Quantum Mechanics 2

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Chapter 1

Orbital Angular Momentum

1.1 Basics of QM

Let us recall some basic facts of quantum mechanics.

The expectation value of an observable $\mathcal{A}$ with an associated operator $\hat{A}$ is given by,

$$\left\langle \hat{A} \right\rangle = \langle \Psi | \hat{A} | \Psi \rangle = \int \Psi^* \hat{A} \Psi \, d\mathbf{r}. \tag{1.1}$$

The fundamental position, momentum, and angular momentum operators are defined as follows,

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Definition 1: Fundamental Operators

$$\hat{\mathbf{r}} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}} \tag{1.2}$$
$$\hat{p} = -i\hbar \boldsymbol{\nabla} \tag{1.3}$$
$$\hat{L}_i = \varepsilon_{ijk} \hat{r}_j \hat{p}_k \tag{1.4}$$

The Hamiltonian is defined,

Definition 2: Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t). \tag{1.5}$$

We obtain the wavefunction Ψ by solving the TDSE,

Definition 3: Time Dependent Schrodinger Equation

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{H}\Psi(\mathbf{r}, t). \tag{1.6}$$

For the static case, this reduces to the TISE,

$$\hat{H}\Psi = E\Psi. \tag{1.7}$$

If $\Psi(\mathbf{r}, 0)$ is written in the energy eigenbasis, i.e., $\Psi(\mathbf{r}, 0) = \sum_i c_i |E_i\rangle$, then the time-dependent solution is trivial,

$$\Psi(\mathbf{r}, t) = \sum_i c_i |E_i\rangle \exp\left(\frac{-iE_i t}{\hbar}\right). \tag{1.8}$$

1.1.1 The Simple Harmonic Oscillator

The SHO has a Hamiltonian,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \tag{1.9}$$

with energy eigenvalues,

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{1.10}$$

and has normalised Eigenfunctions,

$$\psi_n(x) = \left(\frac{1}{n!2^n a\sqrt{\pi}}\right) H_n\left(\frac{x}{a}\right) \exp\left(-\frac{x^2}{2a^2}\right) \tag{1.11}$$

where $a = \sqrt{\hbar/m\omega}$ and $H_n(x/a)$ is a Hermite polynomial.

1.1.2   Simple Perturbation Theory

In simple perturbation theory, we write the Hamiltonian as,

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{1.12}$$

where the Hamiltonian $\hat{H}_0$ is trivial and for which we already have obtained its eigenfunction ψ and eigenvalues $E_n^{(0)}$. We then use this to find the expectation value of the total Hamiltonian,

$$\left\langle \hat{H} \right\rangle = \langle\psi| \hat{H}_0 + \hat{V} |\psi\rangle = E_n^{(0)} + \Delta E. \tag{1.13}$$

Writing this more explicitly,

Definition 4: First Order Perturbation Theory

$$E_n = E_n^{(0)} + \langle\psi| \hat{V} |\psi\rangle \tag{1.14}$$

1.2   Particle in 2D SHO

The Hamiltonian of the 2D SHO is given by,

$$\hat{H}\psi(x,y) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2}m\omega(x^2 + y^2)\psi(x,y) = E\psi(x,y) \tag{1.15}$$

We can separate this Hamiltonian into its x and y components,

$$\hat{H}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega x^2 \qquad\qquad \hat{H}_y - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + \frac{1}{2}m\omega y^2. \tag{1.16}$$

We know the solution to the 1D SHO, as by eq. (1.10). We can intuit that the total solution of the 2D Hamiltonian will be a product of the two 1D wavefunctions. This comes from the fact that to add probabilities, we multiply the probability densities. So, we write,

$$\begin{aligned}
\hat{H}\psi_{n_x}(x)\psi_{n_y}(y) &= \left(\hat{H}_x + \hat{H}_y\right)\psi_{n_x}(x)\psi_{n_y}(y) \\
&= \left(\hat{H}_x\psi_{n_x}(x)\right)\psi_{n_y}(y) + \psi_{n_x}(x)\left(\hat{H}_y\psi_{n_y}(y)\right) \\
&= \left(n_x + \frac{1}{2}\right)\hbar\omega\psi_{n_y}(y) + \left(n_y + \frac{1}{2}\right)\hbar\omega\psi_{n_x}(x) \\
&= (n_x + n_y + 1)\hbar\omega\psi_{n_x}(x)\psi_{n_y}(y) \\
\implies E_{n_x,n_y} &= (n_x + n_y + 1)\hbar\omega.
\end{aligned} \tag{1.17}$$

1.2.1   Degeneracy

This is when there is more than one state with the same energy. The degeneracy D is the number of energy states that share the same energy. Non-degenerate states are those with $D = 1$.

1.3 3D Orbital Angular Momentum

The angular momentum in given direction in a classical system is given by,

$$L_i = \varepsilon_{ijk} r_j p_k. \tag{1.18}$$

The angular momentum operator in quantum mechanics is thus,

$$\hat{L}_i = \varepsilon_{ijk} \hat{r}_j \hat{p}_k. \tag{1.19}$$

We are particularly interested in the case where $i = z$, in which case the operator becomes,

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right). \tag{1.20}$$

Let us consider this operator in plane polar coordinates, (r, θ). We have,

$$x = r\cos\theta \qquad\qquad y = r\sin\theta \tag{1.21}$$

Let us consider the following,

$$\begin{aligned}
\frac{\partial}{\partial\theta} &= \frac{\partial x}{\partial\theta}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\theta}\frac{\partial}{\partial y} = -r\sin\theta\frac{\partial}{\partial x} + r\cos\theta\frac{\partial}{\partial y} \\
&= -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}.
\end{aligned} \tag{1.22}$$

So, in plane polars,

Definition 5: Angular Momentum Operator in Z

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\theta}. \tag{1.23}$$

1.3.1 Eigenfunctions and Eigenvalues of $\hat{L}_z$

We wish to consider the following,

$$\hat{L}_z \Phi(\phi) = L_z \Phi(\phi). \tag{1.24}$$

So,

$$-i\hbar\frac{\mathrm{d}\Phi}{\mathrm{d}\phi} = L_z \Phi \tag{1.25}$$

which we can solve trivially,

$$\Phi(\phi) = Ae^{\frac{L_z\phi}{\hbar}} \tag{1.26}$$

where $A = \frac{1}{\sqrt{2\pi}}$ is a normalisation constant. We require a cyclic boundary condition, such that $\Phi(\phi) = \Phi(\phi + 2\pi)$. So,

$$\begin{aligned}
Ae^{\frac{iL_z(\phi+2\pi)}{\hbar}} &= Ae^{\frac{iL_z\phi}{\hbar}} \\
e^{\frac{iL_z 2\pi}{\hbar}} &= 1.
\end{aligned} \tag{1.27}$$

Not all values of L_z satisfy the eq. (1.27), so we have to impose the following restriction,

$$L_z = \hbar m, \quad m \in \mathbb{Z} \tag{1.28}$$

and thus, we can write the angular momentum eigenfunction as,

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Definition 6: Angular Momentum Eigenfunction

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \tag{1.29}$$

1.3.2   Angular Momentum of the 2D SHO

We wish to express eigenfunctions of the 2D SHO as eigenfunctions of angular momentum. we will find that we require a combination of all degenerate eigenfunctions for a givevn D in order to represent angular momentum eigenfunction. Observing the ground state,

$$\Psi_{00}(x,y) = e^{-\frac{x^2}{2a^2}} \cdot e^{-\frac{y^2}{2a^2}} = e^{-\frac{r^2}{2a^2}}, \qquad a^2 = \frac{\hbar}{2m}. \tag{1.30}$$

Applying the angular momentum operator we find,

$$\hat{L}_z \Psi_{00} = 0 \cdot \Psi_{00} \tag{1.31}$$

which holds, as 0 is an allowed value of m. The first excited states of $D = 2$ are given by,

$$\Psi_{10} = x e^{-\frac{x^2}{2a^2}} \cdot e^{-\frac{y^2}{2a^2}} \qquad\qquad\qquad \Psi_{01} = e^{-\frac{x^2}{2a^2}} \cdot y e^{-\frac{y^2}{2a^2}} \tag{1.32}$$

which we combine to form,

$$\begin{aligned}
\Psi_\pm &= \Psi_{10} \pm i \Psi_{01} \\
&= \left[r\cos\phi \pm ir\sin\phi \right] e^{-\frac{r^2}{2a^2}} = r e^{\pm i\phi} e^{-\frac{r^2}{2a^2}}.
\end{aligned} \tag{1.33}$$

Applying $\hat{L}_z$ to eq. (1.33),

$$\hat{L}_z \Psi_\pm = \pm\hbar \Psi_\pm \tag{1.34}$$

$\implies \Psi_\pm$ is an eigenfunction of $\hat{L}_z$ with eigenvalues $\pm\hbar$. Furthermore, $\Psi_\pm$ is an eigenfunction of $\hat{H}$, so $\hat{H}$ and $\hat{L}_z$ commute. This allows for the 2D SHO to be described by *good quantum numbers*. These satisfy the following,

1. Can be known simultaneously,

2. Fully and uniquely specify the state of a system.

For the 2D SHO, its good quantum numbers are (n, m), where $n = n_x + n_y$. n specifies the energy of the system (as by $E_n = (n+1)\hbar\omega$), and m specifies the angular momentum of the system (as by $L_z = m\hbar$).

1.3.3   Angular Momentum Operators

> **Definition 7: Angular Momentum Commutation Relation**
>
> $$\left[\hat{L}_i, \hat{L}_j \right] = \epsilon_{ijk} i\hbar \hat{L}_k \tag{1.35}$$
>
> where i, j, k indicate orthogonal directions.

The above definition indicates that components of $\hat{L}_i$ do not commute in different directions, however it can be shown that,

$$\left[\hat{L}^2, \hat{L}_i \right] = 0. \tag{1.36}$$

Proof.

$$\begin{aligned}
\hat{L}^2 &= \sum_j \hat{L}^2 \\
\left[\hat{L}^2, \hat{L}_i \right] &= \sum_j \left[\hat{L}_j^2, \hat{L}_i^2 \right] \\
&= \sum_j \left(\hat{L}_j \left[\hat{L}_j, \hat{L}_i \right] + \left[\hat{L}_j, \hat{L}_i \right] \hat{L}_j \right) \\
&= i\hbar \sum_{j,l} \left(\hat{L}_j \varepsilon_{ijk} \hat{L}_k + \underbrace{\hat{L}_k \varepsilon_{ijk} \hat{L}_j}_{-\varepsilon_{ijk} \hat{L}_j \hat{L}_k} \right) \\
&= \sum_{j,l} \left(\hat{L}_j \hat{L}_k - \hat{L}_j \hat{L}_k \right) = 0
\end{aligned} \tag{1.37}$$

$\square$

Eigenvalues and eigenfunctions of Angular Momentum

It can be shown that the angular momentum operators in the 3 cardinal directions expressed in polar coordinates are given by,

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \tag{1.38}$$

$$\hat{L}_y = -i\hbar \left(\cos\phi \frac{\partial}{\partial \theta} - \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right) \tag{1.39}$$

$$\hat{L}_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial \theta} - \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right) \tag{1.40}$$

$$\hat{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) \tag{1.41}$$

We now wish to solve for the eigenfunctions of $\hat{L}^2$, $\hat{L}^2 \psi(r,\theta,\phi) = L^2 \psi(r,\theta,\phi)$. We can consider a separable solution, $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$, and neglect the r dependent term as $\hat{L}^2$ does not depend on r. Furthmore, we wish for $Y(\theta,\phi)$ to be an eigenfunction of $\hat{L}_z$ too, so we can assume that $Y \propto e^{im\phi}$ since we know the eigenfunctons of $\hat{L}_z$. Thus, we can write $Y(\theta,\phi) = P(\theta)e^{im\phi}$. Now,

$$-\hbar^2 \left(\frac{d^2}{d\theta^2} + \cot\theta \frac{d}{d\theta} - \frac{m^2}{\sin^2\theta} \right) P(\theta) = L^P(\theta). \tag{1.42}$$

Let us define $\lambda = L^2/\hbar^2$, and write,

$$\frac{d^2 P}{d\theta^2} + \frac{\cos\theta}{\sin\theta} \frac{dP}{d\theta} + \left(\lambda - \frac{m^2}{\sin^2\theta} \right) P = 0 \tag{1.43}$$

which we recognise as the associated Legendre equation, whose solutions are associated Legendre polynomials $P_l^m(\theta)$. Let us consider the possible eigenfunctions by substituting some known associated Legendre polynomials,

1. $P(\theta) = 1$,

$$\lambda - \frac{m^2}{\sin^2\theta} = 0 \tag{1.44}$$

which is only true for $\lambda = m^2 = 0$.

2. $P(\theta) = \cos\theta$,

$$(\lambda - 2)\cos\theta - m^2 \frac{\cos\theta}{\sin^2\theta} = 0 \tag{1.45}$$

which is only true for $\lambda = 2$, $m^2 = 0$.

Generally,

$$\lambda = l(l+1) \qquad\qquad m = -l, -l+1, -l+2 \dots, 2+l, 1+l, l \tag{1.46}$$

for $l \in \mathbb{Z}$. Thus, for a 3D simple harmonic oscillator, l is the second quantum number. It follows that,

$$\hat{L}_z^2 \leq \hat{L}^2 \implies m^2 \leq l(l+1) \implies |m| \leq l \tag{1.47}$$

and for a given l, there are $2l+1$ values for the quantum number m.

Spherical Harmonic Functions

We have that the eigenfunctions of $\hat{L}^2$ and $\hat{L}_z^2$ is the function,

$$Y_{lm}(\theta\phi) = P_{lm}(\cos\theta)e^{im\phi} \tag{1.48}$$

where $P_{lm}(\cos\theta)$ is an associated Legendre polynomial. Its eigenvalues are,

$$\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}, \tag{1.49}$$

$$\hat{L}_z Y_{lm} = m\hbar Y_{lm}, \tag{1.50}$$

and it is normalised by,

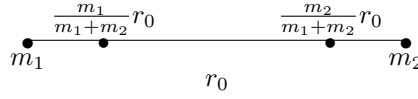$$2\pi \int_{-1}^{1} |P_{lm}(x)|^2 \, dx = 1. \tag{1.51}$$

Figure 1.1

Raising and Lowering Operators

Definition 8: Raising and Lowering Operator

$$\hat{L}^{\pm} = \hat{L}_x \pm i\hat{L}_y \tag{1.52}$$

The raising and lowering operator commutes by,

$$\left[\hat{L}_z, \hat{L}^{\pm}\right] = \pm\hbar\hat{L}^{\pm}. \tag{1.53}$$

Given a function, $Y = \hat{L}^+ Y_{lm}$, it has eigenvalues,

$$\hat{L}_z Y = \hbar(m+1)Y. \tag{1.54}$$

1.4   Rotation of a Diatomic Molecule

We can model the rotation of a diatomic molecule as two masses connected by a massless, rigid rod of length l. In order to find the quantum mechanical solution to this problem, we following the following steps:

1. Consider the classical energy, and express it in terms of conserved quantities (i.e., find the classical Hamiltonian). In our case,

$$E = \frac{1}{2}I\omega^2 = \frac{1}{2I}L^2 \tag{1.55}$$

   where I is the moment of inertia and L is the angular momentum.

2. The quantum Hamiltonian will take on the operator form of the classical Hamiltonian. I.e., in equation (1.55), we see that we can turn L^2 into the operator $\hat{L}^2$, so,

$$\hat{H} = \frac{\hat{L}^2}{2I}. \tag{1.56}$$

The moment of inertia is given by,

$$I = \sum_i m_i r_i \tag{1.57}$$

where m_i is the ith mass of the system, and r_i is the distance of the mass from the centre of mass. In our case, this is,

$$I = m_1 \left(\frac{m_2}{m_1 + m_2} r_0\right)^2 + m_2 \left(\frac{m_1}{m_1 + m_2} r_0\right)^2 = \mu r_0^2 \tag{1.58}$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ which is the reduced mass. We know the eigenfunctions of $\hat{L}$, and its corresponding eigenvalues. We find that,

$$E_l = \frac{l(l+1)\hbar^2}{2I}. \tag{1.59}$$

E_l is independent of l, which implies a degeneracy of $2m+1$ fold, as for every given l, there are $2m+1$ values for the quantum number l.
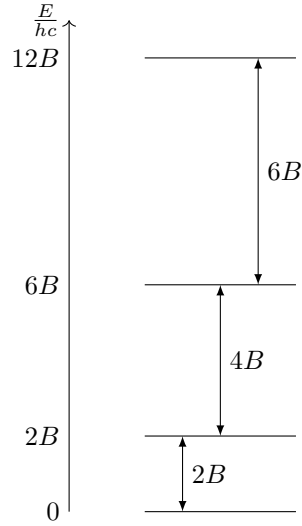
Figure 1.2

1.4.1 Population of Excited States

For a diatomic molecule, we say that the energy of a molecule is of the order $E \sim \frac{\hbar^2}{2I}$, and the thermodynamic energy is $E \sim k_B T$. By equating these, we find that the temperature to which rotational energy corresponds is $T \sim 90k$, thus rotational excited states are populated at room temperature. However, vibrational states are not populated ($\hbar\omega$).

The energy of a molecule corresponds to a certain wavelength, which corresponds to the photon energy the molecule can absorb or emit. This photon energy corresponds to a wavenumber k, which is quantised,

$$k = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{E}{hc} = \frac{h}{8\pi^2 cI}l(l+1) = Bl(l+1). \tag{1.60}$$

These energy level transitions are visualised in figure 1.2. We have that the only allowed transitions due to the absorption or emission of a single photon is $\Delta l = \pm 1$. So, we would observe the emission spectra separated by $2B, 4B, 6B$, etc.

Chapter 2

The Hydrogen Atom

In order to solve the quantum mechanics of the hydrogen atom, we must solve the time independent Schrodinger equation under a central potential, i.e,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi). \tag{2.1}$$

It is most useful for us to work in polar coordinates. When writing the TISE in this way, we find we can write it as,

$$\underbrace{\left(-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right] + \frac{\hat{L}^2}{2mr^2} + V(r)\right)}_{\hat{H}}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi). \tag{2.2}$$

Before we begin attempting to solve this, let us use some intuition,

1. We will expect ψ to have 3 quantum numbers, as there are 3 degrees of freedom.

2. By inspection, $\left[\hat{H},\hat{L}\right] = \left[\hat{H},\hat{L}_z\right] = 0 \implies (l,m)$ are good quantum numbers of hydrogen, since $\hat{L}$ appears in its Hamiltonian. This means that we expect to find a quantum number from solving the r dependence in the TISE.

2.1   Central (Coulomb) Potential

The Coulomb potential between a positively charges nucleus and an electron is given by,

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{2.3}$$

which we will use to solve the radial part of equation (2.2). By attempting a separable solution of the form $\psi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi)$ and noting $\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}$, we can write,

$$\left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}\right)R(r)Y_{lm}(\theta,\phi) = ER(r)Y_{lm}(\theta,\phi). \tag{2.4}$$

Let us use the substitution $R(r) = \frac{U(r)}{r}$ and cancel $Y_{lm}(\theta,\phi)$ to obtain,

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 U}{\mathrm{d}r^2} + \frac{l(l+1)\hbar^2}{2mr^2}U - \frac{e^2}{4\pi\epsilon_0 r}U = EU. \tag{2.5}$$

Let us recall that in the Bohr model of the atom, energy levels depended on the Rydberg energy E_R, and atomic radii depended on a_0, defined,

$$E_R = \frac{m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2} \qquad\qquad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}. \tag{2.6}$$

Let us now define two dimensionless constants,

$$\rho \equiv \frac{r}{a_0} \qquad\qquad \tilde{E} \equiv \frac{E}{E_R} \tag{2.7}$$

and substitute these in equation (2.5),

$$-\frac{\mathrm{d}^2 U}{\mathrm{d}\rho^2} + \frac{l(l+1)}{\rho^2}U - \frac{2}{\rho}U = \tilde{E}U. \tag{2.8}$$

2.1.1 Radial Solutions of the Wavefunction

Before attempting a general solution of equation (2.8), let us consider the solutions in the limits $\rho \gg 1$ and $\rho \ll 1$.

Large ρ

In the limit of large ρ, we find equation (2.8) reduces to,

$$\frac{\mathrm{d}^2 U}{\mathrm{d}\rho^2} = -\tilde{E}U \tag{2.9}$$

which implies a solution,

$$U(\rho) \propto e^{-b\rho} \tag{2.10}$$

where $\tilde{E} = -b^2$. We require the minus sign as we need the wavefunction to go to 0 at large ρ.

Small ρ

For small ρ, we find equation (2.8) reduces to,

$$-\frac{\mathrm{d}^2 U}{\mathrm{d}\rho^2} + \frac{l(l+1)}{\rho^2}U \approx 0 \tag{2.11}$$

for which we require,

$$U \propto \rho^{l+1} \tag{2.12}$$

as $U(0) = 0$.

General Solution

We can attempt a general solution if we consider a combination of the solutions for small and large ρ,

$$U(\rho) = \rho^{l+1}e^{-b\rho}f(\rho) \tag{2.13}$$

where $f_p(\rho)$ is some smooth function. Equation (2.8) then becomes,

$$\rho\frac{\mathrm{d}^2 f_p}{\mathrm{d}\rho^2} + 2(l+1-b\rho)\frac{\mathrm{d}f_p}{\mathrm{d}\rho} + 2(1-b(l+1))f = 0. \tag{2.14}$$

We can solve equation (2.14) by series solution, i.e.,

$$f(\rho) = \sum_{k=0}^{\infty} c_k \rho^k \tag{2.15}$$

by the series expansion of f. Substituting this into equation (2.14), we find,

$$\sum_{k=0}^{\infty}\left[c_{k+1}\left(k^2 + 3k + 2 + 2l(k+1)\right) - 2c_k\left(bk + bl + 2b - 2\right)\right]\rho^k = 0 \tag{2.16}$$

from which we obtain the recursion relation,

$$c_{k+1} = \frac{2bk + 2bl + 2b - 2}{k^2 + 3k + 2 + 2l(k+1)}c_k. \tag{2.17}$$

We will state without proof that the recursion relation (2.17) diverges unless the series expansion of f terminates, i.e., unless f is a polynomial of some degree, let's call it p. By the condition $c_{p+1} = 0$, we find,

$$b = \frac{1}{1+l+p} \qquad\qquad \implies \qquad\qquad \tilde{E} = -\frac{1}{(1+l+p)^2} \tag{2.18}$$

2.2   Energy Eigenvalues of the Hydrogen Atom

From our findings in the previous section, we can define a new quantum number n, such that the energy eigenvalues of the hydrogen atom are,

$$E_n = -\frac{E_R}{n^2} \quad n \geq 1 \tag{2.19}$$

where n is bounded by,

$$0 \leq n \leq n - 1. \tag{2.20}$$

We then have that n, m, l fully parametrise $\psi(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$ and are *good quantum numbers*.

Appendix A

Misc. Formulae

A.1   Commutation Relation

$$\left[\hat{A}\hat{B},\hat{C}\right] = \left[\hat{A},\hat{C}\right]\hat{B} + \hat{A}\left[\hat{B},\hat{C}\right] \tag{A.1}$$

$$\left[\hat{A}+\hat{B},\hat{C}\right] = \left[\hat{A},\hat{C}\right] + \left[\hat{B},\hat{C}\right] \tag{A.2}$$