E_3 \\ 0 & & & \ddots \end{pmatrix}$$

with $E_n \equiv \langle \psi_n | H | \psi_n \rangle$.

What we learned last time is,

$$E_n = \langle \psi_n | H | \psi_n \rangle$$
$$= \langle \psi_n^0 + \psi_n^1 + \psi_n^2 \cdots | H^0 + H' | \psi_n^0 + \psi_n^1 + \psi_n^2 \cdots \rangle$$
$$= \langle \psi_n^0 | H^0 | \psi_n^0 \rangle + \underbrace{\langle \psi_n^0 | H^0 | \psi_n^1 \rangle}_{0} + \underbrace{\langle \psi_n^1 | H^0 | \psi_n^0 \rangle}_{0} + \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

up to the first order

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

But if the unperturbed Hamiltonian is degenerate, that is, if a certain E_n is shared between multiple eigenfunctions, then the procedure has to be modified.

Let's say E_n^0 is two fold degenerate such that

$$E_n^0 = \langle \psi_{na}^0 | H^0 | \psi_{na}^0 \rangle$$
$$= \langle \psi_{nb}^0 | H^0 | \psi_{nb}^0 \rangle$$

Then up to the 1st order, finding the perturbed eigenvalues are equivalent to solving the Schrödinger equation within this subspace defined by these two functions $\{ \psi_{na}^0, \psi_{nb}^0 \}$.

In other words, just solve

$$\begin{pmatrix} H'_{aa} & H'_{ab} \\ H'_{ba} & H'_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_n' \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \equiv \alpha \psi^0_{na} + b \psi^0_{nb}$$

The best way to understand this process is through an example.

Ex. Consider the 3-D infinite cubical well

$$V(x,y,z) = \begin{cases} 0 & \text{if } 0 < x,y,z < a \\ \infty & \text{else} \end{cases}$$

The eigenfctns of the T.I.S.E are

$$\psi^0_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\left(\frac{n_x\pi}{a}x\right) \sin\left(\frac{n_y\pi}{a}y\right) \cdot \sin\left(\frac{n_z\pi}{a}z\right)$$

with the energy eigenvalues

$$E^0_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

The ground state is non degenerate

$$E_{111}^{0} = \frac{\pi^2 \hbar^2}{2ma^2} \cdot 3$$

Let's call E_{111}^{0} by E_0^{0}.

The first excited state is triply degenerate

$$E_1^{0} \equiv E_{112}^{0} = E_{121}^{0} = E_{211}^{0} = \frac{\pi^2 \hbar^2}{ma^2} \cdot 3$$

Let's introduce the perturbation

$$H' = \begin{cases} V_0 , & \text{if } 0<x<\frac{a}{2} \text{ and } 0<y<\frac{a}{2} \\ & (0<z<a) \\ 0 , & \text{else} \end{cases}$$

First order correction to the ground state is simply

$$E_0^{1} = H'_{00} = \langle \psi_{111}^{0} | H' | \psi_{111}^{0} \rangle$$

$$= \left(\frac{2}{a}\right)^3 V_0 \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}x\right) dx \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}y\right) dy \int_0^{a} \sin^2\left(\frac{\pi}{a}z\right) dz$$

$$= \left(\frac{2}{a}\right)^3 V_0 \cdot \frac{a}{4} \cdot \frac{a}{4} \cdot \frac{a}{2}$$

$$= \frac{V_0}{4} , \text{ as expected from the non-degenerate theory}$$

Now for the 1st excited, we need to use the degenerate perturbation theory

Within the subspace spanned by

$$\psi_a \equiv \psi_{112}, \quad \psi_b = \psi_{121}, \quad \psi_c = \psi_{211}$$

We need to solve the Schrödinger Eq. for

$$H' \equiv \begin{pmatrix} H'_{aa} & H'_{ab} & H'_{ac} \\ H'_{ba} & H'_{bb} & H'_{bc} \\ H'_{ca} & H'_{cb} & H'_{cc} \end{pmatrix}$$

Here $H'_{aa} = \langle \psi_{112} | H' | \psi_{112} \rangle$

$$= \left(\frac{2}{a}\right)^3 V_0 \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}x\right) dx \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}y\right) dy \cdot \int_0^{a} \sin^2\left(\frac{2\pi}{a}z\right) dz$$

$$= \left(\frac{2}{a}\right)^3 \cdot V_0 \cdot \frac{a}{4} \cdot \frac{a}{4} \cdot \frac{a}{2} = \frac{V_0}{4}$$

Similarly $H'_{bb} = H'_{cc} = \frac{V_0}{4}$

$$H'_{ab} = \langle \psi_{112} | H' | \psi_{121} \rangle = \left(\frac{2}{a}\right)^3 V_0 \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}x\right) dx \cdot \int_0^{\frac{a}{2}} \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}\right) dy \cdot \int_0^{a} \sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}\right) dz = 0$$

$$H'_{ac} = \langle \psi_{112} | H' | \psi_{211} \rangle = 0$$

due to "z" integral

$$H'_{bc} = \langle \psi_{121} | H' | \psi_{211} \rangle$$

$$= \left(\frac{2}{a}\right)^3 V_0 \int_0^{\frac{a}{2}} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) dx$$

$$\cdot \int_0^{\frac{a}{2}} \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}y\right) dy$$

$$\cdot \int_0^{a} \sin\left(\frac{\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right) dz$$

$$= \frac{16}{9\pi^2} V_0$$

Because H' must be hermitian

$H'_{cb} = H'^{*}_{bc} = H'_{bc}$, etc. ...

So

$$H' \equiv \frac{V_0}{4} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}$$

, $\kappa \equiv \left(\frac{8}{3\pi}\right)^2 \simeq 0.72$

What the perturbation theory is saying is, up to the first order, we just have to solve this small size Schrödinger equation

For the first excited state,

$$H'|\psi\rangle = E'|\psi\rangle$$

$$= \frac{V_0}{4}\cdot\epsilon\,|\psi\rangle$$

$$\Rightarrow \frac{V_0}{4}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \frac{V_0}{4}\epsilon\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

$$\Rightarrow \begin{vmatrix} 1-\epsilon & 0 & 0 \\ 0 & 1-\epsilon & \kappa \\ 0 & \kappa & 1-\epsilon \end{vmatrix} = 0$$

$$\Rightarrow (1-\epsilon)\left((1-\epsilon)^2 - \kappa^2\right) = 0$$

$$\Rightarrow (\epsilon-1)(\epsilon-1-\kappa)(\epsilon-1+\kappa) = 0$$

$$\Rightarrow \epsilon = 1,\ 1+\kappa,\ 1-\kappa$$

And the eigenfunctions are

$$\epsilon = 1,\quad \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \kappa \\ 0 & \kappa & 0 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = 0$$

$$\Rightarrow \gamma = 0,\ \beta = 0 \Rightarrow \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$= \psi_a$$

$\epsilon = 1+\kappa$,
$$\begin{pmatrix} -\kappa & 0 & 0 \\ 0 & -\kappa & \kappa \\ 0 & \kappa & -\kappa \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = 0$$

$$\Rightarrow \alpha = 0, \quad \beta = \gamma \Rightarrow \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$$

$$= \frac{1}{\sqrt{2}} (\psi_b + \psi_c)$$

$\epsilon = 1-\kappa$,
$$\begin{pmatrix} \kappa & 0 & 0 \\ 0 & \kappa & \kappa \\ 0 & \kappa & \kappa \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = 0$$

$$\Rightarrow \alpha = 0, \quad \alpha = -\beta \Rightarrow \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}$$

$$= \frac{1}{\sqrt{2}} (\psi_b - \psi_c)$$

And the ~~total~~ energies are, up to first order

$$E_1 = \begin{cases} E_1^0 + \frac{V_0}{4} & \rightarrow \psi_a \\ E_1^0 + (1+\kappa)\frac{V_0}{4} & \rightarrow \frac{1}{\sqrt{2}}(\psi_b + \psi_c) \\ E_1^0 + (1-\kappa)\frac{V_0}{4} & \rightarrow \frac{1}{\sqrt{2}}(\psi_b - \psi_c) \end{cases}$$

* So with the perturbation, the degeneracy is broken, and ψ_a, $\frac{1}{\sqrt{2}}(\psi_b + \psi_c)$, $\frac{1}{\sqrt{2}}(\psi_b - \psi_c)$ are approximately the new eigen fcns.