

Foundations of Physics 2A

Shaun Cole

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Contents

1 Quantum Mechanics	3
1. Basics of QM	3
2. Operators and Expectation Values	3
3. The Origin Of Uncertainty	3
4. Schrodinger Equation and Eigenfunctions	4
5. Eigenfunctions versus Superpositions	4
Orthogonality	5
Wavefns in Superposition of Eigenstates	5
Expectation for Energy and Time dep	5
6. Superposition of eigenstates and transitions	6
How to find the cm	6
7. Eigenfunctions of various potentials	6
Infinite Square Well	6
Finite Square Well	7
Even Solns	7
Odd Solns	8
Commutator Algebra	8
Consequences of non-commutation	8
The linear harmonic oscillator	9
Ladder Operators	9
Brute Force Solution	10
Properties of Harmonic Potential	10
8. The 3-D Schrodinger Equation	11
ISW Potential	11
Schrodinger in Spherical Polars	11
9. Angular Momentum	12
Combinations	12
Total Angular momentums	12
Spatial Symmetry and L	12
10. Angular Momentum and Spherical Harmonics	13
Angular momentum Operators in Spherical Polars	13
Eigenfunctions of L_z	13
Eigenfunctions of L^2	13
Spherical Harmonics of Y_{lm}	14
11. Finding the Hydrogen Wavefunction	15
Radial Equation for Spherical Potential	15
The Hydrogen Atom	15
Transitions Between Energy Levels	16
12. Generalising Angular Momentum	17
Preview of Spin Concept	17
Review of Angular Momentum	17
Angular Momentum Ladder Operators	17

Properties	17
Overview of general angular momentum, J	17
13. Spin	18
Electron Orbiting Magnetic Field	18
Dirac Notation	18
14. Time-dependent Perturbation Theory	19
Small Modification to Hamiltonian	19
Power expansion	19
First Order correction	19
1D Square Well with Delta Function	20
First Order Correction to Wavefunction	20
15. Degenerate Perturbation Theory	20
Twofold Degeneracy	21
16. Degenerate Perturbation Theory II	21
Link to non-degenerate perturbation theory	21
Higher-order degeneracy	21
Example in 3D Square Well	22
Meaning of Vector components	22
17. Degenerate Perturbation Theory and Hydrogen	22
Spin-Orbit Coupling	22
Commutation Properties	22
Adding Angular Momenta	23
18. Degenerate Perturbation Theory and Hydrogen II	23
Spin Orbit	23
Correction to electron-proton potential (Darwin Term)	23
Relativistic corrections to kinetic energy	24
19. Hydrogen Fine Structure	24
Total First Order Correction	24
Ground State of Hydrogen	25
Quantum Number Sets and Balmer Series	25
Lamb Splitting	25
Hyperfine Splitting	25
20. Formalities and the Correspondence Principle	25
Marginal Probability Distributions	25
Time-energy uncertainty principle	25
The time evolution of expectation values	26
Formalism	26
Ehrenfest Theorems	26
Virial Theorem	27
The Correspondence Principle	27

Chapter 1

Quantum Mechanics

1. Basics of QM

- Useless so just read notes
- Particles described by wave functions, ψ
- $P(x)dx = \psi^2 dx = \psi^* \psi dx$
 - $\int_{-\infty}^{\infty} = 1$

2. Operators and Expectation Values

- Expectation value is average value
 - $\langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx$
 - Doesn't always mean most expected value, just average
 - page 7
- \hat{p} now means $-i\hbar \frac{\partial}{\partial x}$
 - page 8
- Hamiltonian
 - sum of potential and kinetic energy
 - use $-\frac{\hat{p}^2}{2m} + V$ for the operator version
 - $\hat{H}\psi = E\psi$
 - * alternate form of Schrodinger
 - page 8
- Klein-Gordon for relativistic electrons
 - probably won't need it
 - page 9

3. The Origin Of Uncertainty

- Page 10
- Complex conjugate operators of position, momentum, etc operate on the function immediately to the right
- Hermitian – the complex conjugate of the integral for the expectation value is equivalent
 - Swapping positions of variables and taking cplx conjugate
- Any dynamical quantity can be an operator
- Expectation value only real if it is Hermitian
- Can use Hermitian to show uncertainty principle

- try finding $\langle xp \rangle$
- will not get the complex conjugate
- $\hat{x}\hat{p} \neq \hat{p}\hat{x}$
 - they do not commute
- Page 11
- Square bracket notation for commutator
 - $[\hat{a}, \hat{b}] = \hat{a}\hat{b} - \hat{b}\hat{a}$
- The x and p operators don't commute so aren't real and can't be measured
 - can be a test for other operators too to find relations for uncertainty
 - the difference between the two double commutators for x and p is \hbar which is where the $\hbar/2$ comes from for uncertainty
- Use a Gaussian function and find EVs for $\langle x \rangle, \langle p \rangle, \langle x^2 \rangle, \langle p^2 \rangle$ to get minimum Heisenberg values
- Ehrenfest's Theorem fulfils Newton's second law with EVs

4. Schrodinger Equation and Eigenfunctions

- page 14
- $\ln T = \frac{E}{i\hbar}t + K$
- $T = e^{-it\frac{E}{\hbar}}$
- Can convert from time-dep to time-indep if $V = V(x)$, separable fns
- Kronacker delta fn from Maths
 - for distinct eigenfns and orthogonality
- Bra-ket notation for eigen stuff
 - $\langle |$ for cplx conjugate
 - \rangle for normal
 - $\langle | \rangle = \int$
- Eigenfns of the Hamiltonian are stationary

5. Eigenfunctions versus Superpositions

- page 17
- $\Psi(x, t) = \Psi_E(x, t)e^{-\frac{iE}{\hbar}t}$
- $\Psi(x, t) = C_1\Psi_{E_1}(x, t)e^{-\frac{iE_1}{\hbar}t} + C_2\Psi_{E_2}(x, t)e^{-\frac{iE_2}{\hbar}t}$
- Certain harmonics for standing waves
 - only certain wavelengths and energies for these systems
- Infinite square well example
 - see last year's notes
 - normal SHO
 - * sin and cos solns
 - * $\cos = 0$
 - * $\Psi(x) = A \sin(kx)$
 - * $k = \frac{\sqrt{2mE}}{\hbar}$
 - * $A = \sqrt{\frac{2}{L}}$
 - * all usual maths from last year, find Ψ and integrate for constants
 - can make this into a full energy eigenfn:

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{iE_n t}{\hbar}}$$

- Mixture of states leads to time dep
- For any single eigenfn, probability is not time dep
 - we say these are stationary states

- expectation values are not time dep
- General solution to time dep Schrodinger eqn is superposition of eigenstates:

$$\Psi(x, t) = \sum_n c_n \Psi_n(x, t) = \sum_n c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{iE_n t}{\hbar}}$$

- c_n must be chosen so as to normalise total wavefn
 - must equate to one as usual

Orthogonality

- Form an overlap integral of two states n and m:
 - $\langle \Psi_n | \Psi_m \rangle$
 - use !wa as usual for indefinite integral
- when $n \neq m$ both sin terms are for integer π and so both are zero
- when $n = m$, the denominator on the first term goes to zero and the rest tends to 1 as the inside tends to zero
 - this shows it is orthonormal
 - like dot product
- Span the space known from Fourier analysis for expressed as sum of sin waves

Wavefns in Superposition of Eigenstates

- **this is much more thorough in the notes**
- General solution for superpositions:

$$\Psi(x) = \sum_n c_n \Psi_n(x) |\Psi\rangle = \sum_n c_n |\Psi_n\rangle$$

- Normalisation condition for two states:
 - $|c_1|^2 + |c_2|^2 = 1$
 - for general,
 - * use Kronacker delta fn to simplify integrals to get down to:
 - * $\sum_m |c_m|^2$
 - * **always adds up to 1**
- For average energy,
 - using Kronacker delta again

$$\langle E \rangle = \sum_n |c_n|^2 E_n$$

- Only works if $|c_n|^2$ is probability of being in state Ψ_n and measuring energy E_n
- QM predicts only the probability of measuring particular energies
 - non-deterministic

Expectation for Energy and Time dep

- Expectation value of energy is probability weighted sum of energies associated with each state
- A superposed states probability of being in any particular state is

$$\Psi(x, t) = \sum_n c_n \Psi_n e^{-\frac{iE_n t}{\hbar}}$$

- it oscillates with time
- Looking at the probability for a two state system:
 - last two terms contain $e^{\pm \frac{i(E_2 - E_1)t}{\hbar}}$

- write this as $e^{\pm i\omega t}$
- $\hbar\omega = E_2 - E_1$

$$P(x, t) = |c_1|^2 |\Psi_1|^2 + |c_2|^2 |\Psi_2|^2 + c_1^* c_2 \Psi_1^* \Psi_2 e^{-i\omega t} + c_1 c_2^* \Psi_1 \Psi_2^* e^{i\omega t}$$

- This is real as last two terms are cplx conjugate of each other and so, when added together, their imaginary parts cancel.
- Notes that this probability varies with time
- **Superposed states are not stationary states**
- It is still normalised, $\int P(x, t) = 1$, as orthogonality of eigenfns makes last two terms zero when integrated over x

6. Superposition of eigenstates and transitions

- page 21
- All expectation values are constant in time for single eigenfn
 - A general soln which contains multiple is not
- For two terms in the infinite square well, the probability density oscillates with
 - $\omega = \frac{E_2 - E_1}{\hbar}$
- For an electron in ground state of an atom,
 - it can be said it is a single eigenfn so it is not dep on time
 - standing wave
- QM probability distributions solve radiation problem
 - probability density is stationary so the charge is not 'moving' and it doesn't radiate
 - otherwise everything crashes into nucleus
- The mixture of two or more different states, say $n = 1, 2$ then it has a chance of decaying down
 - can't happen at ground state as no lower state to mix with

How to find the cm

- Going from particular soln to general assume that energy eigenfns span the entire space
 - complete set of basis fns
 - any arbitrary fn can be expanded as sum of these
- For any functional form $f(x)$, can decompose it into a weighted sum of energy eigenfns $c_n \Psi_n$ by calculating each $c_n = \int \Psi_n^* f(x) dx$
 - find the overlap of f with the wavefn
 - $\sum_n c_n \delta_{nm} = c_m$

7. Eigenfunctions of various potentials

- page 22
- Consider infinite square well, symmetric about the origin

Infinite Square Well

- For $0 < x < L$, $\Psi_n(x, t) = \Psi_n e^{-i \frac{E_n t}{\hbar}}$:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right); E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

- Can make this symmetric about origin by using a change of variable:
 - $x' = x - \frac{L}{2}$
 - Energy levels are unchanged but solns for odd n will become cos

- * seen by drawing a diagram
- This gives

$$\Psi_n(x)' = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x'}{L} + \frac{n\pi}{2}\right) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x'}{L}\right) \cos\left(\frac{n\pi}{2}\right) + \cos\left(\frac{n\pi x'}{L}\right) \sin\left(\frac{n\pi}{2}\right)$$

- Depends on n
 - odd n wavefns are even fns
 - * $\Psi(x') = \Psi(-x')$
 - even n wavefns are odd fns
 - * $\Psi(x') = -\Psi(-x')$
 - Note that in either case the probability distribution $P(x) = |\Psi(x)|^2$ is symmetric about $x' = 0$

Finite Square Well

- Potential is now V instead of infinity
- Expect bound wavefns to be similar to infinite square well but broader and leak out slightly
- Solve Schrodinger for three regions:
 - $x < -\frac{L}{2}$
 - $-\frac{L}{2} < x < \frac{L}{2}$
 - $x > \frac{L}{2}$
- For central region, $V = 0$:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E\Psi = A \cos ks + B \sin(kx) ; k^2 = \frac{2mE}{\hbar^2}$$

- For $x > \frac{L}{2}$:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V_0\Psi = E\Psi \frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2} (V_0 - E)\Psi = \alpha^2\Psi ; \alpha^2 = \frac{2m}{\hbar^2} (V_0 - E)$$

- Here we have used that for bound states $V_0 > E$
 - $-\alpha^2 < 0$
 - General soln is $\Psi(x) = Ce^{\alpha x} + De^{-\alpha x}$
 - For soln to be normalisable, $C = 0$, or exponent just increases

$$\Psi(x) = De^{-\alpha x} ; x > \frac{L}{2}$$

- Similarly for $x < -\frac{L}{2}$:

$$\Psi(x) = Fe^{\alpha x}$$

- Not an infinite discontinuity in V, then $\frac{\partial\Psi}{\partial x}$ as well as Ψ must be continuous at $x = \pm\frac{L}{2}$
 - In principle, this is all we need for solns
 - solns will either be odd or even - $\Psi(x) = \pm\Psi(-x)$

Even Solns

- page 24
- Only need to consider the join at $x = \frac{L}{2}$ as it's the same at $x = -\frac{L}{2}$ by symmetry
- Applying continuity:
 - In Ψ : $A \cos \frac{kL}{2} = De^{-\frac{\alpha L}{2}}$
 - In $\frac{\partial\Psi}{\partial x}$: $-kA \sin \frac{kL}{2} = -\alpha De^{-\frac{\alpha L}{2}}$
- We find that:

$$\left(\frac{kL}{2} \tan \frac{kL}{2} = \frac{\alpha L}{2}\right)$$

- Meanwhile for defns of k and α , in terms of energy we also have:

$$\left(\frac{\alpha L}{2}\right)^2 + \left(\frac{kL}{2}\right)^2 = \frac{2mV_0}{\hbar^2} \left(\frac{L}{2}\right)^2$$

- Solving for simultaneous eqns finds allowed values for k , energy levels and wavefns
 - Isn't trivial, but can find informative graphical soln by setting

$$X = \frac{kL}{2} ; Y = \frac{\alpha L}{2}$$

- Two eqns become:

$$Y = X \tan X ; X^2 + Y^2 = \frac{2mV_0}{\hbar^2} \left(\frac{L}{2}\right)^2$$

- Plot $Y(X)$ for both eqns and where they intersect are allowed solns

Odd Solns

- Follow same method for odd solns, so sin instead of cos

$$Y = -X \cot X ; X^2 + Y^2 = \frac{2mV_0}{\hbar^2} \left(\frac{L}{2}\right)^2$$

- Look at plot on page 24:
 1. There is always at least one bound state
 - if $R < \frac{\pi}{2} \rightarrow V_0 < \frac{\hbar^2 \pi^2}{2mL^2}$ then this is the only state
 2. For intermediate circle, there are 4 allowed states corresponding to the four points of intersection
 - Reading X and Y values determines k and α
 - Plugging back into eqns above gives D and F (for symmetry) in terms of A
 - To get value for A , use normalisation
 - * split into bounds $-\infty \leq x \leq -\frac{L}{2}$, $-\frac{L}{2} \leq x \leq \frac{L}{2}$, $\frac{L}{2} \leq x \leq \infty$
 3. In lim as $V_0 \rightarrow \infty$, radius of circle becomes very large and intersections occur at
 - $X(= \frac{kL}{2}) = \frac{n\pi}{2}$
 - energy values are same as in infite square well
 - * $E_n = \frac{n^2 \hbar^2 k^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2}$

Commutator Algebra

- $[A, B] = AB - BA = -[B, A]$
 - not necessarily zero
 - operators do not have to commute
 - E.g. $[x, p] = i\hbar$
- See page 25 for commutator identity proofs

$$= AA - AA = 0$$

$$[A + B, C] = [A, C] + [B, C]$$

$$[AB, C] = A[B, C] + [A, C]B$$

$$[A, BC] = [A, B]C + B[A, C]$$

Consequences of non-commutation

- All operators which commute share a common set of eigenfns
 - page 26 for proof
- Tells a bit more about uncertainty principle
 - measuring an operator does not disturb wavefn for measurement of next

- if they don't commute, then in measuring A, we change the wavefn to be one of the eigenfns of A
- * if not eigenfns of B, can still expand f in terms of eigenfns of B

$$f_n = \sum_m c_m g_m ; c_m = \int g_m^* f_n dx$$

- Now if we measure B, don't get a deterministic value of B
 - measure value b_m with probability $|c_m|^2$
- Non-commutation means the two associated variables cannot simultaneously have deterministic values
 - this implies the uncertainty principle

The linear harmonic oscillator

- Potential, $V(x) = \frac{1}{2}kx^2$
 - oscillates with $\omega = \sqrt{\frac{k}{m}}$
 - $V(x) = \frac{1}{2}m\omega^2 x^2$
- Wide applications as about equilibrium psn, x_0 , any arbitrary continuous potential $V(x)$ is harmonic to leading order

$$V(x) \approx V(x_0) + \left[\frac{dV}{dx} \Big|_{x_0} (x - x_0) \right]^{=0} + \frac{1}{2} \frac{d^2V}{dx^2} \Big|_{x_0} (x - x_0)^2 + \dots$$

- Time Indep Schrodinger eqn is:

$$\left(\frac{\hat{p}^2}{2m} + V \right) \Psi = E \Psi$$

$$\frac{1}{2m} (\hat{p}^2 + (m\omega x)^2) \Psi = E \Psi$$

Ladder Operators

- Can't do this factorisation:

$$(a^2 + b^2) = (-ib + a)(-b + a)$$

- These are operators and they don't commute, so this doesn't work
- Consider:

$$a_{\pm} = \frac{1}{\sqrt{2\hbar m \omega}} (\mp i p + m \omega x)$$

- The prefactor is chosen to make things neater later on

$$a_+ a_- = \left(\frac{1}{\hbar \omega} H - \frac{1}{2} \right)$$

$$a_- a_+ = \left(\frac{1}{\hbar \omega} H + \frac{1}{2} \right)$$

- *full derivation on page 27*

$$H = \hbar \omega (a_+ a_- + \frac{1}{2})$$

$$H = \hbar \omega (a_- a_+ - \frac{1}{2})$$

- Hamiltonian does not quite factor properly and we have

$$\hbar \omega (a_{\pm} a_{\mp} \pm \frac{1}{2}) \Psi = E \Psi$$

- Suppose could find soln Ψ_n , with associated energy, E_n
 - operate on this with a_+ for $a_+ \Psi_n$ which is also a soln

$$H(a_+ \Psi_n) = \hbar \omega (a_+ a_- + \frac{1}{2}) a_+ \Psi_n$$

$$H(a_+ \Psi_n) = (E_n + \hbar \omega) a_+ \Psi_n$$

- If Ψ_n satisfies Schrodinger with energy, E_n , then $a_+\Psi_n$ satisfies it with energy, $E_n + \hbar\omega$
 - This works similiary with a_-
- Need one energy to get started and find the rest of them with this method
 - must be a bottom rung

$$a_-\Psi_0 = 0 \frac{1}{\sqrt{2\hbar m\omega}} (\hbar \frac{d}{dx} + m\omega x) \Psi_0 = 0$$

$$\frac{d\Psi_0}{dx} = -\frac{m\omega}{\hbar} x \Psi_0$$

$$\Psi_0 = N e^{-\frac{m\omega x^2}{2\hbar}}$$

$$\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{2\hbar}}$$

- This solution is the Gaussin wavefn used in the first few sections
 - $a = \frac{m\omega}{\hbar}$
 - associated energy is easy to find from $H\Psi = \hbar\omega(a_+a_- + \frac{1}{2})\Psi = E\Psi$

$$a_-\Psi_0 = 0$$

$$\frac{1}{2}\hbar\omega\Psi_0 = E_0\Psi_0$$

$$\therefore E_0 = \frac{\hbar\omega}{2}$$

- Call this state $n = 0$, then all other states follow:

$$\Psi_n = A_n a_+^n \Psi_0$$

$$E_n = (n + \frac{1}{2})\hbar\omega$$

- $n = 0$ is the ground state for SHO

Brute Force Solution

- lots of maths - see page 28
- Can be solved using the Frobenius/Power series technique
- Polynomial solns known as Hermite polynomials $H_n(\zeta)$
 - n denotes order of polynomial
 - will get lots of other terms involved

$$H_{n+2}(\zeta) - 2\zeta H_{n+1}(\zeta) + 2(n+1)H_n(\zeta) = 0$$

- Above eqn fixes this
- Swap between even and odd fns as you go up in n

Properties of Harmonic Potential

- Wavefns for ISW, FSW, and SHO have similar properties

$$E_n = (n + \frac{1}{2})\hbar\omega$$

- Runs from $n = 0$
- System has zero point energy which is non-zero
 - due to Heisenberg uncertainty
 - can't sit motionless at the bottom of well as then psn and momentum are both known
 - ground state of system must satisfy Heisenberg
 - implies energy is greater than the minimum of the pot well

8. The 3-D Schrodinger Equation

- page 30

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V(x, y, z, t) \Psi$$

$$i\hbar \frac{\partial \Psi}{\partial t} - \frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, t) \Psi(\vec{r}, t)$$

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi_n(\vec{r}) + V \Psi_n(\vec{r}) = E_n \Psi_n(\vec{r})$$

- This is separable over space

$$\Psi_n(x, y, z) = X(x)Y(y)Z(z) \text{ if } V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$$

- Can separate into three equations for dimensions

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V_x X(x) = E_x X(x)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial y^2} + V_y Y(y) = E_y Y(y)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial z^2} + V_z Z(z) = E_z Z(z)$$

$$E_x + E_y + E_z = E$$

- Not many useful potentials can be split up like this
 - Harmonic Oscillator can be though

ISW Potential

- Inside the well, we have explicit eqns as above
- Soln is just the same as 1D case in each direction
- Full wavefn and energy level:

$$\Psi(x, y, z) = X(x)Y(y)Z(z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E = E_x + E_y + E_z + \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

- Things simplify a bit for a cube, see notes page 31
- Only one way to get ground state, (1, 1, 1), so it is non-degenerate
 - next energy level can be (1, 1, 2), (1, 2, 1), (2, 1, 1), so it is three-fold degenerate
 - get degeneracies because of symmetries of the potential

Schrodinger in Spherical Polars

- page 32

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

- Usual shit for integration in sphericals

- Usual conversion for everything else too

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

- Solutions are called Spherical Harmonics, $Y(\theta, \phi)$
- Related to angular momentum

9. Angular Momentum

- $\underline{L} = \underline{r} \times \underline{p}$
- The angular momentum operators:

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

- Angular momentum operators are Hermitian
- Heisenberg doesn't apply across these operators, if measuring in different directions

Combinations

- L_x, L_y, L_z do not commute

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

- Same cycle for other permutations
- Non-commutation means can't measure all components at once
- Can't know a pair of the angular momentums
- Uncertainty for this:

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{1}{2} \left| \langle [L_x, L_y] \rangle \right| = \frac{\hbar}{2} \left| \langle L_z \rangle \right|$$

Total Angular momentums

- $L^2 = L_x^2 + L_y^2 + L_z^2$
- L^2 commutes with each of the components, i.e. $[L^2, L_i] = 0$, $i = x, y, z$
- So can measure a single component of angular momentum alongside total magnitude of angular momentum
 - Use L_z as it is the simplest
 - L_z and L^2 commute, so they share a common set of efn's

Spatial Symmetry and L

- page 35
- Angular momentum is zero for any spherically symmetric wavefn
- L about the z-axis is related to angular dependence
 - oscillations between real and imaginary in x-y plane
 - $x + iy = re^{i\theta}$

10. Angular Momentum and Spherical Harmonics

Angular momentum Operators in Spherical Polars

- Use angular momentum operators in polar form:

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

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

- All of these can be obtained using the chain rule
- L^2 is essentially the angular part of the Laplacian
 - use this to rewrite Schrodinger
- Angular dependence of wavefn is related to angular momentum

Eigenfunctions of L_z

- Want to solve

$$L_z \Phi_m = m\hbar \Phi_m$$

- for eigenvalues m and eigenfunctions Φ_m

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

- The equation is satisfied for any value of m but the soln requires periodicity of 2π
 - results that m must be a integer
- Eigenvalues of L_z are $0, \pm n\hbar$, $n \in \mathbb{R}$
 - z-axis could be chosen in any arbitray direction then the orbital angular momentum about any axis is quantised
 - m is the magnetic quantum number in atoms
 - * response to magnetic fields
- These eigenfunctions are orthonormal

$$\int_0^{2\pi} \Phi_n^* \Phi_m d\phi = \delta_{nm}$$

- Can expand any angular function:

$$f(\phi) = \sum c_m \Phi_m$$

Eigenfunctions of L^2

- There is a common set of eigenfunctions for L_z and L^2
 - Call these $Y_{lm}(\theta, \phi)$

$$L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi)$$

$$L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi)$$

- Set the constant to $l(l+1)$
 - will be explained later

- Y_{lm} is separable, otherwise it wouldn't share eigenfunctions with L_z $Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\theta)$
- derivation on page 38
 - will solve this in maths lectures
- When $m = 0$, solutions are called **Legendre polynomials**, $P_l(\cos \theta)$
 - l is the order of the polynomial
- For $m \neq 0$, the solutions are **associated Legendre polynomials**
 - related to the $|m|^{th}$ derivative of the P_l
 - page 39
- Since P_l is a polynomial of degree l , then its $l + 1$ derivative vanishes
 - for a fixed value of l , we require $|m| \leq l$
 - $2l + 1$ values of m for every l
- Normalise all of this to get $\Theta_{lm}(\theta)$

$$\Theta_{lm} = (-1)^m \left(\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \right)^{1/2} P_l^m(\cos \theta)$$

Spherical Harmonics of Y_{lm}

- Eigenfunctions common to L_z and L^2 are given by:
 - with $l \geq 0$ and $-l \leq m \leq l$

$$Y_{lm}(\theta, \phi) = \Theta_{lm}\Phi_m = (-1)^m \left(\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \right)^{1/2} P_l^m(\cos \theta) e^{im\phi}$$

- Convention of:

$$Y_{lm}^*(\theta, \phi) = (-1)^m Y_{l,-m}(\theta, \phi)$$

- page 39 for proof of values of m
- Start with this:

$$\langle L^2 \rangle = \langle L_x^2 + L_y^2 + L_z^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle$$

- Operators are all Hermitian and real and non-negative

$$\langle L^2 \rangle \geq \langle L_z^2 \rangle$$

- Continue from there to get

$$l(l+1) \geq m^2$$

- This implies the physical limit of $|m| \leq l$
- Specifying L_z means that L_x and L_y can't have defined values
 - measuring them will get a quantised level, $\pm n\hbar$, $0 \leq n \leq l$
 - probability varies
- Can explicitly evaluate expectation values of $\langle L_x \rangle$ and $\langle L_y \rangle$
 - both turn out to be zero
 - the probability of $\pm\hbar$ etc are equal
- page 40
- A semi-classical vector model helps understand this behaviour
 - set magnitude to $\sqrt{l(l+1)}\hbar$
 - spherical harmonics as well
 - can deduce m from the length etc

- dipole patterns of ‘heat’
- page 41 for probability distributions
 - more interesting than the wavefunctions

$$P(\theta, \phi) \sin \theta d\theta d\phi = Y_{lm}^* Y_{lm} \sin \theta d\theta d\phi$$

$$P(\theta, \phi) d\Omega = Y_{lm}^* Y_{lm} d\Omega$$

- $d\Omega$ is the element of solid angle
 - $\sin \theta d\theta d\phi$
- Easier to visualise as exponents in Y_{lm} cancel out
- To get θ dependence, integrate over ϕ

$$P(\theta) d\theta = \int_{\phi=0}^{2\pi} |Y_{lm}(\theta, \phi)|^2 d\phi \sin \theta d\theta$$

11. Finding the Hydrogen Wavefunction

Radial Equation for Spherical Potential

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) = \frac{L^2 Y}{\hbar^2 Y}$$

$$L^2 Y = l(l+1) \hbar^2 Y$$

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) - l(l+1) = 0$$

- This is equation for the eigenfunctions, $R(r)$
 - depends on l but not m
 - for each l , different eigenfunctions
 - * can label with index n
 - denote $R_{nl}(r)$
- page 42
 - lots of simplifications to equation
 - $rR(r) = U_{nl}$
- Radial equation:

$$-\frac{\hbar^2}{2m} \frac{d^2 U_{nl}}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] U_{nl} = E U_{nl}$$

- Identical to 1D Schrodinger
 - normal potential replaced with effective potential in square brackets
 - extra term behaves like potential:
 - * Centripetal force: $F = \frac{mv^2}{r}$
 - * $F = \frac{L^2}{mr^3}$; $L = mvr$
 - * integrate from this to get the term

The Hydrogen Atom

- Hydrogen atom
 - electron and proton instead of just one particle
 - replace electron mass with the reduced mass:
 - $\mu = \frac{M_p m_e}{(M_p + m_e)}$

- Use Coulomb potential

$$-\frac{\hbar^2}{2\mu} \frac{d^2 U_{nl}}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} U_{nl} - \frac{Ze^2}{4\pi\epsilon_0 r} U_{nl} = E U_{nl}$$

- Solve this for the eigenfunctions
- Multiply by spherical harmonics for total

$$R_{nl} \propto \rho^l e^{-\rho} L_{n-l-1}^{2l+1}(2\rho)$$

$$\rho = kr$$

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

$$E = -13.6 \frac{Z^2}{n^2} \frac{\mu}{\mu_H} eV$$

- This only depends on n
- Properties of Laguerre polynomials require $n \geq l + 1$ so $l \leq n - 1$
 - only features for $1/r$ potential
 - all have energies dep on n
- Degeneracy
 - For given n, n values of l which have same energy so the level is n degenerate
 - for each l, $2l + 1$ values of m, so in fact each level is
 - $\sum_{l=0}^n (2l + 1)$ degenerate
 - $2n^2$ degenerate later on once spin is added

$$\rho = kr = \frac{\mu Z e^2}{2\pi\epsilon_0 \hbar^2 \rho_0} r = \frac{\mu Z e^2}{4\pi\epsilon_0 \hbar^2 n} r$$

$$a = \frac{4\pi\epsilon_0 \hbar^2}{\mu Z e^2}$$

- a is the Bohr radius for hydrogen of $5.29 \times 10^{-11} m^{-1}$

$$\Psi_{nlm} \propto \left(\frac{r}{2a}\right)^l e^{-\frac{r}{2a}} L_{n-l-1}^{2l+1}\left(\frac{2r}{a}\right) Y_{lm}(\theta, \phi)$$

- Get the normalisation constant by

$$\int_{r=0}^{\infty} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \psi^*(r, \theta, \phi) \psi(r, \theta, \phi) r^2 \sin \theta d\theta d\phi dr = 1$$

$$E = -\frac{\mu}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}$$

Transitions Between Energy Levels

- If Hydrogen is some stationary state, ψ_{nlm} , it should be stable, but perturbations can cause the electron to transition to another stationary state
 - collision with atom/photon/electron
 - either by absorbing energy or emitting it
 - perturbations are always present so transitions - quantum jumps - are constantly occurring
 - transitions are between discrete energy levels of n difference

$$E_\gamma = E_i - E_f = 13.6 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) eV$$

- Transitions to ground state give rise to Lyman series of emissions lines with wavelengths given by

$$E = \frac{hc}{\lambda} = 13.6 \left(1 - \frac{1}{n^2}\right) eV ; n \geq 2$$

- page 45 for table of Lyman series
 - tend to a limit for shortest wavelength possible

12. Generalising Angular Momentum

Preview of Spin Concept

- Spin is the spinning of particles around own axis
 - electron doesn't have internal structure though
 - spin is *intrinsic* angular momentum

Review of Angular Momentum

- Two components of \underline{L} cannot be measured simultaneously
 - one component can be measured with L^2 however
 - Share a common set of eigenstates

Angular Momentum Ladder Operators

- page 47

$$L_{\pm} = L_x \pm iL_y$$

$$[L^2, L_{\pm}] = 0$$

- same principle as other ladder operators

$$\hbar L_+ f_{\lambda, \mu} \implies L_z(L_+ f_{\lambda, \mu}) = (\mu + 1)\hbar L_+ f_{\lambda, \mu}$$

Properties

- Must be a top and bottom rung
 - max and min values for μ
 - $L_+ f_{\lambda, \mu_{max}} = 0$
- $\lambda = \mu_{max}(\mu_{max} + 1)$
 - Legendre polynomial approach
 - $\mu_{min} = -\mu_{max}$
 - this leads to the range of values for m
- μ can take half-integer values
 - comes from addition of intrinsic and extrinsic

Overview of general angular momentum, \underline{J}

- \underline{J} is angular momentum if its operator components, J_x, J_y, J_z satisfy

$$\begin{aligned}
&= i\hbar J_z ; [J_z, J_x] = i\hbar J_y \\
J^2 &= J_x^2 + J_y^2 + J_z^2 \\
[J^2, J_x] &= 0
\end{aligned}$$

- Common eigenfunctions of J^2 and J_z
 - eigenvalues of $j(j+1)\hbar^2$ and $m_j\hbar$ respectively
- Ladder operators
 - $J_z J_{\pm} f_{j,m_j} = (m_j \pm 1)\hbar J_{\pm} f_{j,m_j}$
- Can't go on forever so top and bottom values for m
 - $m_{max} - m_{min} \in \mathbb{N}$
 - $j = \frac{\mathbb{N}}{2}$
- page 49

$$\underline{J} = \underline{L} + \underline{S}$$

13. Spin

- \underline{S} as angular momentum spin operator
 - S^2 eigenvalues, $s(s+1)\hbar^2$
 - do not have spherical harmonic eigenfunctions
 - eigenstates not functions of spatial coordinates
- intrinsic property of particle

Electron Orbiting Magnetic Field

$$\begin{aligned}
\mu_l &= IA = -\frac{evr}{2} = -\frac{e}{2m_e} m_e v r = -\frac{e}{2m_e} L \\
\underline{\mu}_l &= -\frac{e}{2m_e} \underline{L} = -\frac{\mu_B}{\hbar} \underline{L} \\
\mu_B &= \frac{e\hbar}{2m_e}
\end{aligned}$$

- μ_B is the Bohr magneton, natural unit of microscopic magnetic moment
 - $= 9.27 \times 10^{-24} J T^{-1}$
 - $= 5.79 \times 10^{-5} eV T^{-1}$
- $-\frac{\mu_B}{\hbar} \underline{L}$ is quantum mechanical magnetic moment
 - $(\mu_l)_z = -\frac{\mu_B}{\hbar} \underline{L}_z$
- For a hydrogen atom,
 - $(\mu_l)_z = -m_l \mu_B, \quad -l \leq m_l \leq +l, \in \mathbb{N}$

Dirac Notation

$$\begin{aligned}
|\chi_+\rangle &\rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} ; |\chi_-\rangle \rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\
\langle \chi_+ | &\rightarrow (1 \quad 0) ; \langle \chi_- | \rightarrow (0 \quad 1)
\end{aligned}$$

- kets are equivalent to column vectors
- bras to row vectors
- operators to square matrices

- taking complex conjugate of inner product can be seen as taking Hermitian conjugate of three matrices:
 - $(ABC)^\dagger = C^\dagger B^\dagger A^\dagger$
 - $\langle \psi_n | A | \psi_m \rangle^* = \langle \psi_m | A^\dagger | \psi_n \rangle$
 - $\langle \psi_n | A | \psi_m \rangle^* = \langle \psi_m | A | \psi_n \rangle$, if A is Hermitian
- Bra-Ket inner products were introduced earlier as shorthand for integrals
 - more general than this for when there are no spatial coordinates to integrate over
 - * i.e. spin

14. Time-dependent Perturbation Theory

Small Modification to Hamiltonian

- Solved time-dependent Schrodinger for some Hamiltonian, H^0
 - Get eigenfunctions, ψ_n^0 for each energy level
 - $H^0 \psi_n^0 = E_n^0 \psi_n^0$
 - orthonormal
- Perturb the system slightly
 - a small bump in the square well
 - want to find eigenfunctions and eigenvalues for new Hamiltonian
 - can't solve this exactly but can use *perturbation theory* for approx solution
 - * build on known solutions of unperturbed system
- Write new Hamiltonian as
 - $H = H^0 + \lambda H'$
 - * H' is the perturbation

Power expansion

- Want to write E_n and ψ_n as power series in λ

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$

- E_n^1 and ψ_n^1 refer to the first order corrections for the nth eigenfunctions
 - superscript 2 is second order correction etc

$$H\psi_n = E_n\psi_n$$

$$(H = H^0 + \lambda H')(\psi_0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(\psi_0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots)$$

- collect powers of lambda together

$$H^0 \psi_0 + \lambda(H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2(H^0 \psi_n^2 + H' \psi_n^1) + \dots = E_n^0 \psi_n^0 + \lambda(E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2(E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \dots$$

First Order correction

- Zeroth order expansion is just no perturbation
- Look at first order in λ :

$$H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$$

- Take an inner product with ψ_n^0
 - use Dirac notation for maximum generality
 - some terms from this will cancel so:

$$E_n^1 = \langle \psi_n^1 | H' | \psi_n^0 \rangle$$

- Expressing this with integrals instead yields the same result:

$$E_n^1 = \int (\psi_n^0)^* H' \psi_n^0 dx$$

- Either way, the first order correction to an energy eigenvalues is the **expectation value** of the perturbation using the unperturbed eigenfunctions

1D Square Well with Delta Function

- With Kronacker delta, $\delta_{nm} = 1$ if $n = m$, or 0 otherwise
 - The **Dirac Delta** is the continuum version:

$$\int f(x) \delta(x - x_0) dx = f(x_0)$$

- collapses any integral to the point marked out by the function
 - $\int \delta(x - x_0) dx = 1$
- So if we have $H' = \lambda \delta(x - \frac{a}{2})$ then

$$E_n^1 = \int \int (\psi_n^0)^* H' \psi_n^0 dx$$

$$E_n^1 = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \lambda \delta\left(x - \frac{a}{2}\right) \sin\left(\frac{n\pi x}{a}\right) dx = \frac{2\lambda}{a} \sin^2\left(\frac{n\pi}{2}\right)$$

- This is 0 if n is even
 - no correction to even E_n^0
 - but $E_n^1 = \frac{2\lambda}{a}$ for odd n
 - perturbation has no effect for even n
 - odd n gets a peak and energies are shifted

First Order Correction to Wavefunction

- Calc by writing $\psi_n^1 = \sum_{n \neq l} c_{nl} \psi_l^0$
 - substitute this into the first order correction
 - take inner product with ψ_l^0

$$c_{nl} = - \frac{\langle \psi_l^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_l^0)}$$

- To first order, $\psi_n \approx \psi_n^0 + \lambda \psi_n^1$

15. Degenerate Perturbation Theory

- $E_n - E_m \neq 0$ isn't always the case

Twofold Degeneracy

- Suppose energy level with exactly two states, ψ_a^0 and ψ_b^0 , giving same energy of E^0
 - any linear combination of these gives E^0
 - e.g. in Hydrogen, $l = 0$, $m = 0$, $m_s = \pm \frac{1}{2}$
- The perturbation $\lambda H'$ breaks the degeneracy, we want to find these unperturbed states
- Same first order correction:

$$H^0 \psi^1 + \lambda H' \psi^0 = E^0 \psi^1 + \lambda E^1 \psi^0$$

- multiply by conjugate of one of the states, ψ_a^{0*} , or $\langle \psi_a^0 |$, and integrate

$$\langle \psi_a^0 | H' | \psi^0 \rangle = E^1 \langle \psi_a^0 | \psi^0 \rangle$$

- full derivation on page 55
- use $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$:

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = E^1 \alpha$$

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1$$

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle = \int \psi_i^{0*} H' \psi_j^0 dx$$

- can assemble this into eigenvalue matrix equation:

$$\begin{aligned} & \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \\ \implies & (W_{aa} - E^1)(W_{bb} - E^1) - W_{ab}W_{ba} = 0 \\ \implies & (E^1)^2 - (W_{aa} + W_{bb})E^1 + (W_{aa}W_{bb} - |W_{ab}|^2) = 0 \because W_{ab} = W_{ba}^* \\ & E_{\pm}^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right] \end{aligned}$$

- If two states are degenerate, both having the same energy, any linear combination also has the same energy
- A small perturbation H' cause a small change in energy and the first order approximation for this, E^1 is given by the solution of a matrix equation
- see pages 56 & 57 for examples on this

16. Degenerate Perturbation Theory II

Link to non-degenerate perturbation theory

- page 58

Higher-order degeneracy

- For n-fold degeneracy, get $n \times n$ matrix, with n roots
 - some roots may be zero

Example in 3D Square Well

- page 58 and 59
- integration n stuff

$$\begin{pmatrix} 1-\omega & \kappa & 0 \\ \kappa & 1-\omega & 0 \\ 0 & 0 & 1-\omega \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \omega = \frac{4E^1}{V_0}$$

Meaning of Vector components

- α, β, γ are the amplitudes of the states $\psi_{211}, \psi_{121}, \psi_{112}$ in a general superposition state
- page 60 has eigenvector stuff

17. Degenerate Perturbation Theory and Hydrogen

Spin-Orbit Coupling

- Perturbation from magnetic dipole moment generated by electron spin, μ_s is

$$H'_{so} = -\underline{\mu}_s \cdot \underline{B}$$
$$\underline{\mu}_s = -g_s \left(\frac{e}{2m_e} \right) \underline{S}, \quad g_s \approx 2$$
$$\underline{\mu}_s = \frac{-e}{m_e} \underline{S}$$

- From electron's PoV, can see a current loop from the nucleus 'orbiting' it

$$L = \frac{4\pi m_e r^3 B}{\mu_0 e}$$
$$\underline{L} = \frac{4\pi \epsilon_0 c^2 m r^3}{e} \underline{B}$$
$$H'_{so} = \frac{e^2}{4\pi c^2 m^2 r^3} \underline{S} \cdot \underline{L}$$

- Factor of 0.5 due to special relativity as well:

$$H'_{so} = \frac{e^2}{8\pi c^2 m^2 r^3} \underline{S} \cdot \underline{L}$$

Commutation Properties

- pages 61 - 62
- use total angular momentum, J^2

$$[J^2, \underline{L} \cdot \underline{S}] = 0$$

- as all of the components of these commute with each other
- think about joint eigenfunctions of the operators H^0, L^2, J^2, S^2, J_z
 - since J is conserved

Adding Angular Momenta

- max value of $J_z = l + s$
 - $-l - s \leq J_z \leq l + s$, in integer steps
 - correspond to value $j = l + s$
 - * from $j(j+1)\hbar^2$ in J^2
- see page 62 for visualisation and tables

18. Degenerate Perturbation Theory and Hydrogen II

Spin Orbit

$$J^2 = (\underline{L} + \underline{S}) \cdot (\underline{L} + \underline{S}) + L^2 + S^2 + 2\underline{L} \cdot \underline{S}$$

$$\underline{J} \cdot \underline{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

- Eigenvalues of $\underline{L} \cdot \underline{S}$ are eigenvalues of above:

$$\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)] = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$$

- Spin is $\frac{1}{2}$
- Can plug this into the first order correction to the energy eigenvalues
 - page 64
 - can then be pulled outside the expression as just numbers
- Spin-orbit coupling typically leads to $\frac{E_n^1}{E_n^0} \approx \frac{E_n^0}{mc^2}$

Correction to electron-proton potential (Darwin Term)

- Must correct the assumption that these are point particles
- Position certain only to its Compton wavelength

$$\lambda_C = \frac{\hbar}{mc}$$

- Charge of the electron is therefore smeared out over this volume
 - smearing for the proton is smaller by a factor of the mass ratios so is negligible
- The correction made to the potential if the electron is at the same position as the proton is the Darwin term:

$$H_D^1 = \frac{\pi\hbar^2}{2m^2c^2} \frac{e^2}{4\pi\epsilon_0} \delta(\underline{r})$$

- See footnotes on page 65 for explanation on 3D delta function
- Independent of spin
- Commutes with all angular momentum operators
 - can use non-degenerate perturbation theory

$$E_n^1 = \frac{\pi\hbar^2}{2m^2c^2} \frac{e^2}{4\pi\epsilon_0} \int_V \psi_{nlm}^* \delta(\underline{r}) \psi_{nlm} dV$$

- Only acts at the origin
 - therefore only on states which are non-zero at the origin
 - this is only for $l, m = 0$

- Laguerre polynomials for $l = 0$ are $L_{n-1}^1(0)$ so just a constant term in the polynomial
- *simplification maths on page 65*

$$E_n^1 = \frac{2}{mc^2} (E_n^0)^2 n$$

Relativistic corrections to kinetic energy

- Special relativity KE is given by

$$\begin{aligned} E^2 &= (T + mc^2)^2 = p^2 c^2 + m^2 c^4 \\ T + mc^2 &= mc^2 \sqrt{1 + \frac{p^2}{m^2 c^2}} \\ \Rightarrow T &\approx \frac{p^2}{2m} - \frac{1}{8} \frac{p^4}{m^3 c^2} \\ &= T^0 - \frac{1}{2mc^2} (T^0)^2 \end{aligned}$$

- Using a Taylor expansion on the square root
- T^0 is the non-relativistic KE, and the other term is the lowest order correction for relativity
- Commutation here allows for non-degenerate perturbation theory again

$$\begin{aligned} E_n^1 &= -\frac{1}{2mc^2} \int \psi_n^{0*} [H - V(r)]^2 \psi_n^0 dV \\ \Rightarrow &= -\frac{1}{2mc^2} [(E_n^0)^2 - 2E_n^0 \langle V(r) \rangle + \langle V(r)^2 \rangle] \end{aligned}$$

- *Full derivations for this on page 66*

$$E^1 = -\frac{(E_n^0)^2}{2mc^2} \left[\frac{4n}{(l + \frac{1}{2})} - 3 \right]$$

19. Hydrogen Fine Structure

Total First Order Correction

- Can add all the first order correction terms together to get final:

$$E_{nj}^1 = \frac{(E_n^0)^2}{2mc^2} \left(3 - \frac{4n}{j + \frac{1}{2}} \right)$$

Also written as:

$$\begin{aligned} E_n^0 &= -\alpha^2 \frac{mc^2}{2n^2} \\ \alpha &= \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} \end{aligned}$$

- α is a dimensionless fine structure constant
- see page 67
- Collectively, all the extra terms got from expanding E_{nj}^1 , and the additional level of structure they reveal, are known as the fine structure.

Ground State of Hydrogen

- Only one value for j as $l = 0$
 - $j = \frac{1}{2}$, from the spin
 - gives a relative correction to the ground state
 - * page 67

$$\frac{\Delta E_1}{E_1^0} = \frac{\alpha^2}{4}$$

- This means the ground state is slightly lower than -13.6eV

Quantum Number Sets and Balmer Series

- page 68 - 69

Lamb Splitting

- There is a difference between $2s_{1/2}$ and $2p_{1/2}$ not noticed on pages 68 - 69
 - called Lamb shift, of order α^5
 - comes from interaction between electron and vacuum fluctuations of quantised EM field
 - difference for between states of same n, j and different l

Hyperfine Splitting

- Another energy shift
 - $\times 10$ smaller than Lamb
- Arises from proton's spin
 - interaction with electron's magnetic dipole changes potential
 - page 70

20. Formalities and the Correspondence Principle

Marginal Probability Distributions

- Recap of probability distributions for 1D and 3D wavefunctions on page 71
- For wavefunctions split into radial wavefunctions and spherical harmonics, $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$
 - The probability distributions for the radial wavefunction and for the spherical harmonic can be separated entirely

Time-energy uncertainty principle

$$\begin{aligned}\Delta t &= \frac{\Delta x}{v} = \frac{m\Delta x}{p} \\ E &= \frac{p^2}{2m} \therefore \Delta E = \frac{2p\Delta p}{2m} \\ \Delta t \Delta E &= \frac{m\Delta x}{p} \frac{2p\Delta p}{2m} = \Delta x \Delta p \geq \frac{\hbar}{2}\end{aligned}$$

- Note that position, momentum, and energy are all dynamical variables
 - i.e. measurable characteristics of the system

- Time is not a dynamical variable
 - Δt is the time it takes for the system to change substantially
 - **Time is not an operator belonging to the particle, it is a parameter describing the evolution of the system**
- A state existing for a short time cannot have a definite energy
 - $E = \hbar\omega$, so the frequency of the system must be accurately known for the energy to be definite
 - accurately-known frequency requires the system to be around for a long period of time
 - short time \implies unknown frequency \implies high error in energy
- This is essentially

$$\Delta t = \Delta \langle B \rangle / \left(\frac{dB}{dt} \right)$$

- where B is some dynamical operator

The time evolution of expectation values

- Will use Dirac Notation here as:
 - a ket, $|\psi\rangle$, can be thought of as a column vector;
 - a bra, $\langle\psi| = (|\psi\rangle)^\dagger$, as the Hermitian conjugate of a ket, i.e. a row vector;
 - Hermitian operators as square Hermitian matrices
- Take the time derivative of the expectation value of a Hermitian operator, Q, in general:

$$\frac{d\langle Q \rangle}{dt} = \frac{d}{dt} \langle \psi | Q | \psi \rangle = \left(\frac{\partial \langle \psi |}{\partial t} \right) Q | \psi \rangle + \langle \psi | \frac{\partial Q}{\partial t} | \psi \rangle + \langle \psi | Q \left(\frac{\partial | \psi \rangle}{\partial t} \right)$$

- Full derivation on page 72, using

$$\begin{aligned} \frac{\partial | \psi \rangle}{\partial t} &= \left(-\frac{iH}{\hbar} \right) | \psi \rangle ; \quad \frac{\partial \langle \psi |}{\partial t} = \langle \psi | \left(\frac{iH}{\hbar} \right) \\ \implies \frac{d\langle Q \rangle}{dt} &= \frac{i}{\hbar} \langle [H, Q] \rangle + \left\langle \frac{\partial Q}{\partial t} \right\rangle \end{aligned}$$

Formalism

Ehrenfest Theorems

- If $Q = x$, then

$$\frac{d\langle x \rangle}{dt} = \frac{i}{\hbar} \langle [H, x] \rangle + \left\langle \frac{\partial x}{\partial t} \right\rangle$$

- $H = \frac{p^2}{2m} + V(x)$ so $[H, x] = -i\hbar \frac{p}{m}$
- The operator has no explicit time dependence, similarly to a coordinate system, as it is not the actual location of the particle
- Hence, the First Ehrenfest Theorem:

$$\frac{d\langle x \rangle}{dt} = \frac{i}{\hbar} \left\langle -i\hbar \frac{p}{m} \right\rangle = \frac{\langle p \rangle}{m}$$

- The second Ehrenfest Theorem can be proven similarly to get:

$$\frac{d\langle p \rangle}{dt} = - \left\langle \frac{dV}{dx} \right\rangle$$

- Can combine these two together to get a correspondence to the classical $F = ma$:

$$m \frac{d^2 \langle x \rangle}{dt^2} = \langle F \rangle$$

Virial Theorem

- Let $Q = xp$:

$$\begin{aligned} \frac{d\langle xp \rangle}{dt} &= \frac{i}{\hbar} \langle [H, xp] \rangle + \left\langle \frac{\partial \langle xp \rangle}{\partial t} \right\rangle \\ [H, p] &= i\hbar \frac{dV}{dx} \implies [H, xp] = [H, x]p + x[H, p] = \left[-\frac{i\hbar}{m}p\right]p + x\left[i\hbar \frac{dV}{dx}\right] \\ &= \frac{i}{\hbar} \left\langle -\frac{i\hbar}{m}p^2 + i\hbar x \frac{dV}{dx} \right\rangle \\ &= \left\langle \frac{p^2}{m} - x \frac{dV}{dx} \right\rangle \end{aligned}$$

- In equilibrium, i.e. for a stationary state, expectation values do not change with time
 - the time derivative is zero

$$\left\langle \frac{p^2}{m} \right\rangle = \left\langle x \frac{dV}{dx} \right\rangle \iff \langle T \rangle = \frac{1}{2} \left\langle x \frac{dV}{dx} \right\rangle$$

The Correspondence Principle

The correspondence principle states that the behaviour of systems described by the theory of quantum mechanics reproduces classical physics in the limit of large quantum numbers.

In other words, it says that for large orbits and for large energies, quantum calculations must agree with classical calculations.

Classical quantities appear in quantum mechanics in the form of expected values of observables, and as such the Ehrenfest theorems (which predict the time evolution of the expected values) is an example of the correspondence principle.