Problem 4.2

(a) Equation 4.8 $\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)=E\psi$ (inside the box). Separable solutions: $\psi(x,y,z)=X(x)Y(y)Z(z)$. Put this in, and divide by XYZ:

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2X}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}=-\frac{2m}{\hbar^2}E.$$

The three terms on the left are functions of x, y, and z, respectively, so each must be a constant. Call the separation constants k_x^2, k_y^2, and k_z^2 (as we'll soon seen, they must be positive).

$$\frac{d^2X}{dx^2}=-k_x^2X;\quad \frac{d^2Y}{dy^2}=-k_y^2Y;\quad \frac{d^2Z}{dz^2}=-k_z^2Z,\quad \text{with}\quad E=\frac{\hbar^2}{2m}(k_x^2+k_y^2+k_z^2).$$

Solution:

$$X(x)=A_x\sin k_xx+B_x\cos k_xx;\quad Y(y)=A_y\sin k_yy+B_y\cos k_yy;\quad Z(z)=A_z\sin k_zz+B_z\cos k_zz.$$

But $X(0)=0$, so $B_x=0$; $Y(0)=0$, so $B_y=0$; $Z(0)=0$, so $B_z=0$. And $X(a)=0\Rightarrow\sin(k_xa)=0\Rightarrow k_x=n_x\pi/a$ ($n_x=1,2,3,\ldots$). [As before (page 31), $n_x\neq 0$, and negative values are redundant.] Likewise $k_y=n_y\pi/a$ and $k_z=n_z\pi/a$. So

$$\psi(x,y,z)=A_xA_yA_z\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{a}y\right)\sin\left(\frac{n_z\pi}{a}z\right),\quad E=\frac{\hbar^2}{2m}\frac{\pi^2}{a^2}(n_x^2+n_y^2+n_z^2).$$

We might as well normalize X, Y, and Z separately: $A_x=A_y=A_z=\sqrt{2/a}$. *Conclusion:*

$$\boxed{\psi(x,y,z)=\left(\frac{2}{a}\right)^{3/2}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{a}y\right)\sin\left(\frac{n_z\pi}{a}z\right);\quad E=\frac{\pi^2\hbar^2}{2ma^2}(n_x^2+n_y^2+n_z^2);\quad n_x,n_y,n_z=1,2,3,\ldots}$$

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(b)

n_x	n_y	n_z	$(n_x^2+n_y^2+n_z^2)$
1	1	1	3
1	1	2	6
1	2	1	6
2	1	1	6
1	2	2	9
2	1	2	9
2	2	1	9
1	1	3	11
1	3	1	11
3	1	1	11
2	2	2	12
1	2	3	14
1	3	2	14
2	1	3	14
2	3	1	14
3	1	2	14
3	2	1	14

Energy	Degeneracy
$E_1 = 3\dfrac{\pi^2\hbar^2}{2ma^2};$	$d = 1$
$E_2 = 6\dfrac{\pi^2\hbar^2}{2ma^2};$	$d = 3.$
$E_3 = 9\dfrac{\pi^2\hbar^2}{2ma^2};$	$d = 3.$
$E_4 = 11\dfrac{\pi^2\hbar^2}{2ma^2};$	$d = 3.$
$E_5 = 12\dfrac{\pi^2\hbar^2}{2ma^2};$	$d = 1.$
$E_6 = 14\dfrac{\pi^2\hbar^2}{2ma^2};$	$d = 6.$

(c) The next combinations are: $E_7(322)$, $E_8(411)$, $E_9(331)$, $E_{10}(421)$, $E_{11}(332)$, $E_{12}(422)$, $E_{13}(431)$, and $E_{14}(333 \text{ and } 511)$. The degeneracy of E_{14} is $\boxed{4.}$ Simple combinatorics accounts for degeneracies of 1 ($n_x = n_y = n_z$), 3 (two the same, one different), or 6 (all three different). But in the case of E_{14} there is a numerical "accident": $3^2+3^2+3^2 = 27$, but $5^2+1^2+1^2$ is *also* 27, so the degeneracy is greater than combinatorial reasoning alone would suggest.

Problem 4.3

Eq. 4.32 $\Rightarrow Y_0^0 = \frac{1}{\sqrt{4\pi}} P_0^0(\cos\theta)$; Eq. 4.27 $\Rightarrow P_0^0(x) = P_0(x)$; Eq. 4.28 $\Rightarrow P_0(x) = 1$. $\boxed{Y_0^0 = \frac{1}{\sqrt{4\pi}}.}$

$$Y_2^1 = -\sqrt{\frac{5}{4\pi}\frac{1}{3\cdot 2}}\,e^{i\phi}P_2^1(\cos\theta); \quad P_2^1(x) = \sqrt{1-x^2}\frac{d}{dx}P_2(x);$$

$$P_2(x) = \frac{1}{4\cdot 2}\left(\frac{d}{dx}\right)^2 (x^2-1)^2 = \frac{1}{8}\frac{d}{dx}\left[2(x^2-1)2x\right] = \frac{1}{2}\left[x^2-1+x(2x)\right] = \frac{1}{2}\left(3x^2-1\right);$$

$$P_2^1(x) = \sqrt{1-x^2}\frac{d}{dx}\left[\frac{3}{2}x^2-\frac{1}{2}\right] = \sqrt{1-x^2}\,3x; \; P_2^1(\cos\theta) = 3\cos\theta\sin\theta. \; \boxed{Y_2^1 = -\sqrt{\frac{15}{8\pi}}\,e^{i\phi}\sin\theta\cos\theta.}$$

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Normalization: $\iint |Y_0^0|^2 \sin\theta \, d\theta \, d\phi = \frac{1}{4\pi}\left[\int_0^\pi \sin\theta \, d\theta\right]\left[\int_0^{2\pi} d\phi\right] = \frac{1}{4\pi}(2)(2\pi) = 1.$ ✓

$$\iint |Y_2^1|^2 \sin\theta \, d\theta \, d\phi = \frac{15}{8\pi}\int_0^\pi \sin^2\theta\cos^2\theta\sin\theta \, d\theta \int_0^{2\pi} d\phi = \frac{15}{4}\int_0^\pi \cos^2\theta(1-\cos^2\theta)\sin\theta \, d\theta$$

$$= \frac{15}{4}\left[-\frac{\cos^3\theta}{3} + \frac{\cos^5\theta}{5}\right]\Bigg|_0^\pi = \frac{15}{4}\left[\frac{2}{3} - \frac{2}{5}\right] = \frac{5}{2} - \frac{3}{2} = 1 \checkmark$$

Orthogonality: $\iint Y_0^{0*} Y_2^1 \sin\theta \, d\theta \, d\phi = -\frac{1}{\sqrt{4\pi}}\sqrt{\frac{15}{8\pi}}\left[\underbrace{\int_0^\pi \sin\theta\cos\theta\sin\theta \, d\theta}_{(\sin^3\theta/3)|_0^\pi = 0}\right]\left[\underbrace{\int_0^{2\pi} e^{i\phi} d\phi}_{(e^{i\phi}/i)|_0^{2\pi} = 0}\right] = 0.$ ✓

Problem 4.5

$$Y_l^l = (-1)^l\sqrt{\frac{(2l+1)}{4\pi}\frac{1}{(2l)!}}\, e^{il\phi}P_l^l(\cos\theta). \quad P_l^l(x) = (1-x^2)^{l/2}\left(\frac{d}{dx}\right)^l P_l(x).$$

$$P_l(x) = \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l, \quad \text{so } P_l^l(x) = \frac{1}{2^l l!}(1-x^2)^{l/2}\left(\frac{d}{dx}\right)^{2l}(x^2-1)^l.$$

Now $(x^2-1)^l = x^{2l} + \cdots$, where all the other terms involve powers of x *less* than $2l$, and hence give zero when differentiated $2l$ times. So

$$P_l^l(x) = \frac{1}{2^l l!}(1-x^2)^{l/2}\left(\frac{d}{dx}\right)^{2l} x^{2l}. \quad \text{But } \left(\frac{d}{dx}\right)^n x^n = n!, \quad \text{so } P_l^l = \frac{(2l)!}{2^l l!}(1-x^2)^{l/2}.$$

$$\therefore Y_l^l = (-1)^l\sqrt{\frac{(2l+1)}{4\pi(2l)!}}\, e^{il\phi}\frac{(2l)!}{2^l l!}(\sin\theta)^l = \boxed{\frac{1}{l!}\sqrt{\frac{(2l+1)!}{4\pi}}\left(-\frac{1}{2}e^{i\phi}\sin\theta\right)^l.}$$

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$$Y_3^2 = \sqrt{\frac{7}{4\pi}\cdot\frac{1}{5!}}\,e^{2i\phi}P_3^2(\cos\theta);\quad P_3^2(x) = (1-x^2)\left(\frac{d}{dx}\right)^2 P_3(x);\quad P_3(x) = \frac{1}{8\cdot 3!}\left(\frac{d}{dx}\right)^3 (x^2-1)^3.$$

$$P_3 = \frac{1}{8\cdot 3\cdot 2}\left(\frac{d}{dx}\right)^2\left[6x(x^2-1)^2\right] = \frac{1}{8}\frac{d}{dx}\left[(x^2-1)^2 + 4x^2(x^2-1)\right]$$
$$= \frac{1}{8}\left[4x(x^2-1) + 8x(x^2-1) + 4x^2\cdot 2x\right] = \frac{1}{2}\left(x^3 - x + 2x^3 - 2x + 2x^3\right) = \frac{1}{2}\left(5x^3 - 3x\right).$$

$$P_3^2(x) = \frac{1}{2}\left(1-x^2\right)\left(\frac{d}{dx}\right)^2\left(5x^3-3x\right) = \frac{1}{2}\left(1-x^2\right)\frac{d}{dx}\left(15x^2-3\right) = \frac{1}{2}(1-x^2)30x = 15x(1-x^2).$$

$$Y_3^2 = \sqrt{\frac{7}{4\pi}\frac{1}{5!}}\,15e^{2i\phi}\cos\theta\sin^2\theta = \boxed{\frac{1}{4}\sqrt{\frac{105}{2\pi}}\,e^{2i\phi}\sin^2\theta\cos\theta.}$$

Check that Y_l^l satisfies Eq. 4.18: Let $\frac{1}{l!}\sqrt{\frac{(2l+1)!}{4\pi}}\left(-\frac{1}{2}\right)^l \equiv A$, so $Y_l^l = A(e^{i\phi}\sin\theta)^l$.

$$\frac{\partial Y_l^l}{\partial\theta} = Ae^{il\phi}l(\sin\theta)^{l-1}\cos\theta;\quad \sin\theta\frac{\partial Y_l^l}{\partial\theta} = l\cos\theta Y_l^l;$$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_l^l}{\partial\theta}\right) = l\cos\theta\left(\sin\theta\frac{\partial Y_l^l}{\partial\theta}\right) - l\sin^2\theta Y_l^l = \left(l^2\cos^2\theta - l\sin^2\theta\right)Y_l^l.\quad \frac{\partial^2 Y_l^l}{\partial\phi^2} = -l^2 Y_l^l.$$

So the left side of Eq. 4.18 is $\left[l^2(1-\sin^2\theta) - l\sin^2\theta - l^2\right]Y_l^l = -l(l+1)\sin^2\theta\, Y_l^l$, which matches the right side.

Check that Y_3^2 satisfies Eq. 4.18: Let $B \equiv \frac{1}{4}\sqrt{\frac{105}{2\pi}}$, so $Y_3^2 = Be^{2i\phi}\sin^2\theta\cos\theta$.

$$\frac{\partial Y_3^2}{\partial\theta} = Be^{2i\phi}\left(2\sin\theta\cos^2\theta - \sin^3\theta\right);\quad \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_3^2}{\partial\theta}\right) = Be^{2i\phi}\sin\theta\frac{\partial}{\partial\theta}\left(2\sin^2\theta\cos^2\theta - \sin^4\theta\right)$$

$$= Be^{2i\phi}\sin\theta\left(4\sin\theta\cos^3\theta - 4\sin^3\theta\cos\theta - 4\sin^3\theta\cos\theta\right) = 4Be^{2i\phi}\sin^2\theta\cos\theta\left(\cos^2\theta - 2\sin^2\theta\right)$$

$= 4(\cos^2\theta - 2\sin^2\theta)Y_3^2.\quad \frac{\partial^2 Y_3^2}{\partial\phi^2} = -4Y_3^2.$ So the left side of Eq. 4.18 is

$$4(\cos^2\theta - 2\sin^2\theta - 1)Y_3^2 = 4(-3\sin^2\theta)Y_3^2 = -l(l+1)\sin^2\theta\, Y_3^2,$$

where $l = 3$, so it fits the right side of Eq. 4.18.

Problem 4.11

(a)

$$\text{Eq. 4.31} \Rightarrow \int_0^\infty |R|^2 r^2 dr = 1. \quad \text{Eq. 4.82} \Rightarrow R_{20} = \left(\frac{c_0}{2a}\right)\left(1-\frac{r}{2a}\right)e^{-r/2a}. \quad \text{Let } z \equiv \frac{r}{a}.$$

$$1 = \left(\frac{c_0}{2a}\right)^2 a^3 \int_0^\infty \left(1-\frac{z}{2}\right)^2 e^{-z} z^2\, dz = \frac{c_0^2 a}{4}\int_0^\infty \left(z^2 - z^3 + \frac{1}{4}z^4\right)e^{-z}\,dz = \frac{c_0^2 a}{4}\left(2-6+\frac{24}{4}\right) = \frac{a}{2}c_0^2.$$

$$\therefore \boxed{c_0 = \sqrt{\frac{2}{a}}.} \quad \text{Eq. 4.15} \Rightarrow \psi_{200} = R_{20}Y_0^0. \quad \text{Table 4.3} \Rightarrow Y_0^0 = \frac{1}{\sqrt{4\pi}}.$$

$$\therefore \psi_{200} = \frac{1}{\sqrt{4\pi}}\sqrt{\frac{2}{a}}\frac{1}{2a}\left(1-\frac{r}{2a}\right)e^{-r/2a} \Rightarrow \boxed{\psi_{200} = \frac{1}{\sqrt{2\pi a}}\frac{1}{2a}\left(1-\frac{r}{2a}\right)e^{-r/2a}.}$$

(b)

$$R_{21} = \frac{c_0}{4a^2}re^{-r/2a}; \quad 1 = \left(\frac{c_0}{4a^2}\right)^2 a^5 \int_0^\infty z^4 e^{-z}\,dz = \frac{c_0^2 a}{16}24 = \frac{3}{2}ac_0^2, \text{ so } \boxed{c_0 = \sqrt{\frac{2}{3a}}.}$$

$$R_{21} = \frac{1}{\sqrt{6a}}\frac{1}{2a^2}re^{-r/2a}; \quad \psi_{21\pm1} = \frac{1}{\sqrt{6a}}\frac{1}{2a^2}re^{-r/2a}\left(\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}\right) = \boxed{\mp\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}re^{-r/2a}\sin\theta e^{\pm i\phi};}$$

$$\psi_{210} = \frac{1}{\sqrt{6a}}\frac{1}{2a^2}re^{-r/2a}\left(\sqrt{\frac{3}{4\pi}}\cos\theta\right) = \boxed{\frac{1}{\sqrt{2\pi a}}\frac{1}{4a^2}re^{-r/2a}\cos\theta.}$$

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4.12 (c)

Eq. 4.62 $\Rightarrow v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$. Eq. 4.76 $\Rightarrow c_1 = \frac{2(3-5)}{(1)(6)} c_0 = -\frac{2}{3} c_0$.

$c_2 = \frac{2(4-5)}{(2)(7)} c_1 = -\frac{1}{7} c_1 = \frac{2}{21} c_0$; $c_3 = \frac{2(5-5)}{(3)(8)} c_2 = 0$.

$$v(\rho) = c_0 - \frac{2}{3} c_0 \rho + \frac{2}{21} c_0 \rho^2 = \boxed{\frac{c_0}{21}\left(21 - 14\rho + 2\rho^2\right).}$$ ✓