Lecture #11

Degenerate perturbation theory

Problem 1

Consider the three-dimensional infinite cubical well

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

The stationary states are

$$\psi^0_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi_x n}{a}x\right)\sin\left(\frac{\pi_y n}{a}y\right)\sin\left(\frac{\pi_z n}{a}z\right),$$

n_x, n_y, n_z are positive integers. The energies are given by

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

Question for the class:
What are the energies of ground and first excited states?
Are these states degenerate? If so, what are the degeneracies?

The ground state is nondegenerate: $n_x = n_y = n_z = 1$ $\quad \psi_{111}$

$$E^0_{111} \equiv E^0_0 = 3\frac{\pi^2\hbar^2}{2ma^2}$$

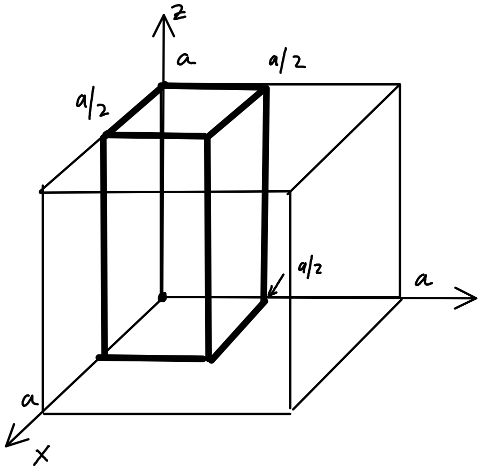
Next three states all share the same energy (triply degenerate):

n_x	n_y	n_z
1	1	2
1	2	1
2	1	1

$$E^0_1 = \frac{\pi^2\hbar^2}{2ma^2}(1+1+4) = \frac{3\pi^2\hbar^2}{2ma^2}$$

$\psi_{112}, \psi_{121}, \psi_{211}$

We now introduce perturbation



$$H' = \begin{cases} V_0, & \text{if } 0 < x < a/2 \\ & \phantom{\text{if }} 0 < y < a/2 \\ & \phantom{\text{if }} 0 < z < a \\ 0 & \text{otherwise} \end{cases}$$

Question for the class:
What is first-order correction to the ground state energy?

$$\int \sin^2(ax)\,dx = -\frac{1}{2a}\cos(ax)\sin(ax) + \frac{x}{2}$$

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

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

$$= \left(\frac{2}{a}\right)^3 \left(\frac{a/2}{2}\right)^2 \frac{a}{2} = \frac{8}{\cancel{a^3}} \frac{\cancel{a}}{2} \frac{\cancel{a^2}}{16} \cdot V_0 = \frac{V_0}{4}$$

Our next mission is to calculate **the first-order correction to the energy of the first excited state**. Here, the states are degenerate and we need to use degenerate perturbation theory, i.e. we need to calculate all elements of the 3 x 3 matrix

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

Class exercise: calculate all elements of the matrix

$$W = \begin{pmatrix} W_{aa} & W_{ab} & W_{ac} \\ W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{pmatrix}$$

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

$$W_{ij} = \langle \psi_i^\circ \,|\, H' \,|\, \psi_j^\circ \rangle$$

$$\int \sin^2(ax)\,dx = -\frac{1}{2a}\cos(ax)\sin(ax) + \frac{x}{2}$$

$$\int \sin(b_1 x)\sin(b_2 x)\,dx = \frac{\sin[(b_1 - b_2)x]}{2(b_1 - b_2)} - \frac{\sin[(b_1 + b_2)x]}{2(b_1 + b_2)}$$

for $|b_1| \neq |b_2|$

Solution:

$$W_{aa} = \langle \psi_{112} \,|\, H' \,|\, \psi_{112} \rangle = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\overset{1}{\frac{\pi}{a}} x\right) dx$$

$$\int_0^{a/2} \sin^2\left(\overset{1}{\frac{\pi}{a}} y\right) dy \int_0^{a} \sin^2\left(\overset{2}{\frac{2\pi}{a}} z\right) dz = \left(\frac{2}{a}\right)^3 V_0 \left(\frac{a/2}{2}\right)^2 \frac{a}{2} = \frac{V_0}{4}$$

Same as the ground state

$$W_{bb} = W_{cc} = W_{aa} = \frac{V_0}{4}$$

$$W_{ab} = \langle \psi_{112} \,|\, H' \,|\, \psi_{121} \rangle = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\overset{1\quad 1}{\frac{\pi}{a}} x\right) dx$$

$$\int_0^{a/2} \sin\left(\overset{1}{\frac{\pi}{a}} y\right) \sin\left(\overset{2}{\frac{2\pi}{a}} y\right) dy \int_0^{a} \sin\left(\frac{2\pi}{a} z\right) \sin\left(\frac{\pi}{a} z\right) dz$$

$$\int_0^{a/2} \sin\left(\frac{\pi}{a}y\right)\sin\left(\frac{2\pi}{a}y\right)dy = \left[\frac{\sin\left(-\frac{\pi}{a}y\right)}{2\cdot\left(-\frac{\pi}{a}\right)} - \frac{\sin\left(\frac{3\pi}{a}y\right)}{2\cdot\frac{3\pi}{a}}\right]\Bigg|_0^{a/2}$$

$$= a\,\frac{\sin\frac{\pi}{2}}{2\pi} - \frac{a}{6\pi}\sin\left(\frac{3\pi}{2}\right) = \frac{a}{2\pi} + \frac{a}{6\pi} = \frac{2a}{3\pi}$$

$$\int \sin(b_1 x)\sin(b_2 x)\,dx = \frac{\sin[(b_1-b_2)x]}{2(b_1-b_2)} - \frac{\sin[(b_1+b_2)x]}{2(b_1+b_2)}$$

$$b_1 = \frac{\pi}{a}, \quad b_2 = \frac{2\pi}{a}$$

$$\int_0^a \sin\left(\frac{2\pi}{a}z\right)\sin\left(\frac{\pi}{a}z\right)dz = 0$$ since we will get $\sin\pi$ and $\sin 3\pi$

$$\boxed{W_{ab} = W_{ba} = 0}$$

$$\boxed{\begin{array}{l} W_{ac} = \langle \psi_{112} | H' | \psi_{211} \rangle = 0 \\ W_{ca} = 0 \end{array}}$$

since we get the same z integral as in W_{ab}

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

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

$$\times \underbrace{\int_0^a \sin^2\left(\frac{\pi}{a}z\right)dz}_{a/2} = \frac{8}{a^3}\,\frac{4a^2}{9\pi^2}\,\frac{a}{2}V_0 = \boxed{\frac{16}{9\pi^2}V_0}$$

$$\boxed{\text{Result:} \quad W = \frac{V_0}{4}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & K \\ 0 & K & 1 \end{pmatrix} \qquad K = \left(\frac{8}{3\pi}\right)^2 \simeq 0.7205}$$

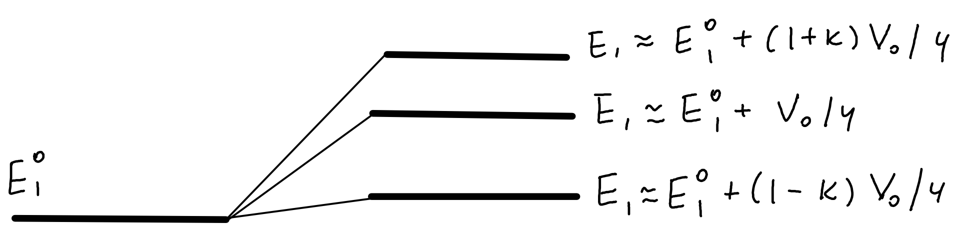
The characteristic equation for $\frac{4W}{V_0}$:

$$\begin{vmatrix} 1-w & 0 & 0 \\ 0 & 1-w & K \\ 0 & K & 1-w \end{vmatrix} = (1-w)\left[(1-w)^2 - K^2\right] = 0$$

$$(1-w)(1-w-K)(1-w+K) = 0$$

$$\boxed{\begin{aligned} w_1 &= 1 \\ w_2 &= 1+K \\ w_3 &= 1-K \end{aligned}} \qquad \begin{aligned} w_2 &\approx 1.705 \\ w_3 &\approx 0.295 \end{aligned}$$

The initial energy level E_1^0 will split into three due to the perturbation:



"Good" unperturbed states are linear combination of the form

$$\psi^0 = \alpha\psi_a + \beta\psi_b + \gamma\psi_c,$$

where the coefficients α, β, γ are the eigenvectors of W.

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & K \\ 0 & K & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

Exercise for the class: find the eigenvectors and write out three resulting states ψ_0 .

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & K \\ 0 & K & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

#1 $\quad w_1 = 1 \qquad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & K \\ 0 & K & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$

$$\begin{pmatrix} \alpha \\ \beta + K\gamma \\ \beta K + \gamma \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \Rightarrow \alpha = 1, \ \beta = \gamma = 0 \qquad \boxed{\psi^0 = \psi_a}$$

#2 $\quad w_2 = 1 + K \qquad \begin{pmatrix} \alpha \\ \beta + K\gamma \\ \beta K + \gamma \end{pmatrix} = 1 + K\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$

$$\alpha = 0 \qquad \beta + K\gamma = \beta + K\beta \Rightarrow \gamma = \beta \Rightarrow \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \Rightarrow$$

$$\boxed{\psi^0 = \frac{1}{\sqrt{2}}(\psi_b + \psi_c)}$$

#3 $\quad w_3 = 1 - K \qquad \begin{pmatrix} \alpha \\ \beta + K\gamma \\ \beta K + \gamma \end{pmatrix} = (1-K)\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \qquad \alpha = 0, \quad \beta + K\gamma = \beta - K\beta \Rightarrow \gamma = -\beta$

$$\begin{pmatrix} 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix} \Rightarrow \boxed{\psi^0 = \frac{1}{\sqrt{2}}(\psi_b - \psi_c)}$$

If we apply nondegenerate perturbation theory to these three states, we will get correct results. We will not get correct results if we apply nondegerate perturbation theory to original unperturbed states ψ_a, ψ_b, and ψ_c.