The Physics of Quantum Mechanics
Solutions to starred problems

3.11* *By expressing the annihilation operator A of the harmonic oscillator in the momentum representation, obtain $\langle p|0\rangle$. Check that your expression agrees with that obtained from the Fourier transform of*

$$\langle x|0\rangle = \frac{1}{(2\pi\ell^2)^{1/4}}\,\mathrm{e}^{-x^2/4\ell^2}, \quad \textit{where} \quad \ell \equiv \sqrt{\frac{\hbar}{2m\omega}}. \tag{3.1}$$

Soln: In the momentum representation $x = \mathrm{i}\hbar\partial/\partial p$ so $[x,p] = \mathrm{i}\hbar\partial p/\partial p = \mathrm{i}\hbar$. Thus from Problem 3.8

$$A = \left(\frac{x}{2\ell} + \mathrm{i}\frac{\ell}{\hbar}p\right) = \mathrm{i}\left(\frac{\ell p}{\hbar} + \frac{\hbar}{2\ell}\frac{\partial}{\partial p}\right)$$

$$0 = Au_0 \quad \Rightarrow \quad \frac{\ell p}{\hbar}u_0 = -\frac{\hbar}{2\ell}\frac{\partial u_0}{\partial p} \quad \Rightarrow \quad u_0(p) \propto \mathrm{e}^{-p^2\ell^2/\hbar^2}$$

Alternatively, transforming $u_0(x)$:

$$\langle p|0\rangle = \int \mathrm{d}x \langle p|x\rangle\langle x|0\rangle = \frac{1}{\sqrt{h}}\int_{-\infty}^{\infty}\mathrm{d}x\,\mathrm{e}^{-\mathrm{i}px/\hbar}\frac{\mathrm{e}^{-x^2/4\ell^2}}{(2\pi\ell^2)^{1/4}}$$

$$= \frac{1}{(2\pi\ell^2h^2)^{1/4}}\int_{-\infty}^{\infty}\mathrm{d}x\,\exp\left(-\left\{\frac{x}{2\ell} + \frac{\mathrm{i}p\ell}{\hbar}\right\}^2\right)\mathrm{e}^{-p^2\ell^2/\hbar^2} = \frac{2\ell\sqrt{\pi}}{(2\pi\ell^2h^2)^{1/4}}\,\mathrm{e}^{-p^2\ell^2/\hbar^2}$$

3.13* *A* **Fermi oscillator** *has Hamiltonian $H = f^\dagger f$, where f is an operator that satisfies*

$$f^2 = 0, \quad ff^\dagger + f^\dagger f = 1. \tag{3.2}$$

Show that $H^2 = H$, and thus find the eigenvalues of H. If the ket $|0\rangle$ satisfies $H|0\rangle = 0$ with $\langle 0|0\rangle = 1$, what are the kets (a) $|a\rangle \equiv f|0\rangle$, and (b) $|b\rangle \equiv f^\dagger|0\rangle$?

In quantum field theory the vacuum is pictured as an assembly of oscillators, one for each possible value of the momentum of each particle type. A boson is an excitation of a harmonic oscillator, while a fermion in an excitation of a Fermi oscillator. Explain the connection between the spectrum of $f^\dagger f$ and the Pauli principle.

Soln:

$$H^2 = f^\dagger ff^\dagger f = f^\dagger(1 - f^\dagger f)f = f^\dagger f = H$$

Since eigenvalues have to satisfy any equations satisfied by their operators, the eigenvalues of H must satisfy $\lambda^2 = \lambda$, which restricts them to the numbers 0 and 1. The Fermi exclusion principle says there can be no more than one particle in a single-particle state, so each such state is a Fermi oscillator that is either excited once or not at all.

$$||a\rangle|^2 = \langle 0|f^\dagger f|0\rangle = 0 \quad \text{so this ket vanishes.}$$

$$||b\rangle|^2 = \langle 0|ff^\dagger|0\rangle = \langle 0|(1 - f^\dagger f)|0\rangle = 1 \quad \text{so } |b\rangle \text{ is more interesting.}$$

Moreover,

$$H|b\rangle = f^\dagger ff^\dagger|0\rangle = f^\dagger(1 - f^\dagger f)|0\rangle = f^\dagger|0\rangle = |b\rangle$$

so $|b\rangle$ is the eigenket with eigenvalue 1.

3.15* *P is the probability that at the end of the experiment described in Problem 3.14, the oscillator is in its second excited state. Show that when $f = \frac{1}{2}$, $P = 0.144$ as follows. First show that the annihilation operator of the original oscillator*

$$A = \tfrac{1}{2}\left\{(f^{-1} + f)A' + (f^{-1} - f)A'^\dagger\right\}, \tag{3.3}$$

where A' and $A'^\dagger$ are the annihilation and creation operators of the final oscillator. Then writing the ground-state ket of the original oscillator as a sum $|0\rangle = \sum_n c_n|n'\rangle$ over the energy eigenkets of the final oscillator, show that the condition $A|0\rangle = 0$ yields the recurrence relation

$$c_{n+1} = -\frac{f^{-1} - f}{f^{-1} + f}\sqrt{\frac{n}{n+1}}\,c_{n-1}. \tag{3.4}$$

Finally using the normalisation of $|0\rangle$*, show numerically that* $c_2 \simeq 0.3795$*. What value do you get for the probability of the oscillator remaining in the ground state?*

Show that at the end of the experiment the expectation value of the energy is $0.2656\hbar\omega$*. Explain physically why this is less than the original ground-state energy* $\frac{1}{2}\hbar\omega$*.*

This example contains the physics behind the inflationary origin of the universe: gravity explosively enlarges the vacuum, which is an infinite collection of harmonic oscillators (Problem 3.13). Excitations of these oscillators correspond to elementary particles. Before inflation the vacuum is unexcited so every oscillator is in its ground state. At the end of inflation, there is non-negligible probability of many oscillators being excited and each excitation implies the existence of a newly created particle.

Soln: From Problem 3.6 we have

$$A \equiv \frac{m\omega x + \mathrm{i}p}{\sqrt{2m\hbar\omega}} \qquad A' \equiv \frac{mf^2\omega x + \mathrm{i}p}{\sqrt{2m\hbar f^2\omega}}$$
$$= \frac{x}{2\ell} + \frac{\mathrm{i}\ell}{\hbar}p \qquad = \frac{fx}{2\ell} + \frac{\mathrm{i}\ell}{f\hbar}p$$

Hence

$$A' + A'^\dagger = \frac{f}{\ell}x \quad A' - A'^\dagger = f\frac{2\mathrm{i}\ell}{f\hbar}p \quad \text{so} \quad A = \frac{1}{2f}(A' + A'^\dagger) + \frac{f}{2}(A' - A'^\dagger)$$

$$0 = A|0\rangle = \tfrac{1}{2}\sum_k \left\{(f^{-1}+f)c_k A'|k'\rangle + (f^{-1}-f)c_k A'^\dagger|k'\rangle\right\}$$
$$= \tfrac{1}{2}\sum_k \left\{(f^{-1}+f)\sqrt{k}c_k|k-1'\rangle + (f^{-1}-f)\sqrt{k+1}c_k|k+1'\rangle\right\}$$

Multiply through by $\langle n'|$:

$$0 = (f^{-1}+f)\sqrt{n+1}c_{n+1} + (f^{-1}-f)\sqrt{n}c_{n-1},$$

which is a recurrence relation from which all non-zero c_n can be determined in terms of c_0. Put $c_0 = 1$ and solve for the c_n. Then evaluate $S \equiv |c_n|^2$ and renormalise: $c_n \to c_n/\sqrt{S}$.

The probability of remaining in the ground state is $|c_0|^2 = 0.8$. $\langle E\rangle = \sum_n |c_n|^2(n+\frac{1}{2})\hbar f^2\omega$. It is less than the original energy because of the chance that energy is in the spring when the stiffness is reduced.

3.16* *In terms of the usual ladder operators* A, $A^\dagger$*, a Hamiltonian can be written*

$$H = \mu A^\dagger A + \lambda(A + A^\dagger). \tag{3.5}$$

What restrictions on the values of the numbers μ *and* λ *follow from the requirement for* H *to be Hermitian?*

Show that for a suitably chosen operator B*,* H *can be rewritten*

$$H = \mu B^\dagger B + \text{constant}, \tag{3.6}$$

where $[B, B^\dagger] = 1$*. Hence determine the spectrum of* H*.*

Soln: Hermiticity requires μ and λ to be real. Defining $B = A + a$ with a a number, we have $[B, B^\dagger] = 1$ and

$H = \mu(B^\dagger - a^*)(B-a) + \lambda(B - a + B^\dagger - a^*) = \mu B^\dagger B + (\lambda - \mu a^*)B + (\lambda - \mu a)B^\dagger + (|a|^2\mu - \lambda(a+a^*))$.

We dispose of the terms linear in B by setting $a = \lambda/\mu$, a real number. Then $H = \mu B^\dagger B - \lambda^2/\mu$. From the theory of the harmonic oscillator we know that the spectrum of $B^\dagger B$ is $0, 1, \ldots$, so the spectrum of H is $n\mu - \lambda^2/\mu$.

3.17* *Numerically calculate the spectrum of the anharmonic oscillator shown in Figure 3.2. From it estimate the period at a sequence of energies. Compare your quantum results with the equivalent classical results.*

Soln:

3.18* *Let $B = cA + sA^\dagger$, where $c \equiv \cosh\theta$, $s \equiv \sinh\theta$ with θ a real constant and A, $A^\dagger$ are the usual ladder operators. Show that $[B, B^\dagger] = 1$.*

Consider the Hamiltonian

$$H = \epsilon A^\dagger A + \tfrac{1}{2}\lambda(A^\dagger A^\dagger + AA), \tag{3.7}$$

where ϵ and λ are real and such that $\epsilon > \lambda > 0$. Show that when

$$\epsilon c - \lambda s = Ec, \quad \lambda c - \epsilon s = Es \tag{3.8}$$

with E a constant, $[B, H] = EB$. Hence determine the spectrum of H in terms of ϵ and λ.

Soln:

$$[B, B^\dagger] = [cA + sA^\dagger, cA^\dagger + sA] = (c^2 - s^2)[A, A^\dagger] = 1$$

$$\begin{aligned}[B, H] &= [cA + sA^\dagger, \epsilon A^\dagger A + \tfrac{1}{2}\lambda(A^\dagger A^\dagger + AA)] = c[A, \epsilon A^\dagger A + \tfrac{1}{2}\lambda A^\dagger A^\dagger] + s[A^\dagger, \epsilon A^\dagger A + \tfrac{1}{2}\lambda AA] \\ &= c(\epsilon A + \lambda A^\dagger) - s(\epsilon A^\dagger + \lambda A) = cEA + sEA^\dagger = EB\end{aligned}$$

as required. Let $H|E_0\rangle = E_0|E_0\rangle$. Then multiplying through by B

$$E_0 B|E_0\rangle = BH|E_0\rangle = (HB + [B, H])|E_0\rangle = (HB + EB)|E_0\rangle$$

So $H(B|E_0\rangle) = (E_0 - E)(B|E_0\rangle)$, which says the $B|E_0\rangle$ is an eigenket for eigenvalue $E_0 - E$.

We assume that the sequence of eigenvalues $E_0, E_0 - E, E_0 - 2E, \ldots$ terminates because $B|E_{\min}\rangle = 0$. Mod-squaring this equation we have

$$\begin{aligned}0 = \langle E_{\min}|B^\dagger B|E_{\min}\rangle &= \langle E_{\min}|(cA^\dagger + sA)(cA + sA^\dagger)|E_{\min}\rangle \\ &= \langle E_{\min}|\{(c^2 + s^2)A^\dagger A + s^2 + cs(A^\dagger A^\dagger + AA)\}|E_{\min}\rangle \\ &= cs\langle E_{\min}|\{(c/s + s/c)A^\dagger A + s/c + (A^\dagger A^\dagger + AA)\}|E_{\min}\rangle\end{aligned}$$

But eliminating E from the given equations, we find $\lambda(c/s + s/c) = 2\epsilon$. Putting this into the last equation

$$0 = \langle E_{\min}| \left\{ \frac{2\epsilon}{\lambda} A^\dagger A + s/c + (A^\dagger A^\dagger + AA) \right\} |E_{\min}\rangle$$

Multiplying through by $\lambda/2$ this becomes

$$0 = \langle E_{\min}|\{H + s\lambda/2c\}|E_{\min}\rangle$$

so $E_{\min} = -s\lambda/2c$. Finally, $x = s/c$ satisfies the quadratic

$$x^2 - 2\frac{\epsilon}{\lambda}x + 1 = 0 \quad \Rightarrow \quad x = \frac{\epsilon}{\lambda} \pm \sqrt{\frac{\epsilon^2}{\lambda^2} - 1}.$$

Also from the above $E = \epsilon - \lambda x$ so the general eigenenergy is

$$\begin{aligned}E_n = E_{\min} + nE &= -\tfrac{1}{2}\lambda x + n\epsilon - n\lambda x = n\epsilon - (n + \tfrac{1}{2})\lambda x = n\epsilon - (n + \tfrac{1}{2})\left(\epsilon \pm \sqrt{\epsilon^2 - \lambda^2}\right) \\ &= -\tfrac{1}{2}\epsilon \mp (n + \tfrac{1}{2})\sqrt{\epsilon^2 - \lambda^2}\end{aligned}$$

We have to choose the plus sign in order to achieve consistency with our previously established value of $E_{\min}$; thus finally

$$E_n = -\tfrac{1}{2}\epsilon + (n + \tfrac{1}{2})\sqrt{\epsilon^2 - \lambda^2}$$

4.2* *Show that the vector product $\mathbf{a} \times \mathbf{b}$ of two classical vectors transforms like a vector under rotations. Hint: A rotation matrix $\mathbf{R}$ satisfies the relations $\mathbf{R} \cdot \mathbf{R}^T = \mathbf{I}$ and det($\mathbf{R}$) $= 1$, which in tensor notation read $\sum_p R_{ip}R_{tp} = \delta_{it}$ and $\sum_{ijk} \epsilon_{ijk} R_{ir} R_{js} R_{kt} = \epsilon_{rst}$.*

Soln: Let the rotated vectors be $\mathbf{a}' = \mathbf{Ra}$ and $\mathbf{b}' = \mathbf{Rb}$. Then

$$\begin{aligned}(\mathbf{a}'\times\mathbf{b}')_i &= \sum_{jklm}\epsilon_{ijk}R_{jl}a_lR_{km}b_m\\ &= \sum_{tjklm}\delta_{it}\epsilon_{tjk}R_{jl}R_{km}a_lb_m\\ &= \sum_{ptjklm}R_{ip}R_{tp}\epsilon_{tjk}R_{jl}R_{km}a_lb_m\\ &= \sum_{plm}R_{ip}\epsilon_{plm}a_lb_m = (\mathbf{Ra}\times\mathbf{b})_i.\end{aligned}$$

4.3* *We have shown that $[v_i, J_j] = \mathrm{i}\sum_k \epsilon_{ijk}v_k$ for any operator whose components v_i form a vector. The expectation value of this operator relation in any state $|\psi\rangle$ is then $\langle\psi|[v_i, J_j]|\psi\rangle = \mathrm{i}\sum_k \epsilon_{ijk}\langle\psi|v_k|\psi\rangle$. Check that with $U(\boldsymbol{\alpha}) = \mathrm{e}^{-\mathrm{i}\boldsymbol{\alpha}\cdot\mathbf{J}}$ this relation is consistent under a further rotation $|\psi\rangle \to |\psi'\rangle = U(\boldsymbol{\alpha})|\psi\rangle$ by evaluating both sides separately.*

Soln: Under the further rotation the LHS $\to \langle\psi|U^\dagger[v_i, J_j]U|\psi\rangle$. Now

$$\begin{aligned}U^\dagger[v_i, J_j]U &= U^\dagger v_iJ_jU - U^\dagger J_jv_iU = (U^\dagger v_iU)(U^\dagger J_jU) - (U^\dagger J_jU)(U^\dagger v_iU)\\ &= \sum_{kl}[R_{ik}v_k, R_{jl}J_l] = \sum_{kl}R_{ik}R_{jl}[v_k, J_l].\end{aligned}$$

Similar $|\psi\rangle \to U|\psi\rangle$ on the RHS yields

$$\mathrm{i}\sum_{km}R_{km}\epsilon_{ijk}\langle\psi|v_m|\psi\rangle.$$

We now multiply each side by $R_{is}R_{jt}$ and sum over i and j. On the LHS this operation yields $[v_s, J_t]$. On the right it yields

$$\mathrm{i}\sum_{ijkm}R_{is}R_{jt}R_{km}\epsilon_{ijk}\langle\psi|v_m|\psi\rangle = \mathrm{i}\sum_m \epsilon_{stm}\langle\psi|v_m|\psi\rangle,$$

which is what our original equation would give for $[v_s, J_t]$.

4.4* *The matrix for rotating an ordinary vector by ϕ around the z-axis is*

$$\mathbf{R}(\phi) \equiv \begin{pmatrix}\cos\phi & -\sin\phi & 0\\ \sin\phi & \cos\phi & 0\\ 0 & 0 & 1\end{pmatrix}. \tag{4.1}$$

By considering the form taken by $\mathbf{R}$ for infinitesimal ϕ calculate from $\mathbf{R}$ the matrix $\boldsymbol{\mathcal{J}}_z$ that appears in $\mathbf{R}(\phi) = \exp(-\mathrm{i}\boldsymbol{\mathcal{J}}_z\phi)$. Introduce new coordinates $u_1 \equiv (-x+\mathrm{i}y)/\sqrt{2}$, $u_2 = z$ and $u_3 \equiv (x+\mathrm{i}y)/\sqrt{2}$. Write down the matrix $\mathbf{M}$ that appears in $\mathbf{u} = \mathbf{M}\cdot\mathbf{x}$ [where $\mathbf{x} \equiv (x, y, z)$] and show that it is unitary. Then show that

$$\boldsymbol{\mathcal{J}}_z' \equiv \mathbf{M}\cdot\boldsymbol{\mathcal{J}}_z\cdot\mathbf{M}^\dagger \tag{4.2}$$

is identical with S_z in the set of spin-one Pauli analogues

$$S_x = \frac{1}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix},\quad S_y = \frac{1}{\sqrt{2}}\begin{pmatrix}0 & -\mathrm{i} & 0\\ \mathrm{i} & 0 & -\mathrm{i}\\ 0 & \mathrm{i} & 0\end{pmatrix},\quad S_z = \begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{pmatrix}. \tag{4.3}$$

Write down the matrix $\boldsymbol{\mathcal{J}}_x$ whose exponential generates rotations around the x-axis, calculate $\boldsymbol{\mathcal{J}}_x'$ by analogy with equation (4.2) and check that your result agrees with S_x in the set (4.3). Explain as fully as you can the meaning of these calculations.

Soln: For an infinitesimal rotation angle $\delta\phi$ to first order in $\delta\phi$ we have

$$1 - \mathrm{i}\boldsymbol{\mathcal{J}}_z\delta\phi = \mathbf{R}(\delta\phi) = \begin{pmatrix}1 & -\delta\phi & 0\\ \delta\phi & 1 & 0\\ 0 & 0 & 1\end{pmatrix}$$

comparing coefficients of $\delta\phi$ we find

$$\boldsymbol{\mathcal{J}}_z = \mathrm{i}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

In components $\mathbf{u} = \mathbf{M}\cdot\mathbf{x}$ reads

$$\begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 & \mathrm{i} & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

so $\mathbf{M}$ is the matrix above. We show that $\mathbf{M}$ is unitary by calculating the product $\mathbf{M}\mathbf{M}^\dagger$. Now we have

$$\begin{aligned}\boldsymbol{\mathcal{J}}'_z &= \tfrac{1}{2}\begin{pmatrix} -1 & \mathrm{i} & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} -1 & 0 & 1 \\ -\mathrm{i} & 0 & -\mathrm{i} \\ 0 & \sqrt{2} & 0 \end{pmatrix} \\ &= \tfrac{1}{2}\begin{pmatrix} -1 & \mathrm{i} & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} -1 & 0 & -1 \\ -\mathrm{i} & 0 & \mathrm{i} \\ 0 & 0 & 0 \end{pmatrix} = \tfrac{1}{2}\begin{pmatrix} 2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -2 \end{pmatrix}\end{aligned}$$

Similarly, we have

$$\boldsymbol{\mathcal{J}}_x = \mathrm{i}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

so

$$\begin{aligned}\boldsymbol{\mathcal{J}}'_x &= \tfrac{1}{2}\begin{pmatrix} -1 & \mathrm{i} & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} -1 & 0 & 1 \\ -\mathrm{i} & 0 & -\mathrm{i} \\ 0 & \sqrt{2} & 0 \end{pmatrix} \\ &= \tfrac{1}{2}\begin{pmatrix} -1 & \mathrm{i} & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 \\ 0 & -\mathrm{i}\sqrt{2} & 0 \\ 1 & 0 & 1 \end{pmatrix} = \tfrac{1}{2}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix}\end{aligned}$$

These results show that the only difference between the generators of rotations of ordinary 3d vectors and the spin-1 representations of the angular-momentum operators, is that for conventional vectors we use a different coordinate system than we do for spin-1 amplitudes. Apart from this, the three amplitudes for the spin of a spin-1 particle to point in various directions are equivalent to the components of a vector, and they transform among themselves when the particle is reoriented for the same reason that the rotation of a vector changes its Cartesian components.

4.6* *Show that if* $\boldsymbol{\alpha}$ *and* $\boldsymbol{\beta}$ *are non-parallel vectors,* $\boldsymbol{\alpha}$ *is not invariant under the combined rotation* $\mathbf{R}(\boldsymbol{\alpha})\mathbf{R}(\boldsymbol{\beta})$. *Hence show that*

$$\mathbf{R}^{\mathrm{T}}(\boldsymbol{\beta})\mathbf{R}^{\mathrm{T}}(\boldsymbol{\alpha})\mathbf{R}(\boldsymbol{\beta})\mathbf{R}(\boldsymbol{\alpha})$$

is not the identity operation. Explain the physical significance of this result.

Soln: $\mathbf{R}(\boldsymbol{\alpha})\boldsymbol{\alpha} = \boldsymbol{\alpha}$ because a rotation leaves its axis invariant. But the only vectors that are invariant under $\mathbf{R}(\boldsymbol{\beta})$ are multiples of the rotation axis $\boldsymbol{\beta}$. So $\mathbf{R}(\boldsymbol{\beta})\boldsymbol{\alpha}$ is not parallel to $\boldsymbol{\alpha}$.

If $\mathbf{R}^{\mathrm{T}}(\boldsymbol{\beta})\mathbf{R}^{\mathrm{T}}(\boldsymbol{\alpha})\mathbf{R}(\boldsymbol{\beta})\mathbf{R}(\boldsymbol{\alpha})$ were the identity, we would have

$$\mathbf{R}^{\mathrm{T}}(\boldsymbol{\beta})\mathbf{R}^{\mathrm{T}}(\boldsymbol{\alpha})\mathbf{R}(\boldsymbol{\beta})\mathbf{R}(\boldsymbol{\alpha})\boldsymbol{\alpha} = \boldsymbol{\alpha} \quad\Rightarrow\quad \mathbf{R}(\boldsymbol{\beta})\mathbf{R}(\boldsymbol{\alpha})\boldsymbol{\alpha} = \mathbf{R}(\boldsymbol{\alpha})\mathbf{R}(\boldsymbol{\beta})\boldsymbol{\alpha} \quad\Rightarrow\quad \mathbf{R}(\boldsymbol{\beta})\boldsymbol{\alpha} = \mathbf{R}(\boldsymbol{\alpha})(\mathbf{R}(\boldsymbol{\beta})\boldsymbol{\alpha})$$

which would imply that $\mathbf{R}(\boldsymbol{\beta})\boldsymbol{\alpha}$ is invariant under $\mathbf{R}(\boldsymbol{\alpha})$. Consequently we would have $\mathbf{R}(\boldsymbol{\beta})\boldsymbol{\alpha} = \boldsymbol{\alpha}$. But this is true only if $\boldsymbol{\alpha}$ is parallel to $\boldsymbol{\beta}$. So our original hypothesis that $\mathbf{R}^{\mathrm{T}}(\boldsymbol{\beta})\mathbf{R}^{\mathrm{T}}(\boldsymbol{\alpha})\mathbf{R}(\boldsymbol{\beta})\mathbf{R}(\boldsymbol{\alpha}) = \mathbf{I}$ is wrong. This demonstrates that when you rotate about two non-parallel axes and then do the reverse rotations in the same order, you always finish with a non-trivial rotation.

4.7* *In this problem you derive the wavefunction*

$$\langle\mathbf{x}|\mathbf{p}\rangle = \mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{x}/\hbar} \tag{4.4}$$

of a state of well-defined momentum from the properties of the translation operator $U(\mathbf{a})$. *The state* $|\mathbf{k}\rangle$ *is one of well-defined momentum* $\hbar\mathbf{k}$. *How would you characterise the state* $|\mathbf{k}'\rangle \equiv U(\mathbf{a})|\mathbf{k}\rangle$? *Show*

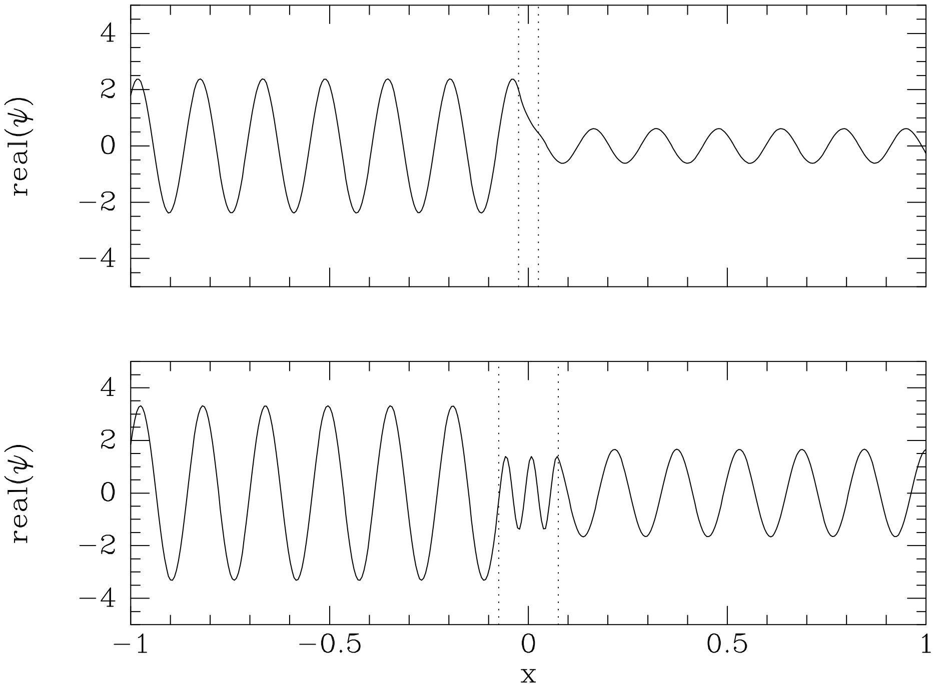

Figure 5.0 The real part of the wavefunction when a free particle of energy E is scattered by a classically forbidden square barrier barrier (top) and a potential well (bottom). The upper panel is for a barrier of height $V_0 = E/0.7$ and half-width a such that $2mEa^2/\hbar^2 = 1$. The lower panel is for a well of depth $V_0 = E/0.2$ and half-width a such that $2mEa^2/\hbar^2 = 9$. In both panels $(2mE/\hbar^2)^{1/2} = 40$.

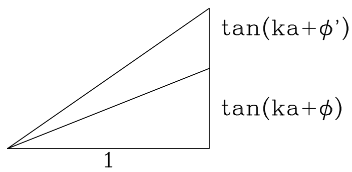

Figure 5.1 A triangle for Problem 5.10

that the wavefunctions of these states are related by $u_{\mathbf{k}'}(\mathbf{x}) = \mathrm{e}^{-\mathrm{i}\mathbf{a}\cdot\mathbf{k}}u_{\mathbf{k}}(\mathbf{x})$ *and* $u_{\mathbf{k}'}(\mathbf{x}) = u_{\mathbf{k}}(\mathbf{x}-\mathbf{a})$. *Hence obtain equation (4.4).*

Soln: $U(\mathbf{a})|\mathbf{k}\rangle$ is the result of translating a state of well-defined momentum by $\mathbf{k}$. Moving to the position representation

$$u_{\mathbf{k}'}(\mathbf{x}) = \langle\mathbf{x}|U(\mathbf{a})|\mathbf{k}\rangle = \langle\mathbf{k}|U^\dagger(\mathbf{a})|\mathbf{x}\rangle^* = \langle\mathbf{k}|\mathbf{x}-\mathbf{a}\rangle^* = u_{\mathbf{k}}(\mathbf{x}-\mathbf{a})$$

Also

$$\langle\mathbf{x}|U(\mathbf{a})|\mathbf{k}\rangle = \langle\mathbf{x}|\mathrm{e}^{-\mathrm{i}\mathbf{a}\cdot\mathbf{p}/\hbar}|\mathbf{k}\rangle = \mathrm{e}^{-\mathrm{i}\mathbf{a}\cdot\mathbf{k}}\langle\mathbf{x}|\mathbf{k}\rangle = \mathrm{e}^{-\mathrm{i}\mathbf{a}\cdot\mathbf{k}}u_{\mathbf{k}}(\mathbf{x})$$

Putting these results together we have $u_{\mathbf{k}}(\mathbf{x}-\mathbf{a}) = \mathrm{e}^{-\mathrm{i}\mathbf{a}\cdot\mathbf{k}}u_{\mathbf{k}}(\mathbf{x})$. Setting $\mathbf{a} = \mathbf{x}$ we find $u_{\mathbf{k}}(\mathbf{x}) = \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}u_{\mathbf{k}}(0)$, as required.

5.13* *This problem is about the coupling of ammonia molecules to electromagnetic waves in an ammonia maser. Let* $|+\rangle$ *be the state in which the N atom lies above the plane of the H atoms and* $|-\rangle$ *be the state in which the N lies below the plane. Then when there is an oscillating electric field* $\mathcal{E}\cos\omega t$ *directed perpendicular to the plane of the hydrogen atoms, the Hamiltonian in the* $|\pm\rangle$ *basis becomes*

$$H = \begin{pmatrix} \overline{E} + q\mathcal{E}s\cos\omega t & -A \\ -A & \overline{E} - q\mathcal{E}s\cos\omega t \end{pmatrix}. \tag{5.1}$$

Transform this Hamiltonian from the $|\pm\rangle$ *basis to the basis provided by the states of well-defined parity* $|\mathrm{e}\rangle$ *and* $|\mathrm{o}\rangle$ *(where* $|\mathrm{e}\rangle = (|+\rangle + |-\rangle)/\sqrt{2}$, *etc). Writing*

$$|\psi\rangle = a_{\mathrm{e}}(t)\mathrm{e}^{-\mathrm{i}E_{\mathrm{e}}t/\hbar}|\mathrm{e}\rangle + a_{\mathrm{o}}(t)\mathrm{e}^{-\mathrm{i}E_{\mathrm{o}}t/\hbar}|\mathrm{o}\rangle, \tag{5.2}$$

show that the equations of motion of the expansion coefficients are

$$\begin{aligned}\frac{\mathrm{d}a_\mathrm{e}}{\mathrm{d}t} &= -\mathrm{i}\Omega a_\mathrm{o}(t)\Big(\mathrm{e}^{\mathrm{i}(\omega-\omega_0)t} + \mathrm{e}^{-\mathrm{i}(\omega+\omega_0)t}\Big)\\ \frac{\mathrm{d}a_\mathrm{o}}{\mathrm{d}t} &= -\mathrm{i}\Omega a_\mathrm{e}(t)\Big(\mathrm{e}^{\mathrm{i}(\omega+\omega_0)t} + \mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}\Big),\end{aligned} \tag{5.3}$$

where $\Omega \equiv q\mathcal{E}s/2\hbar$ and $\omega_0 = (E_\mathrm{o} - E_\mathrm{e})/\hbar$. Explain why in the case of a maser the exponentials involving $\omega + \omega_0$ can be neglected so the equations of motion become

$$\frac{\mathrm{d}a_\mathrm{e}}{\mathrm{d}t} = -\mathrm{i}\Omega a_\mathrm{o}(t)\mathrm{e}^{\mathrm{i}(\omega-\omega_0)t}, \quad \frac{\mathrm{d}a_\mathrm{o}}{\mathrm{d}t} = -\mathrm{i}\Omega a_\mathrm{e}(t)\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}. \tag{5.4}$$

Solve the equations by multiplying the first equation by $\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}$ and differentiating the result. Explain how the solution describes the decay of a population of molecules that are initially all in the higher energy level. Compare your solution to the result of setting $\omega = \omega_0$ in (5.4).

Soln: We have

$$\begin{aligned}\langle \mathrm{e}|H|\mathrm{e}\rangle &= \tfrac{1}{2}\left(\langle +| + \langle -|\right) H \left(|+\rangle + |-\rangle\right)\\ &= \tfrac{1}{2}\left(\langle +|H|+\rangle + \langle -|H|-\rangle + \langle -|H|+\rangle + \langle +|H|-\rangle\right)\\ &= \overline{E} - A = E_\mathrm{e}\\ \langle \mathrm{o}|H|\mathrm{o}\rangle &= \tfrac{1}{2}\left(\langle +| - \langle -|\right) H \left(|+\rangle - |-\rangle\right)\\ &= \tfrac{1}{2}\left(\langle +|H|+\rangle + \langle -|H|-\rangle - \langle -|H|+\rangle - \langle +|H|-\rangle\right)\\ &= \overline{E} + A = E_\mathrm{o}\end{aligned}$$

$$\begin{aligned}\langle \mathrm{o}|H|\mathrm{e}\rangle = \langle \mathrm{e}|H|\mathrm{o}\rangle &= \tfrac{1}{2}\left(\langle +| + \langle -|\right) H \left(|+\rangle - |-\rangle\right)\\ &= \tfrac{1}{2}\left(\langle +|H|+\rangle - \langle -|H|-\rangle + \langle -|H|+\rangle - \langle +|H|-\rangle\right)\\ &= q\mathcal{E}s\cos(\omega t)\end{aligned}$$

Now we use the TDSE to calculate the evolution of $|\psi\rangle = a_\mathrm{e}\mathrm{e}^{-\mathrm{i}E_\mathrm{e}t/\hbar}|\mathrm{e}\rangle + a_\mathrm{o}\mathrm{e}^{-\mathrm{i}E_\mathrm{o}t/\hbar}|\mathrm{o}\rangle$:

$$\begin{aligned}\mathrm{i}\hbar\frac{\partial|\psi\rangle}{\partial t} &= \mathrm{i}\hbar\dot a_\mathrm{e}\mathrm{e}^{-\mathrm{i}E_\mathrm{e}t/\hbar}|\mathrm{e}\rangle + a_\mathrm{e}E_\mathrm{e}\mathrm{e}^{-\mathrm{i}E_\mathrm{e}t/\hbar}|\mathrm{e}\rangle + \mathrm{i}\hbar\dot a_\mathrm{o}\mathrm{e}^{-\mathrm{i}E_\mathrm{o}t/\hbar}|\mathrm{o}\rangle + a_\mathrm{o}E_\mathrm{o}\mathrm{e}^{-\mathrm{i}E_\mathrm{o}t/\hbar}|\mathrm{o}\rangle\\ &= a_\mathrm{e}\mathrm{e}^{-\mathrm{i}E_\mathrm{e}t/\hbar}H|\mathrm{e}\rangle + a_\mathrm{o}\mathrm{e}^{-\mathrm{i}E_\mathrm{o}t/\hbar}H|\mathrm{o}\rangle\end{aligned}$$

We now multiply through by first $\langle \mathrm{e}|$ and then $\langle \mathrm{o}|$. After dividing through by some exponential factors to simplify, we get

$$\begin{aligned}\mathrm{i}\hbar\dot a_\mathrm{e} + a_\mathrm{e}E_\mathrm{e} &= a_\mathrm{e}\langle \mathrm{e}|H|\mathrm{e}\rangle + a_\mathrm{o}\mathrm{e}^{\mathrm{i}(E_\mathrm{e}-E_\mathrm{o})t/\hbar}\langle \mathrm{e}|H|\mathrm{o}\rangle\\ \mathrm{i}\hbar\dot a_\mathrm{o} + a_\mathrm{o}E_\mathrm{o} &= a_\mathrm{e}\mathrm{e}^{\mathrm{i}(E_\mathrm{o}-E_\mathrm{e})t/\hbar}\langle \mathrm{o}|H|\mathrm{e}\rangle + a_\mathrm{o}\langle \mathrm{o}|H|\mathrm{o}\rangle\end{aligned}$$

With the results derived above

$$\begin{aligned}\mathrm{i}\hbar\dot a_\mathrm{e} + a_\mathrm{e}E_\mathrm{e} &= a_\mathrm{e}E_\mathrm{e} + a_\mathrm{o}\mathrm{e}^{\mathrm{i}(E_\mathrm{e}-E_\mathrm{o})t/\hbar}q\mathcal{E}s\cos(\omega t)\\ \mathrm{i}\hbar\dot a_\mathrm{o} + a_\mathrm{o}E_\mathrm{o} &= a_\mathrm{e}\mathrm{e}^{\mathrm{i}(E_\mathrm{o}-E_\mathrm{e})t/\hbar}q\mathcal{E}s\cos(\omega t) + a_\mathrm{o}E_\mathrm{o}\end{aligned}$$

After cancelling terms in each equation, we obtain the desired equations of motion on expressing the cosines in terms of exponentials and using the new notation.

The exponential with frequency $\omega + \omega_0$ oscillates so rapidly that it effectively averages to zero, so we can drop it. Multiplying the first eqn through by $\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}$ and differentiating gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}\dot a_\mathrm{e}\right) = \mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}\left[-\mathrm{i}(\omega-\omega_0)\dot a_\mathrm{e} + \ddot a_\mathrm{e}\right] = -\Omega^2 a_\mathrm{e}\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}$$

The exponentials cancel leaving a homogeneous second-order o.d.e. with constant coefficients. Since initially all molecules are in the higher-energy state $|\mathrm{o}\rangle$, we have to solve subject to the boundary

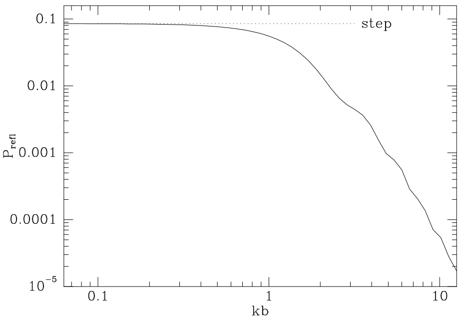

Figure 5.2 The symbols show the ratio of the probability of reflection to the probability of transmission when particles move from $x = -\infty$ in the potential (5.69) with energy $E = \hbar^2 k^2/2m$ and $V_0 = 0.7E$. The dotted line is the value obtained for a step change in the potential

condition $a_e(0) = 0$. With $a_0(0) = 1$ we get from the original equations the second initial condition $\dot{a}_e(0) = -i\Omega$. For trial solution $a_e \propto e^{\alpha t}$ the auxiliary eqn is

$$\alpha^2 - i(\omega - \omega_0)\alpha + \Omega^2 = 0 \quad \Rightarrow \quad \alpha = \tfrac{1}{2}\left[i(\omega - \omega_0) \pm \sqrt{-(\omega - \omega_0)^2 - 4\Omega^2}\right] = i\omega_\pm$$

with $\omega\pm = \frac{1}{2}\left[(\omega - \omega_0) \pm \sqrt{(\omega - \omega_0)^2 + 4\Omega^2}\right]$. When $\omega \simeq \omega_0$, these frequencies both lie close to Ω. From the condition $a_e(0) = 0$, the required solution is $a_e(t) \propto (e^{i\omega_+ t} - e^{i\omega_- t})$ and the constant of proportionality follows from the second initial condition, so finally

$$a_e(t) = \frac{-\Omega}{\sqrt{(\omega - \omega_0)^2 + 4\Omega^2}}(e^{i\omega_+ t} - e^{i\omega_- t}) \qquad (*)$$

The probability oscillates between the odd and even states. First the oscillating field stimulates emission of radiation and decay from $|o\rangle$ to $|e\rangle$. Later the field excites molecules in the ground state to move back up to the first-excited state $|o\rangle$.

If we solve the original equations (1) exactly on resonance ($\omega = \omega_0$), the relevant solution is

$$a_e(t) = \tfrac{1}{2}(e^{-i\Omega t} - e^{i\Omega t}),$$

which is what our general solution $(*)$ reduces to as $\omega \to \omega_0$.

5.15* *Particles of mass m and momentum $\hbar k$ at $x < -a$ move in the potential*

$$V(x) = V_0 \begin{cases} 0 & \text{for } x < -a \\ \frac{1}{2}[1 + \sin(\pi x/2a)] & \text{for } |x| < a \\ 1 & \text{for } x > a, \end{cases} \qquad (5.5)$$

where $V_0 < \hbar^2 k^2/2m$. Numerically reproduce the reflection probabilities plotted in Figure 5.20 as follows. Let $\psi_i \equiv \psi(x_j)$ be the value of the wavefunction at $x_j = j\Delta$, where Δ is a small increment in the x coordinate. From the TISE *show that*

$$\psi_j \simeq (2 - \Delta^2 k^2)\psi_{j+1} - \psi_{j+2}, \qquad (5.6)$$

where $k \equiv \sqrt{2m(E - V)}/\hbar$. Determine ψ_j at the two grid points with the largest values of x from a suitable boundary condition, and use the recurrence relation (5.6) to determine ψ_j at all other grid points. By matching the values of ψ at the points with the smallest values of x to a sum of sinusoidal waves, determine the probabilities required for the figure. Be sure to check the accuracy of your code when $V_0 = 0$, and in the general case explicitly check that your results are consistent with equal fluxes of particles towards and away from the origin.

Equation (12.40) gives an analytical approximation for ψ in the case that there is negligible reflection. Compute this approximate form of ψ and compare it with your numerical results for larger values of a.

Soln:

We discretise the TISE

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \quad \text{by} \quad -\frac{\hbar^2}{2m}\frac{\psi_{j+1} + \psi_{j-1} - 2\psi_j}{\Delta^2} + V_j\psi_j = E\psi_j$$

which readily yields the required recurrence relation. At the right-hand boundary we require a pure outgoing wave, so $\psi_j = \exp(\mathrm{i}jK\Delta)$ gives ψ at the two last grid points. From the recurrence relation we obtain ψ elsewhere. At the left boundary we solve for A_+ and A_- the equations

$$A_+ \exp(\mathrm{i}0k\Delta) + A_- \exp(-\mathrm{i}0k\Delta) = \psi_0$$
$$A_+ \exp(\mathrm{i}1k\Delta) + A_- \exp(-\mathrm{i}1k\Delta) = \psi_1$$

The transmission probability is $(K/k)/|A_+|^2$. The code must reproduce the result of Problem 5.4 in the appropriate limit.

5.16* *In this problem we obtain an analytic estimate of the energy difference between the even- and odd-parity states of a double square well. Show that for large θ, $\coth\theta - \tanh\theta \simeq 4\mathrm{e}^{-2\theta}$. Next letting δk be the difference between the k values that solve*

$$\tan\left[r\pi - k(b-a)\right]\sqrt{\frac{W^2}{(ka)^2}-1} = \begin{cases} \coth\left(\sqrt{W^2-(ka)^2}\right) & \textit{even parity} \\ \tanh\left(\sqrt{W^2-(ka)^2}\right) & \textit{odd parity,} \end{cases} \tag{5.7a}$$

where

$$W \equiv \sqrt{\frac{2mV_0a^2}{\hbar^2}} \tag{5.7b}$$

for given r in the odd- and even-parity cases, deduce that

$$\left\{\left[\left(\frac{W^2}{(ka)^2}-1\right)^{1/2} + \left(\frac{W^2}{(ka)^2}-1\right)^{-1/2}\right](b-a) + \frac{1}{k}\left(1-\frac{(ka)^2}{W^2}\right)^{-1}\right\}\delta k \simeq -4\exp\left[-2\sqrt{W^2-(ka)^2}\right]. \tag{5.8}$$

Hence show that when $W \gg 1$ the fractional difference between the energies of the ground and first excited states is

$$\frac{\delta E}{E} \simeq \frac{-8a}{W(b-a)}\,\mathrm{e}^{-2W\sqrt{1-E/V_0}}. \tag{5.9}$$

Soln: First

$$\coth\theta - \tanh\theta = \frac{\mathrm{e}^\theta+\mathrm{e}^{-\theta}}{\mathrm{e}^\theta-\mathrm{e}^{-\theta}} - \frac{\mathrm{e}^\theta-\mathrm{e}^{-\theta}}{\mathrm{e}^\theta+\mathrm{e}^{-\theta}} = \frac{1+\mathrm{e}^{-2\theta}}{1-\mathrm{e}^{-2\theta}} - \frac{1-\mathrm{e}^{-2\theta}}{1+\mathrm{e}^{-2\theta}} \simeq (1+2\mathrm{e}^{-2\theta}) - (1-2\mathrm{e}^{-2\theta}) = 4\mathrm{e}^{-2\theta}$$

So when $W \gg 1$ the difference in the right side of the equations for k in the cases of even and odd parity is small and we may estimate the difference in the left side by its derivative w.r.t. k times the difference δk in the solutions. That is

$$-\,\mathrm{s}^2[r\pi - k(b-a)](b-a)\delta k\sqrt{\frac{W^2}{(ka)^2}-1} + \tan[r\pi - k(b-a)]\frac{-W^2/(ka)^2\delta k/k}{\sqrt{\frac{W^2}{(ka)^2}-1}} \simeq 4\mathrm{e}^{-2\sqrt{W^2-(ka)^2}}$$

In the case of interest the right side of the original equation is close to unity, so we can simplify the last equation by using

$$\tan\left[r\pi - k(b-a)\right]\sqrt{\frac{W^2}{(ka)^2}-1} \simeq 1$$

With the help of the identity $\mathrm{s}^2\theta = 1 + \tan^2\theta$ we obtain the required relation. We now approximate the left side for $W \gg ka$. This yields

$$\frac{W}{ka}(b-a)\delta k \simeq -4\mathrm{e}^{-2W\sqrt{1-(ka/W)^2}} \tag{\$}$$

Since $E = \hbar^2k^2/2m$, $\delta E/E = 2\delta k/k$ and

$$(ka/W)^2 = \frac{2mEa^2}{\hbar^2} \times \frac{\hbar^2}{2mV_0a^2} = E/V_0.$$

The required relation follows when we use these relations in ($).

6.11* *Show that when the density operator takes the form $\rho = |\psi\rangle\langle\psi|$, the expression $\overline{Q} = \mathrm{Tr}\, Q\rho$ for the expectation value of an observable can be reduced to $\langle\psi|Q|\psi\rangle$. Explain the physical significance of this result. For the given form of the density operator, show that the equation of motion of ρ yields*

$$|\phi\rangle\langle\psi| = |\psi\rangle\langle\phi| \quad \text{where} \quad |\phi\rangle \equiv \mathrm{i}\hbar\frac{\partial|\psi\rangle}{\partial t} - H|\psi\rangle. \tag{6.1}$$

Show from this equation that $|\phi\rangle = a|\psi\rangle$, where a is real. Hence determine the time evolution of $|\psi\rangle$ given the at $t = 0$, $|\psi\rangle = |E\rangle$ is an eigenket of H. Explain why ρ does not depend on the phase of $|\psi\rangle$ and relate this fact to the presence of a in your solution for $|\psi, t\rangle$.

Soln:

$$\mathrm{Tr}(Q\rho) = \sum_n \langle n|Q|\psi\rangle\langle\psi|n\rangle$$

We choose a basis that $|\psi\rangle$ is a member. Then there is only one non-vanishing term in the sum, when $|n\rangle = |\psi\rangle$, and the right side reduces to $\langle\psi|Q|\psi\rangle$ as required. This result shows that density operators recover standard experimental predictions when the system is in a pure state.

Differentiating the given ρ we have

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial|\psi\rangle}{\partial t}\langle\psi| + |\psi\rangle\frac{\partial\langle\psi|}{\partial t} = \frac{1}{\mathrm{i}\hbar}\left(H|\psi\rangle\langle\psi| - |\psi\rangle\langle\psi|H\right)$$

Gathering the terms proportional to $\langle\psi|$ on the left and those proportional to $|\psi\rangle$ on the right we obtain the required expression. Now

$$|\phi\rangle\langle\psi| = |\psi\rangle\langle\phi| \quad\Rightarrow\quad |\phi\rangle\langle\psi|\phi\rangle = |\psi\rangle\langle\phi|\phi\rangle,$$

which establishes that $|\phi\rangle \propto |\psi\rangle$. We define a as the constant of proportionality. Using $|\phi\rangle = a|\psi\rangle$ in $|\phi\rangle\langle\psi| = |\psi\rangle\langle\phi|$ we learn that $a = a^*$ so a is real.

Returning to the definition of $|\phi\rangle$ we now have

$$\mathrm{i}\hbar\frac{\partial|\psi\rangle}{\partial t} = (H - a)|\psi\rangle.$$

This differs from the TDSE in having the term in a. If $|\psi\rangle$ is an eigenfunction of H, we find that its time dependence is $|\psi, t\rangle = |\psi, 0\rangle \mathrm{e}^{-\mathrm{i}(E-a)t/\hbar}$ rather than the expected result $|\psi, t\rangle = |\psi, 0\rangle\mathrm{e}^{-\mathrm{i}Et/\hbar}$. We cannot determine a from the density-matrix formalism because ρ is invariant under the transformation $|\psi\rangle \to \mathrm{e}^{-\mathrm{i}\chi}|\psi\rangle$, where χ is any real number.

7.9* *Repeat the analysis of Problem 7.8 for spin-one particles coming on filters aligned successively along $+z$, 45° from z towards x [i.e. along (1,0,1)], and along x.*

Use classical electromagnetic theory to determine the outcome in the case that the spin-one particles were photons and the filters were Polaroid. Why do you get a different answer?

Soln: We adapt the calculation of Problem 7.8 by replacing the matrix for J_x by that for $\mathbf{n}\cdot\mathbf{J} = (J_x + J_z)/\sqrt{2}$. So if now (a, b, c) is $|+\mathbf{n}\rangle$ in the usual basis, we have

$$\begin{pmatrix} 2^{-1/2} & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & -2^{-1/2} \end{pmatrix}\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix} \quad\Rightarrow\quad \begin{cases} a = \dfrac{b}{2-\sqrt{2}} \\[2ex] c = \dfrac{b}{2+\sqrt{2}} \end{cases}$$

The normalisation yields $b = \frac{1}{2}$, so $a = \frac{1}{2}/(2-\sqrt{2})$ and the required probability is the square of this, $0.25/(6-4\sqrt{2}) \simeq 0.73$. So the probability of getting through all three filters is $\frac{1}{3}\times(0.73)^2 \simeq 0.177$.

In electromagnetism just one of two polarisations gets through the first filter, so we must say that a photon has a probability of half of passing the first filter. Then we resolve its $\mathcal{E}$ field along the direction of the second filter and find that the amplitude of $\mathcal{E}$ falls by $1/\sqrt{2}$ on passing the second filter, so half the energy and therefore photons that pass the first filter pass the second. Of these just a half pass the third filter. Hence in total $\frac{1}{8} = 0.125$ of the photons get right through.

Although photons are spin-one particles, there are two major difference between the two cases. Most obviously, polaroid selects for linear polarisation rather than circular polarisation, and a photon with well-defined angular momentum is circularly polarised. The other difference is that a photon can be in the state $|+z\rangle$ or $|-z\rangle$ but not the state $|0z\rangle$, where the z-axis is parallel to the photon's motion. This fact arises because emag waves are transverse so they do not drive motion in the direction of propagation **k**; an angular momentum vector perpendicular to **k** would require motion along **k**. Our theory does not allow for this case because it is non-relativistic, whereas a photon, having zero rest mass, is an inherently relativistic object; we cannot transform to a frame in which a photon is at rest so all three directions would be equivalent.

7.13* *Write a computer program that determines the amplitudes a_m in*

$$|\mathbf{n}; s, s\rangle = \sum_{m=-s}^{s} a_m |s, m\rangle$$

where $\mathbf{n} = (\sin\theta, 0, \cos\theta)$ with θ any angle and $|\mathbf{n}; s, s\rangle$ is the ket that solves the equation $(\mathbf{n} \cdot \mathbf{S})|\mathbf{n}; s, s\rangle = s|\mathbf{n}; s, s\rangle$. Explain physically the nature of this state.

Use your a_m to evaluate the expectation values $\langle S_x\rangle$ and $\langle S_x^2\rangle$ for this state and hence show that the rms fluctuation in measurements of S_x will be $\sqrt{s/2}\cos\theta$.

Soln: We use a routine `tridiag()` that computes the e-values and e-kets of a real symmetric tri-diagonal matrix – the routine `tqli()` in *Numerical Recipies* by Press et al. is suitable.

```
#define J 100
#define NT 3
double tridiag(double*,double*,int,double**)// evaluates & ekets of real,
//                                     symmetric tridiagonal matrix
double alphap(int j,int m){
  if(m>=j)return 0;
  return sqrt((double)(j*(j+1)-m*(m+1)));
}
double alpham(int j,int m){
  if(m<=-j) return 0;
  return sqrt((double)(j*(j+1)-m*(m-1)));
}
void expect(double *a,int j,double st){//evaluate <Sx> and <Sx^2>
  double s1=0,s2=0;
  for(int n=-j;n<=j;n++){
    int nm2=n-2,nm1=n-1,np1=n+1,np2=n+2;
    if(nm2>=-j) s2+=alpham(j,n)*alpham(j,nm1)*a[nm2]*a[n];
    if(np2<=j) s2+=alphap(j,n)*alphap(j,np1)*a[np2]*a[n];
    s2+=(alphap(j,nm1)*alpham(j,n)+alpham(j,np1)*alphap(j,n))*pow(a[n],2);
    if(nm1>=-j) s1+=alpham(j,n)*a[nm1]*a[n];
    if(np1<=j) s1+=alphap(j,n)*a[np1]*a[n];
  }
  s1*=.5; s2*=.25;
  printf("%f %f %f %f\n",s1,j*st,s2,.5*j*(1-st*st)+pow(j*st,2));
}
int main(void){
  double pi=acos(-1),theta[NT]={80,120,30};
  double *D = new double[2*J+1];
  double *E = new double[2*J+1];
  double **Z = new double*[2*J+1];//allocate storage for square matrix
  for(int i=0; i<2*J+1; i++) Z[i] = new double[2*J+1];
  for(int it=0; it<3; it++){
    theta[it]=theta[it]*pi/180;
    double ct=cos(theta[it]), st=sin(theta[it]);
    for(int m=-J; m<=J; m++){
      D[J+m]=m*ct;//diagonal elements of matrix
      if(m>-J) E[J+m]=st*.5*alpham(J,m);//sub-diagonal elements
    }
    tridiag(D,E,2*J+1,Z);//finds evalues & ekets of tridiagonal matrix
    int mm;
    for(int i=0; i<2*J+1; i++){
      if(fabs(D[i]-J)<.05) mm=i; // identify eket m=J
```

```
        }
        expect(Z[mm]+J,J,st);
    }
}
```

7.14* *We have that*

$$L_+ \equiv L_x + \mathrm{i}L_y = \mathrm{e}^{\mathrm{i}\phi}\Big(\frac{\partial}{\partial\theta} + \mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\Big). \tag{7.1}$$

From the Hermitian nature of $L_z = -\mathrm{i}\partial/\partial\phi$ we infer that derivative operators are anti-Hermitian. So using the rule $(AB)^\dagger = B^\dagger A^\dagger$ on equation (7.1), we infer that

$$L_- \equiv L_+^\dagger = \Big(-\frac{\partial}{\partial\theta} + \mathrm{i}\frac{\partial}{\partial\phi}\cot\theta\Big)\mathrm{e}^{-\mathrm{i}\phi}.$$

This argument and the result it leads to is wrong. Obtain the correct result by integrating by parts $\int \mathrm{d}\theta\,\sin\theta \int \mathrm{d}\phi\,(f^* L_+ g)$, where f and g are arbitrary functions of θ and ϕ. What is the fallacy in the given argument?

Soln:

$$\begin{aligned}\int \mathrm{d}\theta\,\sin\theta \int \mathrm{d}\phi\,(f^* L_+ g) &= \int \mathrm{d}\theta\,\sin\theta \int \mathrm{d}\phi\, f^*\mathrm{e}^{\mathrm{i}\phi}\left(\frac{\partial g}{\partial\theta} + \mathrm{i}\cot\theta\frac{\partial g}{\partial\phi}\right)\\ &= \int \mathrm{d}\phi\,\mathrm{e}^{\mathrm{i}\phi}\int \mathrm{d}\theta\,\sin\theta f^*\frac{\partial g}{\partial\theta} + \mathrm{i}\int \mathrm{d}\theta\,\cos\theta\int \mathrm{d}\phi\, f^*\mathrm{e}^{\mathrm{i}\phi}\frac{\partial g}{\partial\phi}\\ &= \int \mathrm{d}\phi\,\mathrm{e}^{\mathrm{i}\phi}\left([\sin\theta\, f^* g] - \int \mathrm{d}\theta\, g\frac{\partial(\sin\theta f^*)}{\partial\theta}\right)\\ &\quad + \mathrm{i}\int \mathrm{d}\theta\,\cos\theta\left([f^*\mathrm{e}^{\mathrm{i}\phi}g] - \int \mathrm{d}\phi\, g\frac{\partial(f^*\mathrm{e}^{\mathrm{i}\phi})}{\partial\phi}\right)\end{aligned}$$

The square brackets vanish so long f, g are periodic in ϕ. Differentiating out the products we get

$$\begin{aligned}\int \mathrm{d}\theta\,\sin\theta \int \mathrm{d}\phi\,(f^* L_+ g) = &-\int \mathrm{d}\phi\,\mathrm{e}^{\mathrm{i}\phi}\left(\int \mathrm{d}\theta\,\sin\theta g\frac{\partial f^*}{\partial\theta} + \int \mathrm{d}\theta\,\cos\theta g f^*\right)\\ &-\mathrm{i}\int \mathrm{d}\theta\,\cos\theta\left(\int \mathrm{d}\phi\,\mathrm{e}^{\mathrm{i}\phi}g\frac{\partial f^*}{\partial\phi} + \mathrm{i}\int \mathrm{d}\phi\,\mathrm{e}^{\mathrm{i}\phi}g f^*\right)\end{aligned}$$

The two integrals containing f^*g cancel as required leaving us with

$$\int \mathrm{d}\theta\,\sin\theta \int \mathrm{d}\phi\,(f^* L_+ g) = -\int \mathrm{d}\theta\,\sin\theta\int \mathrm{d}\phi\, g\mathrm{e}^{\mathrm{i}\phi}\left(\frac{\partial f^*}{\partial\theta} + \mathrm{i}\cot\theta\frac{\partial f^*}{\partial\phi}\right) = \int \mathrm{d}\theta\,\sin\theta\int \mathrm{d}\phi\, g(L_- f)^*$$

where

$$L_- = -\mathrm{e}^{-\mathrm{i}\phi}\Big(\frac{\partial}{\partial\theta} - \mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\Big).$$

The fallacy is the proposition that $\partial/\partial\theta$ is anti-Hermitian: the inclusion of the factor $\sin\theta$ in the integral prevents this being so.

7.15* *By writing $\hbar^2 L^2 = (\mathbf{x}\times\mathbf{p})\cdot(\mathbf{x}\times\mathbf{p}) = \sum_{ijklm}\epsilon_{ijk}x_j p_k\,\epsilon_{ilm}x_l p_m$ show that*

$$p^2 = \frac{\hbar^2 L^2}{r^2} + \frac{1}{r^2}\left\{(\mathbf{r}\cdot\mathbf{p})^2 - \mathrm{i}\hbar\mathbf{r}\cdot\mathbf{p}\right\}. \tag{7.2}$$

By showing that $\mathbf{p}\cdot\hat{\mathbf{r}} - \hat{\mathbf{r}}\cdot\mathbf{p} = -2\mathrm{i}\hbar/r$, obtain $\mathbf{r}\cdot\mathbf{p} = rp_r + \mathrm{i}\hbar$. Hence obtain

$$p^2 = p_r^2 + \frac{\hbar^2 L^2}{r^2}. \tag{7.3}$$

Give a physical interpretation of one over $2m$ times this equation.

Soln: From the formula for the product of two epsilon symbols we have

$$\hbar^2 L^2 = \sum_{jklm} (\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}) x_j p_k x_l p_m$$
$$= \sum_{jk} \big(x_j p_k x_j p_k - x_j p_k x_k p_j \big).$$

The first term is

$$\sum_{jk} x_j p_k x_j p_k = \sum_{jk} x_j (x_j p_k + [p_k, x_j]) p_k = \sum_{jk} x_j (x_j p_k - \mathrm{i}\hbar \delta_{jk}) p_k$$
$$= r^2 p^2 - \mathrm{i}\hbar \mathbf{r} \cdot \mathbf{p}.$$

The second term is

$$\sum_{jk} x_j p_k x_k p_j = \sum_{jk} x_j (x_k p_k - \mathrm{i}\hbar) p_j$$
$$= \sum_{jk} x_j (p_j x_k p_k + \mathrm{i}\hbar \delta_{jk} p_k) - 3\mathrm{i}\hbar \sum_j x_j p_j$$
$$= (\mathbf{r} \cdot \mathbf{p})(\mathbf{r} \cdot \mathbf{p}) - 2\mathrm{i}\hbar (\mathbf{r} \cdot \mathbf{p}).$$

When these relations are substituted above, the required result follows.

Using the position representaion

$$\mathbf{p} \cdot \hat{\mathbf{r}} - \hat{\mathbf{r}} \cdot \mathbf{p} = -\mathrm{i}\hbar \boldsymbol{\nabla} \cdot (\mathbf{r}/r) = -\frac{3\mathrm{i}\hbar}{r} - \mathrm{i}\hbar \mathbf{r} \cdot \boldsymbol{\nabla}(1/r) = -\frac{3\mathrm{i}\hbar}{r} - \mathrm{i}\hbar r \frac{\partial r^{-1}}{\partial r} = -\frac{3\mathrm{i}\hbar}{r} + \mathrm{i}\hbar r \frac{1}{r^2}$$

Using this relation and the definition of p_r

$$r p_r = \frac{r}{2} (\hat{\mathbf{r}} \cdot \mathbf{p} + \mathbf{p} \cdot \hat{\mathbf{r}}) = \frac{r}{2} \left(2\hat{\mathbf{r}} \cdot \mathbf{p} - \frac{2\mathrm{i}\hbar}{r} \right) = \mathbf{r} \cdot \mathbf{p} - \mathrm{i}\hbar$$

Substituting this into our expression for p^2 we have

$$p^2 = \frac{\hbar^2 L_2}{r^2} + \frac{1}{r^2} \left((r p_r + \mathrm{i}\hbar)(r p_r + \mathrm{i}\hbar) - \mathrm{i}\hbar (r p_r + \mathrm{i}\hbar) \right)$$

When we multiply out the bracket, we encounter $r p_r r p_r = r^2 p_r^2 + r[p_r, r] p_r = r^2 p_r^2 - \mathrm{i}\hbar r p_r$. Now when we clean up we find that all terms in the bracket that are proportional to $\hbar$ cancel and we have desired result.

This equation divided by $2m$ expresses the kinetic energy as a sum of tangetial and radial KE.

7.20* *Show that $[J_i, L_j] = \mathrm{i} \sum_k \epsilon_{ijk} L_k$ and $[J_i, L^2] = 0$ by eliminating L_i using its definition $\mathbf{L} = \hbar^{-1} \mathbf{x} \times \mathbf{p}$, and then using the commutators of J_i with $\mathbf{x}$ and $\mathbf{p}$.*

Soln:

$$\hbar [J_i, L_j] = \epsilon_{jkl} [J_i, x_k p_l] = \epsilon_{jkl} ([J_i, x_k] p_l + x_k [J_i, p_l])$$
$$= \epsilon_{jkl} (\mathrm{i}\epsilon_{ikm} x_m p_l + \mathrm{i}\epsilon_{iln} x_k p_n) = \mathrm{i}(\epsilon_{klj}\epsilon_{kmi} x_m p_l + \epsilon_{ljk}\epsilon_{lni} x_k p_n)$$
$$= \mathrm{i}(\delta_{lm}\delta_{ji} - \delta_{li}\delta_{jm}) x_m p_l + \mathrm{i}(\delta_{jn}\delta_{ki} - \delta_{ji}\delta_{kn}) x_k p_n$$
$$= \mathrm{i}(\mathbf{x} \cdot \mathbf{p} \delta_{ij} - x_j p_i + x_i p_j - \mathbf{x} \cdot \mathbf{p} \delta_{ij}) = \mathrm{i}(x_i p_j - x_j p_i)$$

But

$$\mathrm{i}\hbar \epsilon_{ijk} L_k = \mathrm{i}\epsilon_{ijk}\epsilon_{klm} x_l p_m = \mathrm{i}\epsilon_{kij}\epsilon_{klm} x_l p_m = \mathrm{i}(\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}) x_l p_m = \mathrm{i}(x_i p_j - x_j p_i)$$

7.21* *In this problem you show that many matrix elements of the position operator $\mathbf{x}$ vanish when states of well-defined l, m are used as basis states. These results will lead to selection rules for electric* *dipole radiation. First show that* $[L^2, x_i] = \mathrm{i}\sum_{jk}\epsilon_{jik}(L_j x_k + x_k L_j)$. *Then show that* $\mathbf{L}\cdot\mathbf{x} = 0$ *and using this result derive*

$$[L^2,[L^2,x_i]] = \mathrm{i}\sum_{jk}\epsilon_{jik}\left(L_j[L^2,x_k] + [L^2,x_k]L_j\right) = 2(L^2x_i + x_iL^2). \tag{7.4}$$

By squeezing this equation between angular-momentum eigenstates $\langle l,m|$ *and* $|l',m'\rangle$ *show that*

$$0 = \left\{(\beta-\beta')^2 - 2(\beta+\beta')\right\}\langle l,m|x_i|l',m'\rangle,$$

where $\beta \equiv l(l+1)$ *and* $\beta' = l'(l'+1)$. *By equating the factor in front of* $\langle l,m|x_i|l',m'\rangle$ *to zero, and treating the resulting equation as a quadratic equation for* β *given* β', *show that* $\langle l,m|x_i|l',m'\rangle$ *must vanish unless* $l + l' = 0$ *or* $l = l' \pm 1$. *Explain why the matrix element must also vanish when* $l = l' = 0$.

Soln:

$$\sum_j [L_j^2, x_i] = \sum_j (L_j[L_j,x_i] + [L_j,x_i]L_j) = \mathrm{i}\sum_{jk}\epsilon_{jik}(L_jx_k + x_kL_j)$$

$$\hbar\mathbf{L}\cdot\mathbf{x} = \sum_{ijk}\epsilon_{ijk}x_jp_kx_i = \sum_{ijk}\epsilon_{ijk}(x_jx_ip_k + x_j[p_k,x_i]) = \sum_{ijk}\epsilon_{ijk}(x_jx_ip_k - \mathrm{i}\hbar x_j\delta_{ki})$$

Both terms on the right side of this expression involve $\sum_{ik}\epsilon_{ijk}S_{ik}$ where $S_{ik} = S_{ki}$ so they vanish by Problem 7.3. Hence $\mathbf{x}\cdot\mathbf{L} = 0$ as in classical physics.

Now

$$\begin{aligned}
[L^2,[L^2,x_i]] &= \mathrm{i}\sum_{jk}\epsilon_{jik}[L^2,(L_jx_k + x_kL_j)] = \mathrm{i}\sum_{jk}\epsilon_{jik}(L_j[L^2,x_k] + [L^2,x_k]L_j)\\
&= -\sum_{jklm}\epsilon_{jik}\epsilon_{lkm}(L_j\{L_lx_m + x_mL_l\} + \{L_lx_m + x_mL_l\}L_j)\\
&= -\sum_{jlm}(\delta_{jm}\delta_{il} - \delta_{jl}\delta_{im})(L_j\{L_lx_m + x_mL_l\} + \{L_lx_m + x_mL_l\}L_j)\\
&= -\sum_j(L_j\{L_ix_j + x_jL_i\} + \{L_ix_j + x_jL_i\}L_j - L_j\{L_jx_i + x_iL_j\} - \{L_jx_i + x_iL_j\}L_j)\\
&= -\left\{\sum_j(L_jL_ix_j + x_jL_iL_j) - L^2x_i - \sum_j(L_jx_iL_j + L_jx_iL_j) - x_iL^2\right\}
\end{aligned}$$

where to obtain the last line we have identified occurrences of $\mathbf{L}\cdot\mathbf{x}$ and $\mathbf{x}\cdot\mathbf{L}$. Now

$$\sum_j L_jL_ix_j = \sum_j(L_jx_jL_i + L_j[L_i,x_j]) = \mathrm{i}\sum_{jk}\epsilon_{ijk}L_jx_k$$

Similarly, $\sum_j x_jL_iL_j = \mathrm{i}\sum_{jk}\epsilon_{jik}x_kL_j$. Moreover

$$\begin{aligned}
\sum_j L_jx_iL_j &= \sum_j([L_j,x_i]L_j + x_iL_jL_j) = \mathrm{i}\sum_{jk}\epsilon_{jik}x_kL_j + x_iL^2\\
&= \sum_j(L_j[x_i,L_j] + L_jL_jx_i) = \mathrm{i}\sum_{jk}\epsilon_{ijk}L_jx_k + L^2x_i
\end{aligned}$$

Assembling these results we find

$$\begin{aligned}
[L^2,[L^2,x_i]] &= -\left\{\mathrm{i}\sum_{jk}\epsilon_{ijk}[L_j,x_k] - L^2x_i - \mathrm{i}\sum_{jk}\epsilon_{jik}[x_k,L_j] - x_iL^2 - L^2x_i - x_iL^2\right\}\\
&= 2(L^2x_i + x_iL^2)
\end{aligned}$$

as required. The relevant matrix element is

$$\langle lm|[L^2,[L^2,x_i]]|l'm'\rangle = \langle lm|(L^2L^2x_i - 2L^2x_iL^2 + x_iL^2L^2)|l'm'\rangle = 2\langle lm|(L^2x_i + x_iL^2)|l'm'\rangle$$

which implies

$$\beta^2\langle lm|x_i|l'm'\rangle - 2\beta\langle lm|x_i|l'm'\rangle\beta' + \langle lm|x_i|l'm'\rangle\beta'^2 = 2\beta\langle lm|x_i|l'm'\rangle + 2\langle lm|x_i|l'm'\rangle\beta'$$

Taking out the common factor we obtain the required result.

The quadratic for $\beta(\beta')$ is

$$\beta^2 - 2(\beta'+1)\beta + \beta'(\beta'-2) = 0$$

so

$$\begin{aligned}\beta &= \beta'+1 \pm \sqrt{(\beta'+1)^2 - \beta'(\beta'-2)} = \beta'+1 \pm \sqrt{4\beta'+1}\\ &= l'(l'+1)+1 \pm \sqrt{4l'^2+4l'+1} = l'(l'+1)+1 \pm (2l'+1)\\ &= l'^2+3l'+2 \quad \text{or} \quad l'^2-l'\end{aligned}$$

We now have two quadratic equations to solve

$$\begin{aligned} l^2+l-(l'^2+3l'+2) = 0 \quad &\Rightarrow \quad l = \tfrac{1}{2}[-1 \pm (2l'+3)]\\ l^2+l-(l'^2-l') = 0 \quad &\Rightarrow \quad l = \tfrac{1}{2}[-1 \pm (2l'-1)]\end{aligned}$$

Since $l, l' \geq 0$, the only acceptable solutions are $l+l'=0$ and $l = l' \pm 1$ as required. However, when $l = l' = 0$ the two states have the same (even) parity so the matrix element vanishes by the proof given in eq (4.42) of the book.

7.22* *Show that l excitations can be divided amongst the x, y or z oscillators of a three-dimensional harmonic oscillator in $(\frac{1}{2}l+1)(l+1)$ ways. Verify in the case $l=4$ that this agrees with the number of states of well-defined angular momentum and the given energy.*

Soln: If we assign n_x of the l excitations to the x oscillator, we can assign $0, 1, \ldots, l-n_x$ excitations to the y oscillator [$(l-n_x+1)$ possibilities], and the remaining excitations go to z. So the number of ways is

$$S \equiv \sum_{n_x=0}^{l}(l-n_x+1) = \sum_{n_x=0}^{l}(l+1) - \sum_{n_x=1}^{l} n_x = (l+1)^2 - \tfrac{1}{2}l(l+1) = (l+1)(\tfrac{1}{2}l+1)$$

In the case of 4 excitations, the possible values of l are 4, 2 and 0, so the number of states is $(2*4+1)+(2*2+1)+1 = 15$, which is indeed equal to $(4+1)*(2+1)$.

7.23* *Let*

$$A_l \equiv \frac{1}{\sqrt{2m\hbar\omega}}\left(\mathrm{i}p_r - \frac{(l+1)\hbar}{r} + m\omega r\right). \tag{7.5}$$

be the ladder operator of the three-dimensional harmonic oscillator and $|E,l\rangle$ be the stationary state of the oscillator that has energy E and angular-momentum quantum number l. Show that if we write $A_l|E,l\rangle = \alpha_-|E-\hbar\omega, l+1\rangle$, then $\alpha_- = \sqrt{\mathcal{L}-l}$, where $\mathcal{L}$ is the angular-momentum quantum number of a circular orbit of energy E. Show similarly that if $A^\dagger_{l-1}|E,l\rangle = \alpha_+|E+\hbar\omega, l-1\rangle$, then $\alpha_+ = \sqrt{\mathcal{L}-l+2}$.

Soln: Taking the mod-square of each side of $A_l|E,l\rangle = \alpha_-|E-\hbar\omega, l+1\rangle$ we find

$$|\alpha_-|^2 = \langle E,l|A_l^\dagger A_l|E,l\rangle = \langle E,L|\left(\frac{H_l}{\hbar\omega} - (l+\tfrac{3}{2})\right)|E,l\rangle = \frac{E}{\hbar\omega} - (l+\tfrac{3}{2}).$$

In the case $l = \mathcal{L}$, $|\alpha_-|^2 = 0$, so $\mathcal{L} = (E/\hbar\omega) - \frac{3}{2}$ and therefore $|\alpha_-|^2 = \mathcal{L} - l$ as required. We can choose the phase of α_- at our convenience.

Similarly

$$\begin{aligned}\alpha_+^2 &= \langle E,l|A_{l-1}A^\dagger_{l-1}|E,l\rangle = \langle E,l|(A^\dagger_{l-1}A_{l-1} + [A_{l-1}, A^\dagger_{l-1}])|E,l\rangle\\ &= \langle E,l|\left(\frac{H_{l-1}}{\hbar\omega} - (l+\tfrac{1}{2}) + \frac{H_l - H_{l-1}}{\hbar\omega} + 1\right)|E,l\rangle = \frac{E}{\hbar\omega} - l + \tfrac{1}{2} = \mathcal{L} - l + 2\end{aligned}$$

7.24* *Show that the probability distribution in radius of a particle that orbits in the three-dimensional harmonic oscillator potential on a circular orbit with angular-momentum quantum number l peaks at $r/\ell = \sqrt{2(l+1)}$, where*

$$\ell \equiv \sqrt{\frac{\hbar}{2m\omega}}. \tag{7.6}$$

Derive the corresponding classical result.

Soln: The radial wavefunctions of circular orbits are annihilated by A_l, so $A_l|E,l\rangle = 0$. In the position representation this is

$$\left(\frac{\partial}{\partial r} + \frac{1}{r} - \frac{l+1}{r} + \frac{r}{2\ell^2}\right)u(r) = 0$$

Using the integrating factor,

$$\exp\left\{\int \mathrm{d}r\,\left(-\frac{l}{r} + \frac{r}{2\ell^2}\right)\right\} = r^{-l}\exp\left(r^2/4\ell^2\right), \tag{7.7}$$

to solve the equation, we have $u \propto r^l \mathrm{e}^{-r^2/4\ell^2}$. The radial distribution is $P(r) \propto r^2|u|^2 = r^{2(l+1)}\mathrm{e}^{-r^2/2\ell^2}$. Differentiating to find the maximum, we have

$$2(l+1)r^{2l+1} - r^{2(l+1)}r/\ell^2 = 0 \quad \Rightarrow \quad r = \surd 2(l+1)^{1/2}a$$

For the classical result we have

$$mrv = l\hbar \quad \text{and} \quad \frac{mv^2}{r} = m\omega^2 r \quad \Rightarrow \quad r = v/\omega = \frac{l\hbar}{mr\omega}$$

so $r = (l\hbar/m\omega)^{1/2} = (2l)^{1/2}\ell$ in agreement with the QM result when $l \gg 1$.

7.25* *A particle moves in the three-dimensional harmonic oscillator potential with the second largest angular-momentum quantum number possible at its energy. Show that the radial wavefunction is*

$$u_1 \propto x^l\left(x - \frac{2l+1}{x}\right)\mathrm{e}^{-x^2/4} \quad \textit{where} \quad x \equiv r/\ell \quad \textit{with} \quad \ell \equiv \sqrt{\frac{\hbar}{2m\omega}}. \tag{7.8}$$

How many radial nodes does this wavefunction have?

Soln: From Problem 7.24 we have that the wavefunction of the circular orbit with angular momentum l is $\langle r|E,l\rangle \propto r^l\mathrm{e}^{-r^2/4\ell^2}$. So the required radial wavefunction is

$$\begin{aligned}
&\langle r|E+\hbar\omega, l-1\rangle \propto \langle r|A^\dagger_{l-1}|E,l\rangle \\
&\quad\propto \left(-\frac{\partial}{\partial r} - \frac{l+1}{r} + \frac{r}{2\ell^2}\right) r^l\mathrm{e}^{-r^2/4\ell^2} = \left(-lr^{l-1} + \frac{r^{l+1}}{2\ell^2} - (l+1)r^{l-1} + \frac{r^{l+1}}{2\ell^2}\right)\mathrm{e}^{-r^2/4\ell^2} \\
&\quad= r^l\mathrm{e}^{-r^2/4\ell^2}\left(\frac{r}{\ell^2} - \frac{2l+1}{r}\right) \propto x^l\mathrm{e}^{-x^2/4}\left(x - \frac{2l+1}{x}\right)
\end{aligned}$$

This wavefunction clearly has one node at $x = \sqrt{2l+1}$.

7.28* *The interaction between neighbouring spin-half atoms in a crystal is described by the Hamiltonian*

$$H = K\left(\frac{\mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)}}{a} - 3\frac{(\mathbf{S}^{(1)}\cdot\mathbf{a})(\mathbf{S}^{(2)}\cdot\mathbf{a})}{a^3}\right), \tag{7.9}$$

where K is a constant, $\mathbf{a}$ is the separation of the atoms and $\mathbf{S}^{(1)}$ is the first atom's spin operator. Explain what physical idea underlies this form of H. Show that $S_x^{(1)}S_x^{(2)} + S_y^{(1)}S_y^{(2)} = \frac{1}{2}(S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)})$. Show that the mutual eigenkets of the total spin operators S^2 and S_z are also eigenstates of H and find the corresponding eigenvalues.

At time $t = 0$ particle 1 has its spin parallel to $\mathbf{a}$, while the other particle's spin is antiparallel to $\mathbf{a}$. Find the time required for both spins to reverse their orientations.

Soln: This Hamiltonian recalls the mutual potential energy V of two classical magnetic dipoles $\boldsymbol{\mu}^{(i)}$ that are separated by the vector $\mathbf{a}$, which we can calculate by evaluating the magnetic field $\mathbf{B}$ that the first dipole creates at the location of the second and then recognising that $V = -\boldsymbol{\mu}\cdot\mathbf{B}$.

$$S_+^{(1)}S_-^{(2)} = (S_x^{(1)} + \mathrm{i}S_y^{(1)})(S_x^{(2)} - \mathrm{i}S_y^{(2)}) = S_x^{(1)}S_x^{(2)} + S_y^{(1)}S_y^{(2)} + \mathrm{i}(S_y^{(1)}S_x^{(2)} - S_x^{(1)}S_y^{(2)})$$

Similarly,

$$S_-^{(1)}S_+^{(2)} = S_x^{(1)}S_x^{(2)} + S_y^{(1)}S_y^{(2)} - \mathrm{i}(S_y^{(1)}S_x^{(2)} - S_x^{(1)}S_y^{(2)})$$

Adding these expressions we obtain the desired relation.

We choose to orient the z-axis along $\mathbf{a}$. Then H becomes

$$H = \frac{K}{a}\left(\tfrac{1}{2}(S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)}) + S_z^{(1)}S_z^{(2)} - 3S_z^{(1)}S_z^{(2)}\right). \tag{7.10}$$

The eigenkets of S^2 and S_z are the three spin-one kets $|1,1\rangle$, $|1,0\rangle$ and $|1,-1\rangle$ and the single spin-zero ket $|0,0\rangle$. We multiply each of these kets in turn by H:

$$\begin{aligned} H|1,1\rangle = H|+\rangle|+\rangle &= \frac{K}{a}\left(\tfrac{1}{2}(S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)}) - 2S_z^{(1)}S_z^{(2)}\right)|+\rangle|+\rangle \\ &= -\frac{K}{2a}|1,1\rangle \end{aligned}$$

which uses the fact that $S_+^{(i)}|+\rangle = 0$. Similarly $H|1,-1\rangle = H|-\rangle|-\rangle = -(K/2a)|1,-1\rangle$.

$$\begin{aligned} H|1,0\rangle = H\frac{1}{\sqrt{2}}(|+\rangle|-\rangle + |-\rangle|+\rangle) &= \frac{K}{\sqrt{2}a}\left(\tfrac{1}{2}(S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)}) - 2S_z^{(1)}S_z^{(2)}\right)(|+\rangle|-\rangle + |-\rangle|+\rangle) \\ &= \frac{K}{\sqrt{2}a}\left(\tfrac{1}{2} + 1\right)(|+\rangle|-\rangle + |-\rangle|+\rangle) = \frac{K}{a}|1,0\rangle \end{aligned}$$

where we have used $S_+|-\rangle = |+\rangle$, etc. Finally

$$\begin{aligned} H|0,0\rangle = H\frac{1}{\sqrt{2}}(|+\rangle|-\rangle - |-\rangle|+\rangle) &= \frac{K}{\sqrt{2}a}\left(\tfrac{1}{2}(S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)}) - 2S_z^{(1)}S_z^{(2)}\right)(|+\rangle|-\rangle - |-\rangle|+\rangle) \\ &= \frac{K}{\sqrt{2}a}\left(-\tfrac{1}{2} + \tfrac{1}{2}\right)(|+\rangle|-\rangle - |-\rangle|+\rangle) = 0 \end{aligned}$$

The given initial condition

$$|\psi\rangle = |+\rangle|-\rangle = \frac{1}{\sqrt{2}}(|1,0\rangle + |0,0\rangle),$$

which is a superposition of two stationary states of energies that differ by K/a. By analogy with the symmetrical-well problem, we argue that after time $\pi\hbar/\Delta E = \pi\hbar a/K$ the particle spins will have reversed.

8.10* *A spherical potential well is defined by*

$$V(r) = \begin{cases} 0 & \text{for } r < a \\ V_0 & \text{otherwise,} \end{cases} \tag{8.1}$$

where $V_0 > 0$. Consider a stationary state with angular-momentum quantum number l. By writing the wavefunction $\psi(\mathbf{x}) = R(r)\mathrm{Y}_l^m(\theta,\phi)$ and using $p^2 = p_r^2 + \hbar^2L^2/r^2$, show that the state's radial wavefunction $R(r)$ must satisfy

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{r}\right)^2 R + \frac{l(l+1)\hbar^2}{2mr^2}R + V(r)R = ER. \tag{8.2}$$

Show that in terms of $S(r) \equiv rR(r)$, this can be reduced to

$$\frac{\mathrm{d}^2S}{\mathrm{d}r^2} - l(l+1)\frac{S}{r^2} + \frac{2m}{\hbar^2}(E - V)S = 0. \tag{8.3}$$

Assume that $V_0 > E > 0$. For the case $l = 0$ write down solutions to this equation valid at (a) $r < a$ and (b) $r > a$. Ensure that R does not diverge at the origin. What conditions must S satisfy at $r = a$? Show that these conditions can be simultaneously satisfied if and only if a solution can be found to $k \cot ka = -K$, where $\hbar^2 k^2 = 2mE$ and $\hbar^2 K^2 = 2m(V_0 - E)$. Show graphically that the equation can only be solved when $\sqrt{2mV_0}\, a/\hbar > \pi/2$. Compare this result with that obtained for the corresponding one-dimensional potential well.

The deuteron is a bound state of a proton and a neutron with zero angular momentum. Assume that the strong force that binds them produces a sharp potential step of height V_0 at interparticle distance $a = 2 \times 10^{-15}$ m. Determine in MeV the minimum value of V_0 for the deuteron to exist. Hint: remember to consider the dynamics of the reduced particle.

Soln: In the position representation $p_r = -i\hbar(\partial/\partial r + r^{-1})$, so in this representation and for an eigenfunction of L^2 we get the required form of $E|E\rangle = H|E\rangle = (p^2/2m + V)|E\rangle$. Writing $R = S/r$ we have

$$\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{r}\right) R = \left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{r}\right) \frac{S}{r} = \frac{1}{r}\frac{\mathrm{d}S}{\mathrm{d}r} \quad \Rightarrow \quad \left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{r}\right)^2 R = \left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{r}\right) \frac{1}{r}\frac{\mathrm{d}S}{\mathrm{d}r} = \frac{1}{r}\frac{\mathrm{d}^2 S}{\mathrm{d}r^2}$$

Inserting this into our TISE and multiplying through by r, we obtain the required expression.

When $l = 0$ the equation reduces to either exponential decay or shm, so with the given condition on E we have

$$S \propto \begin{cases} \cos kr \quad \text{or} \quad \sin kr & \text{at } r < a \\ A\mathrm{e}^{-Kr} & \text{at } r > a \end{cases}$$

where $k^2 = 2mE/\hbar^2$ and $K^2 = 2m(V_0 - E)/\hbar^2$. At $r < a$ we must chose $S \propto \sin kr$ because we require $R = S/r$ to be finite at the origin. We require S and its first derivative to be continuous at $r = a$, so

$$\begin{aligned} \sin(ka) &= A\mathrm{e}^{-Ka} \\ k\cos(ka) &= -KA\mathrm{e}^{-Ka} \end{aligned} \quad \Rightarrow \quad \cot(ka) = -\frac{K}{k} = -\sqrt{W^2/(ka)^2 - 1}$$

with $W \equiv \sqrt{2mV_0 a^2/\hbar^2}$. In a plot of each side against ka, the right side starts at $-\infty$ when $ka = 0$ and rises towards the x axis, where it terminates when $ka = W$. The left side starts at ∞ and becomes negative when $ka = \pi/2$. There is a solution iff the right side has not already terminated, i.e. iff $W > \pi/2$.

We obtain the minimum value of V_0 for $W = (a/\hbar)\sqrt{2mV_0} = \pi/2$, so

$$V_0 = \frac{\pi^2\hbar^2}{8ma^2} = \frac{(\pi\hbar/a)^2}{4m_\mathrm{p}} = 25.6\,\mathrm{MeV}$$

where $m \simeq \frac{1}{2}m_\mathrm{p}$ is the reduced mass of the proton.

8.13* *From equation (8.50) show that $l' + \frac{1}{2} = \sqrt{(l + \frac{1}{2})^2 - \beta}$ and that the increment Δ in l' when l is increased by one satisfies $\Delta^2 + \Delta(2l' + 1) = 2(l + 1)$. By considering the amount by which the solution of this equation changes when l' changes from l as a result of β increasing from zero to a small number, show that*

$$\Delta = 1 + \frac{2\beta}{4l^2 - 1} + \mathrm{O}(\beta^2). \tag{8.4}$$

Explain the physical significance of this result.

Soln: The given eqn is a quadratic in l':

$$l'^2 + l' - l(l+1) + \beta = 0 \quad \Rightarrow \quad l' = \frac{-1 \pm \sqrt{1 + 4l(l+1) - 4\beta}}{2} \quad \Rightarrow \quad l' + \tfrac{1}{2} = \sqrt{(l + \tfrac{1}{2})^2 - \beta}, \tag{8.5}$$

where we've chosen the root that makes $l' > 0$.

Squaring up this equation, we have

$$(l' + \tfrac{1}{2})^2 = (l + \tfrac{1}{2})^2 - \beta \quad \Rightarrow \quad (l' + \Delta + \tfrac{1}{2})^2 = (l + \tfrac{3}{2})^2 - \beta$$

Taking the first eqn from the second yields

$$\Delta^2 + 2(l' + \tfrac{1}{2})\Delta = (l + \tfrac{3}{2})^2 - (l + \tfrac{1}{2})^2 = 2(l + 1)$$

This is a quadratic equation for Δ, which is solved by $\Delta = 1$ when $l' = l$. We are interested in the small change $\delta\Delta$ in this solution when l' changes by a small amount $\delta l'$. Differentiating the equation, we have

$$2\Delta\delta\Delta + 2\Delta\delta l' + (2l'+1)\delta\Delta = 0 \quad \Rightarrow \quad \delta\Delta = -\frac{2\Delta\delta l'}{2\Delta + 2l' + 1}$$

Into this we put $\Delta = 1$, $l' = l$, and by binomial expansion of (8.5)

$$\delta l' = -\frac{\beta}{2l+1}$$

and have finally

$$\delta\Delta = \frac{-2\beta}{(2l+1)(2l+3)}$$

Eq (8.55) gives the energy of a circular orbit as

$$E = -\frac{Z_0^2 e^2}{8\pi\epsilon_0 a_0 (l'(l) + k + 1)^2},$$

with k the number of nodes in the radial wavefunction. This differs from Rydberg's formula in that $(l'(l)+k+1)$ is not an integer n. Crucially $l'(l)+k$ does not stay the same if k in decreased by unity and l increased by unity – in fact these changes (which correspond to shifting to a more circular orbit) cause $l'(l)+k$ to increase slightly and therefore E to decrease slightly: on a more circular orbit, the electron is more effectively screened from the nucleus. So in the presence of screening the degeneracy in H under which at the same E there are states of different angular momentum is lifted by screening.

8.15* *(a) A particle of mass m moves in a spherical potential $V(r)$. Show that according to classical mechanics*

$$\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{p} \times \mathbf{L}_\mathrm{c}) = mr^2 \frac{\mathrm{d}V}{\mathrm{d}r}\frac{\mathrm{d}\mathbf{e}_r}{\mathrm{d}t}, \tag{8.6}$$

where $\mathbf{L}_\mathrm{c} = \mathbf{r} \times \mathbf{p}$ is the classical angular-momentum vector and $\mathbf{e}_r$ is the unit vector in the radial direction. Hence show that when $V(r) = -K/r$, with K a constant, the **Runge–Lenz vector** *$\mathbf{M}_\mathrm{c} \equiv \mathbf{p} \times \mathbf{L}_\mathrm{c} - mK\mathbf{e}_r$ is a constant of motion. Deduce that $\mathbf{M}_\mathrm{c}$ lies in the orbital plane, and that for an elliptical orbit it points from the centre of attraction to the pericentre of the orbit, while it vanishes for a circular orbit.*

(b) Show that in quantum mechanics $(\mathbf{p} \times \mathbf{L})^\dagger - \mathbf{p} \times \mathbf{L} = -2\mathrm{i}\mathbf{p}$. Hence explain why in quantum mechanics we take the Runge–Lenz vector operator to be

$$\mathbf{M} \equiv \tfrac{1}{2}\hbar\mathbf{N} - mK\mathbf{e}_r \quad \textit{where} \quad \mathbf{N} \equiv \mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}. \tag{8.7}$$

Explain why we can write down the commutation relation $[L_i, M_j] = \mathrm{i}\sum_k \epsilon_{ijk} M_k$.

(c) Explain why $[p^2, N] = 0$ and why $[1/r, \mathbf{p} \times \mathbf{L}] = [1/r, \mathbf{p}] \times \mathbf{L}$. Hence show that

$$[1/r, \mathbf{N}] = \mathrm{i}\left\{\frac{1}{r^3}(r^2\mathbf{p} - \mathbf{x}\,\mathbf{x}\cdot\mathbf{p}) - \left(\mathbf{p}r^2 - \mathbf{p}\cdot\mathbf{x}\,\mathbf{x}\right)\frac{1}{r^3}\right\}. \tag{8.8}$$

(d) Show that

$$[p^2, \mathbf{e}_r] = \mathrm{i}\hbar\left\{-\left(\mathbf{p}\frac{1}{r} + \frac{1}{r}\mathbf{p}\right) + \sum_j \left(p_j \frac{x_j}{r^3}\mathbf{x} + \mathbf{x}\frac{x_j}{r^3}p_j\right)\right\}. \tag{8.9}$$

(e) Hence show that $[H, \mathbf{M}] = 0$. What is the physical significance of this result?

(f) Show that (i) $[M_i, L^2] = \mathrm{i}\sum_{jk} \epsilon_{ijk}(M_k L_j + L_j M_k)$, (ii) $[L_i, M^2] = 0$, where $M^2 \equiv M_x^2 + M_y^2 + M_z^2$. What are the physical implications of these results?

(g) Show that

$$[N_i, N_j] = -4\mathrm{i}\sum_u \epsilon_{iju} p^2 L_u \tag{8.10}$$

and that

$$[N_i, (\mathbf{e}_r)_j] - [N_j, (\mathbf{e}_r)_i] = -\frac{4\mathrm{i}\hbar}{r}\sum_t \epsilon_{ijt} L_t \tag{8.11}$$

and hence that

$$[M_i, M_j] = -2\mathrm{i}\hbar^2 mH \sum_k \epsilon_{ijk} L_k. \tag{8.12}$$

What physical implication does this equation have?

Soln: (a) Since $\mathbf{L}_\mathrm{c}$ is a constant of motion

$$\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{p}\times\mathbf{L}_\mathrm{c}) = \dot{\mathbf{p}}\times\mathbf{L}_\mathrm{c} = -\frac{\partial V}{\partial \mathbf{x}}\times\mathbf{L}_\mathrm{c} = -\frac{\mathrm{d}V}{\mathrm{d}r}\mathbf{e}_r\times\mathbf{L}_\mathrm{c}, \tag{8.13}$$

where we have used Hamilton's equation $\dot{\mathbf{p}} = -\partial H/\partial\mathbf{x}$ and $\partial r/\partial\mathbf{x} = \mathbf{e}_r$. Also

$$\frac{\mathrm{d}\mathbf{e}_r}{\mathrm{d}t} = \boldsymbol{\omega}\times\mathbf{e}_r,$$

where $\boldsymbol{\omega} = \mathbf{L}_\mathrm{c}/mr^2$ is the particle's instantaneous angular velocity. So $\mathbf{e}_r\times\mathbf{L}_\mathrm{c} = -mr^2\boldsymbol{\omega}\times\mathbf{e}_r = -mr^2\dot{\mathbf{e}}_r$. Using this equation to eliminate $\mathbf{e}_r\times\mathbf{L}_\mathrm{c}$ from (8.13), we find that when $\mathrm{d}V/\mathrm{d}r = Kr^2$, the right side becomes $mK\dot{\mathbf{e}}_r$, which is a total time-derivative, and the invariance of $\mathbf{M}_\mathrm{c}$ follows. Dotting $\mathbf{M}_\mathrm{c}$ with $\mathbf{L}_\mathrm{c}$ we find that $\mathbf{M}_\mathrm{c}$ is perpendicular to $\mathbf{L}_\mathrm{c}$ so it lies in the orbital plane. Also

$$\mathbf{M}_\mathrm{c} + mK\mathbf{e}_r = \mathbf{p}\times(\mathbf{r}\times\mathbf{p}) = p^2\,\mathbf{r} - \mathbf{p}\cdot\mathbf{r}\,\mathbf{p}.$$

Evaluating the right side at pericentre, where $\mathbf{p}\cdot\mathbf{r} = 0$, we have

$$\mathbf{M}_\mathrm{c} = (p^2 r - mK)\mathbf{e}_r.$$

In the case of a circular orbit, by centripetal balance $p^2/mr = K/r^2$ and $\mathbf{M}_\mathrm{c} = 0$. At pericentre, the particle is moving faster than the circular speed, so $p^2 > mK/r$ and the coefficient of $\mathbf{e}_r$ is positive, so $\mathbf{M}_\mathrm{c}$ points to pericentre.

(b) Since both $\mathbf{p}$ and $\mathbf{L}$ are Hermitian,

$$\begin{aligned}(\mathbf{p}\times\mathbf{L})_i^\dagger &= \sum_{jk}\epsilon_{ijk}(p_j L_k)^\dagger = \sum_{jk}\epsilon_{ijk}L_k p_j\\ &= \sum_{jk}\epsilon_{ijk}(p_j L_k + [L_k, p_j]) = \sum_{jk}\epsilon_{ijk}\left(p_j L_k + \mathrm{i}\sum_m \epsilon_{kjm}p_m\right)\\ &= (\mathbf{p}\times\mathbf{L})_i - 2\mathrm{i}p_i.\end{aligned}$$

We want the Runge–Lenz vector to be a Hermitian operator, so we apply the principle that $\frac{1}{2}(AB + BA)$ is Hermitian even when $[A, B] \neq 0$ and write

$$M_i = \tfrac{1}{2}\hbar\sum_{jk}\epsilon_{ijk}(p_j L_k + L_k p_j) - mK\mathbf{e}_r = \tfrac{1}{2}\hbar(\mathbf{p}\times\mathbf{L} - \mathbf{L}\times\mathbf{p}) - mK\mathbf{e}_r$$

$\mathbf{M}$ is a (pseudo) vector operator, so its components have the standard commutation relations with the components of $\mathbf{L}$.

(c) p^2 is a scalar so it commutes with $\mathbf{L}$, and of course it commutes with $\mathbf{p}$, so it must commute with both $\mathbf{p}\times\mathbf{L}$ and $\mathbf{L}\times\mathbf{p}$. As a scalar $1/r$ commutes with $\mathbf{L}$, so

$$[1/r, \mathbf{p}\times\mathbf{L}] = [1/r, \mathbf{p}]\times\mathbf{L} = -\frac{\mathrm{i}\hbar}{2r^3}[r^2, \mathbf{p}]\times\mathbf{L} = -\frac{\mathrm{i}\hbar}{r^3}\mathbf{x}\times\mathbf{L}.$$

Similarly,

$$[1/r, \mathbf{L}\times\mathbf{p}] = -\mathrm{i}\hbar\mathbf{L}\times\mathbf{x}\frac{1}{r^3}.$$

Now

$$(\mathbf{x}\times\mathbf{L})_i = \frac{1}{\hbar}\sum_{jklm}\epsilon_{ijk}\epsilon_{klm}x_jx_lp_m = \frac{1}{\hbar}\sum_{jklm}\epsilon_{ijk}\epsilon_{lmk}x_jx_lp_m = \frac{1}{\hbar}\sum_{jlm}(\delta_{il}\delta_{jm}-\delta_{im}\delta_{jl})x_jx_lp_m$$
$$= \frac{1}{\hbar}(x_i\mathbf{x}\cdot\mathbf{p}-r^2p_i)$$

and

$$(\mathbf{L}\times\mathbf{x})_i = \frac{1}{\hbar}\sum_{jklm}\epsilon_{ijk}\epsilon_{jlm}x_lp_mx_k = \frac{1}{\hbar}\sum_{jklm}\epsilon_{jki}\epsilon_{jlm}x_lp_mx_k = \frac{1}{\hbar}\sum_{klm}(\delta_{kl}\delta_{im}-\delta_{km}\delta_{il})x_lp_mx_k$$
$$= \frac{1}{\hbar}\sum_k(x_kp_ix_k - x_ip_kx_k) = \frac{1}{\hbar}\sum_k(p_ix_kx_k + \mathrm{i}\hbar\delta_{ik}x_k - p_kx_ix_k - \mathrm{i}\hbar\delta_{ki}x_k)$$
$$= \frac{1}{\hbar}\big(p_ir^2 - \mathbf{p}\cdot\mathbf{x}\,x_i\big)$$

Hence

$$[1/r,\mathbf{N}] = [\mathbf{p}\times\mathbf{L},1/r]-[\mathbf{L}\times\mathbf{p},1/r] = \mathrm{i}\Big\{-\frac{1}{r^3}(x_i\mathbf{x}\cdot\mathbf{p}-r^2p_i)+\big(p_ir^2-\mathbf{p}\cdot\mathbf{x}\,x_i\big)\frac{1}{r^3}\} \tag{8.14}$$

(d)

$$[p^2,(\mathbf{e}_r)_n] = [p^2,x_n/r] = \sum_j\left(p_j[p_j,x_n/r]+[p_j,x_n/r]p_j\right)$$
$$= \sum_j\left(p_j[p_j,x_n]/r + p_jx_n[p_j,1/r]+[p_j,x_n]/rp_j + x_n[p_j,1/r]p_j\right)$$
$$= \mathrm{i}\hbar\sum_j\left(-p_j\frac{\delta_{jn}}{r}+p_jx_n\frac{x_j}{r^3}-\frac{\delta_{jn}}{r}p_j+x_n\frac{x_j}{r^3}p_j\right)$$
$$= \mathrm{i}\hbar\left\{-\left(p_n\frac{1}{r}+\frac{1}{r}p_n\right)+\sum_j\left(p_j\frac{x_j}{r^3}x_n+x_n\frac{x_j}{r^3}p_j\right)\right\}$$

(e)

$$[H,\mathbf{M}] = \left[\frac{p^2}{2m}-\frac{K}{r},\tfrac{1}{2}\hbar\{\mathbf{p}\times\mathbf{L}-\mathbf{L}\times\mathbf{p}\}-mK\mathbf{e}_r\right]$$

The results we have in hand imply that when we expand this commutator, there are only two non-zero terms, so

$$[H,\mathbf{M}] = -\tfrac{1}{2}K\left[p^2,\mathbf{e}_r\right]-\tfrac{1}{2}\hbar K\left[\frac{1}{r},\mathbf{p}\times\mathbf{L}-\mathbf{L}\times\mathbf{p}\right]$$
$$= \tfrac{1}{2}\mathrm{i}\hbar K\left\{\left(\mathbf{p}\frac{1}{r}+\frac{1}{r}\mathbf{p}\right)-\sum_j\left(p_j\frac{x_j}{r^3}\mathbf{x}+\mathbf{x}\frac{x_j}{r^3}p_j\right)+\frac{1}{r^3}\left(\mathbf{x}\,\mathbf{x}\cdot\mathbf{p}-r^2\mathbf{p}\right)-\left(\mathbf{p}r^2-\mathbf{p}\cdot\mathbf{x}\,\mathbf{x}\right)\frac{1}{r^3}\right\}$$
$$= 0$$

This result shows: (i) that the eigenvalues of the M_i are good quantum numbers – if the particle starts in an eigenstate of M_i, it will remain in that state; (ii) the unitary transformations $U_i(\theta)\equiv\exp(-\mathrm{i}\theta M_i)$ are dynamical symmetries of a hydrogen atom. In particular, these operators turn stationary states into other stationary states of the same energy.

(f) (i)

$$[M_i,L^2] = \sum_j[M_i,L_j^2] = \sum_j([M_i,L_j]L_j+L_j[M_i,L_j]) = \mathrm{i}\sum_{jk}\epsilon_{ijk}(M_kL_j+L_jM_k)\neq 0.$$

so we do not expect to know the total angular momentum when the atom is in an eigenstate of any of the M_i.

(ii) $[L_i, M^2] = \sum_j [L_i, M_j^2] = \mathrm{i}\sum_{jk}\epsilon_{ijk}(M_kM_j + M_jM_k) = 0$, so there is a complete set of mutual eigenstates of L^2, L_z and M^2.

(g)

$$\begin{aligned}[(\mathbf{p}\times\mathbf{L})_i, p_m] &= \sum_{jk}\epsilon_{ijk}[p_jL_k, p_m] = \sum_{jk}\epsilon_{ijk}p_j[L_k, p_m] = \mathrm{i}\sum_{jkn}\epsilon_{ijk}\epsilon_{kmn}p_jp_n = \mathrm{i}\sum_{jkn}\epsilon_{kij}\epsilon_{kmn}p_jp_n \\ &= \mathrm{i}\sum_{nj}(\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})p_jp_n = \mathrm{i}(p^2\delta_{im} - p_ip_m)\end{aligned}$$

Similarly $[(\mathbf{L}\times\mathbf{p})_i, p_m] = -\mathrm{i}(p^2\delta_{im} - p_ip_m)$, so we have shown that

$$[N_i, p_m] = 2\mathrm{i}(p^2\delta_{im} - p_ip_m).$$

Moreover, since $\mathbf{N}$ is a vector, $[N_i, L_m] = \mathrm{i}\sum_n \epsilon_{imn}N_n$, so

$$\begin{aligned}[N_i, N_s] &= \sum_{tu}\epsilon_{stu}[N_i, p_tL_u - L_tp_u] = \sum_{tu}\epsilon_{stu}\big\{[N_i, p_t]L_u + p_t[N_i, L_u] - [N_i, L_t]p_u - L_t[N_i, p_u]\big\} \\ &= \mathrm{i}\sum_{tu}\epsilon_{stu}\big\{2(p^2\delta_{it} - p_ip_t)L_u - 2L_t(p^2\delta_{iu} - p_ip_u) + \sum_n(\epsilon_{iun}p_tN_n - \epsilon_{itn}N_np_u)\big\} \\ &= 2\mathrm{i}\sum_u\epsilon_{siu}p^2L_u - 2\mathrm{i}\sum_t\epsilon_{sti}L_tp^2 - 2\mathrm{i}\sum_{tu}\epsilon_{stu}(p_ip_tL_u - L_tp_ip_u) \\ &\quad + \mathrm{i}\sum_{tun}\epsilon_{stu}\epsilon_{iun}p_tN_n - \mathrm{i}\sum_{tun}\epsilon_{stu}\epsilon_{itn}N_np_u \\ &= 2\mathrm{i}\sum_u\epsilon_{siu}(p^2L_u + L_up^2) - 2\mathrm{i}\sum_{tu}\epsilon_{stu}(p_ip_tL_u - L_tp_ip_u) \\ &\quad + \mathrm{i}\sum_{tn}(\delta_{sn}\delta_{ti} - \delta_{si}\delta_{nt})p_tN_n - \mathrm{i}\sum_{nu}(\delta_{un}\delta_{si} - \delta_{ui}\delta_{sn})N_np_u \\ &= 4\mathrm{i}\sum_u\epsilon_{siu}p^2L_u - 2\mathrm{i}\sum_{tu}\epsilon_{stu}(p_ip_tL_u - L_tp_ip_u) + \mathrm{i}(p_iN_s + N_sp_i) - \mathrm{i}(\mathbf{p}\cdot\mathbf{N} + \mathbf{N}\cdot\mathbf{p})\delta_{is} \\ &= 4\mathrm{i}\sum_u\epsilon_{siu}p^2L_u + \mathrm{i}\Big(- 2p_i(\mathbf{p}\times\mathbf{L})_s + 2(\mathbf{L}\times\mathbf{p})_sp_i \\ &\quad + p_i(\mathbf{p}\times\mathbf{L})_s - p_i(\mathbf{L}\times\mathbf{p})_s + (\mathbf{p}\times\mathbf{L})_sp_i - (\mathbf{L}\times\mathbf{p})_sp_i\Big) - \mathrm{i}(\mathbf{p}\cdot\mathbf{N} + \mathbf{N}\cdot\mathbf{p})\delta_{is},\end{aligned} \tag{8.15}$$

where we have used the fact that $[p^2, L_u] = 0$. We show that the terms with cross products sum to zero by first ensuring that all terms with p_i on the left contain $\mathbf{p}\times\mathbf{L}$ and all terms with p_i on the right contain $\mathbf{L}\times\mathbf{p}$. We have to amend two terms to achieve this standardisation:

$$\begin{aligned}-p_i(\mathbf{L}\times\mathbf{p})_s + (\mathbf{p}\times\mathbf{L})_sp_i &= \sum_{jk}\epsilon_{sjk}\left(-p_iL_jp_k + p_jL_kp_i\right) \\ &= \sum_{jk}\epsilon_{sjk}\Big(-p_i\Big\{p_kL_j + \mathrm{i}\sum_n\epsilon_{jkn}p_n\Big\} + \Big\{L_kp_j + \mathrm{i}\sum_n\epsilon_{jkn}p_n\Big\}p_i\Big) \\ &= p_i(\mathbf{p}\times\mathbf{L})_s - (\mathbf{L}\times\mathbf{p})_sp_i\end{aligned} \tag{8.16}$$

The standardised sum of cross products in equation (8.15) is now

$$\mathrm{i}\Big(- 2p_i(\mathbf{p}\times\mathbf{L})_s + 2(\mathbf{L}\times\mathbf{p})_sp_i + p_i(\mathbf{p}\times\mathbf{L})_s + p_i(\mathbf{p}\times\mathbf{L})_s - (\mathbf{L}\times\mathbf{p})_sp_i - (\mathbf{L}\times\mathbf{p})_sp_i\Big)$$

and is manifestly zero. The last term in (8.15) *has* to vanish because it alone is symmetric in is, and it's not hard to show that it does:

$$\mathbf{p}\cdot\mathbf{N} + \mathbf{N}\cdot\mathbf{p} = \sum_{ijk}\epsilon_{ijk}\Big(p_i(p_jL_k - L_jp_k) + (p_jL_k - L_jp_k)p_i\Big)$$

The first and last terms trivially vanish because they are symmetric in ij and ik,respectively. The remaining terms can be written

$$-\sum_{ijk}\epsilon_{ijk}p_iL_jp_k + \sum_{jki}\epsilon_{ijk}p_jL_kp_i$$

and they cancel.

Since $\mathbf{e}_r = \mathbf{x}/r$ and in (8.8) we already have $[1/r, \mathbf{N}]$ we prepare for calculating $[N_i, \mathbf{e}_r]$ by calculating

$$[(\mathbf{p}\times\mathbf{L})_i, x_j] = \sum_{st}\epsilon_{ist}[p_sL_t, x_j] = \sum_{st}\epsilon_{ist}(p_s[L_t, x_j] + [p_s, x_j]L_t) = \mathrm{i}\sum_{st}\epsilon_{ist}\Big(p_s\sum_n \epsilon_{tjn}x_n - \hbar\delta_{sj}L_t\Big)$$
$$= \mathrm{i}\Big\{\sum_{sn}(\delta_{ij}\delta_{sn} - \delta_{in}\delta_{sj})p_sx_n - \hbar\sum_t\epsilon_{ijt}L_t\Big\} = \mathrm{i}\Big(\mathbf{p}\cdot\mathbf{x}\,\delta_{ij} - p_jx_i - \hbar\sum_t\epsilon_{ijt}L_t\Big)$$

Similarly

$$[(\mathbf{L}\times\mathbf{p})_i, x_j] = -\mathrm{i}\Big(\mathbf{x}\cdot\mathbf{p}\,\delta_{ij} - x_ip_j - \hbar\sum_t\epsilon_{ijt}L_t\Big)$$

so

$$[N_i, x_j] = \mathrm{i}\Big\{(\mathbf{p}\cdot\mathbf{x} + \mathbf{x}\cdot\mathbf{p})\delta_{ij} - (p_jx_i + x_ip_j) - 2\hbar\sum_t\epsilon_{ijt}L_t\Big\}$$

Now we can compute

$$\begin{aligned}[N_i, (\mathbf{e}_r)_j] &= [N_i, x_j/r] = [N_i, x_j]/r + x_j[N_j, 1/r]\\ &= \mathrm{i}\Big\{(\mathbf{p}\cdot\mathbf{x} + \mathbf{x}\cdot\mathbf{p})\frac{\delta_{ij}}{r} - (p_jx_i + x_ip_j)\frac{1}{r} - \frac{2\hbar}{r}\sum_t\epsilon_{ijt}L_t\Big\}\\ &\quad + x_j[(\mathbf{p}\times\mathbf{L})_i, 1/r] - x_j[(\mathbf{L}\times\mathbf{p})_i, 1/r]\\ &= \mathrm{i}\Big\{(\mathbf{p}\cdot\mathbf{x} + \mathbf{x}\cdot\mathbf{p})\frac{\delta_{ij}}{r} - (p_jx_i + x_ip_j)\frac{1}{r} - \frac{2\hbar}{r}\sum_t\epsilon_{ijt}L_t\\ &\quad + \frac{x_j}{r^3}(x_i\,\mathbf{x}\cdot\mathbf{p} - r^2p_i) - x_j(p_ir^2 - \mathbf{p}\cdot\mathbf{x}\,x_i)\frac{1}{r^3}\Big\}\end{aligned}$$

when we calculate $[N_i, (\mathbf{e}_r)_j] - [N_j, (\mathbf{e}_r)_i]$ all terms above that are symmetric in ij and will vanish and we find

$$\begin{aligned}[N_i, (\mathbf{e}_r)_j] - [N_j, (\mathbf{e}_r)_i] &= \mathrm{i}\Big\{-(p_jx_i + x_ip_j - p_ix_j - x_jp_i)\frac{1}{r} - \frac{4\hbar}{r}\sum_t\epsilon_{ijt}L_t\\ &\quad - \frac{1}{r}(x_jp_i - x_ip_j) - (x_jp_i - x_ip_j)\frac{1}{r} + (x_j\mathbf{p}\cdot\mathbf{x}\,x_i - x_i\mathbf{p}\cdot\mathbf{x}\,x_j)\frac{1}{r^3}\Big\}\\ &= \mathrm{i}\Big\{-\frac{4\hbar}{r}\sum_t\epsilon_{ijt}L_t - (p_jx_i - p_ix_j)\frac{1}{r} - \frac{1}{r}(x_jp_i - x_ip_j) + (x_j\mathbf{p}\cdot\mathbf{x}\,x_i - x_i\mathbf{p}\cdot\mathbf{x}x_j)\frac{1}{r^3}\Big\}\end{aligned} \tag{8.17}$$

Now

$$\begin{aligned}\sum_k x_ip_kx_kx_j &= \sum_k x_i(x_jp_k - \mathrm{i}\hbar\delta_{jk})x_k = \sum_k x_ix_jp_kx_k - \mathrm{i}\hbar x_ix_j = \sum_k x_j(p_kx_i + \mathrm{i}\hbar\delta_{ki})x_k - \mathrm{i}\hbar x_ix_j\\ &= \sum_k x_jp_kx_kx_i\end{aligned}$$

so the terms with dot products in (8.17) cancel. Finally $[1/r, p_j] = -\mathrm{i}\hbar x_j/r^3$ so

$$\frac{1}{r}(x_jp_i - x_ip_j) = x_j(p_i/r - \mathrm{i}\hbar x_i/r^3) - x_i(p_j/r - \mathrm{i}\hbar x_j/r^3) = (x_jp_i - x_ip_j)\frac{1}{r}$$

so the terms with factors $1/r$ in (8.17) cancel and we are left with

$$[N_i, (\mathbf{e}_r)_j] - [N_j, (\mathbf{e}_r)_i] = -\frac{4\mathrm{i}\hbar}{r}\sum_t\epsilon_{ijt}L_t \tag{8.18}$$

From the definition of $\mathbf{M}$ we have

$$\begin{aligned}[M_i, M_j] &= [\tfrac{1}{2}\hbar N_i - mK(\mathbf{e}_r)_i, \tfrac{1}{2}\hbar N_i - mK(\mathbf{e}_r)_i] = \tfrac{1}{4}\hbar^2[N_i, N_j] - \tfrac{1}{2}mK\hbar([N_i, (\mathbf{e}_r)_j] + [(\mathbf{e}_r)_i, N_j])\\ &= \tfrac{1}{4}\hbar^2[N_i, N_j] - \tfrac{1}{2}mK\hbar\big([N_i, (\mathbf{e}_r)_j] - [N_j, (\mathbf{e}_r)_i]\big).\end{aligned}$$

since the components of $\mathbf{e}$ commute with each other. We obtain the required result on substituting from equations (8.10) and (8.11).

A physical consequence of (8.12) is that we will not normally be able to know the values of more than one component of $\mathbf{M}$ – but we can in the exceptional case of completely radial orbits ($L^2|\psi\rangle = 0$).

10.8* *The Hamiltonian of a two-state system can be written*

$$H = \begin{pmatrix} A_1 + B_1\epsilon & B_2\epsilon \\ B_2\epsilon & A_2 \end{pmatrix}, \tag{10.1}$$

where all quantities are real and ϵ is a small parameter. To first order in ϵ, what are the allowed energies in the cases (a) $A_1 \neq A_2$, and (b) $A_1 = A_2$?

Obtain the exact eigenvalues and recover the results of perturbation theory by expanding in powers of ϵ.

Soln: When $A_1 \neq A_2$, the eigenvectors of H_0 are $(1,0)$ and $(0,1)$ so to first-order in ϵ the perturbed energies are the diagonal elements of H, namely $A_1 + B_1\epsilon$ and A_2.

When $A_1 = A_2$ the unperturbed Hamiltonian is degenerate and degenerate perturbation theory applies: we diagonalise the perturbation

$$H_1 = \begin{pmatrix} B_1\epsilon & B_2\epsilon \\ B_2\epsilon & 0 \end{pmatrix} = \epsilon \begin{pmatrix} B_1 & B_2 \\ B_2 & 0 \end{pmatrix}$$

The eigenvalues λ of the last matrix satisfy

$$\lambda^2 - B_1\lambda - B_2^2 = 0 \quad \Rightarrow \quad \lambda = \tfrac{1}{2}\left(B_1 \pm \sqrt{B_1^2 + 4B_2^2}\right)$$

and the perturbed energies are

$$A_1 + \lambda\epsilon = A_1 + \tfrac{1}{2}B_1\epsilon \pm \tfrac{1}{2}\sqrt{B_1^2 + 4B_2^2}\,\epsilon$$

Solving for the exact eigenvalues of the given matrix we find

$$\begin{aligned}\lambda &= \tfrac{1}{2}(A_1 + A_2 + B_1\epsilon) \pm \tfrac{1}{2}\sqrt{(A_1 + A_2 + B_1\epsilon)^2 - 4A_2(A_1 + B_1\epsilon) + 4B_2\epsilon^2} \\ &= \tfrac{1}{2}(A_1 + A_2 + B_1\epsilon) \pm \tfrac{1}{2}\sqrt{(A_1 - A_2)^2 + 2(A_1 - A_2)B_1\epsilon + (B_1^2 + 4B_2^2)\epsilon^2}\end{aligned}$$

If $A_1 = A_2$ this simplifies to

$$\lambda = A_1 + \tfrac{1}{2}B_1\epsilon + \pm\tfrac{1}{2}\sqrt{B_1^2 + 4B_2^2}\,\epsilon$$

in agreement with perturbation theory. If $A_1 \neq A_2$ we expand the radical to first order in ϵ

$$\begin{aligned}\lambda &= \tfrac{1}{2}(A_1 + A_2 + B_1\epsilon) \pm \tfrac{1}{2}(A_1 - A_2)\left(1 + \frac{B_1}{A_1 - A_2}\epsilon + \mathrm{O}(\epsilon^2)\right) \\ &= \begin{cases} A_1 + B_1\epsilon & \text{if } + \\ A_2 & \text{if } - \end{cases}\end{aligned}$$

again in agreement with perturbation theory

10.9* *For the P states of hydrogen, obtain the shift in energy caused by a weak magnetic field (a) by evaluating the Landé g factor, and (b) by use equation (10.28) and the Clebsch–Gordan coefficients calculated in §7.6.2.*

Soln: (a) From $l = 1$ and $s = \frac{1}{2}$ we can construct $j = \frac{3}{2}$ and $\frac{1}{2}$ so we have to evaluate two values of g_{L}. When $j = \frac{3}{2}$, $j(j+1) = 15/4$, and when $j = \frac{1}{2}$, $j(j+1) = 3/4$, so

$$g_{\mathrm{L}} = \tfrac{3}{2} - \tfrac{1}{2}\frac{l(l+1) - s(s+1)}{j(j+1)} = \begin{cases} \frac{4}{3} & \text{for } j = \frac{3}{2} \\ \frac{2}{3} & \text{for } j = \frac{1}{2} \end{cases}$$

So

$$E_B/(\mu_{\mathrm{B}}B) = mg_{\mathrm{L}} = \begin{cases} 2 & \text{for } j = \frac{3}{2}, m = \frac{3}{2} \\ \frac{2}{3} & \text{for } j = \frac{3}{2}, m = \frac{1}{2} \\ \frac{1}{3} & \text{for } j = \frac{1}{2}, m = \frac{1}{2} \end{cases}$$

with the values for negative m being minus the values for positive m.

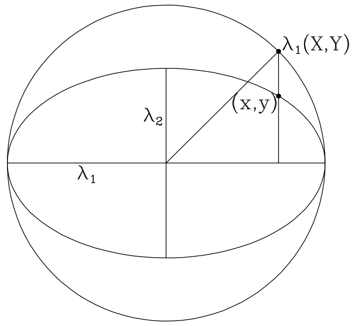

Figure 10.3 The relation of input and output vectors of a 2×2 Hermitian matrix with positive eigenvalues $\lambda_1 > \lambda_2$. An input vector (X, Y) on the unit circle produces the output vector (x, y) that lies on the ellipse that has the eigenvalues as semi-axes.

(b) We have $|\frac{3}{2},\frac{3}{2}\rangle = |+\rangle|11\rangle$ so $\langle\frac{3}{2},\frac{3}{2}|S_z|\frac{3}{2}\frac{3}{2}\rangle = \frac{1}{2}$ and $E_B/(\mu_B B) = m + \langle\psi|S_z|\psi\rangle = \frac{3}{2} + \frac{1}{2} = 2$ in agreement with the Landé factor. Similarly

$$|\tfrac{3}{2},\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}|-\rangle|11\rangle + \sqrt{\tfrac{2}{3}}|+\rangle|10\rangle \quad\Rightarrow\quad \langle\tfrac{3}{2},\tfrac{1}{2}|S_z|\tfrac{3}{2},\tfrac{1}{2}\rangle = \tfrac{1}{3}(-\tfrac{1}{2}) + \tfrac{2}{3}\tfrac{1}{2} = \tfrac{1}{6}$$

so $E_B/(\mu_B B) = \frac{1}{2} + \frac{1}{6} = \frac{2}{3}$ Finally

$$|\tfrac{1}{2},\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}|-\rangle|11\rangle - \sqrt{\tfrac{1}{3}}|+\rangle|10\rangle \quad\Rightarrow\quad \langle\tfrac{1}{2},\tfrac{1}{2}|S_z|\tfrac{1}{2},\tfrac{1}{2}\rangle = \tfrac{2}{3}(-\tfrac{1}{2}) + \tfrac{1}{2}\tfrac{1}{3} = -\tfrac{1}{6}$$

so $E_B/(\mu_B B) = \frac{1}{2} - \frac{1}{6} = \frac{1}{3}$

10.12* *Show that with the trial wavefunction $\psi(x) = (a^2 + x^2)^{-2}$ the variational principle yields an upper limit $E_0 < (\sqrt{7/5})\hbar\omega \simeq 0.529\,\hbar\omega$ on the ground-state energy of the harmonic oscillator.*
Soln: We set $x = a\tan\theta$ and have

$$\int_0^\infty \mathrm{d}x\,|\psi|^2 = a^{-7}\int_0^{\pi/2}\mathrm{d}\theta\,\cos^6\theta = a^{-7}\int_0^{\pi/2}\mathrm{d}\theta\,\{\tfrac{1}{2}(1+\cos 2\theta)\}^3$$
$$= \tfrac{1}{8}a^{-7}\int_0^{\pi/2}\mathrm{d}\theta\,(1 + 3\cos 2\theta + 3\cos^2 2\theta + \cos^3 2\theta) = \tfrac{1}{8}a^{-7}\tfrac{1}{2}\pi(1+\tfrac{3}{2}) = \tfrac{5}{32}\pi a^{-7}$$

where we have used the facts (i) that an odd power of a cosine averages to zero over $(0,\pi)$ and (ii) that $\cos^2\theta$ has average value $\frac{1}{2}$ over this interval.

Similarly

$$\int_0^\infty \mathrm{d}x\,x^2|\psi|^2 = a^{-5}\int_0^{\pi/2}\mathrm{d}\theta\,\cos^4\theta\sin^2\theta = a^{-5}\int_0^{\pi/2}\mathrm{d}\theta\,\tfrac{1}{2}(1+\cos 2\theta)\tfrac{1}{4}\sin^2 2\theta$$
$$= \tfrac{1}{8}a^{-5}\int_0^{\pi/2}\mathrm{d}\theta\,(\sin^2 2\theta + \cos 2\theta\sin^2 2\theta) = \tfrac{1}{8}a^{-5}(\tfrac{1}{4}\pi + \tfrac{1}{6}[\sin^3 2\theta]) = \tfrac{1}{32}\pi a^{-5}$$

and

$$\langle x|p|\psi\rangle = -\mathrm{i}\hbar\frac{-2}{(a^2+x^2)^3}2x$$

so

$$\int_0^\infty \mathrm{d}x\,|p\psi|^2 = 16\hbar^2 a^{-9}\int_0^{\pi/2}\mathrm{d}\theta\,\cos^8\theta\sin^2\theta = 16\hbar^2 a^{-9}\int_0^{\pi/2}\mathrm{d}\theta\,\tfrac{1}{8}(1+\cos 2\theta)^3\tfrac{1}{4}\sin^2 2\theta$$
$$= \tfrac{1}{2}\hbar^2 a^{-9}\left(\int_0^{\pi/2}\mathrm{d}\theta\,(\sin^2 2\theta + 3\cos^2 2\theta\sin^2 2\theta) + \int_0^{\pi/2}\mathrm{d}\theta\,\cos 2\theta(3 + 1 - \sin^2 2\theta)\right)$$
$$= \tfrac{1}{2}\hbar^2 a^{-9}\left(\tfrac{1}{4}\pi(1+\tfrac{3}{4}) + \left[\tfrac{2}{3}\sin^3 2\theta - \tfrac{1}{10}\sin^5 2\theta\right]\right) = \tfrac{7}{32}\hbar^2\pi a^{-9}$$

Hence

$$\langle H\rangle = \frac{\frac{7}{32}\hbar^2 a^{-9}\pi/2m + \frac{1}{2}m\omega^2\frac{1}{32}a^{-5}\pi}{\frac{5}{32}a^{-7}\pi} = \frac{\hbar^2}{2m}\tfrac{7}{5}a^{-2} + \tfrac{1}{10}m\omega^2 a^2$$

$$0 = \frac{\partial \langle H \rangle}{\partial a} = -\frac{\hbar^2}{m}\tfrac{7}{5}a^{-3} + \tfrac{1}{5}m\omega^2 a$$

$$a^4 = 7\left(\frac{\hbar}{m\omega}\right)^2 \quad \Rightarrow \quad a = 7^{1/4}\sqrt{2}\,\ell \quad \langle H \rangle = \frac{\sqrt{7}}{5}\hbar\omega$$

10.14* *Using the result proved in Problem 10.13, show that the trial wavefunction $\psi_b = \mathrm{e}^{-b^2r^2/2}$ yields $-8/(3\pi)\mathcal{R}$ as an estimate of hydrogen's ground-state energy, where $\mathcal{R}$ is the Rydberg constant.*
Soln: With $\psi = \mathrm{e}^{-b^2r^2/2}$, $\mathrm{d}\psi/\mathrm{d}r = -b^2 r\mathrm{e}^{-b^2r^2/2}$, so

$$\begin{aligned}\langle H \rangle &= \left(\frac{\hbar^2 b^4}{2m}\int \mathrm{d}r\, r^4 \mathrm{e}^{-b^2r^2} - \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}r\, r\mathrm{e}^{-b^2r^2}\right)\Big/\int \mathrm{d}r\, r^2\mathrm{e}^{-b^2r^2}\\ &= \left(\frac{\hbar^2}{2mb}\int \mathrm{d}x\, x^4\mathrm{e}^{-x^2} - \frac{e^2}{4\pi\epsilon_0 b^2}\int \mathrm{d}x\, x\mathrm{e}^{-x^2}\right)\Big/\frac{1}{b^3}\int \mathrm{d}x\, x^2\mathrm{e}^{-x^2}\end{aligned}$$

Now

$$\begin{aligned}\int \mathrm{d}x\, x\mathrm{e}^{-x^2} &= \left[\frac{\mathrm{e}^{-x^2}}{-2}\right]_0^\infty = \tfrac{1}{2}\\ \int \mathrm{d}x\, x^2\mathrm{e}^{-x^2} &= \left[\frac{x\mathrm{e}^{-x^2}}{-2}\right]_0^\infty + \tfrac{1}{2}\int \mathrm{d}x\,\mathrm{e}^{-x^2} = \frac{\sqrt{\pi}}{4}\\ \int \mathrm{d}x\, x^4\mathrm{e}^{-x^2} &= \left[\frac{x^3\mathrm{e}^{-x^2}}{-2}\right]_0^\infty + \tfrac{3}{2}\int \mathrm{d}x\, x^2\mathrm{e}^{-x^2} = \frac{3\sqrt{\pi}}{8}\end{aligned}$$

so

$$\langle H \rangle = \left(\frac{\hbar^2}{2mb}\frac{3\sqrt{\pi}}{8} - \frac{e^2}{4\pi\epsilon_0 b^2}\frac{1}{2}\right)\Big/\frac{\sqrt{\pi}}{4b^3} = \frac{3\hbar^2 b^2}{4m} - \frac{e^2 b}{2\pi^{3/2}\epsilon_0}$$

At the stationary point of $\langle H \rangle$ $b = me^2/(3\pi^{3/2}\epsilon_0\hbar^2)$. Plugging this into $\langle H \rangle$ we find

$$\langle H \rangle = \frac{3\hbar^2}{4m}\frac{m^2e^4}{9\pi^3\epsilon_0^2\hbar^4} - \frac{e^2}{2\pi^{3/2}\epsilon_0}\frac{me^2}{3\pi^{3/2}\epsilon_0\hbar^2} = -\frac{8}{3\pi}\frac{m}{2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = \frac{8}{3\pi}\mathcal{R}$$

10.18* *A particle of mass m is initially trapped by the well with potential $V(x) = -V_\delta\delta(x)$, where $V_\delta > 0$. From $t = 0$ it is disturbed by the time-dependent potential $v(x,t) = -Fx\mathrm{e}^{-\mathrm{i}\omega t}$. Its subsequent wavefunction can be written*

$$|\psi\rangle = a(t)\mathrm{e}^{-\mathrm{i}E_0t/\hbar}|0\rangle + \int \mathrm{d}k\;\{b_k(t)|k,\mathrm{e}\rangle + c_k(t)|k,\mathrm{o}\rangle\}\,\mathrm{e}^{-\mathrm{i}E_kt/\hbar}, \tag{10.2}$$

where E_0 is the energy of the bound state $|0\rangle$ and $E_k \equiv \hbar^2k^2/2m$ and $|k,\mathrm{e}\rangle$ and $|k,\mathrm{o}\rangle$ are, respectively the even- and odd-parity states of energy E_k (see Problem 5.17). Obtain the equations of motion

$$\begin{aligned}\mathrm{i}\hbar&\left\{\dot{a}|0\rangle\mathrm{e}^{-\mathrm{i}E_0t/\hbar} + \int \mathrm{d}k\;\left(\dot{b}_k|k,\mathrm{e}\rangle + \dot{c}_k|k,\mathrm{o}\rangle\right)\mathrm{e}^{-\mathrm{i}E_kt/\hbar}\right\}\\ &= v\left\{a|0\rangle\mathrm{e}^{-\mathrm{i}E_0t/\hbar} + \int \mathrm{d}k\;(b_k|k,\mathrm{e}\rangle + c_k|k,\mathrm{o}\rangle)\,\mathrm{e}^{-\mathrm{i}E_kt/\hbar}\right\}.\end{aligned} \tag{10.3}$$

Given that the free states are normalised such that $\langle k',\mathrm{o}|k,\mathrm{o}\rangle = \delta(k-k')$, show that to first order in v, $b_k = 0$ for all t, and that

$$c_k(t) = \frac{\mathrm{i}F}{\hbar}\langle k,\mathrm{o}|x|0\rangle\,\mathrm{e}^{\mathrm{i}\Omega_kt/2}\,\frac{\sin(\Omega_kt/2)}{\Omega_k/2}, \quad \text{where} \quad \Omega_k \equiv \frac{E_k - E_0}{\hbar} - \omega. \tag{10.4}$$

Hence show that at late times the probability that the particle has become free is

$$P_{\mathrm{fr}}(t) = \frac{2\pi mF^2t}{\hbar^3}\left.\frac{|\langle k,\mathrm{o}|x|0\rangle|^2}{k}\right|_{\Omega_k=0}. \tag{10.5}$$

Given that from Problem 5.17 we have

$$\langle x|0\rangle = \sqrt{K}\mathrm{e}^{-K|x|} \quad \textit{where} \quad K = \frac{mV_\delta}{\hbar^2} \quad \textit{and} \quad \langle x|k,\mathrm{o}\rangle = \frac{1}{\sqrt{\pi}}\sin(kx), \tag{10.6}$$

show that

$$\langle k,\mathrm{o}|x|0\rangle = \sqrt{\frac{K}{\pi}}\frac{4kK}{(k^2+K^2)^2}. \tag{10.7}$$

Hence show that the probability of becoming free is

$$P_{\mathrm{fr}}(t) = \frac{8\hbar F^2 t}{mE_0^2}\frac{\sqrt{E_{\mathrm{f}}/|E_0|}}{(1+E_{\mathrm{f}}/|E_0|)^4}, \tag{10.8}$$

where $E_{\mathrm{f}} > 0$ is the final energy. Check that this expression for P_{fr} is dimensionless and give a physical explanation of the general form of the energy-dependence of $P_{\mathrm{fr}}(t)$

Soln: When we substitute the given expansion of $|\psi\rangle$ in stationary states of the unperturbed Hamiltonian H_0 into the TISE, the terms generated by differentiating the exponentials in time cancel on $H_0|\psi\rangle$. The given expression contains the surviving terms, namely the derivatives of the amplitudes a, b_k and c_k on the left and on the right $v|\psi\rangle$. In the first order approximation we put $a = 1$ and $b_k = c_k = 0$ on the right. Then we bra through with $\langle k',\mathrm{e}|$ and $\langle k',\mathrm{o}|$ and exploit the orthonormality of the stationary states to obtain equations for $\dot{b}_k(t)$ and $\dot{c}_k(t)$. The equation for $\dot{b}_k$ is proportional to the matrix element $\langle k,\mathrm{e}|v|0\rangle$, which vanishes by parity because v is an odd-parity operator. Then we replace v by $-xF\mathrm{e}^{-\mathrm{i}\omega t}$ and have

$$\begin{aligned} c_k(t) &= \int_0^t \mathrm{d}t'\,\dot{c}_k = \frac{\mathrm{i}F}{\hbar}\langle k,\mathrm{o}|x|0\rangle \int_0^t \mathrm{d}t'\,\mathrm{e}^{\mathrm{i}[(E_k-E_0)/\hbar-\omega]t'} = \frac{\mathrm{i}F}{\hbar}\langle k,\mathrm{o}|x|0\rangle\frac{\mathrm{e}^{\mathrm{i}\Omega_k t}-1}{\mathrm{i}\Omega_k} \\ &= \frac{\mathrm{i}F}{\hbar}\langle k,\mathrm{o}|x|0\rangle\,\mathrm{e}^{\mathrm{i}\Omega_k t/2}\,\frac{\sin(\Omega_k t/2)}{\Omega_k/2}. \end{aligned}$$

The probability that the particle is free is

$$P_{\mathrm{fr}}(t) = \int \mathrm{d}k\,|c_k|^2 = \frac{F^2}{\hbar^2}\int \mathrm{d}k\,|\langle k,\mathrm{o}|x|0\rangle|^2\frac{\sin^2(\Omega_k t/2)}{(\Omega_k/2)^2}.$$

As $t\to\infty$ we have $\sin^2 xt/x^2 \to \pi t\delta(x)$, so at large t

$$P_{\mathrm{fr}}(t) = \frac{F^2}{\hbar^2}\int \mathrm{d}k\,|\langle k,\mathrm{o}|x|0\rangle|^2\pi t\delta(\Omega_k/2) = \frac{F^2}{\hbar^2}\left.\frac{|\langle k,\mathrm{o}|x|0\rangle|^2\pi t}{\mathrm{d}(\Omega_k/2)/\mathrm{d}k}\right|_{\Omega_k=0}$$

Moreover, $\Omega_k = \frac{1}{2}\hbar k^2/m + \text{constant}$, so $\mathrm{d}\Omega_k/\mathrm{d}k = \hbar k/m$ and therefore

$$P_{\mathrm{fr}}(t) = \frac{2\pi mF^2 t}{\hbar^3}\left.\frac{|\langle k,\mathrm{o}|x|0\rangle|^2}{k}\right|_{\Omega_k=0}.$$

Evaluating $\langle k,\mathrm{o}|x|0\rangle$ in the position representation, we have

$$\begin{aligned} \langle k,\mathrm{o}|x|0\rangle &= 2\int_0^\infty \mathrm{d}x\,\frac{\sin kx}{\sqrt{\pi}}\,x\,\sqrt{K}\mathrm{e}^{-Kx} = 2\sqrt{\frac{K}{\pi}}\frac{1}{2\mathrm{i}}\int_0^\infty \mathrm{d}x\,x\left(\mathrm{e}^{(\mathrm{i}k-K)x}-\mathrm{e}^{-(\mathrm{i}k+K)x}\right) \\ &= -\mathrm{i}\sqrt{\frac{K}{\pi}}\left(\frac{1}{(\mathrm{i}k-K)^2}-\frac{1}{(\mathrm{i}k+K)^2}\right) = \sqrt{\frac{K}{\pi}}\frac{4kK}{(k^2+K^2)^2}. \end{aligned}$$

The probability of becoming free is therefore

$$P_{\mathrm{fr}}(t) = \frac{2\pi mF^2 t}{\hbar^3}\frac{K}{\pi}\frac{16kK^2}{(k^2+K^2)^4} = \frac{32mF^2 t}{\hbar^3K^4}\frac{k/K}{(k^2/K^2+1)^4} \tag{10.9}$$

The required result follows when we substitute into the above $k^2/K^2 = E_{\mathrm{f}}/|E_0|$ and $\hbar^4K^2 = (2mE_0)^2$.

Regarding dimensions, $[F] = E/L$ and $[\hbar] = ET$, so

$$[P_{\rm fr}] = \frac{(E/L)^2 ETT}{ME^2} = \frac{ET^2}{ML^2} = \frac{ML^2T^{-2}T^2}{ML^2}.$$

$P_{\rm fr}(t)$ is small for small E because at such energies the free state, which always has a node at the location of the well, has a long wavelength, so it is practically zero throughout the region of scale $2/K$ within which the bound particle is trapped. Consequently for small E the coupling between the bound and free state is small. At high E the wavelength of the free state is much smaller than $2/K$ and the positive and negative contributions from neighbouring half cycles of the free state nearly cancel, so again the coupling between the bound and free states is small. The coupling is most effective when the wavelength of the free state is just a bit smaller than the size of the bound state.

10.19* *A particle travelling with momentum $p = \hbar k > 0$ from $-\infty$ encounters the steep-sided potential well $V(x) = -V_0 < 0$ for $|x| < a$. Use the Fermi golden rule to show that the probability that a particle will be reflected by the well is*

$$P_{\rm reflect} \simeq \frac{V_0^2}{4E^2}\sin^2(2ka),$$

where $E = p^2/2m$. Show that in the limit $E \gg V_0$ this result is consistent with the exact reflection probability derived in Problem 5.10. Hint: adopt periodic boundary conditions so the wavefunctions of the in and out states can be normalised.

Soln: We consider a length L of the x axis where $L \gg a$ and $k = 2n\pi/L$, where $n \gg 1$ is an integer. Then correctly normalised wavefunctions of the in and out states are

$$\psi_{\rm in}(x) = \frac{1}{\sqrt{L}}{\rm e}^{{\rm i}kx} \quad ; \quad \psi_{\rm out}(x) = \frac{1}{\sqrt{L}}{\rm e}^{-{\rm i}kx}$$

The required matrix element is

$$\frac{1}{L}\int_{-L/2}^{L/2}{\rm d}x\,{\rm e}^{{\rm i}kx}V(x){\rm e}^{{\rm i}kx} = -V_0\int_{-a}^{a}{\rm d}x\,{\rm e}^{2{\rm i}kx} = -V_0\frac{\sin(2ka)}{Lk}$$

so the rate of transitions from the in to the out state is

$$\dot{P} = \frac{2\pi}{\hbar}g(E)|\langle{\rm out}|V|{\rm in}\rangle|^2 = \frac{2\pi}{\hbar}g(E)V_0^2\frac{\sin^2(2ka)}{L^2k^2}$$

Now we need the density of states $g(E)$. $E = p^2/2m = \hbar^2k^2/2m$ is just kinetic energy. Eliminating k in favour of n, we have

$$n = \frac{L}{2\pi\hbar}\sqrt{2mE}$$

As n increases by one, we get one extra state to scatter into, so

$$g = \frac{{\rm d}n}{{\rm d}E} = \frac{L}{4\pi\hbar}\sqrt{\frac{2m}{E}}.$$

Substituting this value into our scattering rate we find

$$\dot{P} = \frac{V_0^2}{2\hbar^2}\sqrt{\frac{2m}{E}}\frac{\sin^2(2ka)}{Lk^2}$$

This vanishes as $L \to \infty$ because the fraction of the available space that is occupied by the scattering potential is $\sim 1/L$. If it is not scattered, the particle covers distance L in a time $\tau = L/v = L/\sqrt{2E/m}$. So the probability that it is scattered on a single encounter is

$$\dot{P}\tau = \frac{V_0^2 m}{2E\hbar^2}\frac{\sin^2(2ka)}{k^2} = \frac{V_0^2}{4E^2}\sin^2(2ka)$$

Equation (5.78) gives the reflection probability as

$$P = \frac{(K/k - k/K)^2 \sin^2(2Ka)}{(K/k + k/K)^2 \sin^2(2Ka) + 4\cos^2(2Ka)}$$

When $V_0 \ll E$, $K^2 - k^2 = 2mV_0/\hbar^2 \ll k^2$, so we approximate Ka with ka and, using $K/k \simeq 1$ in the denominator, the reflection probability becomes

$$P \simeq \left(\frac{K^2 - k^2}{2kK}\right)^2 \sin^2(2ka) \simeq \left(\frac{2mV_0}{2\hbar^2 k^2}\right)^2 \sin^2(2ka) = \frac{V_0^2}{4E^2}\sin^2(2ka),$$

which agrees with the value we obtained from Fermi's rule.

10.20* *Show that the number of states $g(E)\,\mathrm{d}E\,\mathrm{d}^2\Omega$ with energy in $(E, E+\mathrm{d}E)$ and momentum in the solid angle $\mathrm{d}^2\Omega$ around $\mathbf{p} = \hbar\mathbf{k}$ of a particle of mass m that moves freely subject to periodic boundary conditions on the walls of a cubical box of side length L is*

$$g(E)\,\mathrm{d}E\,\mathrm{d}^2\Omega = \left(\frac{L}{2\pi}\right)^3 \frac{m^{3/2}}{\hbar^3}\sqrt{2E}\,\mathrm{d}E\,\mathrm{d}\Omega^2. \tag{10.10}$$

Hence show from Fermi's golden rule that the cross-section for elastic scattering of such particles by a weak potential $V(\mathbf{x})$ from momentum $\hbar\mathbf{k}$ into the solid angle $\mathrm{d}^2\Omega$ around momentum $\hbar\mathbf{k}'$ is

$$\mathrm{d}\sigma = \frac{m^2}{(2\pi)^2\hbar^4}\,\mathrm{d}^2\Omega \left|\int \mathrm{d}^3\mathbf{x}\,\mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}} V(\mathbf{x})\right|^2. \tag{10.11}$$

Explain in what sense the potential has to be 'weak' for this **Born approximation** *to the scattering cross-section to be valid.*

Soln: We have $k_x = 2n_x\pi/L$, where n_x is an integer, and similarly for k_y, k_z. So each state occupies volume $(2\pi/L)^3$ in k-space. So the number of states in the volume element $k^2\,\mathrm{d}k\mathrm{d}^2\Omega$ is

$$g(E)\mathrm{d}E\mathrm{d}^2\Omega = \left(\frac{L}{2\pi}\right)^3 k^2\,\mathrm{d}k\mathrm{d}^2\Omega$$

Using $k^2 = 2mE/\hbar^2$ to eliminate k we obtain the required expression.

In Fermi's formula we must replace $g(E)\,\mathrm{d}E$ by $g(E)\,\mathrm{d}E\,\mathrm{d}^2\Omega$ because this is the density of states that will make our detector ping if $\mathrm{d}^2\Omega$ is its angular resolution. Then the probability per unit time of pinging is

$$\dot{P} = \frac{2\pi}{\hbar} g(E)\mathrm{d}^2\Omega|\langle\mathrm{out}|V|\mathrm{in}\rangle|^2 = \frac{2\pi}{\hbar}\left(\frac{L}{2\pi}\right)^3 k^2\,\frac{\mathrm{d}k}{\mathrm{d}E}\mathrm{d}^2\Omega|\langle\mathrm{out}|V|\mathrm{in}\rangle|^2$$

The matrix element is

$$\langle\mathrm{out}|V|\mathrm{in}\rangle = \frac{1}{L^3}\int \mathrm{d}^3\mathbf{x}\,\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{x}} V(\mathbf{x})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}$$

Now the cross section $\mathrm{d}\sigma$ is defined by $\dot{P} = \mathrm{d}\sigma \times \text{incoming flux} = (v/L^3)\mathrm{d}\sigma = (\hbar k/mL^3)\mathrm{d}\sigma$. Putting everything together, we find

$$\frac{\hbar k}{mL^3}\mathrm{d}\sigma = \frac{1}{L^6}\left|\int \mathrm{d}^3\mathbf{x}\,\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{x}} V(\mathbf{x})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\right|^2 \frac{2\pi}{\hbar}\left(\frac{L}{2\pi}\right)^3 k^2\,\frac{\mathrm{d}k}{\mathrm{d}E}\mathrm{d}^2\Omega$$

$$\Rightarrow \quad \mathrm{d}\sigma = \frac{mk\,\mathrm{d}k/\mathrm{d}E}{(2\pi)^2\hbar^2}\left|\int \mathrm{d}^3\mathbf{x}\,\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{x}} V(\mathbf{x})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\right|^2.$$

Eliminating k with $\hbar^2 k\,\mathrm{d}k = m\mathrm{d}E$ we obtain the desired expression.

The Born approximation is valid providing the unperturbed wavefunction is a reasonable approximation to the true wavefunction throughout the scattering potential. That is, we must be able to neglect "shadowing" by the scattering potential.

11.4* *In terms of the position vectors $\mathbf{x}_\alpha$, $\mathbf{x}_1$ and $\mathbf{x}_2$ of the α particle and two electrons, the centre of mass and relative coordinates of a helium atom are*

$$\mathbf{X} \equiv \frac{m_\alpha \mathbf{x}_\alpha + m_\mathrm{e}(\mathbf{x}_1 + \mathbf{x}_2)}{m_t}, \quad \mathbf{r}_1 \equiv \mathbf{x}_1 - \mathbf{X}, \quad \mathbf{r}_2 \equiv \mathbf{x}_2 - \mathbf{X}, \tag{11.1}$$

where $m_t \equiv m_\alpha + 2m_\mathrm{e}$. Write the atom's potential energy operator in terms of the $\mathbf{r}_i$.

Show that

$$\begin{gathered}\frac{\partial}{\partial \mathbf{X}} = \frac{\partial}{\partial \mathbf{x}_\alpha} + \frac{\partial}{\partial \mathbf{x}_1} + \frac{\partial}{\partial \mathbf{x}_2} \\ \frac{\partial}{\partial \mathbf{r}_1} = \frac{\partial}{\partial \mathbf{x}_1} - \frac{m_\mathrm{e}}{m_\alpha}\frac{\partial}{\partial \mathbf{x}_\alpha} \qquad \frac{\partial}{\partial \mathbf{r}_2} = \frac{\partial}{\partial \mathbf{x}_2} - \frac{m_\mathrm{e}}{m_\alpha}\frac{\partial}{\partial \mathbf{x}_\alpha}\end{gathered} \tag{11.2}$$

and hence that the kinetic energy operator of the helium atom can be written

$$K = -\frac{\hbar^2}{2m_t}\frac{\partial^2}{\partial \mathbf{X}^2} - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial \mathbf{r}_1^2} + \frac{\partial^2}{\partial \mathbf{r}_2^2}\right) - \frac{\hbar^2}{2m_t}\left(\frac{\partial}{\partial \mathbf{x}_1} - \frac{\partial}{\partial \mathbf{x}_2}\right)^2, \tag{11.3}$$

where $\mu \equiv m_\mathrm{e}(1 + 2m_\mathrm{e}/m_\alpha)$. What is the physical interpretation of the third term on the right? Explain why it is reasonable to neglect this term.

Soln: We have from the definitions

$$\begin{aligned}\mathbf{x}_1 &= \mathbf{X} + \mathbf{r}_1 \qquad \mathbf{x}_2 = \mathbf{X} + \mathbf{r}_2 \\ \mathbf{x}_\alpha &= \frac{1}{m_\alpha}\left(m_t\mathbf{X} - m_\mathrm{e}(\mathbf{x}_1 + \mathbf{x}_2)\right) = \frac{1}{m_\alpha}\left(m_t\mathbf{X} - m_\mathrm{e}(2\mathbf{X} + \mathbf{r}_1 + \mathbf{r}_2)\right) \\ &= \mathbf{X} - \frac{m_\mathrm{e}}{m_\alpha}(\mathbf{r}_1 + \mathbf{r}_2)\end{aligned}$$

Directly computing the differences $\mathbf{x}_i - \mathbf{x}_\alpha$, etc, one finds easily that

$$V = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{|\mathbf{r}_1 + (m_\mathrm{e}/m_\alpha)(\mathbf{r}_1 + \mathbf{r}_2)|} + \frac{2}{|\mathbf{r}_1 + (m_\mathrm{e}/m_\alpha)(\mathbf{r}_1 + \mathbf{r}_2)|} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right).$$

By the chain rule

$$\frac{\partial}{\partial \mathbf{X}} = \frac{\partial \mathbf{x}_\alpha}{\partial \mathbf{X}}\cdot\frac{\partial}{\partial \mathbf{x}_\alpha} + \frac{\partial \mathbf{x}_1}{\partial \mathbf{X}}\cdot\frac{\partial}{\partial \mathbf{x}_1} + \frac{\partial \mathbf{x}_2}{\partial \mathbf{X}}\cdot\frac{\partial}{\partial \mathbf{x}_2} = \frac{\partial}{\partial \mathbf{x}_\alpha} + \frac{\partial}{\partial \mathbf{x}_1} + \frac{\partial}{\partial \mathbf{x}_2}$$

as required. Similarly

$$\frac{\partial}{\partial \mathbf{r}_1} = \frac{\partial \mathbf{x}_\alpha}{\partial \mathbf{r}_1}\cdot\frac{\partial}{\partial \mathbf{x}_\alpha} + \frac{\partial \mathbf{x}_1}{\partial \mathbf{r}_1}\cdot\frac{\partial}{\partial \mathbf{x}_1} = -\frac{m_\mathrm{e}}{m_\alpha}\frac{\partial}{\partial \mathbf{x}_\alpha} + \frac{\partial}{\partial \mathbf{x}_1}$$

and similarly for $\partial/\partial\mathbf{r}_2$. Squaring these expressions, we have

$$\begin{aligned}\frac{\partial^2}{\partial \mathbf{X}^2} &= \frac{\partial^2}{\partial \mathbf{x}_\alpha^2} + 2\frac{\partial}{\partial \mathbf{x}_\alpha}\left(\frac{\partial}{\partial \mathbf{x}_1} + \frac{\partial}{\partial \mathbf{x}_2}\right) + \left(\frac{\partial}{\partial \mathbf{x}_1} + \frac{\partial}{\partial \mathbf{x}_2}\right)^2 \\ \frac{\partial^2}{\partial \mathbf{r}_1^2} &= \frac{m_\mathrm{e}^2}{m_\alpha^2}\frac{\partial^2}{\partial \mathbf{x}_\alpha^2} - 2\frac{m_\mathrm{e}}{m_\alpha}\frac{\partial^2}{\partial \mathbf{x}_1\partial \mathbf{x}_\alpha} + \frac{\partial^2}{\partial \mathbf{x}_1^2} \\ \frac{\partial^2}{\partial \mathbf{r}_2^2} &= \frac{m_\mathrm{e}^2}{m_\alpha^2}\frac{\partial^2}{\partial \mathbf{x}_\alpha^2} - 2\frac{m_\mathrm{e}}{m_\alpha}\frac{\partial^2}{\partial \mathbf{x}_2\partial \mathbf{x}_\alpha} + \frac{\partial^2}{\partial \mathbf{x}_2^2}\end{aligned}$$

If we add the first of these eqns to m_α/m_e times the sum of the other two, the mixed derivatives in $\mathbf{x}_\alpha$ cancel and we are left with

$$\frac{\partial^2}{\partial \mathbf{X}^2} + \frac{m_\alpha}{m_\mathrm{e}}\left(\frac{\partial^2}{\partial \mathbf{r}_1^2} + \frac{\partial^2}{\partial \mathbf{r}_2^2}\right) = \left(1 + 2\frac{m_\mathrm{e}}{m_\alpha}\right)\frac{\partial^2}{\partial \mathbf{x}_\alpha^2} + \left(1 + \frac{m_\alpha}{m_\mathrm{e}}\right)\left(\frac{\partial^2}{\partial \mathbf{x}_1^2} + \frac{\partial^2}{\partial \mathbf{x}_2^2}\right) + 2\frac{\partial^2}{\partial \mathbf{x}_1\partial \mathbf{x}_2}$$

Dividing through by m_t we obtain

$$\frac{1}{m_t}\frac{\partial^2}{\partial \mathbf{X}^2} + \frac{m_\alpha}{m_\mathrm{e}m_t}\left(\frac{\partial^2}{\partial \mathbf{r}_1^2} + \frac{\partial^2}{\partial \mathbf{r}_2^2}\right) = \frac{1}{m_\alpha}\frac{\partial^2}{\partial \mathbf{x}_\alpha^2} + \frac{1}{m_\mathrm{e}}\left(1 - \frac{m_\mathrm{e}}{m_t}\right)\left(\frac{\partial^2}{\partial \mathbf{x}_1^2} + \frac{\partial^2}{\partial \mathbf{x}_2^2}\right) + \frac{2}{m_t}\frac{\partial^2}{\partial \mathbf{x}_1\partial \mathbf{x}_2}$$

After multiplication by $-\hbar^2/2$ the first term on the right and the unity part of the second term constitute the atom's KE operator. So we transfer the remaining terms to the left side and have the stated result.

The final term in K must represent the kinetic energy that the α-particle has as it moves around the centre of mass in reflex to the faster motion of the electrons. It will be smaller than the double derivatives with respect to $\mathbf{r}_i$ by at least a factor m_e/m_α. (Classically we'd expect the velocities to be smaller by this factor and therefore the kinetic energies to be in the ratio $m_\mathrm{e}^2/m_\alpha^2$.)

11.7* *Assume that a LiH molecule comprises a Li^+ ion electrostatically bound to an H^- ion, and that in the molecule's ground state the kinetic energies of the ions can be neglected. Let the centres of the two ions be separated by a distance b and calculate the resulting electrostatic binding energy under the assumption that they attract like point charges. Given that the ionisation energy of Li is $0.40\mathcal{R}$ and using the result of Problem 11.6, show that the molecule has less energy than that of well separated hydrogen and lithium atoms for $b < 4.4a_0$. Does this calculation suggest that LiH is a stable molecule? Is it safe to neglect the kinetic energies of the ions within the molecule?*

Soln: When the LI and H are well separated, the energy required to strip an electron from the Li and park it on the H^- is $E = (0.4 + 1 - 0.955)\mathcal{R} = 0.445\mathcal{R}$. Now we recover some of this energy by letting the Li^+ and H^- fall towards each other. When they have reached distance b the energy released is

$$\frac{e^2}{4\pi\epsilon_0 b} = 2\mathcal{R}\frac{a_0}{b}$$

This energy equals our original outlay when $b = (2/0.445)a_0 = 4.49a_0$, which establishes the required proposition.

In LiH the Li-H separation will be $\lesssim 2a_0$, because only at a radius of this order will the electron clouds of the two ions generate sufficient repulsion to balance the electrostatic attraction we have been calculating. At this separation the energy will be decidedly less than that of isolated Li and H, so yes the molecule will be stable.

In its ground state the molecule will have zero angular momentum, so there is no rotational kinetic energy to worry about. However the length of the Li-H bond will oscillate around its equilibrium value, roughly as a harmonic oscillator, so there will be zero-point energy. However, this energy will suffice only to extend the bond length by a fraction of its equilibrium value, so it does not endanger the stability of the molecule.

11.8* *Two spin-one gyros are in a box. Express the states $|j, m\rangle$ in which the box has definite angular momentum as linear combinations of the states $|1, m\rangle|1, m'\rangle$ in which the individual gyros have definite angular momentum. Hence show that*

$$|0, 0\rangle = \frac{1}{\sqrt{3}}(|1, -1\rangle|1, 1\rangle - |1, 0\rangle|1, 0\rangle + |1, 1\rangle|1, -1\rangle). \qquad (11.4)$$

By considering the symmetries of your expressions, explain why the ground state of carbon has $l = 1$ rather than $l = 2$ or 0. What is the total spin angular momentum of a C atom?

Soln: We have that $J_-|2, 2\rangle = 2|2, 1\rangle$, $J_-|2, 1\rangle = \sqrt{6}|2, 0\rangle$, $J_-|1, 1\rangle = \sqrt{2}|1, 0\rangle$, $J_-|1, 0\rangle = \sqrt{2}|1, -1\rangle$. We start from

$$|2, 2\rangle = |1, 1\rangle|1, 1\rangle$$

and apply J_- to both sides, obtaining

$$2|2, 1\rangle = \sqrt{2}(|1, 0\rangle|1, 1\rangle + |1, 1\rangle|1, 0\rangle) \quad \Rightarrow \quad |2, 1\rangle = \frac{1}{\sqrt{2}}(|1, 0\rangle|1, 1\rangle + |1, 1\rangle|1, 0\rangle)$$

Applying J_- again we find

$$|2, 0\rangle = \frac{1}{\sqrt{6}}(|1, -1\rangle|1, 1\rangle + 2|1, 0\rangle|1, 0\rangle + |1, 1\rangle|1, -1\rangle)$$

Next we identify $|1, 1\rangle$ as the linear combination of $|1, 1\rangle|1, 0\rangle$ and $|1, 0\rangle|1, 1\rangle$ that's orthogonal to $|2, 1\rangle$. It clearly is

$$|1, 1\rangle = \frac{1}{\sqrt{2}}(|1, 0\rangle|1, 1\rangle - |1, 1\rangle|1, 0\rangle)$$

We obtain $|1, 0\rangle$ by applying J_- to this

$$|1, 0\rangle = \frac{1}{\sqrt{2}}(|1, -1\rangle|1, 1\rangle - |1, 1\rangle|1, -1\rangle)$$

and applying J_- again we have

$$|1, -1\rangle = \frac{1}{\sqrt{2}}(|1, -1\rangle|1, 0\rangle - |1, 0\rangle|1, -1\rangle)$$

Finally we have that $|0,0\rangle$ is the linear combination of $|1,-1\rangle|1,1\rangle$, $|1,1\rangle|1,-1\rangle$ and $|1,0\rangle|1,0\rangle$ that's orthogonal to both $|2,0\rangle$ and $|1,0\rangle$. By inspection it's the given expression.

The kets for $j=2$ and $j=0$ are symmetric under interchange of the m values of the gyros, while that for $j=1$ is antisymmetric under interchange. Carbon has two valence electrons both in an $l=1$ state, so each electron maps to a gyro and the box to the atom. When the atom is in the $|1,1\rangle$ state, for example, from the above the part of the wavefunction that described the locations of the two valence electrons is

$$\langle \mathbf{x}_1, \mathbf{x}_2|1,1\rangle = \frac{1}{\sqrt{2}}(\langle \mathbf{x}_1|1,0\rangle\langle \mathbf{x}_2|1,1\rangle - \langle \mathbf{x}_1|1,1\rangle\langle \mathbf{x}_2|1,0\rangle)$$

This function is antisymmetric in its arguments so vanishes when $\mathbf{x}_1 = \mathbf{x}_2$. Hence in this state of the atom, the electrons do a good job of keeping out of each other's way and we can expect the electron-electron repulsion to make this state (and the other two $l=1$ states) lower-lying than the $l=2$ or $l=0$ states, which lead to wavefunctions that are symmetric functions of $\mathbf{x}_1$ and $\mathbf{x}_2$.

Since the wavefunction has to be antisymmetric overall, for the $l=1$ state it must be symmetric in the spins of the electrons, so the total spin has to be 1.

11.9* *Suppose we have three spin-one gyros in a box. Express the state $|0,0\rangle$ of the box in which it has no angular momentum as a linear combination of the states $|1,m\rangle|1,m'\rangle|1,m''\rangle$ in which the individual gyros have well-defined angular momenta. Hint: start with just two gyros in the box, giving states $|j,m\rangle$ of the box, and argue that only for a single value of j will it be possible to get $|0,0\rangle$ by adding the third gyro; use results from Problem 11.8.*

Explain the relevance of your result to the fact that the ground state of nitrogen has $l=0$. Deduce the value of the total electron spin of an N atom.

Soln: Since when we add gyros with spins j_1 and j_2 the resulting j satisfies $|j_1-j_2| \le j \le j_1+j_2$, we will be able to construct the state $|0,0\rangle$ on adding the third gyro to the box, only if the box has $j=1$ before adding the last gyro. From Problem 11.8 we have that

$$|0,0\rangle = \frac{1}{\sqrt{3}}(|1,-1\rangle|1,1\rangle - |1,0\rangle|1,0\rangle + |1,1\rangle|1,-1\rangle),$$

where we can consider the first ket in each product is for the combination of 2 gyros and the second ket is for the third gyro. We use Problem 11.8 again to express the kets of the 2-gyro box as linear combinations of the kets of individual gyros:

$$\begin{aligned}|0,0\rangle &= \frac{1}{\sqrt{3}}\bigg(\frac{1}{\sqrt{2}}\big(|1,-1\rangle|1,0\rangle - |1,0\rangle|1,-1\rangle\big)|1,1\rangle - \frac{1}{\sqrt{2}}\big(|1,-1\rangle|1,1\rangle - |1,1\rangle|1,-1\rangle\big)|1,0\rangle \\ &\quad + \frac{1}{\sqrt{2}}\big(|1,0\rangle|1,1\rangle - |1,1\rangle|1,0\rangle\big)|1,-1\rangle\bigg), \\ &= \frac{1}{\sqrt{6}}\Big(|1,-1\rangle|1,0\rangle|1,1\rangle - |1,0\rangle|1,-1\rangle|1,1\rangle - |1,-1\rangle|1,1\rangle|1,0\rangle \\ &\quad + |1,1\rangle|1,-1\rangle|1,0\rangle + |1,0\rangle|1,1\rangle|1,0\rangle - |1,1\rangle|1,0\rangle|1,0\rangle\Big)\end{aligned}$$

This state is totally antisymmetric under exchange of the m values of the gyros.

When we interpret the gyros as electrons and move to the position representation we find that the wavefunction of the valence electrons is a totally antisymmetric function of their coordinates, $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$. Hence the electrons do an excellent job of keeping out of each other's way, and this will be the ground state. To be totally antisymmetric overall, the state must be symmetric in the spin labels of the electrons, so the spin states will be $|+\rangle|+\rangle|+\rangle$ and the states obtained from this by application of J_-. Thus the total spin will be $s=\frac{3}{2}$.

11.10* *Consider a system made of three spin-half particles with individual spin states $|\pm\rangle$. Write down a linear combination of states such as $|+\rangle|+\rangle|-\rangle$ (with two spins up and one down) that is symmetric under any exchange of spin eigenvalues $\pm$. Write down three other totally symmetric states and say what total spin your states correspond to.*

Show that it is not possible to construct a linear combination of products of $|\pm\rangle$ which is totally antisymmetric.

What consequences do these results have for the structure of atoms such as nitrogen that have three valence electrons?

Soln: There are just three of these product states to consider because there are just three places to put the single minus sign. The sum of these states is obviously totally symmetric:

$$|\psi\rangle = \frac{1}{\sqrt{3}}\big(|+\rangle|+\rangle|-\rangle + |+\rangle|-\rangle|+\rangle + |-\rangle|+\rangle|+\rangle\big)$$

Three other totally symmetric state are clearly $|+\rangle|+\rangle|+\rangle$ and what you get from this ket and the one given by everywhere interchanging + and −. These four kets are the kets $|\frac{3}{2}, m\rangle$.

A totally antisymmetric state would have to be constructed from the same three basis kets used above, so we write it as

$$|\psi'\rangle = a|+\rangle|+\rangle|-\rangle + b|+\rangle|-\rangle|+\rangle + c|-\rangle|+\rangle|+\rangle$$

On swapping the spins of the first and the third particles, the first and third kets would interchange, and this would have to generate a change of sign. So $a = -c$ and $b = 0$. Similarly, by swapping the spins on the first and second particles, we can show that $a = 0$. Hence $|\psi\rangle = 0$, and we have shown that no nonzero ket has the required symmetry.

States that satisfy the exchange principle can be constructed by multiplying a spatial wavefunction that is totally antisymmetric in its arguments by a totally symmetric spin function. Such states have maximum total spin. In contrast to the situation with helium, conforming states cannot be analogously constructed by multiplying a symmetric wavefunction by an antisymmetric spin function.

11.11* *In this problem we use the variational principle to estimate the energies of the singlet and triplet states 1s2s of helium by refining the working of Appendix K.*

The idea is to use as the trial wavefunction symmetrised products of the 1s and 2s hydrogenic wavefunctions (Table 8.1) with the scale length a_Z replaced by a_1 in the 1s wavefunction and by a different length a_2 in the 2s wavefunction. Explain physically why with this choice of wavefunction we expect $\langle H\rangle$ to be minimised with $a_1 \sim 0.5a_0$ but a_2 distinctly larger.

Using the scaling properties of the expectation values of the kinetic-energy and potential-energy operators, show that

$$\langle H\rangle = \left\{\frac{a_0^2}{a_1^2} - \frac{4a_0}{a_1} + \frac{a_0^2}{4a_2^2} - \frac{a_0}{a_2} + 2a_0(D(a_1,a_2) \pm E(a_1,a_2))\right\}\mathcal{R},$$

where D and E are the direct and exchange integrals.

Show that the direct integral can be written

$$D = \frac{2}{a_2}\int_0^\infty \mathrm{d}x\, x^2 \mathrm{e}^{-2x}\frac{1}{4y}\{8 - (8 + 6y + 2y^2 + y^3)\mathrm{e}^{-y}\},$$

where $x \equiv r_1/a_1$ and $y = r_1/a_2$. Hence show that with $\alpha \equiv 1 + 2a_2/a_1$ we have

$$D = \frac{1}{a_1}\left\{1 - \frac{a_2^2}{a_1^2}\left(\frac{4}{\alpha^2} + \frac{6}{\alpha^3} + \frac{6}{\alpha^4} + \frac{12}{\alpha^5}\right)\right\}.$$

Show that with $y = r_1/a_2$ and $\rho = \alpha r_2/2a_2$ the exchange integral is

$$E = \frac{\sqrt{2}}{(a_1a_2)^{3/2}}\int \mathrm{d}^3\mathbf{x}_1\, \Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^{0}(\mathbf{x}_1)$$
$$\times\left\{\frac{1}{r_1}\left(\frac{2a_2}{\alpha}\right)^3\int_0^{\alpha y/2}\mathrm{d}\rho\,(\rho^2 - \rho^3/\alpha)\mathrm{e}^{-\rho} + \left(\frac{2a_2}{\alpha}\right)^2\int_{\alpha y/2}^\infty \mathrm{d}\rho\,(\rho - \rho^2/\alpha)\mathrm{e}^{-\rho}\right\}.$$

Using

$$\int_a^b \mathrm{d}\rho\,(\rho^2 - \rho^3/\alpha)\mathrm{e}^{-\rho} = -[\{(1 - \tfrac{3}{\alpha})(2 + 2\rho + \rho^2) - \tfrac{1}{\alpha}\rho^3\}\mathrm{e}^{-\rho}]_a^b$$

and

$$\int_a^b \mathrm{d}\rho\,(\rho - \rho^2/\alpha)\mathrm{e}^{-\rho} = -[\{(1 - \tfrac{2}{\alpha})(1 + \rho) - \tfrac{1}{\alpha}\rho^2\}\mathrm{e}^{-\rho}]_a^b$$

show that

$$
\begin{aligned}
E = &\frac{2}{(a_1a_2)^3}\int_0^\infty \mathrm{d}r_1\, r_1^2\left(1-\frac{r_1}{2a_2}\right)\mathrm{e}^{-\alpha r_1/2a_2}\\
&\times\left\{\frac{1}{r_1}\left(\frac{2a_2}{\alpha}\right)^3\left[2(1-\tfrac{3}{\alpha})-\{(1-\tfrac{3}{\alpha})(2+\alpha y+\tfrac14\alpha^2y^2)-\tfrac18\alpha^2y^3\}\mathrm{e}^{-\alpha y/2}\right]\right.\\
&\qquad\left.+\left(\frac{2a_2}{\alpha}\right)^2\{(1-\tfrac{2}{\alpha})(1+\tfrac12\alpha y)-\tfrac14\alpha y^2\}\mathrm{e}^{-\alpha y/2}\right\}\\
= &\frac{8a_2^2}{\alpha^5a_1^3}\left(10-\frac{50}{\alpha}+\frac{66}{\alpha^2}\right),
\end{aligned}
$$

Using the above results, show numerically that the minimum of $\langle H\rangle$ *occurs near* $a_1 = 0.5a_0$ *and* $a_2 = 0.8a_0$ *in both the singlet and triplet cases. Show that for the triplet the minimum is* $-60.11\,\mathrm{eV}$ *and for the singlet it is* $-57.0\,\mathrm{eV}$. *Compare these results with the experimental values and the values obtained in Appendix K.*

Soln: We'd expect the 2s electron to see a smaller nuclear charge than the 1s electron and therefore to have a longer scale length since the latter scales inversely with the nuclear charge.

The 1s orbit taken on its own has $K = (a_0/a_1)^2\mathcal{R}$ because the kinetic energy is $\mathcal{R}$ for hydrogen and it is proportional to the inverse square of the wavefunction's scale length. The 1s potential energy is $W = -4(a_0/a_1)\mathcal{R}$ because in hydrogen it is $-2\mathcal{R}$, and it's proportional to the nuclear charge and to the inverse of the wavefunction's scale length. Similarly, the 2s orbit taken on its own has $K = \frac14(a_0/a_2)^2\mathcal{R}$ and $W = -(a_0/a_2)\mathcal{R}$, both just $\frac14$ of the 1s values from the $1/n^2$ in the Rydberg formula. The electron-electron energies are $(D \pm E)2a_0\mathcal{R}$ because $\mathcal{R} = e^2/8\pi\epsilon_0 a_0$. The required expression for $\langle H\rangle$ now follows.

When the scale length a_Z is relabelled a_1 where it relates to the 1s electron and is relabelled a_2 where it relates to the 2s electron, equation (K.2) remains valid with ρ redefined to $\rho \equiv r_2/a_2$ and x replaced by $y \equiv r_1/a_2$. With these definitions the first line of equation (K.2) remains valid and the second line becomes

$$
\begin{aligned}
D &= \frac{2}{a_2}\int_0^\infty \mathrm{d}x\, x^2\mathrm{e}^{-2x}\frac{1}{4y}\{8-(8+6y+2y^2+y^3)\mathrm{e}^{-y}\}\\
&= \frac{1}{2a_2}\left\{8\int_0^\infty \mathrm{d}x\, x\frac{x}{y}\mathrm{e}^{-2x}-\int_0^\infty \mathrm{d}x\,\frac{x^2}{y^2}(8y+6y^2+2y^3+y^4)\mathrm{e}^{-(2x+y)}\right\}
\end{aligned}
\tag{11.5}
$$

Now $x/y = a_2/a_1$ and $\int_0^\infty \mathrm{d}y\, y^n\mathrm{e}^{-\alpha y} = \alpha^{-(n+1)}n!$ so with $\alpha \equiv 1+2a_2/a_1$ we have

$$
\begin{aligned}
D &= \frac{1}{2a_2}\left\{2\frac{a_2}{a_1}-\frac{a_2^3}{a_1^3}\left(\frac{8}{\alpha^2}+\frac{6}{\alpha^3}2!+\frac{2}{\alpha^4}3!+\frac{1}{\alpha^5}4!\right)\right\}\\
&= \frac{1}{a_1}\left\{1-\frac{a_2^2}{a_1^2}\left(\frac{4}{\alpha^2}+\frac{6}{\alpha^3}+\frac{6}{\alpha^4}+\frac{12}{\alpha^5}\right)\right\}
\end{aligned}
\tag{11.6}
$$

which agrees with equation (K.2) when $a_1 = a_2 = a_Z$ as it should.

Equation (K.3) for the exchange integral becomes

$$
\begin{aligned}
E = &\frac{1}{\surd 2(a_1a_2)^{3/2}}\int \mathrm{d}^3\mathbf{x}_1\,\Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^0(\mathbf{x}_1)\\
&\times\int \mathrm{d}r_2\mathrm{d}\theta_2\frac{r_2^2(1-r_2/2a_2)\sin\theta_2\mathrm{e}^{-\alpha r_2/2a_2}}{\sqrt{|r_1^2+r_2^2-2r_1r_2\cos\theta_2|}}.
\end{aligned}
\tag{11.7}
$$

After integrating over θ as in Box 11.1, we have

$$
\begin{aligned}
E = &\frac{\surd 2}{(a_1a_2)^{3/2}}\int \mathrm{d}^3\mathbf{x}_1\,\Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^0(\mathbf{x}_1)\\
&\times\left\{\int_0^{r_1}\mathrm{d}r_2\,\frac{r_2^2}{r_1}\left(1-\frac{r_2}{2a_2}\right)\mathrm{e}^{-\alpha r_2/2a_2}+\int_{r_1}^\infty \mathrm{d}r_2\, r_2\left(1-\frac{r_2}{2a_2}\right)\mathrm{e}^{-\alpha r_2/2a_2}\right\}
\end{aligned}
$$

With $y \equiv r_1/a_2$ and $\rho \equiv \alpha r_2/2a_2$

$$E = \frac{\sqrt{2}}{(a_1 a_2)^{3/2}} \int \mathrm{d}^3\mathbf{x}_1\, \Psi^{0*}_{10}(\mathbf{x}_1)\Psi^0_{20}(\mathbf{x}_1) \times \left\{ \frac{1}{r_1}\left(\frac{2a_2}{\alpha}\right)^3 \int_0^{\alpha y/2} \mathrm{d}\rho\, (\rho^2 - \rho^3/\alpha)\mathrm{e}^{-\rho} + \left(\frac{2a_2}{\alpha}\right)^2 \int_{\alpha y/2}^{\infty} \mathrm{d}\rho\, (\rho - \rho^2/\alpha)\mathrm{e}^{-\rho} \right\}.$$

Now

$$\int_a^b \mathrm{d}\rho\, (\rho^2 - \rho^3/\alpha)\mathrm{e}^{-\rho} = -[\{(1 - \tfrac{3}{\alpha})(2 + 2\rho + \rho^2) - \tfrac{1}{\alpha}\rho^3\}\mathrm{e}^{-\rho}]_a^b$$

and

$$\int_a^b \mathrm{d}\rho\, (\rho - \rho^2/\alpha)\mathrm{e}^{-\rho} = -[\{(1 - \tfrac{2}{\alpha})(1 + \rho) - \tfrac{1}{\alpha}\rho^2\}\mathrm{e}^{-\rho}]_a^b$$

Thus

$$\begin{aligned} E &= \frac{\sqrt{2}}{(a_1 a_2)^{3/2}} \int \mathrm{d}^3\mathbf{x}_1\, \Psi^{0*}_{10}(\mathbf{x}_1)\Psi^0_{20}(\mathbf{x}_1) \\ &\times \left\{ \frac{1}{r_1}\left(\frac{2a_2}{\alpha}\right)^3 \left[2(1-\tfrac{3}{\alpha}) - \{(1-\tfrac{3}{\alpha})(2 + \alpha y + \tfrac{1}{4}\alpha^2 y^2) - \tfrac{1}{8}\alpha^2 y^3\}\mathrm{e}^{-\alpha y/2}\right] \right. \\ &\qquad \left. + \left(\frac{2a_2}{\alpha}\right)^2 \{(1-\tfrac{2}{\alpha})(1+\tfrac{1}{2}\alpha y) - \tfrac{1}{4}\alpha y^2\}\mathrm{e}^{-\alpha y/2} \right\} \\ &= \frac{2}{(a_1 a_2)^3} \int \mathrm{d}r_1\, r_1^2 \left(1 - \frac{r_1}{2a_2}\right) \mathrm{e}^{-\alpha r_1/2a_2} \\ &\times \left\{ \frac{1}{r_1}\left(\frac{2a_2}{\alpha}\right)^3 \left[2(1-\tfrac{3}{\alpha}) - \{(1-\tfrac{3}{\alpha})(2 + \alpha y + \tfrac{1}{4}\alpha^2 y^2) - \tfrac{1}{8}\alpha^2 y^3\}\mathrm{e}^{-\alpha y/2}\right] \right. \\ &\qquad \left. + \left(\frac{2a_2}{\alpha}\right)^2 \{(1-\tfrac{2}{\alpha})(1+\tfrac{1}{2}\alpha y) - \tfrac{1}{4}\alpha y^2\}\mathrm{e}^{-\alpha y/2} \right\} \end{aligned}$$

Simplifying further

$$\begin{aligned} E &= \frac{2}{a_1^3}\left(\frac{2a_2}{\alpha}\right)^2 \frac{8}{\alpha^2 a_2}\frac{a_2^3}{a_1^3} \int_0^{\infty} \mathrm{d}y\, y^2 \left(1 - \tfrac{1}{2}y\right) \\ &\times \left\{ \left(\frac{2}{\alpha y}\right) \left[2(1-\tfrac{3}{\alpha})\mathrm{e}^{-\alpha y/2} - \left\{(1-\tfrac{3}{\alpha})(2 + \alpha y + \tfrac{1}{4}\alpha^2 y^2) - \tfrac{1}{8}\alpha^2 y^3\right\} \mathrm{e}^{-\alpha y}\right] \right. \\ &\qquad \left. + \{(1-\tfrac{2}{\alpha})(1+\tfrac{1}{2}\alpha y) - \tfrac{1}{4}\alpha y^2\}\mathrm{e}^{-\alpha y} \right\} \end{aligned}$$

Now let's collect terms with factors

$$\frac{8a_2^2}{\alpha^2 a_1^3} \int_0^{\infty} \mathrm{d}y\, (1 - \tfrac{1}{2}y) y^n \mathrm{e}^{-\alpha y} = \frac{8a_2^2}{\alpha^2 a_1^3} \frac{n!}{\alpha^{n+1}} \left(1 - \frac{n+1}{2\alpha}\right).$$

The two terms with $n = 4$ cancel. The coefficient of the remaining terms are

$$\begin{aligned} n = 3 &\quad : \quad (1 - \tfrac{2}{\alpha})\tfrac{1}{2}\alpha - (1 - \tfrac{3}{\alpha})\tfrac{1}{2}\alpha = \tfrac{1}{2} \\ n = 2 &\quad : \quad (1 - \tfrac{2}{\alpha}) - (1 - \tfrac{3}{\alpha})2 = \tfrac{4}{\alpha} - 1 \\ n = 1 &\quad : \quad -(1 - \tfrac{3}{\alpha})\tfrac{4}{\alpha} \end{aligned}$$

The final contribution to E is

$$\begin{aligned} \frac{8a_2^2}{\alpha^2 a_1^3}\frac{4}{\alpha}(1 - \tfrac{3}{\alpha}) \int \mathrm{d}y\, y(1 - \tfrac{1}{2}y)\mathrm{e}^{-\alpha y/2} &= \frac{8a_2^2}{\alpha^2 a_1^3}\frac{4}{\alpha}\left(1 - \tfrac{3}{\alpha}\right)\left(\frac{2}{\alpha}\right)^2 \left(1 - \tfrac{2}{\alpha}\right) \\ &= \frac{8a_2^2}{\alpha^2 a_1^3}\frac{16}{\alpha^3}\left(1 - \tfrac{3}{\alpha}\right)\left(1 - \tfrac{2}{\alpha}\right) \end{aligned}$$

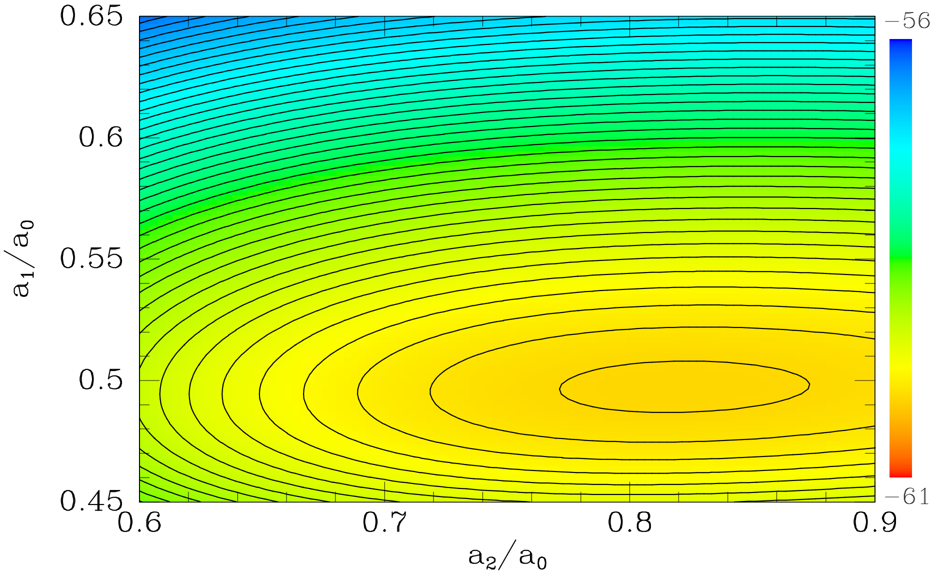

Figure 11.4 Estimates of the energy in electron volts of the 1s2s triplet excited state of helium. The estimates are obtained by taking the expectation of the Hamiltonian using anti-symmetrised products of 1s and 2s hydrogenic wavefunctions that have scale lengths a_1 and a_2, respectively.

our final result is

$$\begin{aligned}E &= \frac{8a_2^2}{\alpha^2 a_1^3}\left[\frac{16}{\alpha^3}\left(1-\tfrac{3}{\alpha}\right)\left(1-\tfrac{2}{\alpha}\right)-(1-\tfrac{3}{\alpha})\tfrac{4}{\alpha}\tfrac{1}{\alpha^2}(1-\tfrac{2}{2\alpha})+(\tfrac{4}{\alpha}-1)\frac{2}{\alpha^3}(1-\tfrac{3}{2\alpha})+\tfrac{1}{2}\frac{6}{\alpha^4}(1-\tfrac{4}{2\alpha})\right]\\ &= \frac{8a_2^2}{\alpha^5 a_1^3}\left[16\left(1-\tfrac{3}{\alpha}\right)\left(1-\tfrac{2}{\alpha}\right)-4(1-\tfrac{3}{\alpha})(1-\tfrac{1}{\alpha})+(\tfrac{4}{\alpha}-1)(2-\tfrac{3}{\alpha})+\tfrac{3}{\alpha}(1-\tfrac{2}{\alpha})\right]\\ &= \frac{8a_2^2}{\alpha^5 a_1^3}\left(10-\frac{50}{\alpha}+\frac{66}{\alpha^2}\right),\end{aligned}$$

which when $a_1 = a_2 = a_Z$ agrees with equation (K.4) as it should.

Figure 11.4 shows $\langle H\rangle$ for the triplet state as a function of a_1 and a_2. The surface has its minimum $-60.11\,\mathrm{eV}$ at $a_1 = 0.50a_0$, $a_2 = 0.82a_0$. As expected, this minimum is deeper than our estimate $-57.8\,\mathrm{eV}$ from perturbation theory, and it occurs when a_2 is significantly greater than $0.5a_0$. It is closer to the experimental value, $-59.2\,\mathrm{eV}$, than the estimate from perturbation theory. A variational value is guaranteed to be larger than the experimental value only for the ground state, and our variational value for the first excited state lies below rather than above the experimental value. The variational estimate of the singlet 1s2s state's energy is $-57.0\,\mathrm{eV}$, which lies between the values from experiment ($-58.4\,\mathrm{eV}$) and perturbation theory ($-55.4\,\mathrm{eV}$).