Quantum Mechanics

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Michælmas Term 1996

Contents

1 Introduction

This section is mandated by the schedules (and was lectured), but it's all A-level physics. So I'll just summarize the salient points *extremely* briefly.

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Planck hypothesised that light of angular frequency ω exists in packets of energy $\hbar\omega$. $\hbar$ is a fundamental constant of nature, and equals $1.05 \times 10^{-34} Js$. Einstein's *photoelectric effect* confirmed Planck's idea, the crucial formula being $\hbar\omega = E + W$. Photons are massless particles, and so move at c.

The Bohr atom. To explain atomic spectra, Bohr suggested that angular momentum was quantized in units of $\hbar$, so using

$$mvR = N\hbar$$

and

$$\frac{mv^2}{R} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{R^2}$$

gives the allowed radii. In good agreement with experiment, but has two major flaws. Firstly, can only be used for hydrogen atom and secondly is a load of rubbish.

De Broglie suggested that associated with a particle of momentum $\mathbf{p}$ is a wave with wave vector $\mathbf{k} = \frac{\mathbf{p}}{\hbar}$.

2 The Schrödinger Equation

This is not relativistic and only works for a single particle in a potential $U(\mathbf{x}, t)$.

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + U(\mathbf{x}, t)\psi$$

It is, however, the remainder of this course...

For a free particle with $U \equiv 0$, the solution is

$$\psi(\mathbf{x}, t) = Ae^{i(\mathbf{k}.\mathbf{x} - \omega t)}.$$

We interpret $\hbar\mathbf{k}$ as the momentum of the particle and $\hbar\omega$ as the kinetic energy.

Note that

- ψ is complex,
- Schrödinger equation is linear,
- ψ is called the state of the particle and
- the Schrödinger equation governs how the state evolves in time.

It is postulated that any solution of the Schrödinger equation is an allowed physical state.

2.1 Probabilistic Interpretation of ψ

The probability of finding the particle in an infinitesimal region dV centered on $\mathbf{x}$ is postulated to be $|\psi(\mathbf{x}, t)|^2 \, dV$.

ψ must be normalised, i.e.

$$\int_{\mathbb{R}^3} |\psi(\mathbf{x}, t)|^2 \, dV = 1.$$

There is still freedom to multiply by $e^{i\alpha}$ – this has no physical consequences. Some wavefunctions are not normalisable, and are regarded as idealisations of physically realisable ones.

2.1.1 Probability Flux and Conservation of probability

If the potential is real, then consider the Schrödinger equation and it's complex conjugate

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + U(\mathbf{x},t)\psi$$

$$i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^* + U(\mathbf{x},t)\psi^*,$$

and calculate $\frac{\partial\psi\psi^*}{\partial t}$ to get

$$\frac{\partial\psi\psi^*}{\partial t} + \nabla.(-\frac{i\hbar}{2m}(\psi^*\nabla\psi - \nabla\psi^*\psi)) = 0,$$

an analogue of conservation of charge.

$$\mathbf{J} = -\frac{i\hbar}{2m}(\psi^*\nabla\psi - \nabla\psi^*\psi)$$

is called the probability current.

2.2 Stationary States

If U is independent of time, we can separate the Schrödinger equation to get

$$\psi(\mathbf{x},t) = \chi(\mathbf{x})e^{-i\omega t},$$

with

$$H\chi = E\chi,$$

where E is the energy $\hbar\omega$ and H is the Hamiltonian operator

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U.$$

This wavefunction is called a stationary state with energy E. ψ is normalised iff χ is normalised. In a stationary state, the probability density is $|\chi|^2$ and depends only on position. Since H is real, E is real. If χ is real, then $\mathbf{J} = 0$.

The general solution of the Schrödinger equation with a static potential is a superposition of stationary states, i.e. suppose H has eigenvalues $E_1, E_2, \ldots$ with corresponding eigenfunctions $\chi_1, \chi_2, \ldots$. Then

$$\psi(\mathbf{x},t) = \sum_{n=1}^{\infty} a_n\chi_n(\mathbf{x})e^{-\frac{iE_nt}{\hbar}}.$$

ψ is normalised iff

$$\sum_{n=1}^{\infty} |a_n|^2 = 1.$$

This can all be generalised to non-normalisable states and continuum and degenerate eigenvalues.

2.3 Gaussian Wave Packet

We superpose plane wave solutions to get a localised particle.

$$\psi(x,t) = \int_{\mathbb{R}} e^{-\frac{\sigma(k-k_0)^2}{2}} e^{i(kx - \frac{\hbar k^2}{2m}t)} dk$$

This integral "simplifies" (honestly!) to give

$$\psi(x,t) = \frac{const}{\sqrt{\sigma + \frac{i\hbar t}{m}}} \exp \frac{1}{2} \left(\frac{k_0 t + ix}{\sigma + \frac{i\hbar t}{m}} \right)^2.$$

$$\psi\psi^* = \frac{const'}{\sqrt{\sigma^2 + \frac{\hbar^2 t^2}{m^2}}} \exp -\sigma \frac{\left(x - \frac{\hbar k_0}{m} t\right)^2}{\sigma^2 + \frac{\hbar^2 t^2}{m^2}},$$

which is a Gaussian in x, centered at $\frac{\hbar k_0}{m} t$. ψ is normalised if $const' = \sqrt{\frac{\sigma}{m}}$.

Particle moves along at a speed $\frac{\hbar k_0}{m} = \frac{\text{average momentum}}{\text{mass}}$. The width of the packet changes with time and is narrowest at $t = 0$.

2.4 Particle in infinite potential well (1–D)

This has a potential

$$U(x) = \begin{cases} 0 & 0 < x < a; \\ \infty & \text{otherwise.} \end{cases}$$

Look for stationary states, i.e. solutions of

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \chi}{\partial x^2} = E\chi,$$

with $\chi(0) = \chi(a) = 0$ since $\chi = 0$ where U is infinite. Not too hard to get

$$\chi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

with

$$E_n = \frac{\hbar^2}{2m} \frac{n^2 \pi^2}{a^2}.$$

2.5 Remarks on bound states

The stationary state equation is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \chi}{\partial x^2} + U(x)\chi = E\chi,$$

with $U \to U_0$ as $x \to \pm\infty$. This equation has 2 linearly independent solutions. If $E > U_0$, both of this are oscillatory as $x \to \pm\infty$ and there is no bound state. If $E < U_0$, one soln decays exponentially one way and grows exponentially the other way. For special E, the eigenvalues, this doesn't happen and there is one solution which decays exponentially as $x \to \pm\infty$. This solution is unique up to normalisation. The other solution is not normalisable. The eigenvalues correspond to bound states with $E < U_0$.

2.6 Remarks on continuity

If U is smooth, so is χ. If U has a finite discontinuity, then χ and χ' are continuous, but χ'' is discontinuous. If U has an infinite discontinuity, usually χ is continuous, χ' discontinuous and $\chi = 0$ where U infinite.

2.7 Remarks on parity

If $U(x) = U(-x)$, then bound states are either even or odd, since if $\chi(x)$ is a solution with energy E, so is $\chi(-x)$ and hence is a multiple of $\chi(x)$.

2.8 Finite Potential Well (1D)

$$U(x) = \begin{cases} 0 & -a < x < a \\ U_0 & \text{otherwise.} \end{cases}$$

Look for even parity bound states. Let $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $\kappa = \sqrt{\frac{2m(U_0-E)}{\hbar^2}}$. Then we have to solve

$$\frac{\partial^2\chi}{\partial x^2} + k^2\chi = 0 \text{ if } |x| < a,$$

and

$$\frac{\partial^2\chi}{\partial x^2} - \kappa^2\chi = 0 \text{ if } |x| > a,$$

with χ and χ' continuous at $x = \pm a$. Easily obtain

$$\chi(x) = \begin{cases} A\cos kx & |x| < a; \\ Be^{-\kappa|x|} & |x| > a. \end{cases}$$

Now impose continuity on $\frac{1}{\chi}\frac{\partial\chi}{\partial x}$ at $x = \pm a$ to get

$$k\tan ka = \kappa.$$

We also have

$$k^2 + \kappa^2 = \frac{2mU_0}{\hbar^2}.$$

Solve numerically or graphically. Number of solutions increases with ka and there is always one solution is $U_0 > 0$. The energy is

$$E = \frac{\hbar^2k^2}{2m}.$$

2.9 Scattering problems

Ideally, we would like to study the scattering of wavepackets on some potential. The evolution of such scattering is complicated, and finding the probabilities for reflection and transmission is not nice... So we look for stationary states.

2.9.1 Potential step

$$U(x) = \begin{cases} 0 & x < 0; \\ U_0 & x > 0. \end{cases}$$

If $E < U_0$, let $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $\kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$. Solve appropriate ode's and impose continuity at $x = 0$ to get

$$\chi(x) = \begin{cases} e^{ikx} + Ae^{-ikx} & x < 0, \\ Be^{-\kappa x} & x > 0. \end{cases}$$

with $A = \frac{k - i\kappa}{k + i\kappa}$ and $B = \frac{2k}{k + i\kappa}$. $|A|^2$ is the probability of reflection, and equals 1.

If $E > U_0$, let $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $\kappa = \sqrt{\frac{2m(E - U_0)}{\hbar^2}}$. Solve appropriate ode's and impose continuity at $x = 0$ to get

$$\chi(x) = \begin{cases} e^{ikx} + Ae^{-ikx} & x < 0, \\ Be^{i\kappa x} & x > 0. \end{cases}$$

with $A = \frac{k - \kappa}{k + \kappa}$ and $B = \frac{2k}{k + \kappa}$. $|A|^2$ is the probability of reflection, and if $E \gg U_0$, $|A|^2 \approx 0$. This is the classical limit.

$|B|^2$ is the probability of finding a particle in $x > 0$. The decrease in speed bunches up the particles and we need to compensate for this. The transition probability is $\frac{\kappa}{k} |B|^2$, which takes account of the change in momentum.

2.9.2 Quantum Tunneling

$$U(x) = \begin{cases} U_0 & 0 < x < a; \\ 0 & \text{otherwise}. \end{cases}$$

Suppose $E < U_0$ and let $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $\kappa = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$. Get

$$\chi(x) = \begin{cases} e^{ikx} + Ae^{-ikx} & x < 0; \\ Be^{-\kappa x} + Ce^{\kappa x} & 0 \le x \le a; \\ De^{ikx} & x > a. \end{cases}$$

Impose continuity and do painful algebra to get...

$$D = \frac{-4ik\kappa}{(\kappa - ik)^2 e^{(ik+\kappa)a} - (\kappa + ik)^2 e^{(ik-\kappa)a}}$$

and

$$\begin{aligned} \text{probability of tunneling} &= |D|^2 \\ &= \frac{4k^2\kappa^2}{(k^2 + \kappa^2)^2 \sinh^2 \kappa a + 4k^2\kappa^2}, \end{aligned}$$

which although exponentially small if ka is large, is non-zero. Tunneling probabilities in real systems exhibit an enormous range, e.g. the half-lives for α decay range from 10^{-8} seconds to 10^{10} years.

2.10 The Quantum Harmonic Oscillator

$$U(x) = \frac{1}{2} m\omega^2 x^2$$

Solve

$$\frac{-\hbar^2}{2m}\frac{\partial^2 \chi}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \chi = E\chi.$$

Put $\xi = \sqrt{\frac{m\omega}{\hbar}} x$ and $\epsilon = \frac{2E}{\hbar\omega}$. Now must solve

$$-\frac{\partial^2 \chi}{\partial \xi^2} + \xi^2 \chi = \epsilon\chi.$$

Try $\chi(\xi) = f(\xi) e^{-\frac{1}{2}\xi^2}$. Solve for f using power series to get

$$f(\xi) = \sum_{n=0}^{\infty} a_n \xi^n$$

and

$$a_{n+2} = \frac{2n+1-\epsilon}{(n+2)(n+1)} a_n.$$

A non-terminating series is unacceptable, since then $\chi \sim e^{\frac{1}{2}\xi^2}$. So series terminates, with implies ϵ is odd. $f_N(\xi)$ is the N^{th} Hermite polynomial $H_N(\xi)$. $E_N = (N+\frac{1}{2})\hbar\omega$. $\frac{\hbar\omega}{2}$ is called the zero-point energy of the oscillator.

N	E_N	$\chi_N(\xi)$
0	$\frac{1}{2}\hbar\omega$	$e^{-\frac{1}{2}\xi^2}$
1	$\frac{3}{2}\hbar\omega$	$\xi e^{-\frac{1}{2}\xi^2}$
2	$\frac{5}{2}\hbar\omega$	$(1-2\xi^2)e^{-\frac{1}{2}\xi^2}$
3	$\frac{7}{2}\hbar\omega$	$(\xi - \frac{2}{3}\xi^3)e^{-\frac{1}{2}\xi^2}$

3 Observables and Operators

In quantum mechanics, physical numbers such as position, velocity etc. are represented by operators. These are chosen such that a state with a definite value for the quantity is an eigenfunction of the operator, with the value being the eigenvalue of the operator.

The operators look the same as their values.

Energy is represented by the Hamiltonian

$$H = \frac{-\hbar^2}{2m}\nabla^2 + U.$$

Momentum is represented by

$$\mathbf{p} = -i\hbar\nabla.$$

Note that

$$H = \frac{1}{2m}\mathbf{p}.\mathbf{p} + U(\mathbf{x}),$$

which is reassuring.

The position operators x_1, x_2, x_3 act by multiplication, so f is an eigenfunction of $\mathbf{x}$ if

$$\mathbf{x} f(x) = \mathbf{X} f(x)$$

for constant $\mathbf{X}$. f must be a delta function, and $\delta(x_1 - X_1)\delta(x_2 - X_2)\delta(x_3 - X_3)$ is an eigenfunction of $\mathbf{x}$ with eigenvalue $\mathbf{X}$.

Angular momentum is defined as expected

$$\begin{aligned} \mathbf{L} &= \mathbf{x} \wedge \mathbf{p} \\ &= -i\hbar \mathbf{x} \wedge \nabla. \end{aligned}$$

In general, a state is not an eigenfunction.

3.1 Canonical Commutation Relations

Operators do not necessarily commute.

The *commutator* of O_1 and O_2 is $O_1 O_2 - O_2 O_1$ and is written $[O_1, O_2]$. O_1 and O_2 commute iff $[O_1, O_2] = 0$.

- $[x_i, x_j] = 0$
- $[p_i, p_j] = 0$
- $[x_i, p_j] = i\hbar\delta_{ij} 1$.

These are easily proven.

3.2 Hermitian Operators

An operator O is Hermitian if

$$\int_{\mathbb{R}^3} \mathbf{v}^*(\mathbf{x})(O\mathbf{u})(\mathbf{x}) d^3x = \int_{\mathbb{R}^3} ((O\mathbf{v})(\mathbf{x}))^* \mathbf{u}(\mathbf{x}) d^3x.$$

for all $\mathbf{u}, \mathbf{v}$ decaying at infinity.

All the operators we have seen so far are Hermitian (easily proven).

3.2.1 Eigenvalues and Eigenfunctions of Hermitian operators

Suppose O is a Hermitian operator, with eigenvalues λ_n and normalised eigenfunctions $U_n(\mathbf{x})$. Then

$$\begin{aligned} \lambda_m \int y_n^* y_m &= \int y_n^* O y_m \\ &= \lambda_n^* \int y_m^* y_n. \end{aligned}$$

Putting $m = n$ gives λ_n real, and $m \neq n$ gives that

$$\int y_n y_m^* = 0.$$

Any decaying $U(\mathbf{x})$ can be written as a linear combination of the U_n.

It is postulated that :-

- Each dynamical variable is represented by a Hermitian operator,

- If the normalised wavefunction at a given time is $\psi(\mathbf{x}) = \sum a_n U_n(\mathbf{x})$, with the U_n normalised eigenfunctions, then the probability that the particle is in state n is $|a_n|^2$.
- If an experiment is carried out and the particle is found to be in state n, then immediately afterwards $\psi(\mathbf{x}) = U_n(\mathbf{x})$. Further evolution of the system is governed by the Schrödinger equation.

We can simultaneously measure observables whose operators commute, since such operators have a complete set of simultaneous eigenfunctions.

3.3 Expection

A measurement of O gives outcome λ_n with probability $|a_n|^2$. The expectation of O, $\langle O \rangle = \sum \lambda_n |a_n|^2$.

It is easy to prove that $\langle O \rangle = \int \psi^* O \psi$.

In a stationary state, $\langle \mathbf{x} \rangle$ and $\langle \mathbf{p} \rangle$ are constant.

It is easy to see that $\langle E \rangle$ is independent of time, and this can be interpreted as conservation of energy.

3.4 Uncertainty Principle

The uncertainty of the observable O is ΔO, where $(\Delta O)^2 = \langle (O - \langle O \rangle)^2 \rangle$. There are wavefunctions which have $\Delta O = 0$. Given two observables with commuting operators, we can make ΔO_1 and ΔO_2 arbitrarily small by choosing simultaneous eigenfunctions. We have an inequality

$$(\Delta O_1)^2 (\Delta O_2)^2 \geq \frac{1}{4} \langle i\,[O_1, O_2] \rangle^2,$$

which gives the Heisenberg Uncertainty principle

$$\Delta x \Delta p \geq \frac{1}{2}\hbar.$$

The Gaussian achieves equality.

4 Schrödinger Equation in Three Dimensions

Assume a spherically symmetric potential $U(r)$ and look at the spherically symmetric stationary states $\chi(r)$. Get

$$\frac{-\hbar^2}{2mr} \frac{\partial^2 r\chi}{\partial r^2} + U(r)\chi = E\chi.$$

with $\chi(0)$ finite and $\lim_{r \to 0} \chi = 0$ for a bound state. Let $\sigma(r) = r\chi(r)$ to get something familiar...

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \sigma}{\partial r^2} + U(r)\sigma = E\sigma,$$

$\sigma(0) = 0$, which gives the 1-D Schrödinger equation on the whole line, with a reflection symmetric potential and an odd parity σ.

The spherical harmonic oscillator ($U(r) = \frac{1}{2} m\omega^2 r^2$) and potential well ($U(r) = 0 (r < a), U_0 (r > a)$) follow through, with the proviso that no bound states need exist for the potential well.

4.1 Spherically symmetric bound states for Hydrogen atom

Let $U(r) = \frac{-\beta}{r}$, with $\beta = \frac{e^2}{4\pi\epsilon_0}$ and solve

$$\frac{-\hbar^2}{2m_e} \left(\frac{\partial^2 \chi}{\partial r^2} + \frac{2}{r} \frac{\partial \chi}{\partial r}\right) - \frac{\beta\chi}{r} = E\chi.$$

Let $\nu^2 = \frac{-2m_e E}{\hbar^2}$ and $\alpha = -\frac{2m_e \beta}{\hbar^2}$.

$$\frac{\partial^2 \chi}{\partial r^2} + \frac{2}{r}\frac{\partial \chi}{\partial r} + \frac{\alpha}{r}\chi - \nu^2 \chi = 0.$$

Asymptotically, $\chi \sim e^{-\nu r}$, so put $\chi(r) = f(r)e^{-\nu r}$ and try a power series solution for f to get

$$\frac{a_n}{a_{n-1}} = \frac{2\nu n - \alpha}{n(n+1)}.$$

The series must terminate, otherwise $\chi \sim e^{\nu r}$, so $\alpha = 2\nu n$ for some n.

$$E_N = \frac{-m_e \beta^2}{2N^2\hbar^2} = \frac{-m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{N^2},$$

as in the Bohr model.

$\chi_N = L_N(\nu r)e^{-\nu r}$, where L_N is the N^{th} Laguerre polynomial. For normalisation,

$$4\pi \int_0^\infty \chi^2(r) r^2 dr = 1.$$

The Bohr radius is $R_0 = \frac{2}{\alpha} = \frac{\hbar^2}{m_e \beta}$. In the N^{th} state, $\langle r \rangle = \frac{3}{2}N^2 R_0$. Get spectral lines etc..

4.2 Angular Momentum Operators

$$\mathbf{L} = \mathbf{x} \wedge \mathbf{p}$$

$$L_j = i\hbar \epsilon_{jkl} x_k \frac{\partial}{\partial x_l}$$

It can be shown by expanding out that

$$[L_j, L_k] = i\hbar \epsilon_{jkl} L_l.$$

Define $\mathbf{L}^2 = L_1^2 + L_2^2 + L_3^2$. Now $\mathbf{L}^2$ commutes with all the L_i (use $\left[A, B^2\right] = [A,B]\,B + B\,[A,B]$).
Now

$$[L_i, x_j] = i\hbar \epsilon_{ijk} x_k,$$

$$[L_i, p_j] = i\hbar \epsilon_{ijk} p_k$$

and

$$[L_i, U(r)] = 0 \text{ for spherically symmetric U.}$$

It is now easy to show that $\left[L_i, \nabla^2\right] = 0$ and so $[L_i, H] = 0$ and $\left[L^2, H\right] = 0$. Thus $H, \mathbf{L}^2$ and L_3 commute if the potential is spherically symmetric. L_3 is the conventional choice of component. Thus the simultaneous eigenfunctions of $H, \mathbf{L}^2$ and L_3 form a complete set of functions.

4.3 Eigenfunctions of $\mathbf{L}^2$ and L_3

For L_3,

$$-i\hbar\frac{\partial f}{\partial\phi} = \lambda f$$

gives

$$f(\phi) = e^{im\phi}.$$

Since the eigenfunction should be unchanged by $\phi \to \phi + 2\pi$, $m \in \mathbb{Z}$. The possible values of L_3 are an integer $\times\,\hbar$, which looks like Bohr's hypothesis. The simultaneous eigenfunctions of L_3 and $\mathbf{L}^2$ are the spherical harmonics, which, un-normalised, are

$$Y_{l,m}(\theta,\phi) = P_{l,m}(\theta)e^{im\phi}, l \geq 0 \text{ and } -l \leq m \leq l.$$

$P_{l,m}$ is an associated Legendre function $P_{l,m}(\theta) = (\sin\theta)^{|m|}\frac{\partial^{|m|}P_l(\cos\theta)}{\partial\theta^{|m|}}$ and P_l is the l^{th} Legendre polynomial.

Or, $P_{l,m}$ is the solution to

$$\left(\frac{-1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}\right)P_{l,m}(\theta) = l(l+1)P_{l,m}(\theta).$$

The eigenvalues are $L_3Y_{l,m} = \hbar m Y_{l,m}$ and $\mathbf{L}^2Y_{l,m} = \hbar^2 l(l+1)$.

4.4 Schrödinger Equation with spherically symmetric potential

$$\frac{-\hbar^2}{2M}\left(\frac{\partial^2\chi}{\partial r^2} + \frac{2}{r}\frac{\partial\chi}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\chi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\chi}{\partial\phi^2}\right)\right) + U(r)\chi = E\chi$$

Separate variables to put $\chi(r,\theta,\phi) = g(r)Y_{l,m}(\theta,\phi)$. This simplifies the above equation to

$$\frac{-\hbar^2}{2M}\left(\frac{\partial^2 g}{\partial r^2} + \frac{2}{r}\frac{\partial g}{\partial r}\right) + \left(U(r) + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2}\right)g = Eg.$$

There is an effective potential of $U(r) + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2}$, giving a centrifugal repulsion. We seek bound states with $E < 0$.

Put $\alpha = \frac{2m_e\beta}{\hbar^2}$ and $\nu^2 = \frac{-2m_eE}{\hbar^2}$. Asymptotically $g(r) = e^{-\nu r}$, so try $g(r) = e^{-\nu r}f(r)$. The equation now simplifies to

$$\frac{\partial^2 f}{\partial r^2} + \left(\frac{2}{r} - 2\nu\right)\frac{\partial f}{\partial r} - \frac{l(l+1)}{r^2}f + \frac{1}{r}\left(\alpha - 2\nu\right)f = 0.$$

Try a series solution $f(r) = \sum_{n=0}^{\infty} a_n r^{n+\sigma}$. The indicial equation gives $\sigma = l$, and the rest reduces to

$$\frac{a_n}{a_{n-1}} = \frac{(n+l)2\nu - \alpha}{n(n+2l+1)}$$

. This must terminate, so $\nu = \frac{\alpha}{2(n+l)}$, or $\alpha = 2\nu N$. $E_N = \frac{-m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{N^2}$ is familiar. The complete unnormalised wavefunction

$$\chi_{N,l,m}(r,\theta,\phi) = r^l L_{N,l}(\frac{\alpha r}{2N})e^{\frac{-\alpha r}{2N}}Y_{l,m}(\theta,\phi).$$

$L_{N,l}$ is a generalised Laguerre polynomial.

4.5 Energy Levels

Energy only depends on N (the principal quantum number).

$$E_N = \frac{-m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{N^2}$$

The allowed values for l, m for given N are $0 \leq l < N$ and $-l \leq m \leq l$. The total degeneracy of E_N is $\sum_{l=0}^{N-1}(2l+1) = N^2$. This large degeneracy is a feature of the Coulomb potential.

N is called the principal quantum number, l is the total angular momentum quantum number and m is the magnetic quantum number (a magnetic field along 3^{rd} axis removes this degeneracy.

4.6 Relation with Bohr orbit

The Bohr picture emerges if N is large, $l \approx N$. If $m = l \approx N$ then the electron has an angular momentum component about the 3^{rd} axis $\approx \hbar N$ and the total angular momentum $\approx \hbar N$.

Consider the radial part of the wavefunction with $l = N-1$, $g(r) = r^l e^{\frac{-\alpha r}{2N}}$. The radial probability density is proportional to $r^2 g^2(r) \approx r^{2N} e^{-\alpha r} N$, which has a maximum at $r = \frac{2N^2}{\alpha} = N^2 R_0$, agreeing with the Bohr model.

The syllabus ends here. The lecturer went on to discuss atoms with more than one electron. It was covered at approximately A-level Chemistry standard (although considerably quicker).