Second Year Quantum Mechanics

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Hilary Term Problems

As with the MT problem set some of the problems given below have a double dagger †† to indicate that they are a bit more challenging. If you can do them you're really on top of the subject. Some of the problems have a single dagger †. They are straightforward extensions and applications of material in the lectures; first time round they will take you some time and may raise difficulties that you'll need to discuss with your tutor but in a couple of years time they'll seem really easy. Finally there are problems with no daggers; these are either really easy or pretty much the same as problems we've done in the lectures.

Your tutor may well tell you to do just a subset of these problems to start with, but you will find it very helpful to have attempted them all before TT exams.

1 Angular Momentum

1. **The Central Potential**
   The 3-D time-independent Schrödinger equation for a particle of mass m in a spherically symmetric potential (i.e. one that only depends on r, not on θ and ϕ) is

$$\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(r)\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}).$$

   (a) By writing $\boldsymbol{\nabla}^2$ in terms of r, θ, ϕ show that this can be written as

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial\psi}{\partial r} + \frac{\boldsymbol{L}^2}{2mr^2}\psi + V\psi = E\psi \qquad (1)$$

   where

$$\boldsymbol{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \qquad (2)$$

   (b) Writing $\psi(\boldsymbol{r}) = R(r)Y(\theta,\phi)$ show that Y must satisfy $\boldsymbol{L}^2 Y = cY$ where c is a constant, and where

$$-\frac{\hbar^2}{2mr^2}\frac{d}{dr}r^2\frac{dR}{dr} + \left(V + \frac{c}{2mr^2}\right)R = ER.$$

   (c) Writing $R = f(r)/r$, show that $f(r)$ satisfies the equation

$$-\frac{\hbar^2}{2m}\frac{d^2 f}{dr^2} + \left(V + \frac{c}{2mr^2}\right)f = Ef.$$

   (d) †This is of exactly the same form as a 1-D time independent Schrödinger equation, with V replaced by $V + c/2mr^2$. So, can we conclude that the spectrum in the original 3-D problem is the same as for this 1-D problem?

2. **The angular momentum operators** L_x, L_y and L_z are defined by $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ where $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$; for example,

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

   (a) Write down the corresponding expressions for L_x and L_y. Check that cyclic interchange of x, y, z also cyclicly interchanges L_x, L_y and L_z

   (b) Show that, for any differentiable function $f(x, y, z)$,

$$(L_x L_y - L_y L_x) f(x, y, z) = i\hbar L_z f(x, y, z).$$

   Since the above relation is true for any f, it is usually written as an operator equation

$$[L_x, L_y] = L_x L_y - L_y L_x = i\hbar L_z.$$

   Use cyclic interchange to infer that also

$$[L_y, L_z] = i\hbar L_x \quad \text{and} \quad [L_z, L_x] = i\hbar L_y.$$

   (c) Changing to spherical polar coordinates show that

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

   [Hint: it is easier to show that the RHS expression is equal to the LHS one, rather than the other way round; use the chain rule

$$\frac{\partial f}{\partial\phi} = \frac{\partial x}{\partial\phi}\frac{\partial f}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial f}{\partial y} + \frac{\partial z}{\partial\phi}\frac{\partial f}{\partial z}$$

   for any f.] Expressions for L_x and L_y can also be worked out but are less pretty.

   (d) Would it make any difference if we defined $\boldsymbol{L} = -\boldsymbol{p} \times \boldsymbol{r}$?

3. **Simple Eigenfunctions of Angular Momentum**
   Consider the three functions $\cos\theta$, $\sin\theta\, e^{i\phi}$ and $\sin\theta\, e^{-i\phi}$.

   (a) Verify by brute force that each of them are eigenfunctions of $\boldsymbol{L}^2$ and of L_z and find the corresponding eigenvalues.

   (b) Find normalisation constants N such that

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} N^2|\psi(\theta,\phi)|^2 \sin\theta\, d\theta\, d\phi = 1$$

   for each of them. (This means that they are normalised over the full 4π solid angle subtended at the centre of the unit sphere). Show also that they are orthogonal to each other.

(c) The normalised eigenfunctions of $\boldsymbol{L}^2$ and L_z with eigenvalues $\ell(\ell+1)\hbar^2$ and $m\hbar$ respectively are called $Y_{\ell m}(\theta,\phi)$. So

$$Y_{10}(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta,\quad Y_{11}(\theta,\phi)=\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi},\quad Y_{1-1}(\theta,\phi)=\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi}.$$

Using $x=r\sin\theta\cos\phi$, $y=r\sin\theta\sin\phi$, $z=r\cos\theta$, show that these functions can also be written as

$$Y_{10}=\sqrt{\frac{3}{4\pi}}\frac{z}{r},\quad Y_{11}=\sqrt{\frac{3}{8\pi}}\frac{(x+iy)}{r},\quad Y_{1-1}=\sqrt{\frac{3}{8\pi}}\frac{(x-iy)}{r}. \tag{3}$$

(d) Sketch $|Y_{10}|^2, |Y_{11}|^2$ and $|Y_{1-1}|^2$ (a cross section in the $x-z$ plane will do - why?)

N.B. It pays to memorize these three functions, which all have $\ell=1$, and $m=0$, $m=1$, $m=-1$ respectively.

4. †**Measuring Angular Momentum**
A particle is in the state with wavefunction

$$\psi=\frac{1}{\sqrt{2}}(Y_{11}(\theta,\phi)+Y_{1-1}(\theta,\phi))$$

(a) What value is obtained if $\boldsymbol{L}^2$ is measured?

(b) Does the particle have a definite value of L_z?

(c) What are the probabilities of getting results $\hbar, -\hbar$ and 0 for L_z? Are any other L_z results possible?

(d) Calculate

$$\langle\psi\mid L_z\mid\psi\rangle=\iint_{\text{unit sphere}}\psi^*(\theta,\phi)L_z\psi(\theta,\phi)\sin\theta\,d\theta\,d\phi \tag{4}$$

and explain the answer.

(e) Suppose that when L_z is measured the result $\hbar$ is obtained. What is the wavefunction afterwards?

5. †**Total Angular Momentum Operator**
The square of the total angular momentum is defined as

$$\boldsymbol{L}^2=L_x^2+L_y^2+L_z^2. \tag{5}$$

(a) Using the result

$$[A,BC]=B[A,C]+[A,B]C, \tag{6}$$

and the commutation rules for the angular momentum operators show that

$$[L_x,\boldsymbol{L}^2]=[L_y,\boldsymbol{L}^2]=[L_z,\boldsymbol{L}^2]=0.$$

(b) Explain why it is *not* possible, in general, to have states for which more than one component of $\boldsymbol{L}$ has a definite value. Also, explain why it *is* possible to have states with simultaneously definite values of $\boldsymbol{L}^2$ and of one component of $\boldsymbol{L}$. (Often the component chosen by convention is L_z.)

(c) Discuss the special case $\psi(x, y, z) = \psi(r)$. What are the values of L_x, L_y and L_z?

6. **††How do we know $\boldsymbol{L}^2$ in (2) is $\boldsymbol{L}^2$ in (5)?**

(a) Let's start with an exercise in classical mechanics. Use the vector product identities you learnt last year to show that

$$\boldsymbol{L}^2 = r^2\boldsymbol{p}^2 - (\boldsymbol{r}.\boldsymbol{p})^2 \tag{7}$$

and hence that

$$\boldsymbol{p}^2 = \frac{(\boldsymbol{r}.\boldsymbol{p})^2}{r^2} + \frac{\boldsymbol{L}^2}{r^2}. \tag{8}$$

The two terms on the RHS are the KE associated with radial motion and with angular motion respectively. This looks rather like what we have in Question 1.1 but actually if we now replaced $\boldsymbol{p}$ on the RHS by $-i\hbar\boldsymbol{\nabla}$ we would get the wrong answer. Why?

(b) Let's repeat the exercise but being quantum mechanical all the way along. So we have

$$\boldsymbol{L}^2 = -\hbar^2(\boldsymbol{r} \times \boldsymbol{\nabla}).(\boldsymbol{r} \times \boldsymbol{\nabla}) \tag{9}$$

Use the vector *operator* identities to show that

$$\boldsymbol{L}^2\Phi = -\hbar^2\left(r^2\boldsymbol{\nabla}^2 - \boldsymbol{r}.\boldsymbol{\nabla} - (\boldsymbol{r}.\boldsymbol{\nabla})^2\right)\Phi. \tag{10}$$

(c) Now using the same method as you did in Question 1.2 show that

$$r\frac{\partial}{\partial r} = x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z} \tag{11}$$

which is of course nothing other than $\boldsymbol{r}.\boldsymbol{\nabla}$. Use this together with (10) and (1) to deduce that the operator $\boldsymbol{L}^2$ is indeed given by (2).

7. **††Particle in a magnetic field**
The Hamiltonian for a particle of charge q, mass m_0, in a constant magnetic field $\boldsymbol{B} = (0, 0, B)$ is (approximately)

$$H = -\frac{\hbar^2\boldsymbol{\nabla}^2}{2m_0} - \frac{qB}{2m_0}L_z.$$

(a) The eigenvalues of which of the following are good quantum numbers: $\boldsymbol{L}^2$, L_x, L_y, L_z?

(b) Show (using the Ehrenfest Theorem result from MT) that the expectation values of L_x, L_y and L_z in a general state $|\psi\rangle$ satisfy the equations

$$\begin{aligned} \frac{d}{dt}\langle\psi|L_x|\psi\rangle &= \frac{qB}{2m_0}\langle\psi|L_y|\psi\rangle \\ \frac{d}{dt}\langle\psi|L_y|\psi\rangle &= -\frac{qB}{2m_0}\langle\psi|L_x|\psi\rangle \\ \frac{d}{dt}\langle\psi|L_z|\psi\rangle &= 0. \end{aligned} \qquad (12)$$

Check that these are the same as the three components of the vector equation

$$\frac{d}{dt}\langle\psi|\boldsymbol{L}|\psi\rangle = \frac{q}{2m_0}\langle\psi|\boldsymbol{L}|\psi\rangle \times \boldsymbol{B}. \qquad (13)$$

(c) The magnetic moment operator $\boldsymbol{\mu}$ is defined by $\boldsymbol{\mu} = \frac{q}{2m_0}\boldsymbol{L}$. Deduce that

$$\frac{d}{dt}\langle\psi|\boldsymbol{\mu}|\psi\rangle = \frac{q}{2m_0}\langle\psi|\boldsymbol{\mu}|\psi\rangle \times \boldsymbol{B}. \qquad (14)$$

(d) You've seen the equation of motion (14) before in the Prelims vector work. Show that (i) the length of the vector $\langle\psi|\boldsymbol{\mu}|\psi\rangle$ is constant in time, and (ii) $\langle\psi|\boldsymbol{\mu}|\psi\rangle.\boldsymbol{B}$ is constant in time. Hence show that $\langle\psi|\boldsymbol{\mu}|\psi\rangle$ precesses around the direction of $\boldsymbol{B}$ with angular frequency $\omega = \frac{qB}{2m_0}$. Calculate ω for the electron in a field of 1 tesla.

8. ††**Another Hamiltonian**
A one particle system has the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r} - e\mathcal{E}x.$$

(a) What is the physical origin of the last term in H ?

(b) Calculate the commutators $[L_x, x]$, $[L_y, x]$, $[L_z, x]$.

(c) Which of the observables represented by the operators $\boldsymbol{L}^2$, L_x, L_y, L_z are constants of the motion assuming (i) $\mathcal{E} = 0$ (ii) $\mathcal{E} \neq 0$?

2 Radial Schrödinger equation

1. **Spherical Box**
The free particle stationary state Schrödinger equation in 3-D, separated in polar coordinates $\psi(r,\theta,\phi) = R_\ell(r)Y_{\ell m}(\theta,\phi)$, leads to the radial equation

$$-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{dR_\ell}{dr}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}R_\ell = ER_\ell$$

(a) Verify that

$$R_0(r) = A_0 \frac{\sin kr}{r} \tag{15}$$

$$R_1(r) = \frac{A_1}{r}\left(\frac{\sin kr}{kr} - \cos kr\right) \tag{16}$$

where A_0 and A_1 are constants, are solutions of the R_ℓ equation for $\ell = 0$ and $\ell = 1$ respectively. [It's easiest to do this by exploiting the result of Question 1.1c.]

(b) The spherical box potential is defined by $V(r) = 0$ for $r \leq a$, $V(r) = \infty$ for $r > a$. This will force the boundary condition $R_\ell(r = a) = 0$. Give approximate numerical values, in units of $\frac{\hbar^2}{2ma^2}$, for the lowest *two* energy eigenvalues in each of the cases (a) $\ell = 0$ (b) $\ell = 1$. [$\ell = 0$ is easy; for $\ell = 1$ you need to solve the equation $\tan x = x$.]

(c) ††What is wrong with the solution $R_0(r) = B_0 \frac{\cos kr}{r}$ in the $l = 0$ case? N.B. This has nothing to do with normalization of the wavefunction. This function is normalizable in three dimensions.

2. †**Finite depth spherical well** potential is given by

$$\begin{aligned} V(r) &= -V_0, \quad r \leq a \\ V(r) &= 0, \qquad r > a. \end{aligned} \tag{17}$$

(a) Satisfy yourself that the wavefunction $\phi(r)$ for a particle of mass m bound in a state with $\ell = 0$ in this well satisfies

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d\phi}{dr} - V_0\phi = -E\phi \text{ for } r \leq a$$

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d\phi}{dr} = -E\phi \text{ for } r > a$$

where E is the binding energy (> 0).

(b) Check that the solution has the form $\phi = \frac{A}{r}\sin kr$ for $r \leq a$, $\phi = \frac{B}{r}e^{-Kr}$ for $r > a$, where $\frac{\hbar^2 k^2}{2m} = (V_0 - E)$ and $\frac{\hbar^2 K^2}{2m} = E$, and where A and B are constants.

(c) Deduce from the boundary conditions at $r = a$ that energy eigenvalues are obtained from the equation $k \cot ka = -K$. Show that there is no allowed E value if $V_0 < \hbar^2\pi^2/8ma^2$. Evaluate this critical value of V_0 (needed to bind a particle) in MeV, for $m = \frac{1}{2}$ mass of proton, and $a = 2 \times 10^{-15}$m (these are roughly the parameters for the deuteron, the neutron-proton bound state which forms the nucleus of deuterium). Why is $\frac{1}{2}$ the proton mass taken? (If in doubt, see Question 4.2 below.)

3. **Coulomb potential**

(a) What quantum numbers are needed to describe the state of an electron (neglecting spin) in hydrogen? Why is it possible to obtain states with simultaneously well defined eigenvalues of H, $\boldsymbol{L}^2$ and of L_z? Draw a diagram of the spectrum up to and including second excited states and label it carefully with all the quantum numbers of the states.

(b) The ground state wavefunction in hydrogen is proportional to $e^{-r/a}$, where $a = 4\pi\epsilon_0\hbar^2/me^2$. Check that this satisfies the time independent Schrödinger equation and normalise it (N.B. get the volume element right!).

(c) $|\psi(x,y,z)|^2 dxdydz$ is the probability for finding a particle between (x,y,z) and $(x+dx, y+dy, z+dz)$. In r,θ,ϕ this becomes $|\psi(r,\theta,\phi)|^2 r^2 \sin\theta \, d\theta \, d\phi dr$. So the probability of finding the particle between r and $r+dr$, without caring about its angular position, is

$$P(r)\,dr = \left[\int_0^\pi d\theta \int_0^{2\pi} d\phi \, |\psi(r,\theta,\phi)|^2 \sin\theta\right] r^2 \, dr. \tag{18}$$

Writing $\psi = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$ show that

$$P(r)\,dr = r^2 |R_{n\ell}(r)|^2 \, dr. \tag{19}$$

(d) Sketch $P(r)$ for the ground state wavefunction. Find the value of r for which it is a maximum and calculate the average value of r in this state.

4. A particle moves in 3-D subject to the potential $V = \frac{1}{2}m\omega^2(x^2+y^2+z^2)$.

(a) Writing $\psi(x,y,z) = X(x)Y(y)Z(z)$ show that the time-independent Schrödinger equation can be solved in terms of the solutions for the 1-D oscillator.

(b) Assuming the 1-D results, show that the energy eigenvalues are

$$E(n_x,n_y,n_z) = \hbar\omega\left(\frac{3}{2} + n_x + n_y + n_z\right)$$

where the n's are integers ≥ 0. What is the degeneracy of the levels with (i) $E = 3\hbar\omega/2$, (ii) $E = 5\hbar\omega/2$, and (iii) $E = 7\hbar\omega/2$? Compare the energy spectrum and degeneracies for the Coulomb problem and the 3-D oscillator problem.

(c) †To save you looking them up the ground and first excited states for the 1-D oscillator have wavefunctions

$$\begin{aligned} \phi_0(x) &= A_0 e^{-x^2/2a^2} \\ \phi_1(x) &= A_1 x e^{-x^2/2a^2}. \end{aligned}$$

Write down the wavefunctions for the ground and first excited states of the 3-D oscillator.

(d) †Rewrite the potential in polar coordinates. Are the eigenvalues of $\boldsymbol{L}^2$ and L_z good quantum numbers for this Hamiltonian?

(e) †Using (3) rewrite the 3-D oscillator wavefunctions you found in part (b) in terms of the spherical harmonics and functions of r. What are the $\boldsymbol{L}^2$ eigenvalues of your wavefunctions? What are the L_z eigenvalues of your wavefunctions?

(f) ††Repeat (4e) for the second excited states. Look up the necessary functions in a book.

3 Spin-$\frac{1}{2}$

1. **The Pauli sigma matrices** are given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

   (a) Verify that the operators

$$S_x = \frac{\hbar}{2}\sigma_x, \quad S_y = \frac{\hbar}{2}\sigma_y, \quad S_z = \frac{\hbar}{2}\sigma_z$$

   satisfy the commutation rules for angular momentum and that

$$\boldsymbol{S}^2 = S_x^2 + S_y^2 + S_z^2 = \frac{3}{4}\hbar^2 I,$$

   where

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

   (b) Find the eigenvalues (which are real), and corresponding normalised eigenvectors (which may be complex), of S_x, S_y, and S_z.

   If you've done this right you should find that the matrices therefore have all the properties required to represent an angular momentum-like degree of freedom, with total angular momentum quantum number $j = \frac{1}{2}\hbar$. So just explain how it all fits with the answers you've got.

2. †**Measuring spin-$\frac{1}{2}$** Let $|\uparrow z\rangle$ and $|\downarrow z\rangle$ denote the eigenstates of $\boldsymbol{S}^2$ and S_z

$$\begin{aligned} \boldsymbol{S}^2|\uparrow z\rangle &= \tfrac{1}{2}(\tfrac{1}{2}+1)\hbar^2|\uparrow z\rangle, \quad S_z|\uparrow z\rangle = +\tfrac{1}{2}\hbar|\uparrow z\rangle \\ \boldsymbol{S}^2|\downarrow z\rangle &= \tfrac{1}{2}(\tfrac{1}{2}+1)\hbar^2|\downarrow z\rangle, \quad S_z|\downarrow z\rangle = -\tfrac{1}{2}\hbar|\downarrow z\rangle \end{aligned} \tag{20}$$

   and similarly $|\uparrow x\rangle$ and $|\downarrow x\rangle$ denote the eigenstates of $\boldsymbol{S}^2$ and S_x.

   (a) Using your results from Question 3.1 express $|\uparrow x\rangle$ and $|\downarrow x\rangle$ as linear combinations of $|\uparrow z\rangle$ and $|\downarrow z\rangle$ and vice versa.

   (b) A system is prepared in the state $|\uparrow x\rangle$. Then a measurement of S_z is made. What are the possible outcomes and their probabilities?

   (c) Suppose that the outcome is in fact $\frac{1}{2}\hbar$. What is now the state of the system? If we now measure S_x what do we find?

3. †**Stern-Gerlach experiment** A spin-$\frac{1}{2}$ particle of charge e has an intrinsic magnetic dipole moment $\boldsymbol{\mu} = g_s\frac{e}{2m}\boldsymbol{S}$. The combination $\mu_B = \frac{e\hbar}{2m}$ is called the *Bohr magneton* and has value $9.3 \times 10^{-24}\,\mathrm{JT}^{-1}$. The number g_s is not determined by non-relativistic QM; Dirac's relativistic wave equation tells us that $g_s = 2$. In fact, it is not exactly 2 but the deviation can be calculated in Quantum Electrodynamics which tells us that we expect $g_s/2 = 1.001\,159\,652\,153(28)$. The best experimental measurement is $g_s/2 = 1.001\,159\,652\,188(4)$. See V.W. Hughes and T. Kinoshita, Rev. Mod. Phys. **71** S133 (1999).

(a) What is the net *force* on a magnetic dipole in a uniform $\boldsymbol{B}$ field?

(b) Explain why there *is* a net force in a non-uniform $\boldsymbol{B}$ field. (Because it's more familiar you may find it easier to explain why there is a net force on an electric dipole in a non-uniform $\boldsymbol{E}$ field.)

(c) The only contribution to the magnetic moment of a silver atom comes from the valence electron so its magnetic moment behaves just like the electron's. Silver atoms with a kinetic energy of about 3×10^{-20}J each travel a distance of 0.03 m through a non-uniform magnetic field of gradient 2.3×10^3 Tm^{-1}. Explain why the beam splits into two and calculate the separation of the two beams at a distance of 0.25 m downstream from the magnet.

4 Quantum Mechanics for two particles

1. **Independent motion.** Write down, but do not try to solve, the time-independent Schrödinger equation for the Helium atom (assuming the nucleus is infinitely heavy). Now suppose you neglect the potential which acts between the electrons. Solve the resulting approximate equation by an appropriate "separation of variables" i.e. write $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$ where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons. Identify the separate equations for $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$ as hydrogen - like Schrödinger equations with e^2 replaced by $2e^2$. Hence calculate the energy of the ground state of the He atom in this approximation, relative to the ground state of the He^{++} ion. The real value is -79 eV; the large discrepancy is due to the electrostatic repulsion between the two electrons.

2. **Relative and centre-of-mass separation**. Consider two particles with masses m_1 and m_2, in 1-D, with the potential energy $V(x_1 - x_2)$. The stationary state Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + V(x_1 - x_2)\right]\Psi(x_1, x_2) = E\Psi(x_1, x_2).$$

(a) Why can this equation *not* be separated in the coordinates x_1 and x_2 ?

(b) Define the centre of mass coordinate $X = (m_1 x_1 + m_2 x_2)/M$ where $M = m_1 + m_2$, and the relative coordinate

$$x = x_1 - x_2.$$

By using the chain rule in the form

$$\frac{\partial f}{\partial x_1} = \frac{\partial f}{\partial X}\frac{\partial X}{\partial x_1} + \frac{\partial f}{\partial x}\frac{\partial x}{\partial x_1}$$

(or, better, in the operator form

$$\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x},$$

and similarly for $\frac{\partial}{\partial x_2}$) show that the Schrödinger equation can be re-written as

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x, X) = E\Psi$$

where the *reduced mass* μ is equal to $m_1 m_2/(m_1+m_2)$.

(c) Show that this equation can be separated in the coordinates x and X i.e. solutions can be found of the form

$$\Psi(x, X) = \psi_{rel}(x)\psi_{CM}(X).$$

Obtain the equation satisfied by $\psi_{rel}(x)$.

(d) What is the solution of the equation for $\psi_{CM}(X)$? Explain the answer physically.

3. †**Addition of angular momenta** All pairs of angular momenta, whether integer or half-integer, combine according to exactly the same rules: if we combine states of angular momentum quantum numbers j_1 and j_2 then the possible total angular momentum quantum numbers are $J = j_1 + j_2$ down to $J = |j_1 - j_2|$ in integer steps. The electron and proton both have intrinsic spin-$\frac{1}{2}$.

   (a) The ground state of hydrogen has no orbital angular momentum so its total angular momentum, quantum number I, comes entirely from the electron and proton spins. What are the possible values of I?

   (b) Now consider an $\ell = 1$ state of the hydrogen atom. Work out the possible values of I by first combining the spins and then combining the results with the orbital angular momentum.

   (c) Repeat but this time first combine the electron spin with the orbital angular momentum and thn combine the results with the proton spin. You should find the same list of possible values for I.

4. †**Two spin-$\frac{1}{2}$ particles**, let's call them a and b. Independent of whether they interact or not the combined system has a basis set of spin state functions which are formed as products of the single spin-$\frac{1}{2}$ states. In particular consider the states

$$\begin{aligned} |1\rangle &= |\uparrow\rangle_{\mathsf{a}}|\uparrow\rangle_{\mathsf{b}} \\ |2\rangle &= |\uparrow\rangle_{\mathsf{a}}|\downarrow\rangle_{\mathsf{b}} \\ |3\rangle &= |\downarrow\rangle_{\mathsf{a}}|\uparrow\rangle_{\mathsf{b}} \\ |4\rangle &= |\downarrow\rangle_{\mathsf{a}}|\downarrow\rangle_{\mathsf{b}}, \end{aligned} \tag{21}$$

where, for example, $|1\rangle$ describes the state in which both particles have spin-up along the z-axis. The spin angular momentum operators for the two particles are $\boldsymbol{S}^{\mathsf{a}}$ and $\boldsymbol{S}^{\mathsf{b}}$ respectively and the total angular momentum operator is now

$$\boldsymbol{S} = \boldsymbol{S}^{\mathsf{a}} + \boldsymbol{S}^{\mathsf{b}}. \tag{22}$$

   (a) Show that $S_z|1\rangle = \hbar|1\rangle$ and $S_z|2\rangle = 0$; find the result of acting with S_z on the other two states.

   (b) How many states do we expect to find with total angular momentum quantum number $S = 1$, and how many with $S = 0$?

   (c) Which of the states *must* have total angular momentum quantum number $S = 1$, and which *may* have $S = 0$?

(d) In fact the states with total angular momentum quantum number $S = 1$ are symmetric under exchange of `a` and `b` whereas those with $S = 0$ are anti-symmetric. Write down the corectly identified states.

5. ††**More addition of angular momenta**
Considering a system of two non-interacting particles with orital angular momentum operators $\boldsymbol{L}^{(1)}$ and $\boldsymbol{L}^{(2)}$ respectively; the total angular momentum operator is

$$\boldsymbol{L} = \boldsymbol{L}^{(1)} + \boldsymbol{L}^{(2)}. \tag{23}$$

We denote the eigenvalues of $\boldsymbol{L}^{(1)}.\boldsymbol{L}^{(1)}$ and $L_z^{(1)}$ by $\ell_1(\ell_1+1)\hbar^2$ and $m_1\hbar$ respectively (and similarly for particle 2). We denote the eigenvalues of $\boldsymbol{L}.\boldsymbol{L}$ and L_z by $L(L+1)\hbar^2$ and $M\hbar$ respectively.

(a) Consider the angular momenta of two particles which are each in $\ell = 1$ states. How many states of the form $\phi_{\ell_1=1,m_1}(\boldsymbol{r}_1)\phi_{\ell_2=1,m_2}(\boldsymbol{r}_2)$ have L_z quantum number $M = 2$? Repeat the exercise for $M = 1, 0, -1, -2$ and comment on any symmetry in the results; how many states do you get altogether? According to the triangle rule the total angular momentum quantum number could be $L = 2, 1$, or 0; how many of these states are there altogether? Now make sure you have the same number of states in the (L, M) labelling as in the $(\ell_1, m_1, \ell_2, m_2)$ labelling.

(b) How many states of the form $\phi_{\ell_1,m_1}(\boldsymbol{r}_1)\phi_{\ell_2,m_2}(\boldsymbol{r}_2)$ have L_z quantum number $M = \ell_1 + \ell_2$? How many have L_z quantum number $M = \ell_1 + \ell_2 - 1$? Carry on until you get to "How many have L_z quantum number $M = 0$?" – why is it not necessary to go any further? Now explain how these results are consistent with the possible L values being $\ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots, |\ell_1 - \ell_2|$ which is what the triangle rule of addition tells us. Why can we not have $L > \ell_1 + \ell_2$?