CHEM344 HW#7
Due: Fri, Mar 14@2pm BEFORE CLASS!

**HW to be handed in:**
Atkins
Chapter 8: Exercises: 8.11(b), 8.16(b), 8.19(b),
Problems: 8.2, 8.4, 8.12, 8.34,
Chapter 9: Exercises: 9.5(b), 9.7(b),

**Extra (do not hand in):**
Chapter 8: Exercises: 8.10(b), 8.14(b), 8.15(b), 8.17(b), 8.21(b), 8.23(b),
Problems: 8.26, 8.38,
Chapter 9: Exercises: 9.6(b), 9.8(b), 9.12(b),

1. [8.11(b)] Calculate the wavelength of a photon needed to excite a transition between neighbouring energy levels of a harmonic oscillator of effective mass equal to that of an oxygen atom (15.9949mu) and force constant 544 N $m^{-1}$.

The requirement for a transition to occur is that $\Delta E(\text{system}) = E(\text{photon})$,

so $\Delta E(\text{system}) = \hbar\omega\,[8.25] = E(\text{photon}) = h\nu = \dfrac{hc}{\lambda}$

Therefore, $\dfrac{hc}{\lambda} = \dfrac{h\omega}{2\pi} = \left(\dfrac{h}{2\pi}\right) \times \left(\dfrac{k_\mathrm{f}}{m}\right)^{1/2}$ [8.24]

Note: by using mass of 16 this is like O  atom vibrating against metal plane (catalyst), not $O_2$. To describe diatomic, need reduced mass

$$\lambda = 2\pi c\left(\frac{m}{k_\mathrm{f}}\right)^{1/2} = (2\pi) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}}) \times \left(\frac{15.9949 \times 1.6605 \times 10^{-27}\ \mathrm{kg}}{544\ \mathrm{N\ m^{-1}}}\right)^{1/2}$$

$$= 1.32 \times 10^{-5}\ \mathrm{m} = \boxed{13.2\ \mu\mathrm{m}}$$

2. [8.16(b)] What are the most probable displacements of a harmonic oscillator with v = 3?

The most probable displacements are the values of $x$ that maximize $\psi^2$. As noted in Exercise 8.6(b), maxima in $\psi^2$ correspond to maxima *and* minima in $\psi$ itself, so one can solve this exercise by finding all points where $\frac{d\psi}{dx} = 0$. From eqn 8.27 and Table 8.1, the wavefunction is

This means positive and negative extrema of $\psi$

$$\psi_3(x) = N_3 H_3(y)\exp\left(-\tfrac{1}{2}y^2\right) \quad \text{with} \quad y = \frac{x}{\alpha},\ \alpha = \left(\frac{\hbar^2}{mk_\mathrm{f}}\right)^{1/4},\ \text{and } H_3(y) = 8y^3 - 12y$$

$$\frac{d\psi_3}{dx} = \frac{dy}{dx}\frac{d\psi_3}{dy} = \frac{N_3}{\alpha}\left\{(24y^2 - 12)\exp\left(-\tfrac{1}{2}y^2\right) - (8y^3 - 12y)y\exp\left(-\tfrac{1}{2}y^2\right)\right\} = 0$$

Dividing through by constants and the exponential functions yields

$$-8y^4 + 36y^2 - 12 = 0$$

Divide out anything common since goes into 0 on other side

Letting $z = y^2$ (and dividing through by −4) yields the quadratic equation

$$2z^2 - 9z + 3 = 0$$

Quadratics easier to solve

so $$z = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{9 \pm \sqrt{9^2 - 2\times 3\times 4}}{2\times 2} = \frac{9 \pm \sqrt{57}}{4}$$

Evaluating the result numerically yields $z = 4.14$ or $0.363$, so $y = \pm 2.03$ or $\pm 0.602$, therefore $x = \boxed{0, \pm 2.03\alpha, \text{ or } \pm 0.602\alpha}$.

3. [8.19(b)] Calculate the value of $|m_l|$ for the system described in the preceding exercise corresponding to a rotational energy equal to the classical average energy at 25°C (which is equal to 1/2kT).*Note: from 8.19(a) the system is a proton constrained to rotate in a circle of radius 100 pm around a fixed point. The energy is ½ kT since 1-D problem.*

The energy levels of a particle on a ring are given by eqn 8.38a:

$$E = \frac{m_l^2\hbar^2}{2I} = \frac{m_l^2\hbar^2}{2mr^2}, \quad m_l = 0, \pm 1, \pm 2, \ldots$$

We set this quantity equal to the classical energy and solve for $|m_l|$:

$$E = \frac{m_l^2\hbar^2}{2mr^2} = \frac{kT}{2} \quad \text{so}$$

$$|m_l| = \frac{r(kTm)^{1/2}}{\hbar}$$

$$= \frac{(100\times 10^{-12}\ \mathrm{m})\times\{(1.381\times 10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})\times(1.6726\times 10^{-27}\ \mathrm{kg})\}^{1/2}}{1.0546\times 10^{-34}\ \mathrm{J\ s}}$$

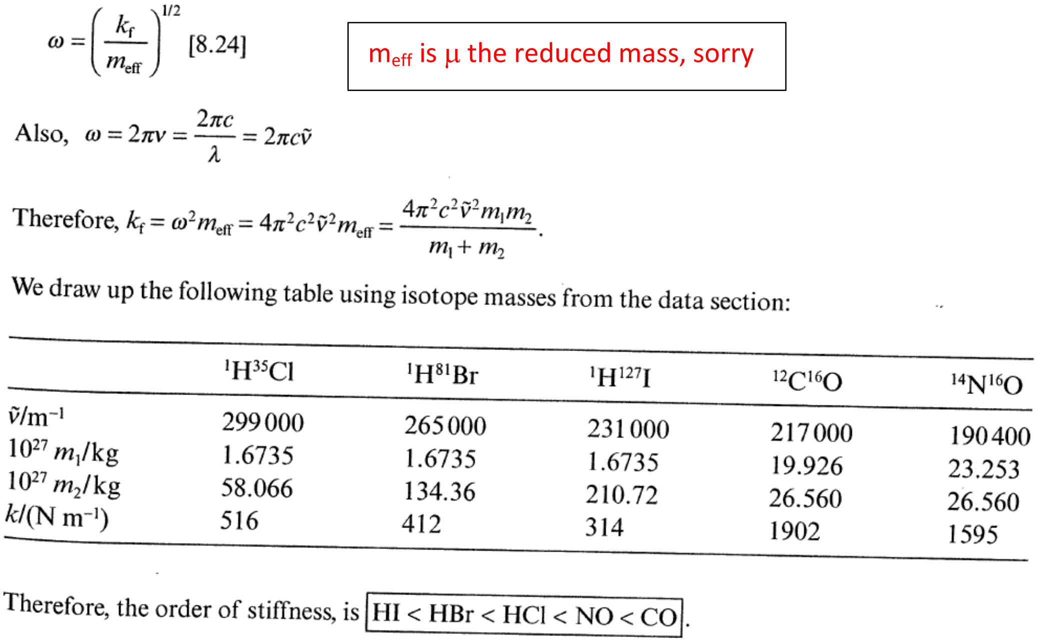
$$= \boxed{2.49}$$

Of course, $m_l$ must be an integer, so $m_l = \pm 2$ is the closest energy level.

4. [8.2] The mass to use in the expression for the vibrational frequency of a diatomic molecule is the effective mass μ = $m_Am_B/(m_A + m_B)$, where $m_A$ and $m_B$ are the masses of the individual atoms. The following data on the infrared absorption wavenumbers (wavenumbers in $cm^{-1}$) of molecules are taken from Spectra of diatomic molecules, G. Herzberg, van Nostrand (1950):

| $H^{35}Cl$ | $H^{81}Br$ | HI | CO | NO |
|---|---|---|---|---|
| 2990 | 2650 | 2310 | 2170 | 1904 |

Calculate the force constants of the bonds and arrange them in order of increasing stiffness.



$$\omega = \left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2} \quad [8.24]$$

$m_{\text{eff}}$ is μ the reduced mass, sorry

Also, $\omega = 2\pi\nu = \dfrac{2\pi c}{\lambda} = 2\pi c\tilde{\nu}$

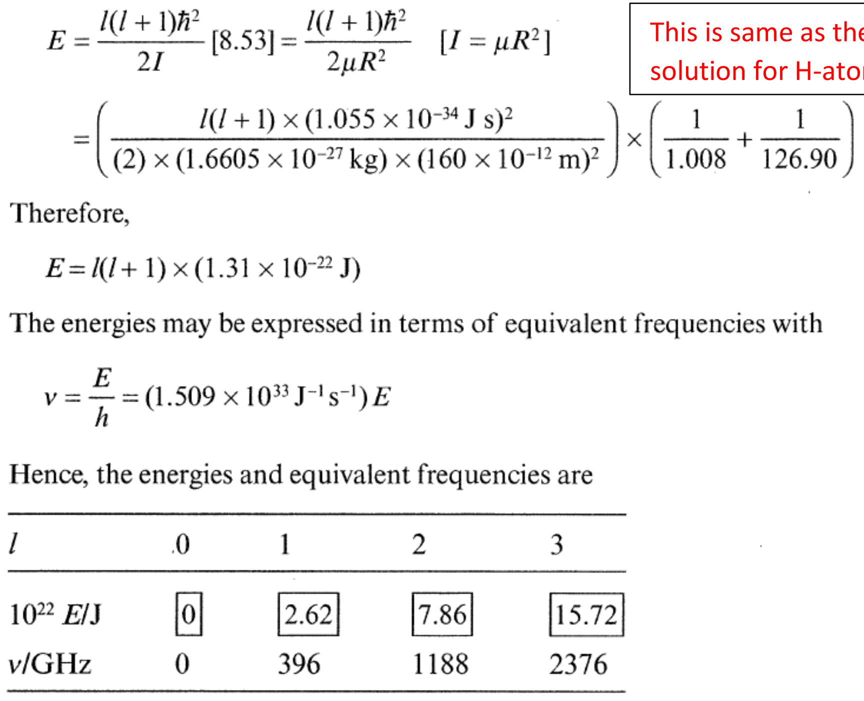
Therefore, $k_f = \omega^2 m_{\text{eff}} = 4\pi^2c^2\tilde{\nu}^2 m_{\text{eff}} = \dfrac{4\pi^2c^2\tilde{\nu}^2 m_1m_2}{m_1 + m_2}$.

We draw up the following table using isotope masses from the data section:

| | $^1H^{35}Cl$ | $^1H^{81}Br$ | $^1H^{127}I$ | $^{12}C^{16}O$ | $^{14}N^{16}O$ |
|---|---|---|---|---|---|
| $\tilde{\nu}/m^{-1}$ | 299 000 | 265 000 | 231 000 | 217 000 | 190 400 |
| $10^{27}\, m_1/kg$ | 1.6735 | 1.6735 | 1.6735 | 19.926 | 23.253 |
| $10^{27}\, m_2/kg$ | 58.066 | 134.36 | 210.72 | 26.560 | 26.560 |
| $k/(N\, m^{-1})$ | 516 | 412 | 314 | 1902 | 1595 |

Therefore, the order of stiffness, is $\boxed{HI < HBr < HCl < NO < CO}$.

5. [8.4] Calculate the energies of the first four rotational levels of $^1H^{127}I$ free to rotate in three dimensions, using for its moment of inertia I = $\mu R^2$, with μ= $m_Hm_I/(m_H + m_I)$ and R = 160 pm.



$$E = \frac{l(l+1)\hbar^2}{2I}\,[8.53] = \frac{l(l+1)\hbar^2}{2\mu R^2} \quad [I = \mu R^2]$$

This is same as the orbital angular momentum solution for H-atom, but R constant, E = $E_\ell$ only

$$= \left(\frac{l(l+1)\times(1.055\times10^{-34}\ \text{J s})^2}{(2)\times(1.6605\times10^{-27}\ \text{kg})\times(160\times10^{-12}\ \text{m})^2}\right)\times\left(\frac{1}{1.008}+\frac{1}{126.90}\right)$$

If it were particle on a ring, 1-D, then get E ~ $n^2$ instead of E ~ $\ell(\ell+1)$, 2-D

Therefore,

$$E = l(l+1)\times(1.31\times10^{-22}\ \text{J})$$

The energies may be expressed in terms of equivalent frequencies with

$$\nu = \frac{E}{h} = (1.509\times10^{33}\ \text{J}^{-1}\text{s}^{-1})E$$

Hence, the energies and equivalent frequencies are

| $l$ | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| $10^{22}\, E/J$ | $\boxed{0}$ | $\boxed{2.62}$ | $\boxed{7.86}$ | $\boxed{15.72}$ |
| $\nu/GHz$ | 0 | 396 | 1188 | 2376 |

6. [8.12] Calculate the mean kinetic energy of a harmonic oscillator by using the relations in Table 8.1.

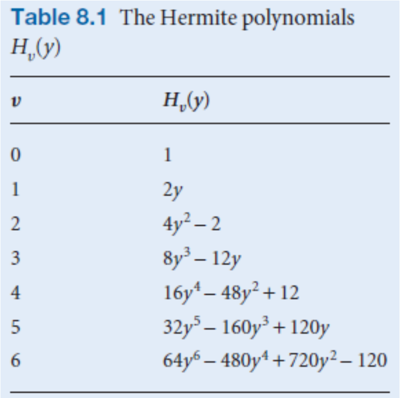
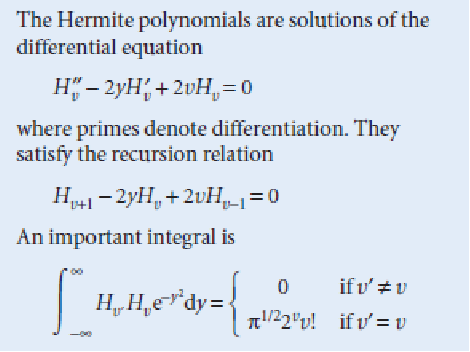


**Table 8.1** The Hermite polynomials $H_v(y)$

| $v$ | $H_v(y)$ |
|---|---|
| 0 | 1 |
| 1 | $2y$ |
| 2 | $4y^2-2$ |
| 3 | $8y^3-12y$ |
| 4 | $16y^4-48y^2+12$ |
| 5 | $32y^5-160y^3+120y$ |
| 6 | $64y^6-480y^4+720y^2-120$ |



The Hermite polynomials are solutions of the differential equation

$$H_v''-2yH_v'+2vH_v=0$$

where primes denote differentiation. They satisfy the recursion relation

$$H_{v+1}-2yH_v+2vH_{v-1}=0$$

An important integral is

$$\int_{-\infty}^{\infty} H_{v'}H_v e^{-y^2}\mathrm{d}y=\begin{cases}0 & \text{if } v'\neq v\\ \pi^{1/2}2^v v! & \text{if } v'=v\end{cases}$$

$$\langle E_{\mathrm{K}}\rangle=\int_{-\infty}^{+\infty}\psi^*\hat{E}_{\mathrm{K}}\,\psi\,\mathrm{d}x$$

Kinetic energy is T or in q.m. is $-\hbar^2/2m\ \mathrm{d}^2/\mathrm{d}x^2$

$$\hat{E}_{\mathrm{K}}=-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}[7.31]=-\frac{\hbar^2}{2m\alpha^2}\frac{\mathrm{d}^2}{\mathrm{d}y^2}=-\frac{\hbar\omega}{2}\frac{\mathrm{d}^2}{\mathrm{d}y^2},\quad\left[x=\alpha y,\ \alpha^2=\frac{\hbar}{m\omega}\right]$$

which implies that

$$\hat{E}_{\mathrm{K}}\psi=-\frac{\hbar\omega}{2}\left(\frac{\mathrm{d}^2\psi}{\mathrm{d}y^2}\right)$$

We then use $\psi=NHe^{-y^2/2}$, and obtain

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}y^2}=N\frac{\mathrm{d}^2}{\mathrm{d}y^2}(He^{-y^2/2})=N\{H''-2yH'-H+y^2H\}e^{-y^2/2}$$

From Table 8.1

$$H_v''-2yH_v'=-2vH_v$$

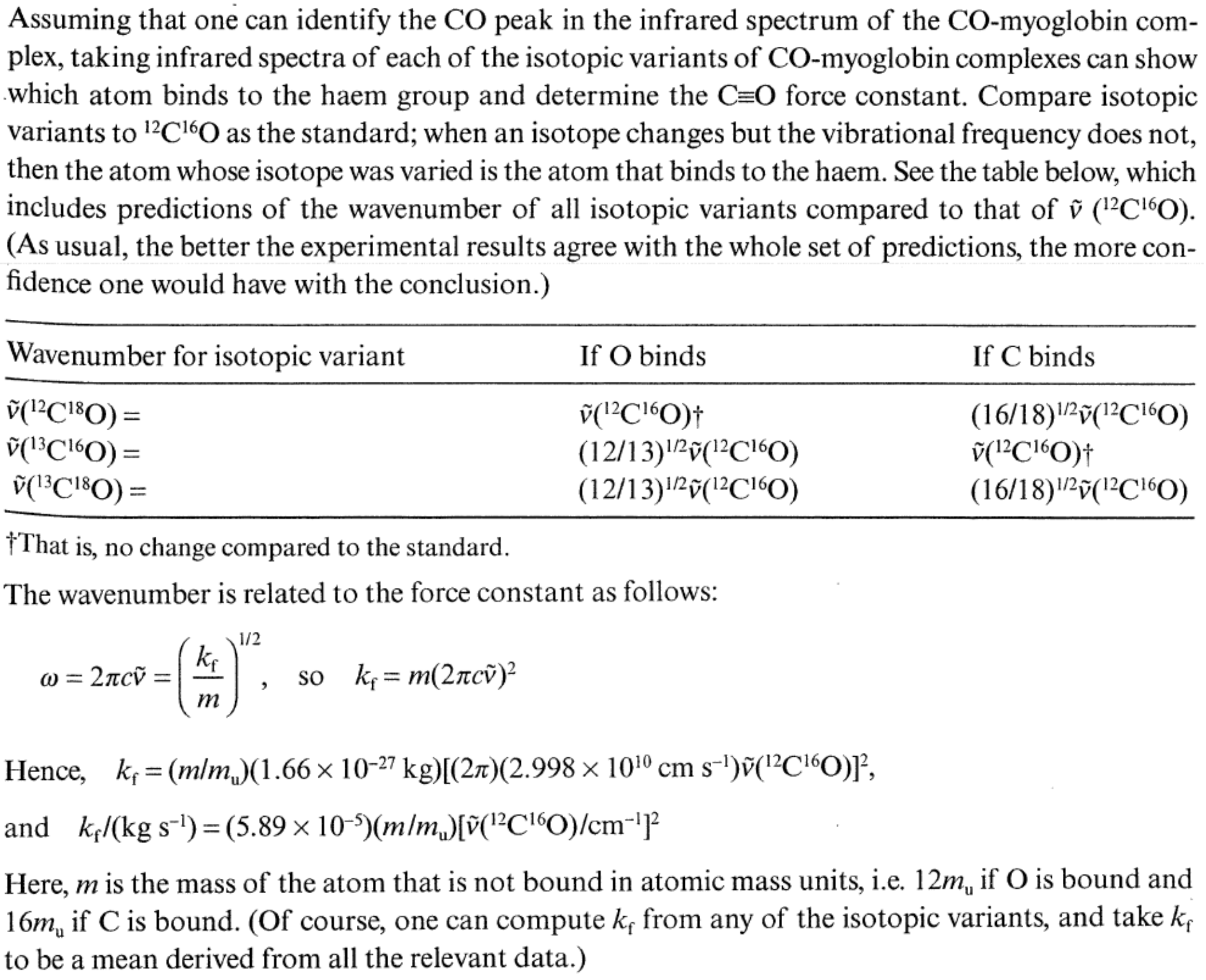
$$\begin{aligned}y^2H_v&=y(\tfrac{1}{2}H_{v+1}+vH_{v-1})=\tfrac{1}{2}(\tfrac{1}{2}H_{v+2}+(v+1)H_v)+v(\tfrac{1}{2}H_v+(v-1)H_{v-2})\\&=\tfrac{1}{4}H_{v+2}+v(v-1)H_{v-2}+(v+\tfrac{1}{2})H_v\end{aligned}$$

Hence, $$\frac{\mathrm{d}^2\psi}{\mathrm{d}y^2}=N\left[\tfrac{1}{4}H_{v+2}+v(v-1)H_{v-2}-\left(v+\frac{1}{2}\right)H_v\right]e^{-y^2/2}$$

Therefore,

$$\begin{aligned}\langle E_{\mathrm{K}}\rangle&=N_v^2\left(-\frac{\hbar\omega}{2}\right)\int_{-\infty}^{+\infty}H_v\left\{\frac{1}{4}H_{v+2}+v(v-1)H_{v-2}-\left(v+\frac{1}{2}\right)H_v\right\}e^{-y^2}\mathrm{d}x\ [\mathrm{d}x=\alpha\mathrm{d}y]\\&=\alpha N_v^2(-\tfrac{1}{2}\hbar\omega)\{0+0-(v+\tfrac{1}{2})\pi^{1/2}2^v v!\}\ [\text{Hermite polynomials orthogonal}]\\&=\boxed{\frac{1}{2}\left(v+\frac{1}{2}\right)\hbar\omega}\left[N_v^2=\frac{1}{\alpha\pi^{1/2}2^v v!},\ \text{Example 8.3}\right]\end{aligned}$$

7. [8.34] Of the four assumptions made in Problem 8.33, the last two are questionable. Suppose that the first two assumptions are still reasonable and that you have at your disposal a supply of myoglobin, a suitable buffer in which to suspend the protein, $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{18}O$, and an infrared spectrometer. Assuming that isotopic substitution does not affect the force constant of the C≡O bond, describe a set of experiments that: (a) proves which atom, C or O, binds to the haem group of myoglobin, and (b) allows for the determination of the force constant of the C≡O bond for myoglobin-bound carbon monoxide.



Assuming that one can identify the CO peak in the infrared spectrum of the CO-myoglobin complex, taking infrared spectra of each of the isotopic variants of CO-myoglobin complexes can show which atom binds to the haem group and determine the C≡O force constant. Compare isotopic variants to $^{12}C^{16}O$ as the standard; when an isotope changes but the vibrational frequency does not, then the atom whose isotope was varied is the atom that binds to the haem. See the table below, which includes predictions of the wavenumber of all isotopic variants compared to that of $\tilde{\nu}$ ($^{12}C^{16}O$). (As usual, the better the experimental results agree with the whole set of predictions, the more confidence one would have with the conclusion.)

| Wavenumber for isotopic variant | If O binds | If C binds |
|---|---|---|
| $\tilde{\nu}(^{12}C^{18}O) =$ | $\tilde{\nu}(^{12}C^{16}O)$† | $(16/18)^{1/2}\tilde{\nu}(^{12}C^{16}O)$ |
| $\tilde{\nu}(^{13}C^{16}O) =$ | $(12/13)^{1/2}\tilde{\nu}(^{12}C^{16}O)$ | $\tilde{\nu}(^{12}C^{16}O)$† |
| $\tilde{\nu}(^{13}C^{18}O) =$ | $(12/13)^{1/2}\tilde{\nu}(^{12}C^{16}O)$ | $(16/18)^{1/2}\tilde{\nu}(^{12}C^{16}O)$ |

†That is, no change compared to the standard.

The wavenumber is related to the force constant as follows:

$$\omega = 2\pi c\tilde{\nu} = \left(\frac{k_f}{m}\right)^{1/2}, \quad \text{so} \quad k_f = m(2\pi c\tilde{\nu})^2$$

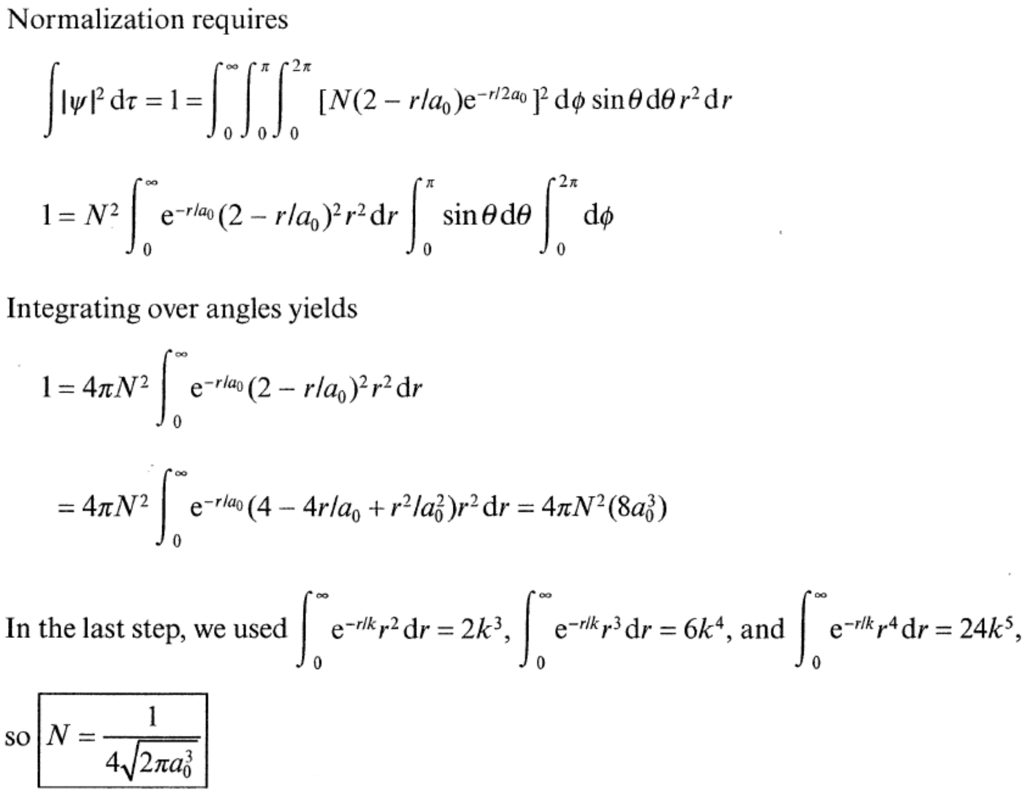
Hence, $k_f = (m/m_u)(1.66\times10^{-27}\text{ kg})[(2\pi)(2.998\times10^{10}\text{ cm s}^{-1})\tilde{\nu}(^{12}C^{16}O)]^2$,

and $k_f/(\text{kg s}^{-1}) = (5.89\times10^{-5})(m/m_u)[\tilde{\nu}(^{12}C^{16}O)/\text{cm}^{-1}]^2$

Here, $m$ is the mass of the atom that is not bound in atomic mass units, i.e. $12m_u$ if O is bound and $16m_u$ if C is bound. (Of course, one can compute $k_f$ from any of the isotopic variants, and take $k_f$ to be a mean derived from all the relevant data.)

In reality the bond between CO and the heam is not rigid, and the mass of both C and O will affect the frequency, but this is a good logic problem none the less. The difference between this simple assumption and reality is not so great since the frequency of the CO—heam vibration is very different from the CO vibration, so they do not couple very well. This is like a triple mass connected by two springs problem.  Try it out.

8. [9.5(b)] The wavefunction for the 2s orbital of a hydrogen atom is $N(2 - r/a_0)e^{-r/2a0}$. Determine the normalization constant N.



Normalization requires

$$\int |\psi|^2\,\mathrm{d}\tau = 1 = \int_0^\infty\int_0^\pi\int_0^{2\pi} [N(2 - r/a_0)\mathrm{e}^{-r/2a_0}]^2\,\mathrm{d}\phi\,\sin\theta\,\mathrm{d}\theta\,r^2\,\mathrm{d}r$$

$$1 = N^2\int_0^\infty \mathrm{e}^{-r/a_0}(2 - r/a_0)^2 r^2\,\mathrm{d}r\int_0^\pi \sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi$$

Integrating over angles yields

$$1 = 4\pi N^2\int_0^\infty \mathrm{e}^{-r/a_0}(2 - r/a_0)^2 r^2\,\mathrm{d}r$$

$$= 4\pi N^2\int_0^\infty \mathrm{e}^{-r/a_0}(4 - 4r/a_0 + r^2/a_0^2)r^2\,\mathrm{d}r = 4\pi N^2(8a_0^3)$$

In the last step, we used $\int_0^\infty \mathrm{e}^{-r/k}r^2\,\mathrm{d}r = 2k^3$, $\int_0^\infty \mathrm{e}^{-r/k}r^3\,\mathrm{d}r = 6k^4$, and $\int_0^\infty \mathrm{e}^{-r/k}r^4\,\mathrm{d}r = 24k^5$,

so $\boxed{N = \dfrac{1}{4\sqrt{2\pi a_0^3}}}$

Recall:

$\int_0^{2\pi} d\phi = (2\pi - 0) = 2\pi$ $\int_0^{\pi} \sin\theta\, d\theta = -\cos\theta|_0^{\pi} = -(-1 - 1) = 2$ so $\int_0^{2\pi}\int_0^{\pi} \sin\theta\, d\theta\, d\phi = 4\pi$

9. [9.7(b)] At what radius in the H atom does the radial distribution function of the ground state have (a) 50 per cent, (b) 75 per cent of its maximum value.

The radial distribution function varies as

$$P = 4\pi r^2 \psi^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0} \text{ [9.17]}$$

The maximum value of $P$ occurs at $r = a_0$ since

$$\frac{dP}{dr} \propto \left(2r - \frac{2r^2}{a_0}\right) e^{-2r/a_0} = 0 \quad \text{at} \quad r = a_0 \text{ and } P_{\max} = \frac{4}{a_0} e^{-2}$$

$P$ falls to a fraction $f$ of its maximum given by

$$f = \frac{\frac{4r^2}{a_0^3} e^{-2r/a_0}}{\frac{4}{a_0} e^{-2}} = \frac{r^2}{a_0^2} e^2 e^{-2r/a_0}$$

and hence we must solve for $r$ in

$$\frac{f^{1/2}}{e} = \frac{r}{a_0} e^{-r/a_0}$$

(a) $f = 0.50$

$$0.260 = \frac{r}{a_0} e^{-r/a_0} \text{ solves to } r = 2.08a_0 = \boxed{110 \text{ pm}} \text{ and to } r = 0.380a_0 = \boxed{20.1 \text{ pm}}$$

(b) $f = 0.75$

$$0.319 = \frac{r}{a_0} e^{-r/a_0} \text{ solves to } r = 1.63a_0 = \boxed{86 \text{ pm}} \text{ and to } r = 0.555a_0 = \boxed{29.4 \text{ pm}}$$

In each case the equation is solved numerically (or graphically) with readily available personal computer software. The solutions above are easily checked by substitution into the equation for $f$. The radial distribution function is readily plotted and is shown in Figure 9.1.

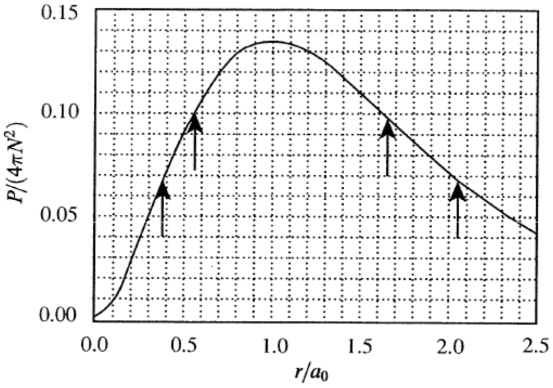


**Figure 9.1**

**Extra (do not hand in):**

10. [8.10(b)] For a certain harmonic oscillator of effective mass 2.88 × $10^{-25}$ kg, the difference in adjacent energy levels is 3.17 zJ. Calculate the force constant of the oscillator.

The difference in adjacent energy levels is

$$\Delta E = E_{v+1} - E_v = \hbar\omega\ [8.25] = \hbar\left(\frac{k_f}{m}\right)^{1/2} \quad [8.24]$$

so $$k_f = \frac{m(\Delta E)^2}{\hbar^2} = \frac{(2.88\times10^{-25}\ \text{kg})\times(3.17\times10^{-21}\ \text{J})^2}{(1.0546\times10^{-34}\ \text{J s})^2} = 260\ \text{kg s}^{-2} = \boxed{260\ \text{N m}^{-1}}$$

11. [8.14(b)] Confirm that the wavefunction for the first excited state of a one-dimensional linear harmonic oscillator given in Table 8.1 is a solution of the Schrödinger equation for the oscillator and that its energy is $\frac{3}{2}\hbar\omega$.

The first excited-state wavefunction has the form

$$\psi_1 = 2N_1 y \exp(-\tfrac{1}{2}y^2)\ [8.30]$$

where $N_1$ is a collection of constants and $y \equiv x\left(\frac{m\omega}{\hbar}\right)^{1/2}$. To see if it satisfies the Schrödinger equation, we apply the energy operator to this function

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \tfrac{1}{2}m\omega^2x^2\psi$$

We need derivatives of $\psi$

$$\frac{d\psi}{dx} = \frac{d\psi}{dy}\frac{dy}{dx} = \left(\frac{m\omega}{\hbar}\right)^{1/2}(2N_1)\times(1-y^2)\times\exp(-\tfrac{1}{2}y^2)$$

and $$\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dy^2}\left(\frac{dy}{dx}\right)^2 = \left(\frac{m\omega}{\hbar}\right)\times(2N_1)\times(-3y+y^3)\times\exp(-\tfrac{1}{2}y^2) = \left(\frac{m\omega}{\hbar}\right)\times(y^2-3)\psi$$

So, $$\hat{H}\psi = -\frac{\hbar^2}{2m}\times\left(\frac{m\omega}{\hbar}\right)\times(y^2-3)\psi + \tfrac{1}{2}m\omega^2x^2\psi$$

$$= -\tfrac{1}{2}\hbar\omega\times(y^2-3)\times\psi + \tfrac{1}{2}\hbar\omega y^2\psi = \tfrac{3}{2}\hbar\omega\psi$$

Thus, $\psi$ is a solution the Schrödinger equation with energy eigenvalue $E = \frac{3}{2}\hbar\omega$.

12. [8.15(b)] Locate the nodes of the harmonic oscillator wavefunction with v = 5.

The harmonic oscillator wavefunctions have the form

$$\psi_v(x) = N_v H_v(y)\exp(-\tfrac{1}{2}y^2) \quad \text{with} \quad y = \frac{x}{\alpha} \quad \text{and} \quad \alpha = \left(\frac{\hbar^2}{mk_f}\right)^{1/4} \quad [8.27]$$

The exponential function approaches zero only as $x$ approaches $\pm\infty$, so the nodes of the wavefunction are the nodes of the Hermite polynomials.

$$H_5(y) = 32y^5 - 160y^3 + 120y = 0 \text{ [Table 8.1]} = 8y(4y^4 - 20y^2 + 15)$$

So, one solution is $y = 0$, which leads to $x = 0$. The other factor can be made into a quadratic equation by letting $z = y^2$

$$4z^2 - 20z + 15 = 0$$

so $$z = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{20 \pm \sqrt{20^2 - 4\times 4\times 15}}{2\times 4} = \frac{5 \pm \sqrt{10}}{2}$$

Evaluating the result numerically yields $z = 0.92$ or $4.08$, so $y = \pm 0.96$ or $\pm 2.02$. Therefore $x = \boxed{0, \pm 0.96\alpha, \text{ or } \pm 2.02\alpha}$.

**COMMENT.** Numerical values could also be obtained graphically by plotting $H_5(y)$.

13. [8.17(b)] Assuming that the vibrations of a $^{14}N_2$ molecule are equivalent to those of a harmonic oscillator with a force constant k = 2293.8 N m$^{-1}$, what is the zero-point energy of vibration of this molecule? The effective mass of a homonuclear diatomic molecule is half its total mass, and m($^{14}$N) = 14.0031$m_u$.

The zero-point energy is

$$E_0 = \frac{1}{2}\hbar\omega \text{ [8.26]} = \frac{\hbar}{2}\left(\frac{k}{m_{\text{eff}}}\right)^{1/2} \quad [8.24]$$

$$m_{\text{eff}} = 14.0031 \times (1.6605 \times 10^{-27}\text{ kg})/2 = 1.1626 \times 10^{-26}\text{ kg}$$

$$E_0 = \frac{1.0546 \times 10^{-34}\text{ J s}}{2} \times \left(\frac{2293.8\text{ N m}^{-1}}{1.1626 \times 10^{-26}\text{ kg}}\right)^{1/2} = \boxed{2.3422 \times 10^{-20}\text{ J}}$$

14. [8.21(b)] The moment of inertia of an $SF_6$ molecule is $3.07 \times 10^{-45}$ kg m$^2$. What is the minimum energy needed to start it rotating?

In Chapter 12, we will see that the results on rotational motion developed in this chapter apply to rigid rotors of various shapes, not just to point masses. The rotor in this case is not a disk-like object (as in Exercise 8.20(b)), so we use results derived for rotation in three dimensions. The energy levels are

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \ldots \text{ [8.53]}$$

The minimum energy to start it rotating is the minimum excitation energy, the energy to take it from the motionless $l = 0$ to the rotating $l = 1$ state:

$$\Delta E = E_1 = \frac{1 \times 2 \times (1.0546 \times 10^{-34}\text{ J s})^2}{2 \times (3.07 \times 10^{-45}\text{ kg m}^2)} = \boxed{3.62 \times 10^{-24}\text{ J}}$$

15. [8.23(b)] What is the magnitude of the angular momentum of an $SF_6$ molecule when it is rotating with its minimum energy?

The energy levels are

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \ldots \text{ [8.53]}$$

So, the minimum energy *allowed* for this system is zero—but that corresponds to rest, not rotation. So, the minimum energy of rotation occurs for the state that has $l = 1$. The angular momentum in that state is

$$J = \{l(l+1)\}^{1/2}\hbar \text{ [8.54a]} = \boxed{2^{1/2}\hbar} = 2^{\frac{1}{2}} \times (1.0546 \times 10^{-34}\text{ J s}) = \boxed{1.49 \times 10^{-34}\text{ J s}}.$$

16. [8.26] Show that the function f = cos ax cos by cos cz is an eigenfunction of $\nabla^2$, and determine its eigenvalue.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \text{ [Table 7.1]}$$

$$\frac{\partial^2}{\partial x^2} f = -a^2 \cos ax \cos by \cos cz = -a^2 f$$

Similarly, $\frac{\partial^2}{\partial y^2} f = -b^2 f \quad \frac{\partial^2}{\partial y^2} f = -c^2 f$

so $f$ is an eigenfunction with eigenvalue $\boxed{-(a^2 + b^2 + c^2)}$.

17. [8.38] We remarked in Impact I8.1 that the particle in a sphere is a reasonable starting point for the discussion of the electronic properties of spherical metal nanoparticles. Here, we justify the expression for the energy levels with l = 0.

(a) The Hamiltonian for a particle free to move inside a sphere of radius R is

$$\hat{H} = -\frac{\hbar}{2m}\nabla^2$$

Show that the Schrödinger equation is separable into radial and angular components. That is, begin by writing ψ(r,θ,φ) = u(r)Y(θ,φ), where u(r) depends only on the distance of the particle away from the centre of the sphere, and Y(θ,φ) is a spherical harmonic. Then show that the Schrödinger equation can be separated into two equations, one for u, the radial equation, and the other for Y, the angular equation:

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2u(r)}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}u(r)}{\mathrm{d}r}\right) + \frac{l(l+1)\hbar^2}{2mr^2}u(r) = Eu(r)$$

$$\Lambda^2 Y = -l(l+1)Y$$

(b) Consider the case l = 0. Show by differentiation that the solution of the radial equation has the form

$$u(r) = (2\pi R)^{-1/2}\frac{\sin(n\pi r/R)}{r}$$

(c) Now go on to show that the allowed energies are given by:

$$E_n = \frac{n^2h^2}{8mR^2}$$

(a) In the sphere, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right)\psi = E\psi \ \text{[8.49 and 8.51a]}$$

where $\Lambda^2$ is an operator that contains derivatives with respect to $\theta$ and $\phi$ only.

Let $\psi(r,\theta,\phi) = u(r)\,Y(\theta,\phi)$

Substituting into the Schrödinger equation gives

$$-\frac{\hbar^2}{2m}\left(Y\frac{\partial^2 u}{\partial r^2} + \frac{2Y}{r}\frac{\partial u}{\partial r} + \frac{u}{r^2}\Lambda^2 Y\right) = EuY$$

Divide both sides by $uY$:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{u}\frac{\partial^2 u}{\partial r^2} + \frac{2}{ur}\frac{\partial u}{\partial r} + \frac{1}{Yr^2}\Lambda^2 Y\right) = E$$

The first two terms in parentheses depend only on $r$, but the last one depends on both $r$ and angles however, multiplying both sides of the equation by $r^2$ will effect the desired separation:

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{u}\frac{\partial^2 u}{\partial r^2}+\frac{2r}{u}\frac{\partial u}{\partial r}+\frac{1}{Y}\Lambda^2 Y\right)=Er^2$$

Put all of the terms involving angles on the right-hand side and the terms involving distance on the left:

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{u}\frac{\partial^2 u}{\partial r^2}+\frac{2r}{u}\frac{\partial u}{\partial r}\right)-Er^2=\frac{\hbar^2}{2mY}\Lambda^2 Y$$

Note that the right side depends only on $\theta$ and $\phi$, while the left side depends only on $r$. The two sides can be equal to each other for all $r,\theta$, and $\phi$ only if they are both equal to a constant. Call that constant $-\frac{\hbar^2 l(l+1)}{2m}$ (with $l$ as yet undefined) and we have, from the right side of the equation:

$$\frac{\hbar^2}{2mY}\Lambda^2 Y=-\frac{\hbar^2 l(l+1)}{2m}, \quad \text{so} \quad \Lambda^2 Y=-l(l+1)Y$$

From the left side of the equation, we have

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{u}\frac{\partial^2 u}{\partial r^2}+\frac{2r}{u}\frac{\partial u}{\partial r}\right)-Er^2=-\frac{\hbar^2 l(l+1)}{2m}$$

After multiplying both sides by $u/r^2$ and rearranging, we get the desired radial equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 u}{\partial r^2}+\frac{2}{r}\frac{\partial u}{\partial r}\right)+\frac{\hbar^2 l(l+1)}{2mr^2}u=Eu$$

Thus, the assumption that the wavefunction can be written as a product of functions is a valid one, for we can find separate differential equations for the assumed factors. That is what it means for a partial differential equation to be separable.

(b) The radial equation with $l=0$ can be rearranged to read:

$$\frac{\partial^2 u}{\partial r^2}+\frac{2}{r}\frac{\partial u}{\partial r}=-\frac{2mEu}{\hbar^2}$$

Form the following derivatives of the proposed solution:

$$\frac{\partial u}{\partial r} = (2\pi R)^{-1/2}\left\{\frac{\cos(n\pi r/R)}{r}\left(\frac{n\pi}{R}\right) - \frac{\sin(n\pi r/R)}{r^2}\right\}$$

and $$\frac{\partial^2 u}{\partial r^2} = (2\pi R)^{-1/2}\left\{-\frac{\sin(n\pi r/R)}{r}\left(\frac{n\pi}{R}\right)^2 - \frac{2\cos(n\pi r/R)}{r^2}\left(\frac{n\pi}{R}\right) + \frac{2\sin(n\pi r/R)}{r^3}\right\}$$

Substituting into the left side of the rearranged radial equation yields

$$(2\pi R)^{-1/2}\left[-\frac{\sin(n\pi r/R)}{r}\left(\frac{n\pi}{R}\right)^2 - \frac{2\cos(n\pi r/R)}{r^2}\left(\frac{n\pi}{R}\right) + \frac{2\sin(n\pi r/R)}{r^3}\right]$$

$$+(2\pi R)^{-1/2}\left[\frac{2\cos(n\pi r/R)}{r^2}\left(\frac{n\pi}{R}\right) - \frac{2\sin(n\pi r/R)}{r^3}\right]$$

$$= -(2\pi R)^{-1/2}\frac{\sin(n\pi r/R)}{r}\left(\frac{n\pi}{R}\right)^2 = -\left(\frac{n\pi}{R}\right)^2 u$$

Acting on the proposed solution by taking the prescribed derivatives yields the function back multiplied by a constant, so the proposed solution is in fact a solution.

(c) Comparing this result to the right side of the rearranged radial equation gives an equation for the energy

$$\left(\frac{n\pi}{R}\right)^2 = \frac{2mE}{\hbar^2}, \quad \text{so} \quad E = \left(\frac{n\pi}{R}\right)^2\frac{\hbar^2}{2m} = \frac{n^2\pi^2}{2mR^2}\left(\frac{h}{2\pi}\right)^2 = \frac{n^2h^2}{8mR^2}$$

18. [9.6(b)] By differentiation of the 3s radial wavefunction, show that it has three extrema in its amplitude, and locate them.

The radial wavefunction is [Table 9.1]

$$R_{3,0} = A(6 - 2\rho + \tfrac{1}{9}\rho^2)e^{-\rho/6}, \text{ where } \rho \equiv \frac{2Zr}{a_0}, \text{ and } A \text{ is a collection of constants.}$$

(**Note:** $\rho$ defined here is $3 \times \rho$ as defined in Table 9.1.)

Differentiating with respect to $\rho$ yields

$$\frac{dR_{3,0}}{d\rho} = 0 = A(6 - 2\rho + \tfrac{1}{9}\rho^2) \times (-\tfrac{1}{6})e^{-\rho/6} + (-2 + \tfrac{2}{9}\rho)Ae^{-\rho/6}$$

$$= Ae^{-\rho/6}(-\tfrac{\rho^2}{54} + \tfrac{5}{9}\rho - 3)$$

This is a quadratic equation

$$0 = a\rho^2 + b\rho + c, \quad \text{where} \quad a = -\frac{1}{54}, \; b = \frac{5}{9}, \text{ and } c = -3.$$

The solution is

$$\rho = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = 15 \pm 3\sqrt{7}$$

so $r = \boxed{\left(\frac{15}{2} \pm \frac{3(7^{1/2})}{2}\right)\frac{a_0}{Z}}$.

Numerically, this works out to $\rho = 22.94$ and $7.06$, so $r = \boxed{11.5a_0/Z}$ and $\boxed{3.53a_0/Z}$. Substituting $Z = 1$ and $a_0 = 5.292 \times 10^{-11}$ m, $r = \boxed{607 \text{ pm}}$ and $\boxed{187 \text{ pm}}$.

The other maximum in the wavefunction is at $\boxed{r = 0}$. It is a physical maximum, but not a calculus maximum: the first derivative of the wavefunction does not vanish there, so it cannot be found by differentiation.

19. [9.8(b)] Locate the radial nodes in the 4p orbital of an H atom.

The complete radial wavefunction, $R_{4,1}$ is not given in Table 9.1, but by consulting other references, such as *Introduction to Quantum Mechanics* by Pauling and Wilson, we learn that $R_{4,1}$ is proportional to

$$(20 - 10\rho + \rho^2)\rho, \quad \text{where} \quad \rho = \frac{2Zr}{na_0}$$

The radial nodes occur where the radial wavefunction vanishes, namely where

$$(20 - 10\rho + \rho^2)\rho = 0.$$

The zeros of this function occur at

$$\rho = 0, \quad \boxed{r = 0}$$

and when

$$(20 - 10\rho + \rho^2) = 0, \quad \text{with roots} \quad \rho = 2.764, \quad \text{and} \quad \rho = 7.236$$

$$\text{then } r = \frac{4\rho a_0}{2Z} = \frac{4\rho a_0}{2} = \frac{11.056a_0}{2} = \boxed{5.528a_0} \text{ and } \frac{28.944a_0}{2} = \boxed{14.472a_0}$$

$$\text{or } r = \boxed{2.92 \times 10^{-10}\ \text{m}} \text{ and } \boxed{7.66 \times 10^{-10}\ \text{m}}$$

20. [9.12(b)] What is the orbital angular momentum of an electron in the orbitals (a) 4d, (b) 2p, (c) 3p? Give the numbers of angular and radial nodes in each case.

Orbital angular momentum is

$$\langle \hat{L}^2 \rangle^{1/2} = \hbar(l(l+1))^{1/2}$$

There are $l$ angular nodes and $n - l - 1$ radial nodes.

(a) $n = 4,\ l = 2$, so $\langle \hat{L}^2 \rangle^{1/2} = 6^{1/2}\hbar = \boxed{2.45 \times 10^{-34}\ \text{J s}}$ $\boxed{2}$ angular nodes $\boxed{1}$ radial node

(b) $n = 2,\ l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34}\ \text{J s}}$ $\boxed{1}$ angular nodes $\boxed{0}$ radial nodes

(c) $n = 3,\ l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34}\ \text{J s}}$ $\boxed{1}$ angular node $\boxed{1}$ radial node