Answers to the Problems in Chapter 3

Problem 3.1.

(a and α are numbers)

$\partial\vartheta/\partial\vartheta^2 \sin\vartheta = -\sin\vartheta$

$\partial\vartheta/\partial\vartheta \sin^2\vartheta = 2\cos\vartheta \sin\vartheta$

$(\partial/\partial x + \alpha)\exp(-ax) = -a\exp(-ax) + \alpha\exp(-ax) = (-a + \alpha)\exp(-ax)$

$(x\partial/\partial x + \alpha)x^2 = 2x^2 + \alpha x^2 = (2 + \alpha)x^2$

$(x\partial/\partial x + y\partial/\partial y)\, xy = xy + yx = 2xy$

$xy(\partial/\partial x + \partial/\partial y)\, xy = xy(y + x)$

Problem 3.2.

Equation 3.6.2 gives the energy operator for an electron in a linear box as:

$$\hat{H} = -(\hbar^2/2m_e)\partial^2/\partial x^2$$

Applying this operator to the two wavefunctions we have:

$$\hat{H}\, e^{+inx} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}e^{+inx} = -\frac{\hbar^2}{2m_e}(+in)^2 e^{+inx} = \frac{n^2\hbar^2}{2m_e}e^{+inx}$$

$$\hat{H}\, e^{-inx} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}e^{-inx} = -\frac{\hbar^2}{2m_e}(-in)^2 e^{-inx} = \frac{n^2\hbar^2}{2m_e}e^{-inx}$$

Therefore $\exp(+inx)$ and $\exp(-inx)$ are eigenfunctions of $\hat{H}$ with eigenvalues of $n^2\hbar^2/2m_e$.

Problem 3.3.

A table of the required derivatives is useful.

Function Φ	1	$\cos\vartheta$	$3\cos^2\vartheta - 1$	$5\cos^3\vartheta - 3\cos\vartheta$
$\partial\Phi/\partial\vartheta$	0	$-\sin\vartheta$	$-6\sin\vartheta\cos\vartheta$	$3\sin\vartheta\,(1-5\cos^2\vartheta)$
$\partial^2\Phi/\partial\vartheta^2$	0	$-\cos\vartheta$	$6(\sin^2\vartheta-\cos^2\vartheta)$ $= 6(1-2\cos^2\vartheta)$	$3\cos\vartheta\,(11\sin^2\vartheta-4\cos^2\vartheta)$ $= 3\cos\vartheta\,(11-15\cos^2\vartheta)$

Using the derivatives from the table we find:

$$\hat{L}^2_\vartheta\Psi_s = \hat{L}^2_\vartheta\sqrt{\frac{1}{2}} = 0\Psi_s$$

$$\hat{L}^2_\vartheta\Psi_p = \hat{L}^2_\vartheta\sqrt{\frac{3}{2}}\cos\vartheta = \sqrt{\frac{3}{2}}\left(-\cos\vartheta - \cos\vartheta\right) = -2\Psi_p$$

$$\hat{L}^2_\vartheta\Psi_d = \hat{L}^2_\vartheta\sqrt{\frac{5}{8}}(3\cos^2\vartheta - 1) = \sqrt{\frac{5}{8}}\left(-6\cos^2\vartheta + 6[1-2\cos^2\vartheta]\right)$$

$$= \sqrt{\frac{5}{8}}(-18\cos^2\vartheta + 6) - \sqrt{\frac{5}{8}}6(3\cos^2\vartheta - 1) = -6\Psi_d$$

$$\hat{L}^2_\vartheta\Psi_f = \hat{L}^2_\vartheta\sqrt{\frac{7}{8}}(5\cos^3\vartheta - 3\cos\vartheta) = \sqrt{\frac{7}{8}}\{3\cos\vartheta(1-5\cos^2\vartheta) + 3\cos\vartheta(11-15\cos^2\vartheta)$$

$$= \sqrt{\frac{7}{8}}(3\cos\vartheta - 15\cos^3\vartheta + 33\cos\vartheta - 45\cos^3\vartheta) - 12\sqrt{\frac{7}{8}}(5\cos^3\vartheta - 3\cos\vartheta) = -12\Psi_f$$

From these results we see that the eigenvalues are 0, –2, –6 and –12 for s, p, d and f respectively, as required by the formula $l(l+1)$ for $l = 0, 1, 2$ and 3.

Problem 3.4.

a) Normalisation and orthogonality of Ψ_a and Ψ_b.

$$1.0 = N_a^2\int_0^L x(L-x)^2 dx = N_a^2\left[\frac{x^4}{4}-\frac{2Lx^3}{3}+\frac{L^2x^2}{2}\right]_0^L = N_a^2\frac{L^4}{12} \qquad \therefore N_a = \frac{2\sqrt{3}}{L^2}$$

$$1.0 = N_b^2\int_0^L x^2(L-x)^2 dx = N_b^2\left[\frac{x^5}{5}-\frac{2Lx^4}{4}+\frac{L^2x^3}{3}\right]_0^L = N_b^2\frac{L^5}{30} \qquad \therefore N_b = \sqrt{\frac{30}{L^5}}$$

$$N_aN_b\int_0^L x\sqrt{x}(L-x)^2 dx = N_aN_b\left[\frac{2x^{9/2}}{9}-\frac{4Lx^{7/2}}{7}+\frac{2L^2x^{5/2}}{5}\right]_0^L = N_aN_bL^{9/2}\frac{16}{315} = \frac{32\sqrt{10}}{105}$$

b) The expectation value of x for Ψ_a and Ψ_b.

$$\overline{x}_a = \frac{12}{L^4}\int_0^L \sqrt{x}(L-x)\hat{x}\sqrt{x}(L-x)dx = \frac{12}{L^4}\int_0^L x^2(L-x)^2dx \quad \text{because } \hat{x} = x.$$

$$= \frac{12}{L^4}\left[\frac{x^5}{5}-\frac{2Lx^4}{4}+\frac{L^2x^3}{3}\right]_0^L = \frac{2L}{5}$$

$$\overline{x}_b = \frac{30}{L^5}\int_0^L x(L-x)\hat{x}\, x(L-x)dx = \frac{30}{L^5}\int_0^L x^3(L-x)^2dx \quad \text{because } \hat{x} = x.$$

$$= \frac{30}{L^5}\left[\frac{x^6}{6}-\frac{2Lx^5}{5}+\frac{L^2x^4}{4}\right]_0^L = \frac{L}{2}$$

A good way to illustrate these two functions is to plot them on the same axes using a spread sheet. You will find the maximum value of Ψ_b is at x = L/2 whereas that of Ψ_a lies at x = L/3. This can also be shown by differentiating the functions and setting the derivatives equal to zero.

c) The values of $<\psi_b|\hat{x}^2|\psi_b>$ and $(<\psi_b|\hat{x}|\psi_b>)^2$

$$<\psi_b|\hat{x}^2|\psi_b> = \frac{30}{L^5}\int_0^L\{x^6-2Lx^5+L^2x^4\}dx = \frac{30L^7}{L^5}\cdot\frac{2}{210} = \frac{2L^2}{7}$$

$$(<\psi_b|\hat{x}|\psi_b>)^2 = \left(\frac{L}{2}\right)^2 = \frac{L^2}{4}$$

Problem 3.5.

$$E_b = \int_0^L \Psi_b^* \hat{H} \Psi_b dx = \frac{30}{L^5}\int_0^L x(x-L)\left(\frac{-\hbar^2}{2m_e}\right)\frac{\partial^2}{\partial x^2}x(x-L)dx = \frac{-30\hbar^2}{2m_e L^5}\int_0^L x(x-L)\cdot 2dx$$

$$= \frac{-30\hbar^2}{m_e L^5}\left[\frac{x^3}{3}-\frac{Lx^2}{2}\right]_0^L = \frac{5\hbar^2}{m_e L^2} = \frac{5h^2}{4\pi^2 m_e L^2}$$

The lowest exact energy is, $E_1 = h^2/8m_e L^2$.
Therefore $E_b/E_1 = (5h^2/4\pi^2 m_e L^2)\times(8m_e L^2/h^2) = 10/\pi^2 = 1.0132$

Problem 3.6.

I don't think that it is either necessary or possible to reproduce a quantitatively accurate energy-level diagram *here*. The important point to note is that (see Figure 3.6), for benzene the six π electrons fill the n = 0 and the two n = 1 levels, for naphthalene the two n = 2 levels are also filled and for anthracene the two n = 3 levels as well.

We also require the values of $m_e = 9.109\times10^{-31}$ kg and $\hbar = 1.0546\times10^{-34}$ J s from which we calculate that $\hbar^2/2m_e = 6.1044\times10^{-39}$ J^2 s^2 kg^{-1}.

	Benzene	Naphthalene	Anthracene
Ring circ:/pm	6×139 = 834	10×139 = 1390	14×139 = 1946
Ring radius (r)/pm	$834/2\pi = 132.7$	$1390/2\pi = 212.2$	$1946/2\pi = 309.7$
Radius^2/m^2	1.761×10^{-20}	4.893×10^{-20}	9.591×10^{-20}
$\hbar^2/2m_e r^2$/J^2 s^2 kg^{-1}	3.466×10^{-19}	1.248×10^{-19}	0.636×10^{-19}
Transition n→m	1→2	2→3	3→4
$m^2 - n^2$	3	5	7
ΔE/J	10.40×10^{-19}	6.24×10^{-19}	4.45×10^{-19}
para-band/J	9.55×10^{-19}	6.87×10^{-19}	5.24×10^{-19}