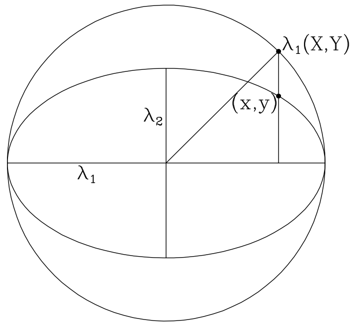

Figure 1.0 The relation of input and output vectors of a 2×2 Hermitian matrix with positive eigenvalues $\lambda_1 > \lambda_2$. An input vector (X, Y) on the unit circle produces the output vector (x, y) that lies on the ellipse that has the eigenvalues as semi-axes.

Further Quantum Mechanics HT 2014
Problems 1 (HT weeks 6 – 8)

Degenerate perturbation theory

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

$$H = \begin{pmatrix} A_1 + B_1\epsilon & B_2\epsilon \\ B_2\epsilon & A_2 \end{pmatrix}, \tag{1.1}$$

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

Variational Principle

1.10* *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

$$\int_0^\infty \mathrm{d}x\,|\psi|^2 = a^{-7}\int_0^{\pi/2}\mathrm{d}\theta\,\cos^6\theta = a^{-7}\int_0^{\pi/2}\mathrm{d}\theta\,\{\tfrac12(1+\cos 2\theta)\}^3$$
$$= \tfrac18 a^{-7}\int_0^{\pi/2}\mathrm{d}\theta\,(1 + 3\cos 2\theta + 3\cos^2 2\theta + \cos^3 2\theta) = \tfrac18 a^{-7}\tfrac12\pi(1+\tfrac32) = \tfrac{5}{32}\pi a^{-7}$$

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 $\frac12$ over this interval.

Similarly

$$\int_0^\infty \mathrm{d}x\,x^2|\psi|^2 = a^{-5}\int_0^{\pi/2}\mathrm{d}\theta\,\cos^4\theta\sin^2\theta = a^{-5}\int_0^{\pi/2}\mathrm{d}\theta\,\tfrac12(1+\cos 2\theta)\tfrac14\sin^2 2\theta$$
$$= \tfrac18 a^{-5}\int_0^{\pi/2}\mathrm{d}\theta\,(\sin^2 2\theta + \cos 2\theta\sin^2 2\theta) = \tfrac18 a^{-5}(\tfrac14\pi + \tfrac16[\sin^3 2\theta]) = \tfrac{1}{32}\pi a^{-5}$$

and

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

so

$$\int_0^\infty \mathrm{d}x\,|p\psi|^2 = 16\hbar^2 a^{-9}\int_0^{\pi/2}\mathrm{d}\theta\,\cos^8\theta\sin^2\theta = 16\hbar^2 a^{-9}\int_0^{\pi/2}\mathrm{d}\theta\,\tfrac18(1+\cos 2\theta)^3\tfrac14\sin^2 2\theta$$
$$= \tfrac12\hbar^2 a^{-9}\left(\int_0^{\pi/2}\mathrm{d}\theta\,(\sin^2 2\theta + 3\cos^2 2\theta\sin^2 2\theta) + \int_0^{\pi/2}\mathrm{d}\theta\,\cos 2\theta(3 + 1 - \sin^2 2\theta)\right)$$
$$= \tfrac12\hbar^2 a^{-9}\left(\tfrac14\pi(1+\tfrac34) + \left[\tfrac23\sin^3 2\theta - \tfrac{1}{10}\sin^5 2\theta\right]\right) = \tfrac{7}{32}\hbar^2\pi a^{-9}$$

Hence

$$\langle H\rangle = \frac{\frac{7}{32}\hbar^2 a^{-9}\pi/2m + \frac12 m\omega^2\frac{1}{32}a^{-5}\pi}{\frac{5}{32}a^{-7}\pi} = \frac{\hbar^2}{2m}\tfrac75 a^{-2} + \tfrac{1}{10}m\omega^2 a^2$$
$$0 = \frac{\partial\langle H\rangle}{\partial a} = -\frac{\hbar^2}{m}\tfrac75 a^{-3} + \tfrac15 m\omega^2 a$$
$$a^4 = 7\left(\frac{\hbar}{m\omega}\right)^2 \quad\Rightarrow\quad a = 7^{1/4}\sqrt{2}\,\ell \quad \langle H\rangle = \frac{\sqrt7}{5}\hbar\omega$$

1.12* *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 $\psi = \mathrm{e}^{-b^2r^2/2}$, $\mathrm{d}\psi/\mathrm{d}r = -b^2r\mathrm{e}^{-b^2r^2/2}$, so

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

Now

$$\int\mathrm{d}x\,x\mathrm{e}^{-x^2} = \left[\frac{\mathrm{e}^{-x^2}}{-2}\right]_0^\infty = \tfrac12$$
$$\int\mathrm{d}x\,x^2\mathrm{e}^{-x^2} = \left[\frac{x\mathrm{e}^{-x^2}}{-2}\right]_0^\infty + \tfrac12\int\mathrm{d}x\,\mathrm{e}^{-x^2} = \frac{\sqrt\pi}{4}$$
$$\int\mathrm{d}x\,x^4\mathrm{e}^{-x^2} = \left[\frac{x^3\mathrm{e}^{-x^2}}{-2}\right]_0^\infty + \tfrac32\int\mathrm{d}x\,x^2\mathrm{e}^{-x^2} = \frac{3\sqrt\pi}{8}$$

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

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

Time-dependent perturbation theory

1.16* *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*

$$|\psi\rangle = a(t)\mathrm{e}^{-\mathrm{i}E_0t/\hbar}|0\rangle + \int \mathrm{d}k\ \{b_k(t)|k,\mathrm{e}\rangle + c_k(t)|k,\mathrm{o}\rangle\}\,\mathrm{e}^{-\mathrm{i}E_kt/\hbar}, \tag{1.2}$$

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

$$\begin{aligned}\mathrm{i}\hbar\left\{\dot a|0\rangle\mathrm{e}^{-\mathrm{i}E_0t/\hbar} + \int \mathrm{d}k\ \left(\dot b_k|k,\mathrm{e}\rangle + \dot c_k|k,\mathrm{o}\rangle\right)\mathrm{e}^{-\mathrm{i}E_kt/\hbar}\right\}\\ = v\left\{a|0\rangle\mathrm{e}^{-\mathrm{i}E_0t/\hbar} + \int \mathrm{d}k\ (b_k|k,\mathrm{e}\rangle + c_k|k,\mathrm{o}\rangle)\,\mathrm{e}^{-\mathrm{i}E_kt/\hbar}\right\}.\end{aligned} \tag{1.3}$$

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

$$c_k(t) = \frac{\mathrm{i}F}{\hbar}\langle k,\mathrm{o}|x|0\rangle\,\mathrm{e}^{\mathrm{i}\Omega_kt/2}\,\frac{\sin(\Omega_kt/2)}{\Omega_k/2}, \quad \text{where} \quad \Omega_k \equiv \frac{E_k - E_0}{\hbar} - \omega. \tag{1.4}$$

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

$$P_{\mathrm{fr}}(t) = \frac{2\pi mF^2t}{\hbar^3}\left.\frac{|\langle k,\mathrm{o}|x|0\rangle|^2}{k}\right|_{\Omega_k=0}. \tag{1.5}$$

Given that from Problem 5.17 we have

$$\langle x|0\rangle = \sqrt{K}\mathrm{e}^{-K|x|} \quad \text{where} \quad K = \frac{mV_\delta}{\hbar^2} \quad \text{and} \quad \langle x|k,\mathrm{o}\rangle = \frac{1}{\sqrt{\pi}}\sin(kx), \tag{1.6}$$

show that

$$\langle k,\mathrm{o}|x|0\rangle = \sqrt{\frac{K}{\pi}}\frac{4kK}{(k^2+K^2)^2}. \tag{1.7}$$

Hence show that the probability of becoming free is

$$P_{\mathrm{fr}}(t) = \frac{8\hbar F^2t}{mE_0^2}\frac{\sqrt{E_\mathrm{f}/|E_0|}}{(1+E_\mathrm{f}/|E_0|)^4}, \tag{1.8}$$

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

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

The probability that the particle is free is

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

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

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

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

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

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

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

The probability of becoming free is therefore

$$P_{\rm fr}(t)=\frac{2\pi mF^2t}{\hbar^3}\frac{K}{\pi}\frac{16kK^2}{(k^2+K^2)^4}=\frac{32mF^2t}{\hbar^3K^4}\frac{k/K}{(k^2/K^2+1)^4}\qquad(1.9)$$

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

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

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

$P_{\rm fr}(t)$ 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.

1.17* *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

$$\langle x|\mathrm{in}\rangle = \frac{1}{\sqrt{L}}\mathrm{e}^{\mathrm{i}kx} \quad ; \quad \langle x|\mathrm{out}\rangle = \frac{1}{\sqrt{L}}\mathrm{e}^{-\mathrm{i}kx}$$

The required matrix element is

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

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

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

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

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

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

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

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

1.18* *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*

$$g(E)\,\mathrm{d}E\,\mathrm{d}^2\Omega = \left(\frac{L}{2\pi}\right)^3\frac{m^{3/2}}{\hbar^3}\sqrt{2E}\,\mathrm{d}E\,\mathrm{d}\Omega^2. \tag{1.10}$$

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

$$\mathrm{d}\sigma = \frac{m^2}{(2\pi)^2\hbar^4}\,\mathrm{d}^2\Omega\left|\int\mathrm{d}^3\mathbf{x}\,\mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}}V(\mathbf{x})\right|^2. \tag{1.11}$$

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.

Further Quantum Mechanics HT 2014

Problems 2 (Easter Vacation)

Radiative transitions

2.1* *Let $|E,l,m\rangle$ denote a stationary state of an atom with orbital angular-momentum quantum numbers l,m, and let $x_\pm = x \pm \mathrm{i}y$ be complex position operators while $L_\pm = L_x \pm \mathrm{i}L_y$ are the usual orbital angular-momentum ladder operators. Show that $x_\pm|E,l,m\rangle$ is an eigenket of L_z with eigenvalue $m\pm 1$. Show also that*

$$[L_+, x_+] = [L_-, x_-] = 0 \quad \text{and} \quad [L_+, x_-] = -[L_-, x_+] = 2z.$$

Hence show that

$$\langle E', l', m|z|E, l, m\rangle = \alpha_+(l, m)\langle E', l', m|x|E, l, m+1\rangle - \alpha_-(l', m)\langle E', l', m-1|x|E, l, m\rangle.$$

where $\alpha_\pm(l,m) \equiv \sqrt{l(l+1) - m(m\pm 1)}$. [Hint: compute $\langle E', l', m|x|E, l, m+1\rangle$]

Soln:

$$[L_z, x_\pm] = [L_z, x] \pm \mathrm{i}[L_z, y] = \mathrm{i}y \pm \mathrm{i}(-\mathrm{i}x) = \pm x_\pm.$$

So

$$L_z x_\pm|E, l, m\rangle = (x_\pm L_z + [L_z, x_\pm])|E, l, m\rangle = (m\pm 1)x_\pm|E, l, m\rangle$$

as required.

$$[L_+, x_\pm] = [L_x + \mathrm{i}L_y, x \pm \mathrm{i}y] = \mathrm{i}([L_y, x] \pm [L_x, y]) = \mathrm{i}(-\mathrm{i}z \pm \mathrm{i}z) = z \mp z$$

as required. The corresponding results for L_- can be obtained by taking the complex conjugate of this equation.

Expressing z as a quarter of the difference of the non-zero commutators, we have

$$\begin{aligned}
\langle E', l', m|x|E, l, m+1\rangle &= \tfrac{1}{2}\langle E', l', m|(x_+ - x_-)|E, l, m+1\rangle \\
&= \frac{1}{2\alpha_+(l,m)}\langle E', l', m|(x_+ - x_-)L_+|E, l, m\rangle \\
&= \frac{1}{2\alpha_+(l,m)}\langle E', l', m|\big\{L_+(x_+ - x_-) + [L_+, x_-]\big\}|E, l, m\rangle \\
&= \frac{\alpha_-(l',m)}{2\alpha_+(l,m)}\langle E', l', m-1|(x_+ - x_-)|E, l, m\rangle + \frac{1}{\alpha_+(l,m)}\langle E', l', m|z|E, l, m\rangle
\end{aligned}$$

Hence

$$\langle E', l', m|z|E, l, m\rangle = \alpha_+(l, m)\langle E', l', m|x|E, l, m+1\rangle - \alpha_-(l', m)\langle E', l', m-1|x|E, l, m\rangle.$$

Oxford Physics Prof J Binney

Further Quantum Mechanics TT 2014
Problems 3 (TT)

Exchange Symmetry

Helium

3.6* *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*

$$\mathbf{X} \equiv \frac{m_\alpha \mathbf{x}_\alpha + m_\mathrm{e}(\mathbf{x}_1 + \mathbf{x}_2)}{m_t}, \quad \mathbf{r}_1 \equiv \mathbf{x}_1 - \mathbf{X}, \quad \mathbf{r}_2 \equiv \mathbf{x}_2 - \mathbf{X}, \tag{3.1}$$

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

$$\begin{gathered}\frac{\partial}{\partial \mathbf{X}} = \frac{\partial}{\partial \mathbf{x}_\alpha} + \frac{\partial}{\partial \mathbf{x}_1} + \frac{\partial}{\partial \mathbf{x}_2} \\ \frac{\partial}{\partial \mathbf{r}_1} = \frac{\partial}{\partial \mathbf{x}_1} - \frac{m_\mathrm{e}}{m_\alpha}\frac{\partial}{\partial \mathbf{x}_\alpha} \qquad \frac{\partial}{\partial \mathbf{r}_2} = \frac{\partial}{\partial \mathbf{x}_2} - \frac{m_\mathrm{e}}{m_\alpha}\frac{\partial}{\partial \mathbf{x}_\alpha}\end{gathered} \tag{3.2}$$

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

$$K = -\frac{\hbar^2}{2m_t}\frac{\partial^2}{\partial \mathbf{X}^2} - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial \mathbf{r}_1^2} + \frac{\partial^2}{\partial \mathbf{r}_2^2}\right) - \frac{\hbar^2}{2m_t}\left(\frac{\partial}{\partial \mathbf{x}_1} - \frac{\partial}{\partial \mathbf{x}_2}\right)^2, \tag{3.3}$$

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 $m_\alpha/m_{\rm e}$ times the sum of the other two, the mixed derivatives in $\mathbf{x}_\alpha$ cancel and we are left with

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

Dividing through by m_t we obtain

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

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 $m_{\rm e}/m_\alpha$. (Classically we'd expect the velocities to be smaller by this factor and therefore the kinetic energies to be in the ratio $m_{\rm e}^2/m_\alpha^2$.)

3.7* *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

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

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

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

Using

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

and

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

show that

$$E = \frac{2}{(a_1a_2)^3}\int_0^\infty \mathrm{d}r_1\, r_1^2\left(1-\frac{r_1}{2a_2}\right)\mathrm{e}^{-\alpha r_1/2a_2}$$

$$\times\left\{\frac{1}{r_1}\left(\frac{2a_2}{\alpha}\right)^3\left[2(1-\tfrac{3}{\alpha}) - \{(1-\tfrac{3}{\alpha})(2+\alpha y+\tfrac14\alpha^2y^2) - \tfrac18\alpha^2y^3\}\mathrm{e}^{-\alpha y/2}\right]\right.$$

$$\left. + \left(\frac{2a_2}{\alpha}\right)^2\{(1-\tfrac{2}{\alpha})(1+\tfrac12\alpha y) - \tfrac14\alpha y^2\}\mathrm{e}^{-\alpha y/2}\right\}$$

$$= \frac{8a_2^2}{\alpha^5 a_1^3}\left(10 - \frac{50}{\alpha} + \frac{66}{\alpha^2}\right),$$

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

$$\begin{aligned} D &= \frac{2}{a_2}\int_0^\infty \mathrm{d}x\, x^2\mathrm{e}^{-2x}\frac{1}{4y}\{8-(8+6y+2y^2+y^3)\mathrm{e}^{-y}\} \\ &= \frac{1}{2a_2}\left\{8\int_0^\infty \mathrm{d}x\, x\frac{x}{y}\mathrm{e}^{-2x} - \int_0^\infty \mathrm{d}x\,\frac{x^2}{y^2}(8y+6y^2+2y^3+y^4)\mathrm{e}^{-(2x+y)}\right\}\end{aligned} \tag{3.4}$$

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

$$\begin{aligned} D &= \frac{1}{2a_2}\left\{2\frac{a_2}{a_1} - \frac{a_2^3}{a_1^3}\left(\frac{8}{\alpha^2}+\frac{6}{\alpha^3}2!+\frac{2}{\alpha^4}3!+\frac{1}{\alpha^5}4!\right)\right\} \\ &= \frac{1}{a_1}\left\{1-\frac{a_2^2}{a_1^2}\left(\frac{4}{\alpha^2}+\frac{6}{\alpha^3}+\frac{6}{\alpha^4}+\frac{12}{\alpha^5}\right)\right\}\end{aligned} \tag{3.5}$$

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

Equation (K.3) for the exchange integral becomes

$$\begin{aligned} E &= \frac{1}{\surd 2(a_1a_2)^{3/2}}\int \mathrm{d}^3\mathbf{x}_1\,\Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^0(\mathbf{x}_1) \\ &\quad\times\int \mathrm{d}r_2\mathrm{d}\theta_2\frac{r_2^2(1-r_2/2a_2)\sin\theta_2\mathrm{e}^{-\alpha r_2/2a_2}}{\sqrt{|r_1^2+r_2^2-2r_1r_2\cos\theta_2|}}.\end{aligned} \tag{3.6}$$

After integrating over θ as in Box 11.1, we have

$$E = \frac{\surd 2}{(a_1a_2)^{3/2}}\int \mathrm{d}^3\mathbf{x}_1\,\Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^0(\mathbf{x}_1)$$

$$\times\left\{\int_0^{r_1}\mathrm{d}r_2\,\frac{r_2^2}{r_1}\left(1-\frac{r_2}{2a_2}\right)\mathrm{e}^{-\alpha r_2/2a_2} + \int_{r_1}^\infty \mathrm{d}r_2\, r_2\left(1-\frac{r_2}{2a_2}\right)\mathrm{e}^{-\alpha r_2/2a_2}\right\}$$

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

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

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

$$\begin{aligned} E &= \frac{\surd 2}{(a_1 a_2)^{3/2}} \int \mathrm{d}^3\mathbf{x}_1\, \Psi^{0*}_{10}(\mathbf{x}_1)\Psi^0_{20}(\mathbf{x}_1) \\ &\times \left\{ \frac{1}{r_1}\left(\frac{2a_2}{\alpha}\right)^3 \Big[2(1-\tfrac{3}{\alpha}) - \{(1-\tfrac{3}{\alpha})(2+\alpha y+\tfrac14\alpha^2y^2) - \tfrac18\alpha^2y^3\}\mathrm{e}^{-\alpha y/2}\Big] \right. \\ &\qquad \left. + \left(\frac{2a_2}{\alpha}\right)^2 \{(1-\tfrac{2}{\alpha})(1+\tfrac12\alpha y) - \tfrac14\alpha y^2\}\mathrm{e}^{-\alpha y/2} \right\} \\ &= \frac{2}{(a_1a_2)^3}\int \mathrm{d}r_1\, r_1^2 \left(1 - \frac{r_1}{2a_2}\right)\mathrm{e}^{-\alpha r_1/2a_2} \\ &\times \left\{ \frac{1}{r_1}\left(\frac{2a_2}{\alpha}\right)^3 \Big[2(1-\tfrac{3}{\alpha}) - \{(1-\tfrac{3}{\alpha})(2+\alpha y+\tfrac14\alpha^2y^2) - \tfrac18\alpha^2y^3\}\mathrm{e}^{-\alpha y/2}\Big] \right. \\ &\qquad \left. + \left(\frac{2a_2}{\alpha}\right)^2 \{(1-\tfrac{2}{\alpha})(1+\tfrac12\alpha y) - \tfrac14\alpha y^2\}\mathrm{e}^{-\alpha y/2} \right\} \end{aligned}$$

Simplifying further

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

Now let's collect terms with factors

$$\frac{8a_2^2}{\alpha^2 a_1^3}\int_0^\infty \mathrm{d}y\,(1-\tfrac12 y)y^n\mathrm{e}^{-\alpha y} = \frac{8a_2^2}{\alpha^2a_1^3}\frac{n!}{\alpha^{n+1}}\left(1 - \frac{n+1}{2\alpha}\right).$$

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

$$\begin{aligned} n=3 &\quad : \quad (1-\tfrac{2}{\alpha})\tfrac12\alpha - (1-\tfrac{3}{\alpha})\tfrac12\alpha = \tfrac12 \\ n=2 &\quad : \quad (1-\tfrac{2}{\alpha}) - (1-\tfrac{3}{\alpha})2 = \tfrac{4}{\alpha} - 1 \\ n=1 &\quad : \quad -(1-\tfrac{3}{\alpha})\tfrac{4}{\alpha} \end{aligned}$$

The final contribution to E is

$$\begin{aligned} \frac{8a_2^2}{\alpha^2a_1^3}\frac{4}{\alpha}(1-\tfrac{3}{\alpha})\int \mathrm{d}y\,y(1-\tfrac12 y)\mathrm{e}^{-\alpha y/2} &= \frac{8a_2^2}{\alpha^2a_1^3}\frac{4}{\alpha}\left(1-\tfrac{3}{\alpha}\right)\left(\frac{2}{\alpha}\right)^2\left(1-\tfrac{2}{\alpha}\right) \\ &= \frac{8a_2^2}{\alpha^2a_1^3}\frac{16}{\alpha^3}\left(1-\tfrac{3}{\alpha}\right)\left(1-\tfrac{2}{\alpha}\right) \end{aligned}$$

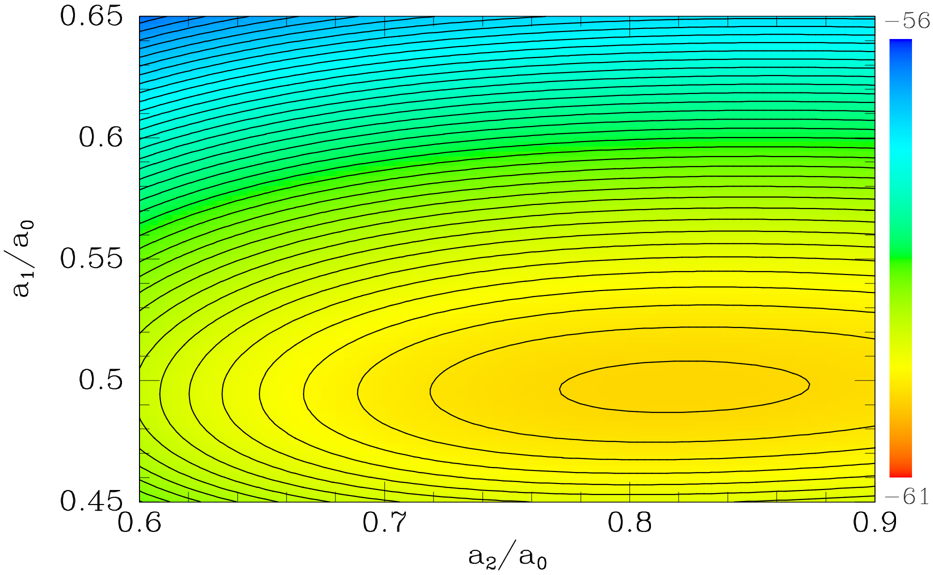

Figure 3.1 Estimates of the energy in electron volts of the 1s2s triplet excited state of helium. The estimates are obtained by taking the expectation of the Hamiltonian using anti-symmetrised products of 1s and 2s hydrogenic wavefunctions that have scale lengths a_1 and a_2, respectively.

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 3.1 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 ($-55.4\,\mathrm{eV}$).

Adiabatic Principle