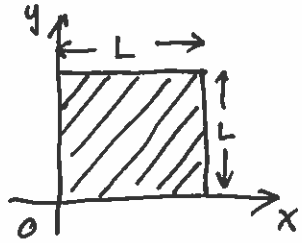
$\boxed{P31.4}$ The 2-dimensional box :



outside the shaded region $V = \infty$,
inside the shaded region $V = 0$.

Schrödinger equation (inside the box) is given by

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y) = E\,\psi(x,y) \quad \text{——} \quad (1)$$

outside the box, $\psi(x,y) = 0$.

Eq. (1) is separable by writing

$$\psi(x,y) = \psi_x(x)\psi_y(y) \quad \text{——} \quad (2)$$

Using (2) in (1) results in

$$\underbrace{\frac{1}{\psi_x}\frac{d^2\psi_x}{dx^2}}_{\text{function of } x \text{ only}} + \underbrace{\frac{1}{\psi_y}\frac{d^2\psi_y}{dy^2}}_{\text{function of } y \text{ only}} = -\frac{2mE}{\hbar^2} = -k^2 \quad \text{——} \quad (3)$$

$$(3) \Rightarrow \quad \frac{1}{\psi_x}\frac{d^2\psi_x}{dx^2} = -k_x^2 \quad \text{——} \quad (4)$$

constants

$$\frac{1}{\psi_y}\frac{d^2\psi_y}{dy^2} = -k_y^2 \quad \text{——} \quad (5)$$

with $\quad k_x^2 + k_y^2 = k^2 \quad$ —— (6)

(4) & (5) are equivalent to

$$\frac{d^2\psi_x}{dx^2} + k_x^2\psi_x = 0 \quad \text{——} \quad (7)$$

$$\frac{d^2\psi_y}{dy^2} + k_y^2\psi_y = 0 \quad \text{——} \quad (8)$$

Solutions to (7) and (8) are

$$\psi_x(x) = A\sin k_x x \quad ; \quad \psi_y(y) = B\sin k_y y \quad \text{——} \quad (9)$$

P31.4 cont'd.

$$\therefore\ \psi(x,y) = \psi_x(x)\psi_y(y) = \underbrace{AB}\ \sin k_x x\ \sin k_y y$$
$$= C\ \sin k_x x\ \sin k_y y \qquad \text{—— (10)}$$

Boundary conditions on the walls $x = L$ and $y = L$ dictate

$$\psi(L, y) = \psi(x, L) = 0 \qquad \text{—— (11)}$$

$$\Rightarrow \quad \sin k_x L = \sin k_y L = 0 \qquad \text{—— (12)}$$

$$\Rightarrow \quad k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L}; \quad \left.\begin{array}{l} n_x = 0, \pm 1, \pm 2, \ldots \\ n_y = 0, \pm 1, \pm 2, \ldots \end{array}\right\} \text{— (13)}$$

$n_x = n_y = 0$ can be excluded since this gives $\psi = 0$. Also, negative values of n_x, n_y do not lead to new independent wave functions from those given by $n_x, n_y > 0$, since

$$\psi(n_x, n_y < 0) = -\psi(n_x, n_y > 0) \qquad \text{—— (14)}$$

$\therefore$ We can restrict n_x, n_y to be positive integers:

$$k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L}; \quad \left.\begin{array}{l} n_x = 1, 2, 3, \ldots \\ n_y = 1, 2, 3, \ldots \end{array}\right\} \text{— (15)}$$

The normalization condition

$$\int_0^L dx \int_0^L dy\ \psi^2(x,y) = 1$$

$$\Rightarrow C^2 \int_0^L dx \sin^2\left(\frac{n_x \pi}{L} x\right) \int_0^L dy \sin^2\left(\frac{n_y \pi}{L} x\right) = C^2 \cdot \frac{L}{2} \cdot \frac{L}{2} = 1$$

$\Rightarrow C = \frac{2}{L}$. So the solution to the unperturbed Sch. eq. (1) is

$$\boxed{\psi_{n_x, n_y}(x,y) = \frac{2}{L} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \quad \begin{array}{l} n_x = 1, 2, 3, \ldots \\ n_y = 1, 2, 3, \ldots \end{array}} \qquad \text{— (16)}$$

P31.4 cont'd

From (3) ~~and~~ (6) and (15) The energy eigenvalues are given by

$$\boxed{E_{n_x n_y} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2+n_y^2) \; ; \quad \begin{matrix} n_x = 1,2,3,\ldots \\ n_y = 1,2,3,\ldots \end{matrix}} \qquad \text{—— (17)}$$

Now introduce the perturbation potential $\boxed{V = \alpha\, xy}$ (α small)

The ground state unperturbed energy is when $n_x = n_y = 1$:

$$E_{11}^{(0)} = \frac{\hbar^2\pi^2}{2mL^2}(1^2+1^2) = \frac{\hbar^2\pi^2}{mL^2} \qquad \text{—— (18)}$$

The unperturbed state $\psi_{11}^{(0)}(x,y)$ is non-degenerate.

$\therefore$ We can use non-degenerate perturbation theory to get (to first order) [see Eq. (31.13)] of text :

$$E_{11}^{(1)} = E_{11}^{(0)} + \langle 1\,1|V|1\,1\rangle \qquad \left(\text{on denoting the unperturbed states by } |n_x n_y\rangle\right) \; (19)$$

$$\langle 1\,1|V|1\,1\rangle = \alpha\int_0^L dx\int_0^L dy\; \psi_{11}^{(0)}(x,y)\, xy\, \psi_{11}^{(0)}(x,y)$$

$$= \frac{4}{L^2}\alpha\int_0^L dx\; x\sin^2\left(\frac{\pi x}{L}\right)\int_0^L dy\cdot y\sin^2\left(\frac{\pi y}{L}\right)$$

use the result
$$\int d\theta\, \theta \sin^2\theta = \frac{\theta^2}{4} - \frac{\theta\sin 2\theta}{4} - \frac{1}{8}\cos 2\theta$$

$$= \frac{4\alpha}{L^2}\left(\int_0^L dx\; x\sin^2\left(\frac{\pi x}{L}\right)\right)^2 = \frac{4\alpha}{L^2}\cdot\left(\frac{L}{2}\right)^4 = \frac{\alpha L^2}{4} \qquad \text{—— (20)}$$

$$\therefore \boxed{E_{11}^{(1)} = \frac{\hbar^2\pi^2}{mL^2} + \frac{\alpha L^2}{4}} \qquad \text{—— (21)}$$

The first excited unperturbed energy is

$$E_{12}^{(0)} = E_{21}^{(0)} = \frac{\hbar^2\pi^2}{2mL^2}(1^2+2^2) = \frac{5\hbar^2\pi^2}{2mL^2} \qquad \text{—— (22)}$$

This level is doubly degenerate, with the different unperturbed states $|n_x n_y\rangle = |1,2\rangle$ and $|n_x n_y\rangle = |2,1\rangle$.

$\boxed{P31.4}$ ∴ To find the perturbed energy we have to use degenerate perturbation theory.

$E_{12}^{(0)}$ will be split by the perturbation potential $V = \alpha xy$. The energy changes ΔE of the split levels are solutions of the secular equation: (see Eq. (31.52) of text)

$$\begin{vmatrix} \langle 12|V|12\rangle - \Delta E & \langle 12|V|21\rangle \\ \langle 21|V|12\rangle & \langle 21|V|21\rangle - \Delta E \end{vmatrix} = 0 \qquad \text{— (23)}$$

$$\langle 12|V|12\rangle = \langle 21|V|21\rangle$$

$$= \left(\frac{2}{L}\right)^2 \alpha \underbrace{\int_0^L dx\, x \sin^2\left(\frac{\pi x}{L}\right)}_{(L/2)^2} \underbrace{\int_0^L dy\, y \sin^2\left(\frac{2\pi y}{L}\right)}_{(L/2)^2}$$

$$= \frac{\alpha L^2}{4} \qquad \text{— (24)}$$

$$\langle 12|V|21\rangle = \langle 21|V|12\rangle$$

$$= \left(\frac{2}{L}\right)^2 \alpha \int_0^L dx \int_0^L dy\, \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi y}{L}\right) x\, y \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right)$$

$$= \left(\frac{2}{L}\right)^2 \alpha \left(\int_0^L dx\, x \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right)\right)^2 \qquad \text{— (25)}$$

$$\int_0^L dx\, x \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) = \left(\frac{L}{\pi}\right)^2 \int_0^\pi d\theta\, \theta \sin\theta \sin 2\theta,$$

$$\int d\theta\, \theta \sin\theta \sin 2\theta \overset{\text{by parts}}{=} \theta\left(\frac{\sin\theta}{2} - \frac{\sin 3\theta}{2.3}\right) - \int d\theta \left(\frac{\sin\theta}{2} - \frac{\sin 3\theta}{6}\right)$$

$$= \frac{\theta \sin\theta}{2} - \frac{\theta \sin 3\theta}{6} + \frac{1}{2}\cos\theta - \frac{1}{18}\cos 3\theta$$

$\boxed{P31.4}$ cont'd

$$\int_0^{\pi} d\theta\ \theta \sin\theta \sin 2\theta = \frac{1}{2}\cos\theta\Big|_0^{\pi} - \frac{1}{18}\cos 3\theta\Big|_0^{\pi} = \frac{1}{2}(-1-1) - \frac{1}{18}(-1-1)$$

$$= -1 + \frac{1}{9} = -\frac{8}{9}$$

$$\therefore \int_0^{L} dx\ x \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) = -\frac{8}{9}\left(\frac{L}{\pi}\right)^2$$

$$\langle 12|V|21\rangle = \langle 21|V|12\rangle$$

$$= \left(\frac{2}{L}\right)^2 \cdot \alpha \left(\frac{64}{81}\right)\frac{L^4}{\pi^4} = \frac{256}{81}\alpha\frac{L^2}{\pi^4} \qquad \text{——— (26)}$$

We can write (23) as

$$\begin{vmatrix} a-\Delta E & b \\ b & a-\Delta E \end{vmatrix} = 0 \qquad \text{——— (27)}$$

where $a = \dfrac{\alpha L^2}{4}$, $b = \dfrac{256}{81}\dfrac{\alpha L^2}{\pi^4}$ ——— (28)

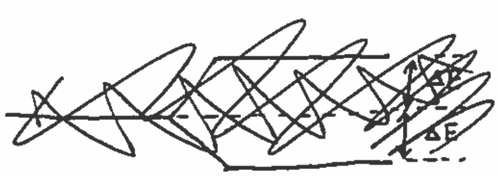
which implies

$$(a-\Delta E)^2 - b^2 = 0$$

$$\Rightarrow (\Delta E - a) = \pm b \Rightarrow \Delta E^{\pm} = a \pm b$$

or $$\Delta E^{\pm} = \alpha L^2\left(\frac{1}{4} \pm \frac{256}{81\pi^4}\right) \qquad \text{——— (29)}$$

$\therefore$ The unperturbed energy level $E_{12}^{(0)}$ is split into 2 levels: $E_{12}^{(1)+}$ and $E_{12}^{(1)-}$



P31.4 cont'd

where

$$\left.\begin{aligned} E_{12}^{(1)+} &= E_{12}^{(0)} + \Delta E^{+} \\ E_{12}^{(1)-} &= E_{12}^{(0)} + \Delta E^{-} \end{aligned}\right\} \quad \text{———} \quad (30)$$

or, using (22) for $E_{12}^{(0)}$ and (29) for $\Delta E^{\pm}$

$$\boxed{\left.\begin{aligned} E_{12}^{(1)+} &= \frac{5\hbar^2\pi^2}{2mL^2} + \alpha L^2 \underbrace{\left(\frac{1}{4} + \overset{\sim 0.032}{\frac{256}{81\pi^4}}\right)}_{\sim 0.282} \\ E_{12}^{(1)-} &= \frac{5\hbar^2\pi^2}{2mL^2} + \alpha L^2 \underbrace{\left(\frac{1}{4} - \frac{256}{81\pi^4}\right)}_{\sim 0.218} \end{aligned}\right\}} \quad \text{———} \quad (31)$$

The zero-th order wave functions with perturbation for the first excited state

$$\left.\begin{aligned} \psi_{\{1,2\}}^{(0)+} &= C_{1+}\,\psi_{12}^{(0)} + C_{2+}\,\psi_{21}^{(0)} \\ \psi_{\{1,2\}}^{(0)-} &= C_{1-}\,\psi_{12}^{(0)} + C_{2-}\,\psi_{21}^{(0)} \end{aligned}\right\} \quad (32)$$

this bracket means the order of (1,2) does not matter

The coefficients $C_{1+}, C_{2+}, C_{1-}, C_{2-}$ are then solutions to the following matrix equations [see Eq. (31.52) in text]

P31.4 cont'd.

$$\begin{pmatrix} a & b \\ b & a \end{pmatrix}\begin{pmatrix} c_{1+} \\ c_{2+} \end{pmatrix} = \Delta E^{+}\begin{pmatrix} c_{1+} \\ c_{2+} \end{pmatrix} \qquad \text{— (33)}$$

$$\begin{pmatrix} a & b \\ b & a \end{pmatrix}\begin{pmatrix} c_{1-} \\ c_{2-} \end{pmatrix} = \Delta E^{-}\begin{pmatrix} c_{1-} \\ c_{2-} \end{pmatrix} \qquad \text{— (34)}$$

Write $\Delta E^{\pm} = \lambda_{\pm}\alpha L^2$, where $\lambda_{\pm} = \left(\frac{1}{4} \pm \frac{256}{81\pi^4}\right)$

$a = a'\alpha L^2$, $b = b'\alpha L^2$, where

$a' = \frac{1}{4}$, $b' = \frac{256}{81\pi^4}$

Then Eq. (33) can be written as

$$\left.\begin{aligned} (a'-\lambda_+)c_{1+} + b' c_{2+} &= 0 \\ b' c_{1+} + (a'-\lambda_+)c_{2+} &= 0 \end{aligned}\right\} \quad (35)$$

and Eq. (34) as

$$\left.\begin{aligned} (a'-\lambda_-)c_{1-} + b' c_{2-} &= 0 \\ b' c_{1-} + (a'-\lambda_-)c_{2-} &= 0 \end{aligned}\right\} \quad (36)$$

$$(35) \Rightarrow \frac{c_{1+}}{c_{2+}} = \frac{b'}{\lambda_+ - a'} = \frac{b'}{b'} = 1$$

normalization of the state $\psi^{(0)+}_{\{1,2\}}$ (Eq. (32)) then implies

$$\boxed{c_{1+} = c_{2+} = \frac{1}{\sqrt{2}}} \qquad \text{— (37)}$$

$$(36) \Rightarrow \frac{c_{1-}}{c_{2-}} = \frac{b'}{\lambda_- - a'} = -1$$

normalization of the state $\psi^{(0)-}_{\{1,2\}}$ (Eq. (32)) then implies

$$\boxed{c_{1-} = \frac{1}{\sqrt{2}}, \quad c_{2-} = -\frac{1}{\sqrt{2}}} \qquad \text{— (38)}$$

P31.4 cont'd

Finally, the zeroth-order perturbed wave functions corresponding to the degenerate wave functions $\psi_{12}^{(0)}$ and $\psi_{21}^{(0)}$ are given by

$$\boxed{\begin{aligned} \psi_{\{1,2\}}^{(0)+}(x,y) &= \frac{\sqrt{2}}{L}\left\{\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)+\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\right\} \\ \psi_{\{1,2\}}^{(0)-}(x,y) &= \frac{\sqrt{2}}{L}\left\{\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)-\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\right\} \end{aligned}} \quad (39)$$

To first-order in the perturbation,

$\psi_{\{1,2\}}^{(0)+}$ has energy eigenvalue $E_{12}^{(1)+}$ and

$\psi_{\{1,2\}}^{(0)-}$ has energy eigenvalue $E_{12}^{(1)-}$.