Chem 403—Physical Chemistry Homework Solutions
Chapter 9

Solutions to problems

Solutions to numerical problems

P9.2 $\omega = \left(\frac{k}{\mu}\right)^{1/2}$ [9.25 with μ in place of m]

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

Therefore $k = \omega^2\mu = 4\pi^2c^2\tilde{\nu}^2\mu = \frac{4\pi^2c^2\tilde{\nu}^2 m_1 m_2}{m_1 + m_2}$.

We draw up the following table using information from the Data Section, p. 991.

	$^1H^{35}Cl$	$^1H^{81}Br$	$^1H^{127}I$	$^{12}C^{16}O$	$^{14}N^{16}O$
$\tilde{\nu}/m^{-1}$	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 $\boxed{HI < HBr < HCl < NO < CO}$.

P9.4 $E = \frac{l(l+1)\hbar^2}{2I}$ [9.53] $= \frac{l(l+1)\hbar^2}{2m_{eff}R^2}$ [$I = m_{eff}R^2$, m_{eff} in place of m]

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

$$\left[\frac{1}{m_{eff}} = \frac{1}{m_1} + \frac{1}{m_2}\right]$$

Therefore,

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

The energies may be expressed in terms of equivalent frequencies with

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

Hence, the energies and equivalent frequencies are

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

$$H^{(1)} = \begin{cases} 0 & \text{for } 0 \le x \le (1/2)(L-a) \text{ and } (1/2)(L+a) \le x \le L \\ \varepsilon & \text{for } (1/2)(L-a) \le x \le (1/2)(L+a). \end{cases}$$

The first-order correction to the ground-state energy, E_1, is

$$E_1^{(1)} = \int_0^L \psi_1^{(0)*} H^{(1)} \psi_1^{(0)} \mathrm{d}x = \int_{(1/2)(L-a)}^{(1/2)(L+a)} \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) \varepsilon \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) \mathrm{d}x,$$

$$E_1^{(1)} = \frac{2\varepsilon}{L} \int_{(1/2)(L-a)}^{(1/2)(L+a)} \sin^2\left(\frac{\pi x}{L}\right) \mathrm{d}x = \frac{\varepsilon}{L\pi}\left(\pi x - L\cos\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)\right)\Bigg|_{1/2(L-a)}^{1/2(L+a)},$$

$$E_1^{(1)} = \frac{\varepsilon a}{L} - \frac{\varepsilon}{\pi}\cos\left(\frac{\pi(L+a)}{2L}\right)\sin\left(\frac{\pi(L+a)}{2L}\right) + \frac{\varepsilon}{\pi}\cos\left(\frac{\pi(L-a)}{2L}\right)\sin\left(\frac{\pi(L-a)}{2L}\right).$$

This expression can be simplified considerably with a few trigonometric identities. The product of sine and cosine is related to the sine of twice the angle:

$$\cos\left(\frac{\pi(L\pm a)}{2L}\right)\sin\left(\frac{\pi(L\pm a)}{2L}\right) = \frac{1}{2}\sin\left(\frac{\pi(L\pm a)}{L}\right) = \frac{1}{2}\sin\left(\pi \pm \frac{\pi a}{L}\right),$$

and the sine of a sum can be written in a particularly simple form since one of the terms in the sum is π:

$$\sin\left(\pi \pm \frac{\pi a}{L}\right) = \sin\pi\cos\left(\frac{\pi a}{L}\right) \pm \cos\pi\sin\left(\frac{\pi a}{L}\right) = \mp\sin\left(\frac{\pi a}{L}\right).$$

Thus $E_1^{(1)} = \boxed{\frac{\varepsilon a}{L} + \frac{\varepsilon}{\pi}\sin\left(\frac{\pi a}{L}\right)}$.

(b) If $a = L/10$, the first-order correction to the ground-state energy is

$$E_1^{(1)} = \boxed{\frac{\varepsilon}{10} + \frac{\varepsilon}{\pi}\sin\left(\frac{\pi}{10}\right)} = \boxed{0.1984\,\varepsilon}.$$

P9.7 The second-order correction to the ground-state energy, E_1, is

$$E_1^{(2)} = \sum_{n=2}^{\infty} \frac{\left|\int_L^0 \psi_n^{(0)*} H^{(1)} \psi_1^{(0)} \mathrm{d}x\right|^2}{E_1^{(0)} - E_n^{(0)}},$$

where $H^{(1)} = mgx$, $\psi_n^{(0)} = \sin\frac{n\pi x}{L}$, and $E_n = \frac{n^2h^2}{8mL^2}$.

The denominator in the sum is

$$E_1^{(0)} - E_n^{(0)} = \frac{h^2}{8mL^2} - \frac{n^2h^2}{8mL^2} = \frac{(1-n^2)h^2}{8mL^2}.$$

average particle-in-a-box energy. To summarize, reversible adiabatic work for a gas of particle-in-a-box molecules is $dw = -pdV$, where the pressure is

$$p = \frac{Nn^2h^2}{12mL^5} = \frac{2}{3}\frac{N}{V}E$$

In expansion, the volume increases, meaning that the box gets bigger. Equation 9.12b tells us that the kinetic energy decreases, even as the quantum numbers remain constant. This is also consistent with what we know of adiabatic expansion and the kinetic model of gases: the temperature of the sample drops on expansion, and temperature is related to the kinetic energy ($T^2 \propto E$).

In isothermal expansion, energy must enter the system as heat to maintain the temperature. We can interpret this influx of heat as an increase in quantum numbers (an excitation of the molecules) that offsets the falling energy levels.

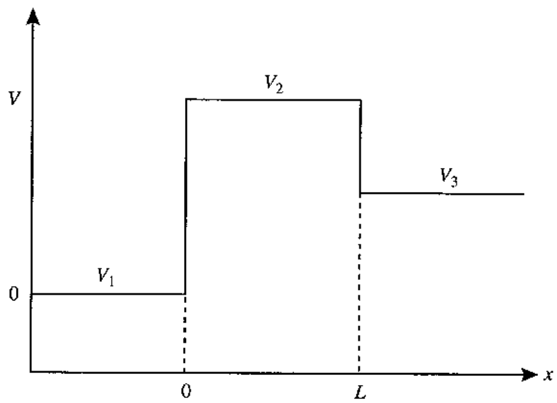

Figure 9.2a

P9.10 **(a)** The wavefunctions in each region (see Figure 9.2(a)) are (eqns 9.14, 9.16, and 9.17):

$$\psi_1(x) = e^{ik_1x} + B_1e^{-ik_2x}$$

$$\psi_2(x) = A_2e^{k_2x} + B_2e^{-k_2x}$$

$$\psi_3(x) = A_3e^{ik_3x}$$

With the above choice of $A_1 = 1$ the transmission probability is simply $T = |A_3|^2$. The wavefunction coefficients are determined by the criteria that both the wavefunctions and their first derivatives with respect to x be continuous at potential boundaries

$$\psi_1(0) = \psi_2(0); \quad \psi_2(L) = \psi_3(L)$$

$$\frac{d\psi_1(0)}{dx} = \frac{d\psi_2(0)}{dx}; \quad \frac{d\psi_2(L)}{dx} = \frac{d\psi_3(L)}{dx}$$

These criteria establish the algebraic relationships:

$$1 + B_1 - A_2 - B_2 = 0$$

$$(-ik_1 - k_2)A_2 + (-ik_1 + k_2)B_2 + 2ik_1 = 0$$

$$A_2e^{k_2L} + B_2e^{-k_2L} - A_3e^{ik_3L} = 0$$

$$A_2k_2e^{k_2L} - B_2k_2e^{-k_2L} - iA_3k_3e^{ik_3L} = 0$$

Solving the simultaneous equations for A_3 gives

$$A_3 = \frac{4k_1k_2 e^{ik_3L}}{(ia+b)\,e^{k_2L} - (ia-b)\,e^{-k_2L}}$$

where $a = k_2^2 - k_1k_3$ and $b = k_1k_2 + k_2k_3$.

Since $\sinh(z) = (e^z - e^{-z})/2$ or $e^z = 2\sinh(z) + e^{-z}$, substitute $e^{k_2L} = 2\sinh(k_2L) + e^{-k_2L}$ giving:

$$A_3 = \frac{2k_1k_2 e^{ik_3L}}{(ia+b)\sinh(k_2L) + be^{-k_2L}}$$

$$T = |A_3|^2 = A_3 \times A_3^* = \frac{4k_1^2k_2^2}{(a^2+b^2)\sinh^2(k_2L) + b^2}$$

where $a^2 + b^2 = (k_1^2 + k_2^2)(k_2^2 + k_3^2)$ and $b^2 = k_2^2(k_1 + k_3)^2$

(b) In the special case for which $V_1 = V_3 = 0$, eqns 9.14 and 9.17 require that $k_1 = k_3$. Additionally,

$$\left(\frac{k_1}{k_2}\right)^2 = \frac{E}{V_2 - E} = \frac{\varepsilon}{1-\varepsilon} \quad \text{where} \quad \varepsilon = E/V_2.$$

$$a^2 + b^2 = (k_1^2 + k_2^2)^2 = k_2^4\left\{1 + \left(\frac{k_1}{k_2}\right)^2\right\}^2$$

$$b^2 = 4k_1^2k_2^2$$

$$\frac{a^2+b^2}{b^2} = \frac{k_2^2\left\{1 + \left(\frac{k_1}{k_2}\right)^2\right\}^2}{4k_1^2} = \frac{1}{4\varepsilon(1-\varepsilon)}$$

$$T = \frac{b^2}{b^2 + (a^2+b^2)\sinh^2(k_2L)} = \frac{1}{1 + \left(\frac{a^2+b^2}{b^2}\right)\sinh^2(k_2L)}$$

$$T = \left\{1 + \frac{\sinh^2(k_2L)}{4\varepsilon(1-\varepsilon)}\right\}^{-1} = \left\{1 + \frac{(e^{k_2L} - e^{-k_2L})^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1}$$

This proves eqn 9.20a where $V_1 = V_3 = 0$.

In the high wide barrier limit $k_2L \gg 1$. This implies both that e^{-k_2L} is negligibly small compared to e^{k_2L} and that 1 is negligibly small compared to $e^{2k_2L}/\{16\varepsilon(1-\varepsilon)\}$. The previous equation simplifies to

$$T = 16\varepsilon(1-\varepsilon)e^{-2k_2L} \text{ [9.20b]}$$

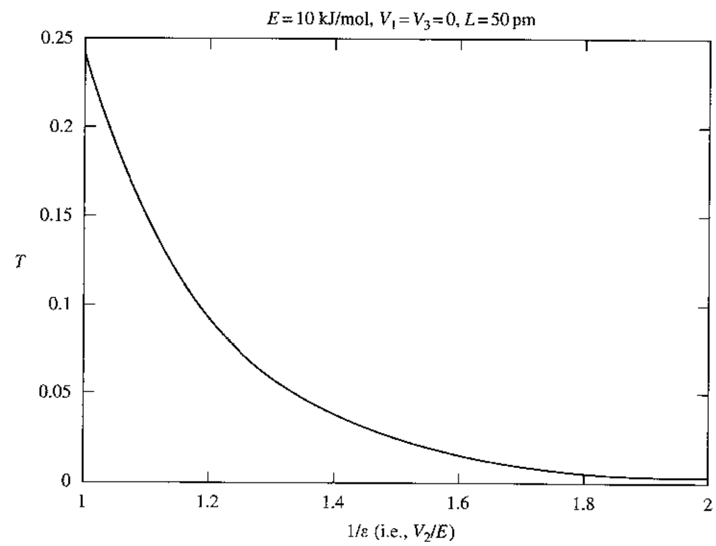

Figure 9.2(b)

P9.12 The Schrödinger equation is $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2}+\dfrac{1}{2}kx^2\psi=E\psi$

and we write $\psi = e^{-gx^2}$, so $\dfrac{d\psi}{dx} = -2gxe^{-gx^2}$

$$\frac{d^2\psi}{dx^2} = -2ge^{-gx^2} + 4g^2x^2e^{-gx^2} = -2g\psi + 4g^2x^2\psi$$

$$\left(\frac{\hbar^2 g}{m}\right)\psi - \left(\frac{2\hbar^2 g^2}{m}\right)x^2\psi + \frac{1}{2}kx^2\psi = E\psi$$

$$\left[\left(\frac{\hbar^2 g}{m}\right) - E\right]\psi + \left(\frac{1}{2}k - \frac{2\hbar^2 g^2}{m}\right)x^2\psi = 0$$

This equation is satisfied if

$$E = \frac{\hbar^2 g}{m} \quad \text{and} \quad 2\hbar^2 g^2 = \frac{1}{2}mk, \quad \text{or} \quad \boxed{g = \frac{1}{2}\left(\frac{mk}{\hbar^2}\right)^{1/2}}$$

Therefore,

$$E = \frac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \frac{1}{2}\hbar\omega \quad \text{if } \omega = \left(\frac{k}{m}\right)^{1/2}$$

P9.14

$$\langle x^n\rangle = \alpha^n\langle y^n\rangle = \alpha^n\int_{-\infty}^{+\infty}\psi y^n\psi\,dx = \alpha^{n+1}\int_{-\infty}^{+\infty}\psi^2 y^n\,dy \quad [x=\alpha y]$$

$$\langle x^3\rangle \propto \int_{-\infty}^{+\infty}\psi^2 y^3\,dy = \boxed{0} \text{ by symmetry} \quad [y^3 \text{ is an odd function of } y]$$

$$\langle x^4\rangle = \alpha^5\int_{-\infty}^{+\infty}\psi y^4\psi\,dy$$

$$y^4\psi = y^4 N H_v e^{-y^2/2}$$

$$
\begin{aligned}
y^4H_v &= y^3\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right) = y^2\left[\tfrac{1}{2}\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + v\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right] \\
&= y^2\left[\tfrac{1}{4}H_{v+2} + \left(v+\tfrac{1}{2}\right)H_v + v(v-1)H_{v-2}\right] \\
&= y\left[\tfrac{1}{4}\left(\tfrac{1}{2}H_{v+3} + (v+2)H_{v+1}\right) + \left(v+\tfrac{1}{2}\right) \times \left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right)\right. \\
&\quad \left. + v(v-1) \times \left(\tfrac{1}{2}H_{v-1} + (v-2)H_{v-3}\right)\right] \\
&= y\left(\tfrac{1}{8}H_{v+3} + \tfrac{3}{4}(v+1)H_{v+1} + \tfrac{3}{2}v^2H_{v-1} + v(v-1) \times (v-2)H_{v-3}\right)
\end{aligned}
$$

Only yH_{v+1} and yH_{v-1} lead to H_v and contribute to the expectation value (since H_v is orthogonal to all except H_v) [Table 9.1]; hence

$$
\begin{aligned}
y^4H_v &= \tfrac{3}{4}y\{(v+1)H_{v+1} + 2v^2H_{v-1}\} + \cdots \\
&= \tfrac{3}{4}\left[(v+1)\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + 2v^2\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right] + \cdots \\
&= \tfrac{3}{4}\{(v+1)^2H_v + v^2H_v\} + \cdots \\
&= \tfrac{3}{4}(2v^2 + 2v + 1)H_v + \cdots
\end{aligned}
$$

Therefore

$$\int_{-\infty}^{+\infty} \psi y^4 \psi \, dy = \tfrac{3}{4}(2v^2 + 2v + 1)N^2 \int_{-\infty}^{+\infty} H_v^2 e^{-y^2} \, dy = \frac{3}{4\alpha}(2v^2 + 2v + 1)$$

and so

$$\langle x^4 \rangle = (\alpha^5) \times \left(\frac{3}{4\alpha}\right) \times (2v^2 + 2v + 1) = \boxed{\frac{3}{4}(2v^2 + 2v + 1)\alpha^4}$$

P9.16

$$\mu \equiv \int \psi_{v'} x \psi_v \, dx = \alpha^2 \int \psi_{v'} y \psi_v \, dy \quad [x = \alpha y]$$

$$y\psi_v = N_v\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right)e^{-y^2/2} \text{ [Table 9.1]}$$

Hence $\mu = \alpha^2 N_v N_{v'} \int \left(\frac{1}{2}H_{v'}H_{v+1} + vH_{v'}H_{v-1}\right)e^{-y^2} \, dy = 0$ unless $v' = v \pm 1$ [Table 9.1]

For $v' = v + 1$

$$\mu = \frac{1}{2}\alpha^2 N_v N_{v+1} \int H_{v+1}^2 e^{-y^2} \, dy = \frac{1}{2}\alpha^2 N_v N_{v+1} \pi^{1/2} 2^{v+1}(v+1)! = \boxed{\alpha\left(\frac{v+1}{2}\right)^{1/2}}$$

For $v' = v - 1$

$$\mu = v\alpha^2 N_v N_{v-1} \int H_{v-1}^2 e^{-y^2} \, dy = v\alpha^2 N_v N_{v-1} \pi^{1/2} 2^{v-1}(v-1)! = \boxed{\alpha\left(\frac{v}{2}\right)^{1/2}}$$

No other values of v' result in a non-zero value for μ; hence, no other transitions are allowed.

Therefore,

$$\langle T\rangle = N^2\left(-\frac{1}{2}\hbar\omega\right)\int_{-\infty}^{+\infty} H_v\left[\frac{1}{4}H_{v+2}+v(v-1)H_{v-2}-\left(v+\frac{1}{2}\right)H_v\right]\mathrm{e}^{-y^2}\,\mathrm{d}x$$

$[\mathrm{d}x = \alpha\mathrm{d}y]$

$$= \alpha N^2(-\tfrac{1}{2}\hbar\omega)\left[0+0-(v+\tfrac{1}{2})\pi^{1/2}2^v v!\right]$$

$$\left[\int_{-\infty}^{+\infty} H_v H_{v'}\mathrm{e}^{-y^2}\,\mathrm{d}y = 0 \quad \text{if } v' \neq v, \text{ Comment 9.2}\right]$$

$$= \boxed{\frac{1}{2}\left(v+\frac{1}{2}\right)\hbar\omega}\ \left[N_v^2 = \frac{1}{\alpha\pi^{1/2}2^v v!},\ \text{Example 9.3}\right].$$

P9.15 **(a)**

$$\langle x\rangle = \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)x\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

$$= \left(\frac{2}{L}\right)\int_0^L x\sin^2 ax\,\mathrm{d}x\left[a=\frac{n\pi}{L}\right]$$

$$= \left(\frac{2}{L}\right)\times\left(\frac{x^2}{4}-\frac{x\sin 2ax}{4a}-\frac{\cos 2ax}{8a^2}\right)\Bigg|_0^L = \left(\frac{2}{L}\right)\times\left(\frac{L^2}{4}\right)$$

$$= \frac{L}{2}\ \text{[by symmetry also]}.$$

$$\left\langle x^2\right\rangle = \frac{2}{L}\int_0^L x^2\sin^2 ax\,\mathrm{d}x = \left(\frac{2}{L}\right)\times\left[\frac{x^3}{6}-\left(\frac{x^2}{4a}-\frac{1}{8a^3}\right)\sin 2ax-\frac{x\cos 2ax}{4a^2}\right]\Bigg|_0^L$$

$$= \left(\frac{2}{L}\right)\times\left(\frac{L^3}{6}-\frac{L^3}{4n^2\pi}\right) = \frac{L^2}{3}\left(1-\frac{1}{6n^2\pi^2}\right).$$

$$\delta x = \left[\frac{L^2}{3}\left(1-\frac{1}{6n^2\pi^2}\right)-\frac{L^2}{4}\right]^{1/2} = \boxed{L\left(\frac{1}{12}-\frac{1}{2\pi^2 n^2}\right)^{1/2}}.$$

$\langle p\rangle = 0$ [by symmetry, also see Exercise 9.2(a)],

$\left\langle p^2\right\rangle = n^2h^2/4L^2$ [from $E = p^2/2m$, also Exercise 9.2(a)].

$$\delta p = \left(\frac{n^2h^2}{4L^2}\right)^{1/2} = \boxed{\frac{nh}{2L}}.$$

$$\delta p\delta x = \frac{nh}{2L}\times L\left(\frac{1}{12}-\frac{1}{2\pi^2n^2}\right)^{1/2} = \frac{nh}{2\sqrt{3}}\left(1-\frac{1}{24\pi^2n^2}\right)^{1/2} > \frac{\hbar}{2}.$$

(b) $\langle x\rangle = \alpha^2\int_{-\infty}^{+\infty}\psi^2 y\,\mathrm{d}y\ [x=\alpha y] = 0$ [by symmetry, y is an odd function].

$$\left\langle x^2\right\rangle = \frac{2}{k}\left\langle\frac{1}{2}kx^2\right\rangle = \frac{2}{k}\langle V\rangle$$

since $2\langle T\rangle = b\langle V\rangle$ [9.35, $\langle T\rangle \equiv E_K$] $= 2\langle V\rangle$ $\left[V = ax^b = \frac{1}{2}kx^2, b = 2\right]$

or $\langle V\rangle = \langle T\rangle = \frac{1}{2}\left(v + \frac{1}{2}\right)\hbar\omega$ [Problem 9.13].

$$\langle x^2\rangle = \left(v+\frac{1}{2}\right)\times\left(\frac{\hbar\omega}{k}\right) = \left(v+\frac{1}{2}\right)\times\left(\frac{\hbar}{\omega m}\right) = \left(v+\frac{1}{2}\right)\times\left(\frac{\hbar^2}{mk}\right)^{1/2} \text{ [9.32].}$$

$$\delta x = \boxed{\left[\left(v+\frac{1}{2}\right)\frac{\hbar}{\omega m}\right]^{1/2}}.$$

$\langle p\rangle = 0$ [by symmetry, or by noting that the integrand is an odd function of x].

$$\langle p^2\rangle = 2m\langle T\rangle = (2m)\times\left(\frac{1}{2}\right)\times\left(v+\frac{1}{2}\right)\times\hbar\omega \text{ [Problem 9.13].}$$

$$\delta p = \boxed{\left[\left(v+\frac{1}{2}\right)\hbar\omega m\right]^{1/2}}.$$

$$\delta p\delta x = \left(v+\frac{1}{2}\right)\hbar \geq \frac{\hbar}{2}.$$

COMMENT. Both results show a consistency with the uncertainty principle in the form $\Delta p\Delta q \geq \frac{\hbar}{2}$ as given in Section 8.6, eqn 8.36a.

P9.17 Use the first two terms of the Taylor series expansion of cosine:

$$V = V_0(1-\cos 3\phi) \approx V_0\left(1 - 1 + \frac{(3\phi)^2}{2}\right) = \frac{9V_0}{2}\phi^2.$$

The Schrödinger equation becomes

$$-\frac{\hbar^2}{2I}\frac{\partial^2\psi}{\partial\phi^2} + \frac{9V_0}{2}\phi^2\psi = E\psi \text{ [9.40 with a non-zero potential energy].}$$

This has the form of the harmonic-oscillator wavefunction (eqn 9.24). The difference in adjacent energy levels is:

$$E_1 - E_0 = \hbar\omega \text{ [9.26] where } \omega = \left(\frac{9V_0}{I}\right)^{1/2} \text{ [adapting 9.25].}$$

If the displacements are sufficiently large, the potential energy does not rise as rapidly with the angle as would a harmonic potential. Each successive energy level would become lower than that of a harmonic oscillator, so the energy levels will become progressively closer together.

Question. The next term in the Taylor series for the potential energy is $-\frac{(27V_0)}{8}\phi^4$. Treat this as a perturbation to the harmonic oscillator wavefunction and compute the first-order correction to the energy.

P9.20 In each case, if the function is an eigenfunction of the operator, the eigenvalue is also the expectation value; if it is not an eigenfunction we form

$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi \, d\tau \ [8.34]$$

(a) $\hat{l}_z e^{i\phi} = \frac{\hbar}{i}\frac{d}{d\phi} e^{i\phi} = \hbar e^{i\phi}$; hence $l_z = \boxed{+\hbar}$

(b) $\hat{l}_z e^{-2i\phi} = \frac{\hbar}{i}\frac{d}{d\phi} e^{-2i\phi} = -2\hbar e^{-2i\phi}$; hence $l_z = \boxed{-2\hbar}$

(c) $\langle l_z \rangle \propto \int_0^{2\pi} \cos\phi \left(\frac{\hbar}{i}\frac{d}{d\phi}\cos\phi\right) d\phi \propto -\frac{\hbar}{i}\int_0^{2\pi} \cos\phi \, \sin\phi \, d\phi = \boxed{0}$

(d)
$$\langle l_z \rangle = N^2 \int_0^{2\pi} (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})^* \left(\frac{\hbar}{i}\frac{d}{d\phi}\right) \times (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi}) \, d\phi$$

$$= \frac{\hbar}{i} N^2 \int_0^{2\pi} (\cos\chi e^{-i\phi} + \sin\chi e^{i\phi}) \times (i\cos\chi e^{i\phi} - \sin\chi e^{-i\phi}) \, d\phi$$

$$= \hbar N^2 \int_0^{2\pi} (\cos^2\chi - \sin^2\chi + \cos\chi \, \sin\chi [e^{2i\phi} - e^{-2i\phi}]) \, d\phi$$

$$= \hbar N^2 (\cos^2\chi - \sin^2\chi) \times (2\pi) = 2\pi\hbar N^2 \cos 2\chi$$

We must evaluate the normalization constant:

$$N^2 \int_0^{2\pi} (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})^* (\cos\chi e^{i\phi} + \sin\chi e^{-i\phi}) \, d\phi = 1$$

$$1 = N^2 \int_0^{2\pi} (\cos^2\chi + \sin^2\chi + \cos\chi \, \sin\chi \, [e^{2i\phi} + e^{-2i\phi}]) \, d\phi$$

$$= 2\pi N^2 (\cos^2\chi + \sin^2\chi) = 2\pi N^2 \quad \text{so } N^2 = \frac{1}{2\pi}$$

Therefore

$$\langle l_z \rangle = \boxed{\hbar \cos 2\chi} \ [\chi \text{ is a parameter}]$$

For the kinetic energy we use $\hat{T} \equiv \hat{E}_K = \frac{\hat{J}_z^2}{2I}$ [9.36] $= -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$ [9.40]

(a) $\hat{T} e^{i\phi} = -\frac{\hbar^2}{2I}(i^2 e^{i\phi}) = \frac{\hbar^2}{2I} e^{i\phi}$; hence $\langle T \rangle = \boxed{\frac{\hbar^2}{2I}}$

(b) $\hat{T} e^{-2i\phi} = -\frac{\hbar^2}{2I}(2i)^2 e^{-2i\phi} = \frac{4\hbar^2}{2I} e^{-2i\phi}$; hence $\langle T \rangle = \boxed{\frac{2\hbar^2}{I}}$

(c) $\hat{T} \cos\phi = -\frac{\hbar^2}{2I}(-\cos\phi) = \frac{\hbar^2}{2I}\cos\phi$; hence $\langle T \rangle = \boxed{\frac{\hbar^2}{2I}}$

(d) $\hat{T}(\cos\chi e^{i\phi} + \sin\chi e^{-i\phi}) = -\frac{\hbar^2}{2I}(-\cos\chi e^{i\phi} - \sin\chi e^{-i\phi}) = \frac{\hbar^2}{2I}(\cos\chi e^{i\phi} + \sin\chi e^{-i\phi})$

and hence $\langle T \rangle = \boxed{\frac{\hbar^2}{2I}}$

P9.23 The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \text{ [9.48 with } V = 0\text{]}.$$

$$\nabla^2\psi = \frac{1}{r}\frac{\partial^2(r\psi)}{\partial r^2} + \frac{1}{r^2}\Lambda^2\psi \text{ [Table 8.1]}.$$

Since r = constant, the first term is eliminated and the Schrödinger equation may be rewritten

$$-\frac{\hbar^2}{2mr^2}\Lambda^2\psi = E\psi \quad \text{or} \quad -\frac{\hbar^2}{2I}\Lambda^2\psi = E\psi \; [I = mr^2] \quad \text{or} \quad \Lambda^2\psi = -\frac{2IE\psi}{\hbar^2}$$

where $\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$.

Now use the specified $\psi = Y_{l,m_l}$ from Table 9.3, and see if they satisfy this equation.

(a) Because $Y_{0,0}$ is a constant, all derivatives with respect to angles are zero, so $\Lambda^2 Y_{0,0} = \boxed{0}$ implying that $E = \boxed{0}$ and angular momentum = $\boxed{0}$ [from $\{l(l+1)\}^{1/2}\hbar$].

(b) $$\Lambda^2 Y_{2,-1} = \frac{1}{\sin^2\theta}\frac{\partial^2 Y_{2,-1}}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{2,-1}}{\partial\theta} \quad \text{where } Y_{2,-1} = N\cos\theta\sin\theta e^{-i\phi}.$$

$$\frac{\partial Y_{2,-1}}{\partial\theta} = Ne^{-i\phi}(\cos^2\theta - \sin^2\theta).$$

$$\begin{aligned}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{2,-1}}{\partial\theta} &= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta Ne^{-i\phi}(\cos^2\theta - \sin^2\theta)\\ &= \frac{Ne^{-i\phi}}{\sin\theta}\left(\sin\theta(-4\cos\theta\sin\theta) + \cos\theta(\cos^2\theta - \sin^2\theta)\right)\\ &= Ne^{-i\phi}\left(-6\cos\theta\sin\theta + \frac{\cos\theta}{\sin\theta}\right) \quad [\cos^3\theta = \cos\theta(1-\sin^2\theta)].\end{aligned}$$

$$\frac{1}{\sin^2\theta}\frac{\partial^2 Y_{2,-1}}{\partial\phi^2} = \frac{-N\cos\theta\sin\theta e^{-i\phi}}{\sin^2\theta} = \frac{-N\cos\theta e^{-i\phi}}{\sin\theta}$$

so $\Lambda^2 Y_{2,-1} = Ne^{-i\phi}(-6\cos\theta\sin\theta) = -6\,Y_{2,-1} = -2(2+1)\,Y_{2,-1}$ [i.e. $l = 2$]
and hence

$$-6Y_{2,-1} = -\frac{2IE}{\hbar^2}Y_{2,-1}, \text{ implying that } \boxed{E = \frac{3\hbar^2}{I}}$$

and the angular momentum is $\{2(2+1)\}^{1/2}\hbar = \boxed{6^{1/2}\hbar}$.

(c) $$\Lambda^2 Y_{3,3} = \frac{1}{\sin^2\theta}\frac{\partial^2 Y_{3,3}}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{3,3}}{\partial\theta} \quad \text{where } Y_{3,3} = N\sin^3\theta e^{3i\phi}.$$

$$\frac{\partial Y_{3,3}}{\partial\theta} = 3N\sin^2\theta\cos\theta e^{3i\phi}.$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{3,3}}{\partial\theta} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}3N\sin^3\theta\cos\theta e^{3i\phi}$$

$$= \frac{3Ne^{3i\phi}}{\sin\theta}(3\sin^2\theta\cos^2\theta - \sin^4\theta) = 3Ne^{3i\phi}\sin\theta(3\cos^2\theta - \sin^2\theta)$$

$$= 3Ne^{3i\phi}\sin\theta(3 - 4\sin^2\theta) \quad [\cos^3\theta = \cos\theta(1-\sin^2\theta)].$$

$$\frac{1}{\sin^2\theta}\frac{\partial^2 Y_{3,3}}{\partial\phi^2} = \frac{-9N\sin^3\theta e^{3i\phi}}{\sin^2\theta} = -9N\sin\theta e^{3i\phi}$$

so $\Lambda^2 Y_{3,3} = -12N\sin^3\theta\, e^{3i\phi} = -12Y_{3,3} = -3(3+1)Y_{3,3}$ [i.e. $l = 3$]
and hence

$$-12Y_{3,3} = -\frac{2IE}{\hbar^2}Y_{3,3}, \text{ implying that } \boxed{E = \frac{6\hbar^2}{I}}$$

and the angular momentum is $\{3(3+1)\}^{1/2}\hbar = \boxed{2\sqrt{3}\hbar}$.

P9.25 From the diagram in Fig. 9.2, $\cos\theta = m_l/\{l(l+1)\}^{1/2}$ and hence $\boxed{\theta = \arccos\frac{m_l}{\{l(l+1)\}^{1/2}}}$.

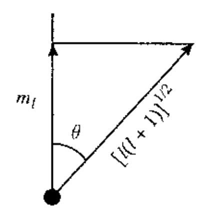

Figure 9.2

For an α electron, $m_s = +\frac{1}{2}$, $s = \frac{1}{2}$ and (with $m_l \to m_s$, $l \to s$)

$$\theta = \arccos\frac{\frac{1}{2}}{\left(\frac{3}{4}\right)^{1/2}} = \arccos\frac{1}{\sqrt{3}} = \boxed{54°44'}.$$

The minimum angle occurs for $m_l = l$:

$$\lim_{l\to\infty}\theta_{\min} = \lim_{l\to\infty}\arccos\left(\frac{l}{\{l(l+1)\}^{1/2}}\right) = \lim_{l\to\infty}\arccos\frac{l}{l} = \arccos 1 = \boxed{0}.$$

P9.27
$$\hat{l} = \hat{r}\times\hat{p} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix} \quad \text{[see any book treating the vector product of vectors]}$$

$$= \mathbf{i}(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y) + \mathbf{j}(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) + \mathbf{k}(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)$$