Chapter 3

Rotational motion and the hydrogen atom

Exercises

3.1

$$E = m_l^2(\hbar^2/2I) \text{ [eqn 3.6]}; \quad I = m_H R^2$$

$$E = m_l^2(\hbar^2/2m_H R^2)$$

$$m_H = 1.674 \times 10^{-27} \text{ kg}, \quad R = 160 \text{ pm}; \quad \hbar^2/2m_H R^2 = 1.30 \times 10^{-22} \text{ J}$$

Hence,

$$E = \underline{(1.30 \times 10^{-22} \text{ J})m_l^2}$$

3.2 Using the energy levels from Exercise 3.1, we obtain

$$\Delta E = (1.30 \times 10^{-22} \text{ J})(1 - 0) = 1.30 \times 10^{-22} \text{ J}$$

$$\lambda = hc/\Delta E = 1.53 \times 10^{-3} \text{ m} = \underline{1.53 \text{ mm}}$$

This wavelength corresponds to microwave radiation.

Exercise: Calculate the effect of deuteration on E and $\lambda(1 \leftarrow 0)$.

3.3 $x = r \cos \phi, \quad y = r \sin \phi, \quad r = (x^2 + y^2)^{1/2}$

$$l_z = \frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$= \frac{\hbar}{\mathrm{i}}\left(x\left\{\frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi}\right\} - y\left\{\frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}\right\}\right)$$

$$= \frac{\hbar}{\mathrm{i}}\left(\left\{\frac{xy}{r}\frac{\partial}{\partial r} + x\frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi}\right\} - \left\{y\frac{x}{r}\frac{\partial}{\partial r} + y\frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}\right\}\right)$$

$$= \frac{\hbar}{\mathrm{i}}\left(x\frac{\partial \phi}{\partial y} - y\frac{\partial \phi}{\partial x}\right)\frac{\partial}{\partial \phi}$$

$$= \frac{\hbar}{\mathrm{i}}\left(\frac{x}{\partial y/\partial \phi} - \frac{y}{\partial x/\partial \phi}\right)\frac{\partial}{\partial \phi}$$

$$= \frac{\hbar}{\mathrm{i}}\left(\frac{r\cos\phi}{r/\cos\phi} + \frac{r\sin\phi}{r/\sin\phi}\right)\frac{\partial}{\partial \phi} = \underline{\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \phi}}$$

3.4

$$\int_0^{2\pi} \phi_{m_l'}^{*}\phi_{m_l}\,\mathrm{d}\phi = (1/2\pi)\int_0^{2\pi} \mathrm{e}^{\mathrm{i}(m_l - m_l')\phi}\mathrm{d}\phi$$

$$= (1/2\pi)\left\{\frac{\mathrm{e}^{2\mathrm{i}(m_l - m_l')\pi} - 1}{(m_l - m_l')\mathrm{i}}\right\} = 0 \quad \text{if } m_l' \neq m_l$$

$$[\mathrm{e}^{2\mathrm{i}n\pi} = 1, n \text{ an integer}]$$

(Note that when $m_l' = m_l$ the integral has the value 2π.)

Exercise: Normalize the wavefunction $\mathrm{e}^{\mathrm{i}\phi}\cos\beta + \mathrm{e}^{-\mathrm{i}\phi}\sin\beta$, and find an orthogonal linear combination of $\mathrm{e}^{+\mathrm{i}\phi}$ and $\mathrm{e}^{-\mathrm{i}\phi}$.

3.5 The moment of inertia of a solid uniform disc of mass M and radius R is

$$I = \tfrac{1}{2}MR^2; \quad \text{hence } I = 2.5 \times 10^{-4}\ \mathrm{kg\ m^2}$$

Then

$$E = m_l^2(\hbar^2/2I) = \underline{(2.2\times10^{-65}\ \text{J})m_l^2}$$

The rotation rate is 100 Hz. Hence $\omega = 2\pi\nu = 628\ \text{s}^{-1}$. The angular momentum is $I\omega =$ 0.16 kg m^2 s^{-1}. If this is set equal to $|m_l|\hbar$ we require $|m_l| = 1.5\times10^{33}$. Since the disc rotates anticlockwise when seen from below, m_l is negative. Hence, $\underline{m_l = -1.5\times10^{33}}$.

Exercise: How much more energy is required to raise the disc into its next rotational state?

3.6 See Fig. 3.1. We have plotted

$$\text{re}\ \phi_{m_l} = (1/2\pi)^{1/2}\cos m_l\phi = \begin{cases}(1/2\pi)^{1/2}\cos 3\phi & \text{for } m_l = 3\\ (1/2\pi)^{1/2}\cos 4\phi & \text{for } m_l = 4\end{cases}$$

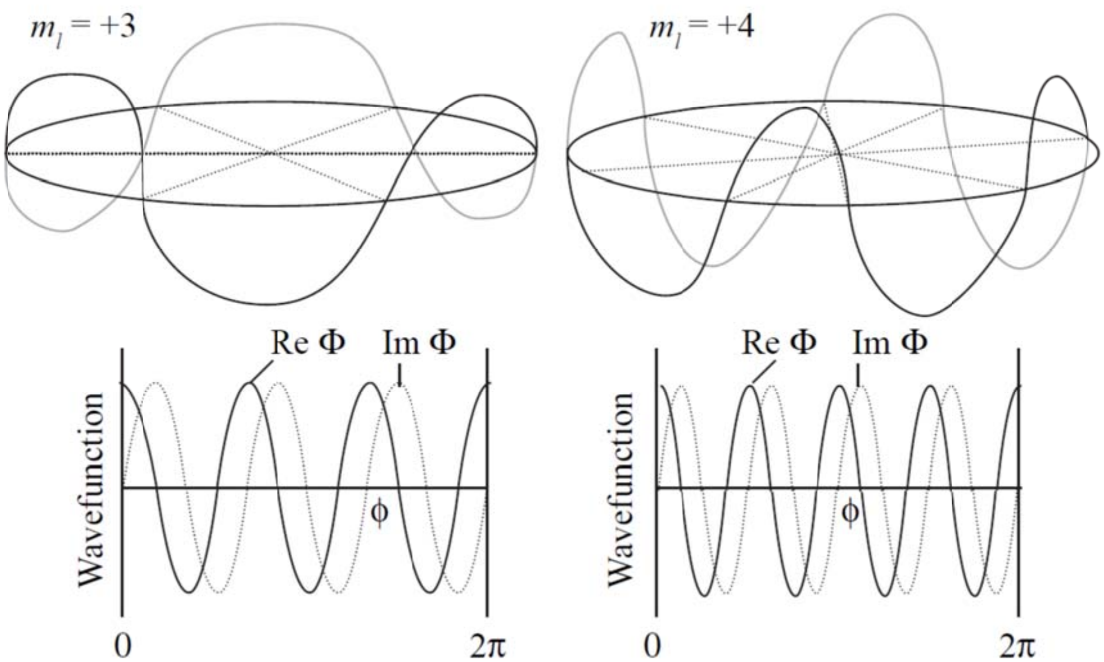

Figure 3.1: A representation of the amplitudes and phases of the wavefunction of a particle on a ring (red, real; green, imaginary).

Exercise: Superimpose the imaginary parts of ϕ_{m_l} on the diagrams. Draw re ϕ for the superposition $e^{i\phi}\cos\beta + e^{-i\phi}\sin\beta$.

3.7 The Schrödinger equation is given in eqn 3.31:

$$\Lambda^2\psi = -(2IE/\hbar^2)\psi\,; \quad \Lambda^2 = (1/\sin^2\theta)(\partial^2/\partial\phi^2) + (1/\sin\theta)(\partial/\partial\theta)\sin\theta(\partial/\partial\theta)$$

Write $\psi = \Theta\Phi$; then with $\Theta' = d\Theta/d\theta$ and $\Phi' = d\Phi/d\phi$, etc.

$$(1/\sin^2\theta)\Theta\Phi'' + (1/\sin\theta)\Phi(d/d\theta)\sin\theta\,\Theta' = -(2IE/\hbar^2)\Theta\Phi$$

$$\Phi''/\Phi + (1/\Theta)\sin\theta(d/d\theta)\sin\theta\,\Theta' = -(2IE/\hbar^2)\sin^2\theta$$

Write $\Phi''/\Phi = -m_l^2$, a constant; then

$$(1/\Theta)\sin\theta(d/d\theta)\sin\theta\,\Theta' = m_l^2 - (2IE/\hbar^2)\sin^2\theta$$

Because $(d/d\theta)\sin\theta\,\Theta' = \Theta'\cos\theta + \Theta''\sin\theta$, this rearranges into

$$\Theta''\sin^2\theta + \Theta'\sin\theta\cos\theta = \{m_l^2 - (2IE/\hbar^2)\sin^2\theta\}\Theta$$

Exercise: Identify this equation in M. Abramowitz and I.A. Stegun, *Handbook of mathematical functions*, and wite down its solutions.

3.8 The Schrödinger equation is

$$\Lambda^2\psi = -(2IE/\hbar)^2\psi \quad \text{[eqn 3.31]}$$

Write $\psi = \Theta(\theta)\Phi(\phi)$, $\Lambda^2 = \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\phi^2} + \dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\sin\theta\dfrac{\partial}{\partial\theta}$ [eqn 3.29], and $2IE/\hbar^2 = \varepsilon^2$;

then

$$\frac{1}{\sin^2\theta}\Theta\frac{d^2\Phi}{d\phi^2} + \frac{\Phi}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} = -\varepsilon^2\Phi\Theta$$

Divide through by $\Theta\Phi$ and multiply through by $\sin^2\theta$:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon^2\sin^2\theta = 0$$

Write $\dfrac{1}{\Phi}\dfrac{d^2\Phi}{d\phi^2} = -m_l^2$, so $\dfrac{d^2\Phi}{d\phi^2} = -m_l^2\Phi$ which implies that

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon^2\sin^2\theta = m_l^2$$

and hence that

$$\sin\theta\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon^2\sin^2\theta\Theta - m_l^2\Theta = 0$$

and the equation is separable.

Exercise: Is the equation separable if $V(\theta, \phi) = af(\theta) + bg(\phi)$?

3.9 It is sufficient to show that the Y_{lm_l} satisfy $\Lambda^2 Y_{lm_l} = -l(l+1)Y_{lm_l}$ [eqn 3.33].

$Y_{11} = -\frac{1}{2}(3/2\pi)^{1/2}\sin\theta\, e^{i\phi}$

$$\Lambda^2 \sin\theta\, e^{i\phi} = (1/\sin^2\theta)(\partial^2/\partial\phi^2)\sin\theta\, e^{i\phi} + (1/\sin\theta)(\partial/\partial\theta)\sin\theta(\partial/\partial\theta)\sin\theta\, e^{i\phi}$$

$$= -(1/\sin\theta)e^{i\phi} + (1/\sin\theta)e^{i\phi}(d/d\theta)\sin\theta\cos\theta$$

$$= -(1/\sin\theta)e^{i\phi} + (1/\sin\theta)e^{i\phi}(\cos^2\theta - \sin^2\theta)$$

$$= -(1/\sin\theta)e^{i\phi} + (1/\sin\theta)e^{i\phi}(1 - 2\sin^2\theta) = -2\sin\theta\, e^{i\phi}$$

Hence, $\Lambda^2 Y_{11} = -2Y_{11}$, in accord with $l = 1$.

$Y_{20} = \frac{1}{4}(5/\pi)^{1/2}(3\cos^2\theta - 1)$

$$\Lambda^2(3\cos^2\theta - 1) = (1/\sin\theta)(d/d\theta)\sin\theta(d/d\theta)(3\cos^2\theta - 1)$$

$$= -6(1/\sin\theta)(d/d\theta)\sin^2\theta\cos\theta$$

$$= -6(1/\sin\theta)\{2\sin\theta\cos^2\theta - \sin^3\theta\}$$

$$= -6\{2\cos^2\theta - \sin^2\theta\} = -6(3\cos^2\theta - 1)$$

Hence, $\Lambda^2 Y_{20} = -6Y_{20}$, in accord with $l = 2$.

3.10

$$\int |Y_{11}|^2\, d\tau = \tfrac{1}{4}(3/2\pi)\int_0^{\pi}\sin^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi$$

$$= \tfrac{3}{4}\int_{-1}^{1}(1-x^2)dx\; [x = \cos\theta] = 1$$

$$\int |Y_{20}|^2\, d\tau = \tfrac{1}{16}(5/\pi)\int_0^{\pi}(3\cos^2\theta - 1)^2\sin\theta d\theta\int_0^{2\pi}d\phi$$

$$= \tfrac{5}{8}\int_{-1}^{1}(3x^2-1)^2 dx = 1$$

$$\int Y_{11}^{*}Y_{20}d\tau \propto \int_0^{2\pi}e^{-i\phi}d\phi = 0$$

Exercise: Repeat the calculation for Y_{21} and Y_{31}.

3.11 From eqn 3.44, $E = J(J + 1)(\hbar^2/2I) = (1.30 \times 10^{-22}\ \text{J})J(J + 1)$ [Exercise 3.1]. Draw up the following Table, using degeneracy $g_J = 2J + 1$:

J	$E/(10^{-22}\ \text{J})$	g_J
0	0	1
1	2.60	3
2	7.80	5

3.12 Using the energies in Exercise 3.11, we find

$$\Delta E(1 - 0) = 2.60 \times 10^{-22}\ \text{J}$$

$$\lambda(1 - 0) = hc/\Delta E(1 - 0) = 7.64 \times 10^{-4}\ \text{m} = \underline{0.764\ \text{mm}}\ (\underline{\text{far infrared}})$$

Exercise: Calculate the same quantities for the deuterated species.

3.13 See Fig. 3.2. From Problem 3.11, when $l = 3$ and $m_l = 0$, $\theta = 90°$, and the angular momentum vector lies in the equatorial plane; therefore $|Y|^2$ will have maxima on the z-axis, as seen in Fig. 3.2. We also see from Problem 3.11 that as $|m_l|$ increases, the deviation of θ from 90° increases; as the projection of the angular momentum vector on the z-axis increases, $|Y|^2$ becomes larger in the equatorial plane.

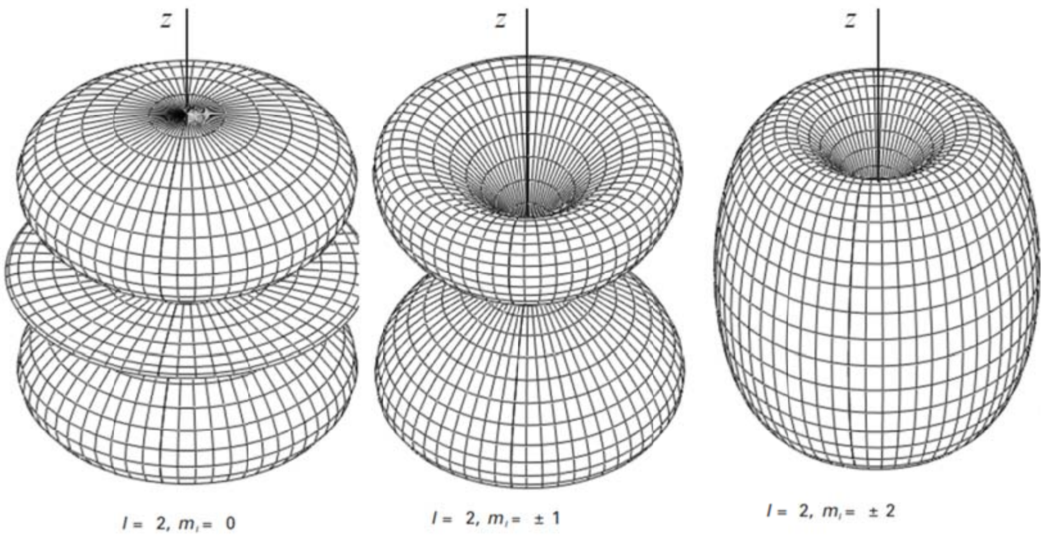

Figure 3.2: A representation of the wavefunctions and the location of the angular nodes for a particle on a sphere with $l = 2$.

Exercise: Draw the corresponding diagrams for $l = 4$.

3.14 Start with eqn 3.45

$$-\frac{\hbar^2}{2m}\nabla^2\psi = -\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2\right)\psi = E\psi$$

and use the form of the wavefunction in eqn 3.46:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

This yields (using eqn 3.33):

$$\begin{aligned} -\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}rRY + \frac{1}{r^2}\Lambda^2 RY\right) &= -\frac{\hbar^2}{2m}\left(\frac{Y}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}rR + \frac{R}{r^2}\Lambda^2 Y\right) \\ &= -\frac{\hbar^2}{2m}\left(\frac{Y}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}rR + \frac{-Rl(l+1)}{r^2}Y\right) \\ &= ERY \end{aligned}$$

Dividing the last two lines above by Y and multiplying by $-\hbar^2/2m$ results in

$$\frac{1}{r}\frac{\mathrm{d}^2(rR)}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2}R = -\frac{2m}{\hbar^2}ER$$

which is eqn 3.47a. Writing $k^2 = 2mE/\hbar^2$ and $z = kr$ gives eqn 3.47b.

3.15 Use eqn 3.57 in the form (with $Z = 1$)

$$(1/r)(\mathrm{d}^2/\mathrm{d}r^2)rR + \{(\mu e^2/2\pi\varepsilon_0\hbar^2 r) - l(l+1)/r^2\}R = -(2\mu E/\hbar^2)R$$

with

$$E = -(\mu e^4/32\pi^2\varepsilon_0^2\hbar^2)(1/n^2) \quad \text{[eqn 3.66]}$$

(a) R_{10} : $n = 1$, $l = 0$; $E = -(\mu e^4/32\pi^2\varepsilon_0^2\hbar^2)$; $l = 0$

$$(1/r)(\mathrm{d}^2/\mathrm{d}r^2)rR_{10} + (\mu e^2/2\pi\varepsilon_0\hbar^2)(1/r)R_{10} = -(2\mu E/\hbar^2)R_{10}$$

Then, because $R_{10} \propto \mathrm{e}^{-r/a}$,

$$(\mathrm{d}^2/\mathrm{d}r^2)rR_{10} = 2R'_{10} + rR''_{10} = -(2/a)R_{10} + (r/a^2)R_{10}$$

$$-(2/ar) + (1/a^2) + (\mu e^2/2\pi\varepsilon_0\hbar^2)(1/r) = -(2\mu E/\hbar^2)$$

But $2/a = \mu e^2/2\pi\varepsilon_0\hbar^2$; hence $1/a^2 = -2\mu E/\hbar^2$, so $E = -\hbar^2/2\mu a^2$, as required.

(b) $R_{20} \propto (2-\rho)\mathrm{e}^{-\rho/2} = (2 - r/a)\mathrm{e}^{-r/2a}$; $E_{2s} = -\frac{1}{4}(\hbar^2/2\mu a^2)$

$$(\mathrm{d}^2/\mathrm{d}r^2)rR_{20} = 2R'_{20} + rR''_{20} \propto \{-(4/a) + (5r/2a^2) - (r^2/4a^3)\}\mathrm{e}^{-r/2a}$$

$$-(4/ar) + (5/2a^2) - (r/4a^3) + \underbrace{(\mu e^2/2\pi\varepsilon_0\hbar^2)}_{2/a}(1/r)(2 - r/a)$$

$$= -(2\mu E/\hbar^2)(2 - r/a)$$

$$-(4/ar) + (5/2a^2) - (r/4a^3) + (4/ar) - (2/a^2) = (1/2a^2) - (r/4a^3)$$

$$= (1/4a^2)(2 - r/a)$$

Hence, $-2\mu E/\hbar^2 = 1/4a^2$, as required.

(c) $R_{31} \propto (4-\rho)\rho e^{-\rho/2}$, $\rho = 2r/3a$, $l(l+1) = 2$; then proceed as above, obtaining $-2\mu E/\hbar^2 = 1/9a^2$.

Exercise: Confirm that R_{11} and R_{30} satisfy the wave equation.

3.16 The radial nodes are at the zeros of R_{nl}; denote them r_0.

(a) ψ_{2s} : $R_{2s} = 0$ when $2 - \rho = 0$; $\rho = r/a$.

Hence, $r_0/a = 2$ or $\underline{r_0 = 2a = 105.8\text{ pm}}$

(b) ψ_{3s} : $R_{3s} = 0$ when $6 - 6\rho + \rho^2 = 0$, $\rho = 2r/3a$. The solutions are

$$\rho_0 = 3 \pm \sqrt{3}\text{, or } r_0 = (3 \pm \sqrt{3})(3a/2) = \underline{1.90a,\ 7.10a \text{ or } 101\text{ pm},\ 376\text{ pm}}$$

Exercise: Find **(a)** the Z-dependence of these node locations, **(b)** the location of the radial nodes of (i) 2p-orbitals, (ii) 4s-orbitals. [A general point in this connection is that A & S lists the locations of zeros of many functions.]

3.17

$$\int \psi_{2s}^{*}\psi_{1s}\,d\tau \propto \int_0^{\infty} R_{20}R_{10}r^2 dr \propto \int_0^{\infty} (2 - Zr/a)e^{-Zr/2a}e^{-Zr/a}r^2 dr$$

$$\propto \int_0^{\infty} (2r^2 - Zr^3/a)e^{-3Zr/2a}dr = (2^5a^3/3^3Z^3) - (2^5a^3/3^3Z^3) = 0$$

Exercise: Confirm that ψ_{2s} and ψ_{3s} are orthogonal.

3.18 Evaluate $|\psi_{ns}|^2 = |Y_{00}|^2 R_{n0}^2 = R_{n0}^2/4\pi$.

$$\psi_{1s}^2(0) = 4(Z/a)^3/4\pi = \underline{(1/\pi)(Z/a)^3} = 2.15 \times 10^{-6}\ \text{pm}^{-3} \text{ for hydrogen}$$

$$\psi_{2s}^2(0) = \tfrac{1}{2}(Z/a)^3/4\pi = \underline{(1/8\pi)(Z/a)^3} = 2.69 \times 10^{-7}\ \text{pm}^{-3}$$

$$\psi_{3s}^2(0) = (6/9\sqrt{3})^2(Z/a)^3/4\pi = \underline{(1/27\pi)(Z/a)^3} = 7.96 \times 10^{-8}\ \text{pm}^{-3}$$

Exercise: Evalute the probability density for a 4s-orbital.

3.19

$$\langle 1/r^3\rangle = \int_0^\infty (1/r^3)R_{21}^2 r^2\text{d}r = \int_0^\infty (1/r)R_{21}^2\text{d}r$$

$$= (Z/a)^3(1/2\sqrt{6})^2(Z/a)^2\int_0^\infty (1/r)r^2\text{e}^{-Zr/a}\text{d}r = \underline{(1/24)(Z/a)^3}$$

For a hydrogen atom, this is 2.82×10^{-7} pm^{-3}.

The *general expression* is

$$\langle 1/r^3\rangle_{nlm_l} = \frac{(Z/a)^3}{n^3 l(l+\frac{1}{2})(1+1)}$$

Exercise: Evaluate **(a)** $\langle 1/r^2\rangle$ for a 2p$_z$-orbital, **and (b)** $\langle(1 - 3\cos^2\theta)/r^3\rangle$ for (i) a 2s-orbital, (ii) a 2p$_z$-orbital.

3.20 $I = hcR$ (i.e. $I = -E_{1s}$)

$$I(\text{H}) - I(\text{D}) = hc(R_\text{H} - R_\text{D}) = hc(\mu_\text{H} - \mu_\text{D})e^4/8h^3\varepsilon_0^2 c$$

$$= (\mu_\text{H} - \mu_\text{D})hcR_\infty/m_\text{e}$$

$$\mu_\text{H} = m_\text{e}m_\text{p}/(m_\text{e} + m_\text{p}),\ \mu_\text{D} = m_\text{e}m_\text{d}/(m_\text{e} + m_\text{d})$$

$$(\mu_{\rm H} - \mu_{\rm D})/m_{\rm e} = \frac{m_{\rm p}}{m_{\rm e}+m_{\rm p}} - \frac{m_{\rm d}}{m_{\rm e}+m_{\rm d}}$$

$$= \frac{m_{\rm e}(m_{\rm p}-m_{\rm d})}{(m_{\rm e}+m_{\rm p})(m_{\rm e}+m_{\rm d})} = \frac{m_{\rm e}(m_{\rm H}-m_{\rm D})}{m_{\rm H}m_{\rm D}}$$

$m_{\rm e} = 9.109\ 38 \times 10^{-31}$ kg, $m_{\rm H} = 1.6735 \times 10^{-27}$ kg, $m_{\rm D} = 3.3443 \times 10^{-27}$ kg;

$(\mu_{\rm H} - \mu_{\rm D})/m_{\rm e} = -2.7195 \times 10^{-4}$

Consequently,

$$I(\mathrm{H}) - I(\mathrm{D}) = -(2.7195 \times 10^{-4}) \times (2.1799 \times 10^{-18}\ \mathrm{J})$$

$$= -5.9282 \times 10^{-22}\ \mathrm{J} = \underline{-0.357\ \mathrm{kJ\ mol^{-1}}}(-3.70\ \mathrm{meV})$$

The experimental values are 109 678.758 $\mathrm{cm^{-1}}$ and 109 708.596 $\mathrm{cm^{-1}}$, so

$$\{I(\mathrm{H}) - I(\mathrm{D})\}/\mathrm{cm^{-1}} = -29.838\ \mathrm{cm^{-1}}(-0.357\ \mathrm{kJ\ mol^{-1}})$$

Exercise: Evaluate the ionization energy of positronium on the basis of the ionization energy of ^{1}H.

3.21 For a given value of l there are $2l + 1$ values of m_l. For a given n there are n values of l. Hence, the degeneracy g is

$$g = \sum_{l=0}^{n-1}(2l+1) = n(n-1) + n = \underline{n^2}$$

Exercise: Calculate the average value of m_l^2 for an atom in a state with principal quantum number equal to n but with l, m_l unspecified.

Problems

3.1 Write $x = r\cos\phi$, $y = r\sin\phi$, $r = (x^2 + y^2)^{1/2}$, $\phi = \arctan(y/x)$. Then

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial f}{\partial \phi}\frac{\partial \phi}{\partial x} = \left(\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial \phi}\right)f$$

or

$$\frac{\partial}{\partial x} = \cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial \phi}$$

Similarly,

$$\frac{\partial}{\partial y} = \sin\phi\frac{\partial}{\partial r} + \frac{\cos\phi}{r}\frac{\partial}{\partial \phi}$$

Therefore,

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) = \left(\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial \phi}\right)\left(\cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial \phi}\right)f$$

$$= \left\{\cos^2\phi\frac{\partial^2}{\partial r^2} - \sin\phi\cos\phi\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial \phi}\right)\right.$$

$$\left. - \frac{\sin\phi}{r}\frac{\partial}{\partial \phi}\left(\cos\phi\frac{\partial}{\partial r}\right) + \frac{\sin\phi}{r^2}\frac{\partial}{\partial \phi}\left(\sin\phi\frac{\partial}{\partial \phi}\right)\right\}f$$

That is,

$$\frac{\partial^2}{\partial x^2} = \cos^2\phi\frac{\partial^2}{\partial r^2} - \frac{2\sin\phi\cos\phi}{r}\frac{\partial^2}{\partial r\partial \phi} + \frac{\sin^2\phi}{r^2}\frac{\partial^2}{\partial \phi^2}$$

$$+ \frac{\sin^2\phi}{r}\frac{\partial}{\partial r} + \frac{2\sin\phi\cos\phi}{r^2}\frac{\partial}{\partial \phi}$$

Similarly,

$$\frac{\partial^2}{\partial y^2} = \sin^2\phi\frac{\partial^2}{\partial r^2} + \frac{2\sin\phi\cos\phi}{r}\frac{\partial^2}{\partial r\partial\phi} + \frac{\cos^2\phi}{r^2}\frac{\partial^2}{\partial\phi^2}$$

$$+\frac{\cos^2\phi}{r}\frac{\partial}{\partial r} - \frac{2\sin\phi\cos\phi}{r^2}\frac{\partial}{\partial\phi}$$

It then follows that

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}$$

as in eqn 3.2.

Exercise: Derive an expression for ∇^2 in cylindrical polar coordinates, $x = r\cos\phi$, $y = r\sin\phi$, z.

3.4

$$\langle r\rangle = \int_0^\infty rP(r)\mathrm{d}r = \int_0^\infty R^2r^3\mathrm{d}r \qquad \text{[eqn 3.69]}$$

$$\langle 1/r\rangle = \int_0^\infty r^{-1}P(r)\mathrm{d}r = \int_0^\infty R^2r\mathrm{d}r \qquad \text{[eqn 3.69]}$$

As in Problem 3.3,

(a)

$$\langle r\rangle = \left(\frac{Z^3}{243a_0^3}\right)\left(\frac{3a_0}{2Z}\right)^4\int_0^\infty(6-6\rho+\rho)^2\rho^3\mathrm{e}^{-\rho}\mathrm{d}\rho = \underline{\frac{27a_0}{2Z}}$$

$$\langle 1/r\rangle = \left(\frac{Z^3}{243a_0^3}\right)\left(\frac{3a_0}{2Z}\right)^2\int_0^\infty(6-6\rho+\rho^2)^2\rho\mathrm{e}^{-\rho}\mathrm{d}\rho = \underline{\frac{Z}{9a_0}}$$

(b)

$$\langle r\rangle = \left(\frac{Z^3}{81\times 6a_0^3}\right)\left(\frac{3a_0}{2Z}\right)^4 \int_0^\infty (4-\rho)^2\rho^5 e^{-\rho}d\rho = \underline{\frac{25a_0}{2Z}}$$

$$\langle 1/r\rangle = \left(\frac{Z^3}{81\times 6a_0^3}\right)\left(\frac{3a_0}{2Z}\right)^2 \int_0^\infty (4-\rho)^2\rho^3 e^{-\rho}d\rho = \underline{\frac{Z}{9a_0}}$$

We have used the integrals

$$\int_0^\infty (6-6x+x^2)^2 x^3 e^{-x}dx = 648$$

$$\int_0^\infty (6-6x+x^2)^2 x e^{-x}dx = 12$$

$$\int_0^\infty (4-x)^2 x^5 e^{-x}dx = 1200$$

$$\int_0^\infty (4-x)^2 x^3 e^{-x}dx = 24$$

as obtained by using the symbolic integration procedure in mathematical software.

Exercise: Evaluate $\langle 1/r^3\rangle$ for each orbital.

3.7 Use available mathematical software to find zeroes of the Bessel functions; in particular find values of z such that $J(z) = 0$. With z identified as ka (see eqn 3.25), the energies can be expressed in terms of z as

$$E = \frac{k^2\hbar^2}{2m} = \frac{z^2\hbar^2}{2ma^2}$$

3.10 **(a)** The moment of inertia of a sphere is $I = \frac{2}{5}MR^2$ [Problem 10.1]; therefore, on writing this value as Mr^2, we see that $r = (2/5)^{1/2}R$.

(b) Consider rotation perpendicular to the axis. The mass of a disc of thickness dx, radius R is $\pi\rho R^2 dx$ where ρ is the mass density of the disc. Therefore,

$$I = \int_{-l/2}^{l/2} \pi\rho R^2 x^2 dx = \tfrac{1}{12}\pi\rho R^2 l^3$$

The mass of the cylinder is $M = \pi\rho R^2 l$; therefore $I = \tfrac{1}{12} Ml^2$.

Setting this value equal to $M r^2$ gives $\underline{r = l/(12)^{1/2}}$

3.13 The wavefunction for a particle in a spherical cavity is given by

$$\psi = Nj(r)Y(\theta,\phi)$$

The ground-state wavefunction is therefore given by $Nj_0 Y_{0,0}$. (i) Proceeding as in Problem 3.8, (ii) using eqn 3.48 for j_0 with $k = \pi/a$ (Table 3.3) and (iii) recognizing that the volume element contains a factor of r^2dr, we write the probability for finding the particle within a sphere of radius a/2 as:

$$P = \frac{\int_0^{a/2} \frac{\sin^2 kr}{(kr)^2} r^2 dr}{\int_0^{a} \frac{\sin^2 kr}{(kr)^2} r^2 dr} = \frac{\int_0^{a/2} \sin^2 kr\, dr}{\int_0^{a} \sin^2 kr\, dr} = \frac{\int_0^{a/2} \sin^2(\frac{\pi r}{a})\, dr}{\int_0^{a} \sin^2(\frac{\pi r}{a})\, dr}$$

Using mathematical software or standard integration tables yields $\underline{P = ½}$.

3.16 Refer to Fig. 3.5. The rotation (a)→(b) corresponds to 3p becoming 3d, the rotation (b)→(c) corresponds to 3d becoming 3s.

Exercise: Identify the patterning of the ball that would account for the degeneracy of two-dimensional f-orbitals.

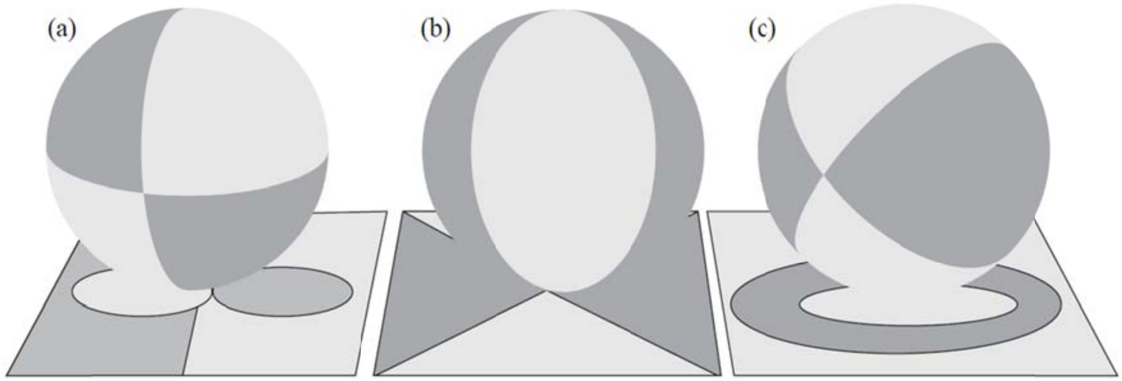

Figure 3.5: The projections of a patterned sphere on a plane (the projection stems from the North Pole).