# Quantum Mechanics Summary Notes

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Notes are based on lectures by Jonathan Pritchard.

# Contents

# 1 Introduction, Recap and Background

## 1.1 The Schrödinger Equation

**Definition** (The Schrödinger Equation)**.** *The time-dependent Schrödinger equation for a particle of mass $m$ in a potential $V : \mathbb{R}^3 \to \mathbb{R}$ is given by:*

$$i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r},t) + V(\boldsymbol{r})\psi(\boldsymbol{r},t) = \hat{H}\psi(\boldsymbol{r},t), \tag{1.1}$$

where $\psi : \mathbb{R}^4 \to \mathbb{C}$ is the *wavefunction.*

**Definition** (Wavefunction)**.** *The wavefunction is defined so that the probability of finding a particle in volume $\Omega \subseteq \mathbb{R}^3$ at time $t$ is*

$$P(\boldsymbol{r} \in \Omega) = \int_\Omega d\Omega\, |\psi(\boldsymbol{r},t)|^2 . \tag{1.2}$$

**Corollary** (Normalization)**.** *Equation* (1.2) *implies the normalization condition:*

$$\int_{\mathbb{R}^3} d\Omega\, |\psi(\boldsymbol{r},t)|^2 = 1 \quad \forall t \in \mathbb{R}. \tag{1.3}$$

If the potential function is time independent, then equation (1.1) can be separated in position and time to yield an *eigenvalue problem.* The general solution is then given by

$$\psi(\boldsymbol{r},t) = \sum_n u_n(\boldsymbol{r})e^{-iE_nt/\hbar}, \tag{1.4}$$

where $u_n(\boldsymbol{r})$ is a solution to the *time-independent Schrödinger equation.*

**Definition** (Time-independent Schrödinger Equation)**.** *The TISE is an eigenvalue equation of the following form:*

$$-\frac{\hbar^2}{2m}\nabla^2 u(\boldsymbol{r}) + V(\boldsymbol{r})u(\boldsymbol{r}) = E_n u(\boldsymbol{r}). \tag{1.5}$$

The eigenvalues $E_n$ are discrete if the boundaries of the problem are finite, continuous if they are infinite.

## 1.2 Solutions to the Schrödinger Equation

### 1.2.1 Free particle

For a free particle, the equation reduces to the wave equation with the solution

$$\psi(\boldsymbol{r},t) = \int A(\boldsymbol{k}) \exp i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t) d^3\boldsymbol{k},$$

where $|\boldsymbol{k}| = \sqrt{2mE/\hbar^2}$.

### 1.2.2 Infinite square well

The solutions are sines and cosines satisfying the boundary conditions. We have quantised energy and wavenumber:

$$k_n = \frac{n\pi}{2a}, n \in \mathbb{Z},$$
$$E_n = \frac{\hbar^2 k_n^2}{2m}.$$

where $2a$ is the width of the well. The results generalise to higher dimensions.

# 2 The Finite Square Well (1-D)

Define the potential to be

$$V(x) = -V_0 \text{ for } |x| \leq a, \quad V(x) = 0 \text{ for } |x| > a$$

for a (positive) constant $V_0$.

## 2.1 Unbound states

If $E > 0$, the solutions are oscillatory in all space. There is no energy quantisation.

## 2.2 Bound states

If $-V_0 < E < 0$, the solutions are bound. Inside the well, we have

$$\frac{d^2u}{dx^2} + k^2 u = 0,$$

and on the outside

$$\frac{d^2u}{dx^2} - \gamma^2 u = 0$$

where

$$k = \frac{\sqrt{2m\,(E + V_0)}}{\hbar}, \quad \gamma = \frac{\sqrt{-2mE}}{\hbar}.$$

Solving the equations and imposing boundary conditions (continuous $u$ and $u'$) leads to two relationships between $\gamma$ and $k$. These relations come from treating even and odd parity solutions separately. This is justified since the potential is even, a solution must be either even or odd.

Even parity:

$$\gamma = k \tan(ka).$$

Odd parity:

$$\gamma = -k \cot(ka)$$

Using the expressions for $k$ and $\gamma$ in terms of the energy, we obtain conditions for energy.

## 2.3 Energy values

It can be shown that

$$\gamma^2 + k^2 = \frac{2mV_0}{\hbar^2}$$

$$\gamma = \sqrt{\frac{2mV_0}{\hbar^2} - k^2}.$$

The expression for $\gamma$ above is independent of $a$, and the expressions involving tangents and cotangents were independent of $V_0$. This means on $\gamma$-$k$ axis, the expressions can be plotted and the solutions will be the intersections.

## 2.4 Comparison with the infinite square well

It can be shown that in the limit $V_0 \to \infty$, the solutions converge to an infinite square well.

# 3 Potential Step and Barrier

Simple to solve step. Barrier is more algebra but conceptually as simple. I will only state the results.

### 3.1 Potential step

The potential is defined as: $V = 0$ for $x < 0$ and $V = V_0$ for $x > 0$.
**Case 1:** $E < V_0$.

$$r = \left(\frac{k - i\gamma}{k + i\gamma}\right),$$

$$t = \left(\frac{2k}{k + i\gamma}\right),$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}, \quad \gamma = \frac{\sqrt{2m\left(V_0 - E\right)}}{\hbar}.$$

**Case 2:** $E > V_0$

$$r = \left(\frac{k_L - k_R}{k_L + k_R}\right),$$

$$t = \left(\frac{2k_L}{k_L + k_R}\right),$$

where

$$k_L = \frac{\sqrt{2mE}}{\hbar}, \quad k_R = \frac{\sqrt{2m\left(E - V_0\right)}}{\hbar}.$$

The transmission and reflection amplitudes can be used to find transmission and reflection coefficients as follows:

$$R = |r|^2 = \frac{\left(k_L - k_R\right)^2}{\left(k_L + k_R\right)^2} < 1$$

$$T = \frac{4k_L^2}{\left(k_L + k_R\right)^2}\frac{k_R}{k_L} = \frac{4k_L k_R}{\left(k_L + k_R\right)^2},$$

where for the transmission coefficient the ratio of the fluxes was used (as the wavenumbers are different).

### 3.2 Potential barrier

We can define a barrier potential as: $V = 0$ for $x < 0$ and $x > w$, $V = V_0$ for $0 < x < w$.

The critical result is that for large $\gamma$, i.e. for $E \ll V_0$, then the transmission coefficient goes as

$$T \sim e^{-2\gamma w}.$$

## 4 The Simple Harmonic Oscillator

The normalised energy eigenstates in terms of Hermite polynomials are given by:

$$u_n(y) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(y) e^{-y^2/2}.$$

The solution is obtained by asymtotic analysis, followed by variation of parameters and a series solution to the resulting simplified equation.

# 5 Postulates of QM

**Postulate 1.** *For every dynamical system, there exists a wavefunction that is a continuous, square-integrable, single valued function of the parameters of the system and of time and from which all possible predictions about the physical properties of the system can be obtained.*

# 6 Hermitian Operators

**Postulate 2.** *Every dynamical variable may be represented by an Hermitian operator whose eigenvalues represent the possible results of carrying out a measurement of the value of the dynamical variable. Immediately after such a measurement, the wavefunction of the system will be identical to the eigenstate corresponding to the eigenvalue obtained as a result of the measurement.*

**Definition** (Hermitian operator)**.** *An operator $\hat{Q}$ is said to be Hermitian if it is equal to its Hermitian conjugate. This can be stated as:*

$$\langle\phi|Q|\psi\rangle = \overline{\langle\psi|Q|\phi\rangle} \quad \forall\, |\phi\rangle, |\psi\rangle \in \mathcal{H}.$$

**Corollary** (Real eigenvalues)**.** *It follows from the definition of an Hermitian operator that its eigenvalues must be real.*

**Corollary** (Orthogonal eigenstates)**.** *Assuming the eigenvalues are not degenerate, it can be shown that the eigenstates of Hermitian operators are orthogonal.*

**Postulate 3.** *The operators representing the position and momentum of a particle are $x$ and $-i\hbar d/dx$ respectively. Operators representing other dynamical variables bear the same function relation to these as do the corresponding classical quantities to the classical position and momentum variables.*

# 7 Complete Orthonormal Sets

Any Hermitian operator forms a self-adjoint eigenvalue problem. By extension, the set of orthogonal eigenstates are complete. Then, any function can be represented as a sum of the eigenstates as

$$\psi = \sum_n c_n \phi_n.$$

The coefficients $c_n$ are given by

$$c_n = \int \overline{\phi}_n \psi dx.$$

This can be written in Dirac notation as:

$$|\psi\rangle = \sum_n |\phi_n\rangle\langle\phi_n|\psi\rangle.$$

We state that $|c_n|^2$ is the *probability* that a measurement of the physical quantity related to the Hermitian operator would give the eigenvalue of the $n^{\text{th}}$ eigenstate.

**Postulate 4.** *When a measurement of a dynamic variable represented by a Hermitian operator is carried out on a system whose wavefunction is $\psi$, then the probability of the result being equal to a particular eigenvalue $\lambda_n$ will be $|c_n|^2$, where $\psi = \sum_n c_n\phi_n$ and the $\phi_n$ are the eigenstates of the operator corresponding to the $\lambda_n$.*

# 8 Time Dependence

**Postulate 5.** *Between measurements, the development of the wavefunction with time is governed by the time-dependent Schrödinger equation.*

**Corollary.** *If the future wavefunction only depends on the initial condition, i.e. on the eigenstate of the measured eigenvalue, then it cannot have any dependence on what the wavefunction was before the collapse. Hence, any wavefunction which could have given the measured eigenvalue may have existed before, but this information is completely lost. Hence, the previous wavefunction is in general "forgotten", along with any properties it may have had.*

## 8.1 TDSE solutions

We know that energy eigenstates evolve as $u_n(x)e^{-iE_nt/\hbar}$, so the time evolution of a general solution has the form

$$\psi(x,t) = \sum_n a_n u_n(x) e^{-iE_nt/\hbar}.$$

Since the wavefunction evolves with time, the expansion coefficients can be considered as a function of time. We can rewrite the expression above as

$$\psi(x,t) = \sum_n \left(a_n e^{-iE_nt/\hbar}\right) u_n(x) = \sum_n a_n(t) u_n(x)$$

The probabilities for measuring the energy values are time-independent, since

$$P_n(t) = |a_n(t)|^2 = |a_n(0)|^2 \, e^{iE_nt/\hbar} e^{-iE_nt/\hbar} = |a_n(0)|^2 = P_n(0).$$

## 8.2 Measurements with time dependence

Suppose we measure the momentum of a state at time $t = 0$. The wavefunction collapses to the momentum state corresponding to the result of our measurement, such that

$$\phi_{measured}(x) = \psi(x, t=0) = \sum_n b_n u_n(x)$$

for some coefficients $b_n$. Now suppose we let the wavefunction evolve for some time and measure the momentum again at time $t = t_1$. The wavefunction at $t = t_1$ is given by

$$\psi(x,t_1) = \sum_n b_n u_n(x) e^{-iE_nt_1/\hbar}.$$

We can represent this in terms of momentum states:

$$\psi(x,t_1) = \sum_p c_p \phi_p(x),$$

where the coefficients $c_p$ are given by

$$c_p = \int \overline{\phi_p}(x)\psi(x,t_1)dx.$$

In general, several of the $c_p$ will be non-zero, so the momentum is uncertain even though it follows from a previous momentum measurement.

# 9 Commutators and Anticommutators

**Definition** (Commutator)**.** *Given two operators $\hat{Q}$ and $\hat{P}$, the commutator is an operator defined by*

$$\left[\hat{Q},\hat{P}\right] = \hat{Q}\hat{P} - \hat{P}\hat{Q}.$$

**Corollary.** *It is trivial to show the following properties of commutators, $\forall\, \hat{Q},\hat{P}$ we have*

$$\left[\hat{Q},\hat{P}\right] = -\left[\hat{Q},\hat{P}\right],$$

$$\left[\hat{Q},\hat{Q}\right] = 0,$$

$$\left[\hat{Q}^m,\hat{Q}^n\right] = 0, \quad n,m \in \mathbb{N}.$$

**Definition** (Commuting operators)**.** *Operators that have a commutator which is zero are said to commute.*

**Definition** (Conjugate operators)**.** *Operators that have a commutator which is $i\hbar$ are said to be conjugate variables.*

The commutator of $\hat{x}$ and $\hat{p}$ is

$$[\hat{x},\hat{p}] = i\hbar.$$

Note that as the commutator is on the order of $\hbar$, in the classical limit it tends to zero.

## 9.1 Hermitian combinations

**Proposition.** *The commutator of two Hermitian operators is anti-Hermitian.*

Let $\hat{Q}$ and $\hat{P}$ be two Hermitian operators. Then, for any $|\psi\rangle, |\phi\rangle \in \mathcal{H}$, we have the following relations:

$$\langle\phi|\hat{Q}\hat{P}|\psi\rangle = \langle\hat{P}\hat{Q}\phi|\psi\rangle, \quad \langle\phi|\hat{P}\hat{Q}|\psi\rangle = \langle\hat{Q}\hat{P}\phi|\psi\rangle.$$

Hence, subtracting

$$\langle\phi|[\hat{Q},\hat{P}|\psi\rangle = \langle[\hat{P},\hat{Q}]\phi|\psi\rangle = -\langle[\hat{Q},\hat{P}]\phi|\psi\rangle.$$

Therefore, we conclude $[\hat{Q},\hat{P}]$ is anti-Hermitian.

Since the commutator is anti-Hermitian, it cannot represent a physical variable. However, we can convert any anti-Hermitian operator to a Hermitian operator by multiplying by $i$. This is easy to show, let $\hat{R}$ be an anti-Hermitian operator. Then, we have for all $|\psi\rangle, |\phi\rangle \in \mathcal{H}$

$$\langle\phi|i\hat{R}\psi\rangle = i\langle\phi|\hat{R}\psi\rangle = -i\langle\hat{R}\phi|\psi\rangle = \langle i\hat{R}\phi|\psi\rangle.$$

This means $i$ times the commutator of two observables can itself correspond to an observable.

**Definition** (Anticommutator)**.** *Given two operators $\hat{Q}$ and $\hat{P}$, the anticommutator is defined as*

$$\left\{\hat{Q},\hat{P}\right\} = \hat{Q}\hat{P} + \hat{P}\hat{Q}.$$

It is easy to show that

$$\left\{\hat{Q},\hat{P}\right\} = \left\{\hat{P},\hat{Q}\right\}$$

and

$$\left\{\hat{Q},\hat{Q}\right\} = 2\hat{Q}.$$

Similarly, it can be shown that the anticommutator of Hermitian operators is also Hermitian.

Finally, we can write the product of two operators in terms of commutators and anticommutators as follows:

$$\hat{Q}\hat{P} = \frac{1}{2}\left\{\hat{Q},\hat{P}\right\} + \left[\hat{Q},\hat{P}\right]/.$$

### 9.2 Further examples

We look at the commutator of momentum and Hamiltonian. We know $\hat{H} = \hat{T} + \hat{V}$ so

$$\left[\hat{H}, \hat{p}\right] = \left[\hat{T}, \hat{p}\right] + \left[\hat{V}, \hat{p}\right].$$

The first is

$$\left[\hat{T}, \hat{p}\right] = \frac{1}{2m}\left[\hat{p}^2, \hat{p}\right] = 0.$$

It is also straightforward to show that

$$\left[\hat{V}, \hat{p}\right] = i\hbar\frac{dV}{dx}.$$

Hence,

$$\left[\hat{H}, \hat{p}\right] = i\hbar\frac{dV}{dx}.$$

The commutator of the Hamiltonian with position is

$$\left[\hat{H}, \hat{x}\right] = \left[\hat{T}, \hat{x}\right] = -\frac{i\hbar}{m}\hat{p}.$$

## 10 Compatibility, Expectation Values, Dirac Notation

**Definition** (Compatible observables)**.** *Two observables are called compatible if they share a common set of eigenstates.*

One example is the free particle Hamiltonian and momentum, where plane waves are eigenstates of both.

If two operators $\hat{Q}$ and $\hat{P}$ have a common set of eigenstates $phi_n$, then we can express any state as

$$\psi = \sum_n a_n \phi_n.$$

Then, we have for $\hat{Q}\hat{P}$ acting on $\psi$

$$\hat{Q}\hat{P}\psi = \sum_n a_n q_n p_n \phi_n = \sum a_n p_n q_n \phi_n = \hat{P}\hat{Q}\psi$$

where $r_n, q_n \in \mathbb{C}$. Therefore, we have for any two compatible observables

$$\left[\hat{Q}, \hat{P}\right] = 0.$$

It is also easy to show, assuming no degeneracies, that if the commutator of two operators is zero, they must be compatible.

### 10.1 Expectation values

**Definition** (Expectation value)**.** *The expectation value of an observable $\hat{Q}$, denoted $\langle\hat{Q}\rangle_\psi$ is given by*

$$\langle\psi|\hat{Q}|\psi\rangle,$$

*where $|\psi\rangle \in \mathcal{H}$.*

Expanding $|\psi\rangle$ in an orthonormal basis of eigenvectors of $\hat{Q}$ yields

$$\langle\hat{Q}\rangle_\psi = \sum_n q_n |c_n|^2$$

where $q_n$ are eigenvalues of $\hat{Q}$.

### 10.2 Dirac notation

This courses treatment of Dirac's formulation of QM is just shameful. I will include some definitions from David Skinner's "Principle of QM" notes.

**Definition** (Ket)**.** *Dirac denotes an element of $\mathcal{H}$ as $|\psi\rangle$, where the symbol "$|\ \rangle$" is known as a ket.*

**Definition** (Bra)**.** *An element of the dual space is written $\langle\phi|$, where the symbol "$\langle\ |$" is known as a bra.*

The relation between the ket $|\phi\rangle \in \mathcal{H}$ and the bra $\langle\phi| \in \mathcal{H}^*$ is the same as $\phi$ *vs* $(\phi, )$. The ket is a vector, whereas a bra is a functional.

Expanding a general state $|\psi\rangle$ as an integral

$$|\psi\rangle = \int_{\mathbb{R}} \psi(x')|x'\rangle dx',$$

we see that the complex coefficients are

$$\langle x|\psi\rangle = \int_{\mathbb{R}} \psi(x')\langle x|x'\rangle dx' = \psi(x).$$

In other words, the position space wavefunctions are nothing but the coefficients of a state $|\psi\rangle \in \mathcal{H}$ in a position continuum basis.

## 11 The Ehrenfest Theorem

It can be shown that the time derivative of the expectation value of an operator $\hat{Q}$ is

$$\frac{d\langle\hat{Q}\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H}, \hat{Q}]\rangle$$

where $\hat{H}$ is the Hamiltonian. Now, we can look at the time dependences of position and momentum operators. Using the commutation relations, we get

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

for position, and

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

for momentum. This leads us to the Ehrenfest theorem: *The equations of motion for the expectation values of observables are identical to the equations of motion for their classical counterparts.*

### 11.1 Conserved variables

The condition for an observable associated with $\hat{Q}$ to be conserved is that its expectation value must be constant in time, in other words

$$\langle[\hat{H}, \hat{Q}]\rangle_\psi = 0.$$

There are two cases under which this is satisfied. Firstly, it is satisfied for all $\hat{Q}$ when the wavefunction is an energy eigenstate - this is why energy eigenstates are stationary states. This case is state dependent.

The more interesting case is if the commutator of $\hat{Q}$ and $\hat{H}$ is zero. Then, the expectation value is constant for all states.

# 12 Measurement Spread

**Definition** (Rms deviation)**.** *We define the rms deviation $\Delta_\psi \hat{Q}$ of $\hat{Q}$ from its mean $\langle \hat{Q} \rangle_\psi$ in state $|\psi\rangle$ as*

$$(\Delta_\psi \hat{Q})^2 = \langle \psi | (\hat{Q} - \langle \hat{Q} \rangle_\psi)^2 | \psi \rangle$$

It is straightforward to show that the definition above reduces to

$$(\Delta_\psi \hat{Q})^2 = \langle \hat{Q}^2 \rangle_\psi - \langle \hat{Q} \rangle_\psi^2.$$

## 12.1 The difference operator

**Definition** (The difference operator)**.** *It is convenient to deal with a difference operator, defined given an operator $\hat{Q}$ and a state $|\psi\rangle$ as*

$$\hat{Q}'_\psi = \hat{Q} - \langle \hat{Q} \rangle_\psi$$

**Proposition.** *The difference operator of a Hermitian operator is also Hermitian.*

*Proof.* Since the expectation value term is just a real number, the proposition holds trivially.

# 13 The Uncertainty Principle

**Definition** (Cauchy-Schwarz inequality)**.** *Given $|\psi\rangle, |\phi\rangle \in \mathcal{H}$, the Cauchy-Schwarz inequality states that*

$$\||\psi\rangle\|^2 \||\phi\rangle\|^2 \geq |\langle \psi | \phi \rangle|^2.$$

We now make use of the difference operators. Since they are Hermitian, we have for all $|\psi\rangle \in \mathcal{H}$

$$(\Delta_\psi \hat{Q})^2 = \langle \psi | \hat{Q}'_\psi | \psi \rangle = \langle \hat{Q}'_\psi \psi | \hat{Q}'_\psi \psi \rangle = \||\hat{Q}'_\psi \psi\rangle\|^2.$$

Let $\hat{Q}$ and $\hat{R}$ be two Hermitian operators. Then, we have

$$\Delta_\psi \hat{Q}^2 \Delta_\psi \hat{R}^2 \geq \left| \langle \psi | \hat{Q}'_\psi \hat{R}'_\psi | \psi \rangle \right|^2.$$

Now, we write $\hat{Q}'_\psi \hat{R}'_\psi$ as

$$\hat{Q}'_\psi \hat{R}'_\psi = \frac{1}{2} \left( [\hat{Q}'_\psi, \hat{R}'_\psi] + \{\hat{Q}'_\psi, \hat{R}'_\psi\} \right).$$

The inequality now becomes

$$\Delta_\psi \hat{Q}^2 \Delta_\psi \hat{R}^2 \geq \frac{1}{4} \left| \left\langle [\hat{Q}'_\psi, \hat{R}'_\psi] \right\rangle_\psi + \left\langle \{\hat{Q}'_\psi, \hat{R}'_\psi\} \right\rangle_\psi \right|^2.$$

We would like to make use of the fact that the expectation values of Hermitian operators are real, to simplfy the expression above. The anti-commutator of two Hermitian operators is Hermitian, whereas the commutator of two Hermitian operators is anti-Hermitian. We make the commutator Hermitian by multiplying by $i$, hence the inequality becomes

$$\begin{aligned} \Delta_\psi \hat{Q}^2 \Delta_\psi \hat{R}^2 &\geq \frac{1}{4} \left| -i \left\langle i[\hat{Q}'_\psi, \hat{R}'_\psi] \right\rangle_\psi + \left\langle \{\hat{Q}'_\psi, \hat{R}'_\psi\} \right\rangle_\psi \right|^2 \\ &= \frac{1}{4} \left( \left\langle i[\hat{Q}'_\psi, \hat{R}'_\psi] \right\rangle_\psi^2 + \left\langle \{\hat{Q}'_\psi, \hat{R}'_\psi\} \right\rangle_\psi^2 \right). \end{aligned}$$

Rewriting in terms of $\hat{Q}$ and $\hat{R}$ yields

$$\left\langle [\hat{Q}'_\psi, \hat{R}'_\psi] \right\rangle_\psi = \left\langle [\hat{Q}, \hat{R}] \right\rangle_\psi$$

and

$$\left\langle \{\hat{Q}'_\psi, \hat{R}'_\psi\} \right\rangle_\psi = \left\langle \{\hat{Q}, \hat{R}\} \right\rangle_\psi - 2\langle \hat{Q} \rangle_\psi \langle \hat{R} \rangle_\psi.$$

Hence, we get the general form for the Heisenberg Uncertainty Principle:

$$\Delta_\psi \hat{Q}^2 \Delta_\psi \hat{R}^2 \geq \left( \left\langle \frac{1}{2}\{\hat{Q}, \hat{R}\} \right\rangle_\psi - \langle \hat{Q} \rangle_\psi \langle \hat{R} \rangle_\psi \right)^2 + \left\langle \frac{i}{2}[\hat{Q}, \hat{R}] \right\rangle_\psi^2.$$

It is important to make the following distinction between the two terms: the first term depends on the expectation values of the operators, which depends on the state $\psi$ whereas the second term only depends on the commutator of the two operators which is independent of the state (if the commutator is a constant, which it is for position and momentum). Therefore, we can equally write the uncertainty principle ignoring the first term (since it is strictly positive, it is mathematically allowed) to obtain:

$$\Delta_\psi \hat{Q} \Delta_\psi \hat{R} \geq \left\langle \frac{i}{2}[\hat{Q}, \hat{R}] \right\rangle_\psi.$$

# 14 Continuous Eigenvalues

This section again follows from David Skinner's "Principles of Quantum Mechanics" notes.

Given a complete orthonormal basis $\{|e_a\rangle\}$ of $\mathcal{H}$, we can expand a general ket $|\psi\rangle$ as

$$|\psi\rangle = \sum_a \psi_a |e_a\rangle$$

in terms of this basis. Then $\langle \chi|\psi\rangle = \sum_{a,b} \overline{\chi}_b \psi_a \langle e_b|e_a\rangle = \sum_a \overline{\chi}_a \psi_a$ as usual.

It's very useful to extend this idea to function spaces. In this case, we introduce a 'continuum basis' with elements $|a\rangle$ labelled by a continuous variable $a$, normalised so that

$$\langle a'|a\rangle = \delta(a' - a)$$

using the Dirac *delta*-function. Then we write

$$|\psi\rangle = \int \psi(a)|a\rangle da$$

to expand a general $|\psi\rangle$ in terms of the $|a\rangle$'s. The point of the normalization is that

$$\langle \chi|\psi\rangle = \int \overline{\chi(b)}\psi(a)\langle b|a\rangle dbda = \int \overline{\chi(b)}\psi(a)\delta(b-a)dbda = \int \overline{\chi(a)}\psi(a)da$$

which is the inner product we defined.

A key example of a 'continuum basis' is the *position* basis $\{|x\rangle\}$, where $x \in \mathbb{R}$. Expanding a general state as an integral

$$|\psi\rangle = \int_{\mathbb{R}} \psi(x')\,|x'\rangle dx'$$

we see that the complex coefficients are

$$\langle x|\psi\rangle = \int_{\mathbb{R}} \psi(x')\,\langle x|x'\rangle dx' = \psi(x).$$

The position space wavefunctions are coefficients of a state $|\psi\rangle \in \mathcal{H}$ in position continuum basis.

We could choose to expand the same vector in any basis. For example, we can expand in the momentum basis as $|\psi\rangle = \int_{\mathbb{R}} \tilde{\psi}(p)|p\rangle dp$ where the new coefficients $\tilde{\psi}(p) = \langle p|\psi\rangle$ are the *momentum space wavefunction.* Given that $\langle x|p\rangle = \mathrm{e}^{ixp/\hbar}/\sqrt{2\pi\hbar}$ so these two sets of coefficients are related by

$$\psi(x) = \langle x|\psi\rangle = \int_{\tilde{\mathbb{R}}} \tilde{\psi}(p)\langle x|p\rangle dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{\tilde{\mathbb{R}}} \mathrm{e}^{\mathrm{i}xp/\hbar}\tilde{\psi}(p)dp$$

$$\tilde{\psi}(p) = \langle p|\psi\rangle = \int_{\mathbb{R}} \psi(x)\langle p|x\rangle dx = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} \mathrm{e}^{-\mathrm{i}xp/\hbar}\psi(x)dx.$$

This is just the statement that the position and momentum space wavefunctions are each other's Fourier transforms.

# 15 QnA Lecture

# 16 Representations and Ladder Operators

## 16.1 Representations

In the momentum representation, we take $\hat{p} = p$, and to find $\hat{x}$ we use the commutator. The commutators are representation independent, so

$$[\hat{x}, \hat{p}] = i\hbar$$

is always true. Therefore

$$\hat{x} = i\hbar\frac{d}{dp}.$$

The momentum eigenstates are

$$\delta(p_m - p)$$

and the position eigenstates are

$$\frac{1}{\sqrt{2\pi\hbar}}\mathrm{e}^{ipx/\hbar}$$

## 16.2 SHO ladder operators

We define the ladder operators as

$$\hat{a} = \sqrt{\frac{m\omega_0}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega_0}}\hat{p}, \quad \hat{a}^\dagger = \sqrt{\frac{m\omega_0}{2\hbar}}\hat{x} - i\sqrt{\frac{1}{2m\hbar\omega_0}}\hat{p}.$$

They are not Hermitian, so they do not correspond to observables. We have

$$\left[\hat{a}, \hat{a}^\dagger\right] = 1, \quad \left\{\hat{a}, \hat{a}^\dagger\right\} = \frac{2\hat{H}}{\hbar\omega_0}.$$

We can write the Hamiltonian as

$$\hat{H} = \hbar\omega_0\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) = \hbar\omega_0\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right) = \frac{\hbar\omega_0}{2}\left(\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\right)$$

It can be shown, from the commutator of $\hat{a}$ with $\hat{H}$, that

$$\hat{H}\left(\hat{a}u_n\right) = \left(E_n - \hbar\omega_0\right)\left(\hat{a}u_n\right).$$

Hence $\hat{a}u_n$ is an eigenstate of $\hat{H}$ with energy $E_n - \hbar\omega_0$. The operator $\hat{a}$ is called a *lowering operator*. Similarly,

$$\hat{H}\left(\hat{a}^\dagger u_n\right) = \left(E_n + \hbar\omega_0\right)\left(\hat{a}^\dagger u_n\right)$$

so $\hat{a}^\dagger$ is called a *raising operator*. We then must have

$$\hat{a}u_0 = 0$$

so we have

$$0 = \hat{a}^\dagger \hat{a} u_0 = \left(\frac{\hat{H}}{\hbar\omega_0} - \frac{1}{2}\right) u_0 = \left(\frac{E_0}{\hbar\omega_0} - \frac{1}{2}\right) u_0$$

hence

$$E_0 = \frac{\hbar\omega_0}{2}.$$

We can solve for $u_0$ and obtain the set of eigenstates for the harmonic oscillator by applying the raising operator on the ground state.

# 17 Time Independent Perturbation Theory

The treatment of perturbation theory in Pritchard's notes is a joke. This section will be based on David Skinner's notes.

## 17.1 Analytic expansion

Let $\hat{H}$ be the Hamiltonian of the system we wish to understand, and $\hat{H}_0$ be the Hamiltonian of our model system whose eigenstates and eigenvalues we already know. We hope that $\hat{\Delta} = \hat{H} - \hat{H}_0$ is in some sense 'small'. For some $\lambda \in [0, 1]$, we define

$$\hat{H}_\lambda = \hat{H}_0 + \lambda\hat{\Delta}.$$

At $\lambda = 0$, the system is our model case, and at $\lambda = 1$, it's the system we are interested in.

We now seek the eigenstates $|E_\lambda\rangle$ of $\hat{H}_\lambda$. Our key assumption is that *since $\hat{H}_\lambda$ depends analytically on $\lambda$, so too do its eigenstates.* In essence, this amounts to the assumption that small changes in the system will lead to small changes in the outcome.

If $|E_\lambda\rangle$ depends analytically on $\lambda$, then we can expand it as

$$|E_\lambda\rangle = |\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \cdots$$

for some $|\alpha\rangle, \cdots \in \mathcal{H}$, and similarly expand the eigenvalues

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots.$$

Plugging these into the equation $\hat{H}_\lambda|E_\lambda\rangle = E(\lambda)|E_\lambda\rangle$ gives

$$\begin{aligned}\left(\hat{H}_0 + \lambda\hat{\Delta}\right)&\left(|\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \cdots\right) \\ &= \left(E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots\right)\left(|\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \cdots\right).\end{aligned}$$

Since we require this to hold as $\lambda$ varies, it must hold for each power of $\lambda$. Hence, we get

$$\begin{aligned}\hat{H}_0|\alpha\rangle &= E^{(0)}|\alpha\rangle \\ \hat{H}_0|\beta\rangle + \hat{\Delta}|\alpha\rangle &= E^{(0)}|\beta\rangle + E^{(1)}|\alpha\rangle \\ \hat{H}_0|\gamma\rangle + \hat{\Delta}|\beta\rangle &= E^{(0)}|\gamma\rangle + E^{(1)}|\beta\rangle + E^{(0)}|\gamma\rangle \\ &\vdots\end{aligned}$$

and so on.

$\lambda^0$: This equation states that $|\alpha\rangle$ is an eigenstate of our model system, with energy $E^{(0)}$. To state this, we relabel $|\alpha\rangle \to |n\rangle$ and $E^{(0)} \to E_n$ where $n$ stands for the $n^{\text{th}}$ eigenstate.

$\lambda^1$: To find $E^{(1)}$, we operate on the second equation with $\langle n|$:

$$\langle n|H_0|\beta\rangle + \langle n|\Delta|n\rangle = E_n\langle n|\beta\rangle + E^{(1)},$$

since $H_0$ is Hermitian,

$$E_n^{(1)} = \langle n|\Delta|n\rangle.$$

To find the perturbed state, we expand $|\beta\rangle$ in the complete set $\{|n\rangle\}$ of eigenstates of the original system as

$$|\beta\rangle = \sum_n \langle n|\beta\rangle|n\rangle.$$

Now, operating with $\langle m|$ (where $m \neq n$) gives

$$\langle m|\beta\rangle = \frac{\langle m|\Delta|n\rangle}{E_n - E_m}.$$

Hence, we get for $|\beta\rangle$

$$|\beta\rangle = \sum_{m\neq n} \frac{\langle m|\Delta|n\rangle}{E_n - E_m}|m\rangle$$

We can argue that when $m = n$, the expansion coefficient is zero from the requirement that $|E_\lambda\rangle$ remains normalised.

We can go for higher orders but we won't (because the course is essentially QM for dummies?)

# 18 QM in Two Dimensions

It is easy to generalise to three dimensions.

## 18.1 Two dimensional SHO

The energy eigenstate equation is

$$\hat{H}u = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{m\omega_x^2 x^2}{2} + \frac{m\omega_y^2 y^2}{2}\right] u = Eu.$$

Separation of variables, we let

$$u(x, y) = X(x)Y(y)$$

so the equation becomes

$$\left(-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} + \frac{m\omega_x^2 x^2}{2}\right) + \left(-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{m\omega_y^2 y^2}{2}\right) = E$$

Hence, we get

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} + \frac{m\omega_x^2 x^2}{2}X = E_x X$$

and similarly for $y$ where $E = E_x + E_y$. We know the eigenvalues:

$$E_x = \left(n_x + \frac{1}{2}\right)\hbar\omega_x, \quad E_y = \left(n_y + \frac{1}{2}\right)\hbar\omega_y$$

and the eigenstate is:

$$u_{n_x n_y} = u_{n_x}(x)u_{n_y}(y).$$

## 18.2 Degeneracy

There can be multiple eigenstates that correspond to the same energy. This is called degeneracy, and happens for the SHO case above for the following general condition:

$$n_x - m_x = \frac{\omega_y}{\omega_x}(m_y - n_y)$$

where $n_x, n_y, m_x, m_y \in \mathbb{N}$ are the quantum numbers describing the two states.

If $\omega_x = \omega_y = \omega$, then we have a central potential

$$V(x,y) = \frac{m\omega_x^2 x^2}{2} + \frac{m\omega_y^2 y^2}{2} = \frac{m\omega_0^2\left(x^2+y^2\right)}{2} = \frac{m\omega_0^2 r^2}{2} = V(r)$$

and so the energies are given by

$$E = E_x + E_y = (n_x + n_y + 1)\,\hbar\omega_0.$$

There are now two first excited states, given by $n_x = 1, n_y = 0$ and $n_x = 0, n_y = 1$ both of which have $E = 2\hbar\omega_0$.

Let $u_{10}$ and $u_{01}$ be the two degenerate states. Consider the superposition

$$\psi = \alpha u_{10} + \beta u_{01}$$

for some constants $\alpha, \beta$, hence we have

$$\hat{H}\psi = \alpha\hat{H}u_{10} + \beta\hat{H}u_{01} = \alpha E_1 u_{10} + \beta E_1 u_{01} = E_1(\alpha u_{10} + \beta u_{01}) = E_1\psi.$$

*Any superposition of degenerate eigenstates is also a degenerate eigenstate.*

## 18.3 Angular momentum

In two dimensions,

$$\hat{L} = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x.$$

We can look at this in polar coordinates, where

$$\hat{L} = -i\hbar\frac{\partial}{\partial\phi}.$$

We can find eigenstates of angular momentum from the eigenstate equation:

$$-i\hbar\frac{\partial\psi}{\partial\phi} = \hbar m_l\psi$$

where we wrote the eigenvalue as $\hbar m_l$ for convenience. Solving the equation yields

$$\psi = C(r)\mathrm{e}^{im_l\phi}$$

From the boundary condition $\psi(r,\phi+2\pi) = \psi(r,\phi)$, we conclude $m_l \in \mathbb{Z}$. So angular momentum must be quantized.

# 19 Degeneracy

## 19.1 Orthogonality

When we proved that the eigenstates of any Hermitian operator are orthogonal, we assumed distinct eigenvalues. However, this assumption does not always hold when there are degeneracies involved.

We can use *Gram-Schmidt process* to construct an orthogonal basis out of degenerate eigenstates.

### 19.1.1 Gram-Schmidt process for degenerate eigenstates

Let $\{|\psi_i\rangle | i = 1, 2, \cdots, n\}$ be a set of $n$ degenerate eigenstates. We note that any linear combination of degenerate eigenstates is itself an eigenstate with the same energy. We label the orthogonal states as $|\psi_i'\rangle$.

First, we let

$$|\psi_1'\rangle = |\psi_1\rangle.$$

Now, let $|\psi_2'\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$. We require $\langle\psi_1'|\psi_2'\rangle = 0$, hence we get

$$c_1\langle\psi_1|\psi_1\rangle + c_2\langle\psi_1|\psi_2\rangle = 0$$

and so

$$|\psi_2'\rangle = c_2\left(|\psi_2\rangle - \frac{\langle\psi_1|\psi_2\rangle|\psi_1\rangle}{\langle\psi_1|\psi_1\rangle}\right).$$

We then repeat the same procedure for the remaining states. The arbitrary constants can be fixed by normalisation.

## 19.2 Compatibility

We showed that if two operators were compatible, they commuted and vice versa. The proof of this, however, assumed no degeneracies. When there are degenerate states involved, there is no guarantee that a particular degenerate state will be an eigenstate of another commuting operator. However, we can *always* construct another degenerate state as the set of degenerate states are complete in the subspace they span, such that said state will be an eigenstate of a commuting operator.

Hence, a commutator being zero is still a good test of the possibility of compatibility, but any given set of degenerate eigenstates may not exhibit it directly.

## 19.3 Collapse

In general, we won't collapse the wavefunction completely by doing a single measurement when degenerate states are involved. As we have two quantum numbers that describe our system, we would need two measurements to know exactly which state the wavefunction is in. In three dimensions, there are three quantum numbers and so we would need three measurements.

## 19.4 Symmetry

If the potential has a symmetry, then there is no reason for the probability density to be asymmetric when considering all the possible solutions. We find that while the probability densities of each of the degenerate eigenstates do not (necessarily) reflect the symmetry of the system, the sum of them does. In three dimensions, then

$$\sum |u_{nlm}(r)|^2$$

will show the symmetry of the system, where the sum is over all the orthogonal degenerate eigenstates of a particular energy.

# 20 Properties of 3D Angular Momentum Operators

The angular momentum operator is found from Postulate 3:

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}.$$

Explicitly in Cartesians

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$$
$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z.$$
$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

We should consider if the angular momentum operators are compatible. Consider

$$\left[\hat{L}_x, \hat{L}_y\right] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x.$$

It is straightforward to show that

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z, \quad \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x, \quad \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y.$$

Hence the angular momentum operators for orthogonal bases are not compatible. At most only one of the $L_i$ can have a definite value at a given time.

The commutation relations can be written as

$$i\hbar\hat{\mathbf{L}} = \hat{\mathbf{L}} \times \hat{\mathbf{L}}.$$

### 20.1 Angular momentum magnitude

Consider

$$\hat{L}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}}$$

It can be shown that this commutes with the $\hat{L}_i$. Hence, the total angular momentum is compatible with the angular momentum components, whereas the components are not compatible with each other. This means that we *require* there to be degeneracies.

## 21 Eigenvalues of Angular Momentum

This section is bit useless, ladder operators for angular momentum are introduced.

### 21.1 Angular momentum ladder operators

We will consider an eigenstate of $\hat{L}^2$ and $\hat{L}_z$, denoted $Y(\theta, \phi)$ such that we have

$$\hat{L}^2 Y = \alpha Y, \quad \hat{L}_z Y = \beta Y.$$

**Definition** (Angular momentum ladders)**.** *We define the ladder operators for angular momentum as*

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y, \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y.$$

We have the commutator relations:

$$[\hat{L}_z, \hat{L}_+] = \hbar\hat{L}_+, \quad [\hat{L}_z, \hat{L}_-] = -\hbar\hat{L}_-.$$

It can then be shown that

$$\hat{L}_z\left(\hat{L}_+ Y\right) = \beta\left(\hat{L}_+ Y\right) + \hbar\left(\hat{L}_+ Y\right) = (\beta + \hbar)\left(\hat{L}_+ Y\right)$$

and similarly

$$\hat{L}_z\left(\hat{L}_- Y\right) = (\beta - \hbar)\left(\hat{L}_- Y\right).$$

Hence, the angular momentum in $L_z$ is quantized in units of $\hbar$. It is trivial to show that the ladder operators commute with $\hat{L}^2$ and so they do not change the total angular momentum. They rotate the angular momentum to increment or decrement the $z$ component.

### 21.2 Eigenvalues

By operating on the maximum and minimum $z$-component of angular momentum states with the ladder operators, eigenvalues of $\hat{L}_z$ can be obtained as

$$\beta = m_l\hbar, \quad m_l = 0, \pm 1, \pm 2, \ldots \pm l$$

for some $l \in \mathbb{N}^+$ and the eigenvalues of $\alpha$ is then

$$l(l+1)\hbar^2.$$

## 22 Angular Momentum in Spherical Polar Coordinates

The angular momentum operators in spherical coordinates are:

$$\begin{aligned}
\hat{L}_x &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right) \\
\hat{L}_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right) \\
\hat{L}_z &= -i\hbar\frac{\partial}{\partial\phi}
\end{aligned}$$

from which it can be shown that the $\hat{L}^2$ operator is

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

We would like to solve the eigenvalue equation

$$\hat{L}^2 Y(\theta,\phi) = \alpha Y(\theta,\phi).$$

This can be reduced to *associated Legendre equation*, and the solutions are

$$P_l^{|m_l|} = \left(1-\mu^2\right)^{|m_l|/2}\frac{d^{|m_l|}P_l^0}{d\mu^{|m_l|}},$$

where $\mu = \cos\theta$, and the general solution is given by

$$Y_{l,m_l}(\theta,\phi) = AP_l^{|m_l|}(\cos\theta)\mathrm{e}^{im_l\phi}$$

for some constant $A$. These functions are called the *spherical harmonics*.

### 22.1 Properties of spherical harmonics

They are orthonormal, i.e.

$$\int_0^\pi\int_0^{2\pi} Y^*_{lm_l}Y_{l'm'_l}\sin\theta d\theta d\phi = \delta_{ll'}\delta_{m_lm'_l}.$$

They are also isotropic when all the degenerate states are summed:

$$\sum_{m_l=-l}^{m_l=+l}|Y_{lm_l}|^2 = \frac{2l+1}{4\pi}$$

such that it is not a function of $\theta$ or $\phi$.

The wavefunction is $\psi(r,\theta,\phi)$, which can be written as

$$\psi = f(r)Y_{lm_l}(\theta,\phi)$$

The spherical harmonics form a complete orthonormal set, hence every angular momentum state can be represented as a sum of the spherical harmonics.

# 23 Central Potentials

## 23.1 Classical effective potential

Assume that a classical particle is traveling in a certain trajectory in a central potential (so $V(\mathbf{r}) = V(r)$). We know angular momentum is conserved, and writing the linear momentum as a sum of its radial and transverse components we get

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times (\mathbf{p}_R + \mathbf{p}_T).$$

Since the radial component of momentum is by definition parallel to position, we have

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}_T.$$

We also know that, by definition, the transverse component of linear momentum is perpendicular to $\mathbf{r}$, hence we deduce

$$|\mathbf{L}| = |\mathbf{r}||\mathbf{p}_T|, \quad p_T^2 = \frac{L^2}{r^2}$$

The total energy is

$$E = \frac{p^2}{2m} + V(r) = \frac{p_R^2}{2m} + \frac{p_T^2}{2m} + V(r)$$

and so

$$E = \frac{p_R^2}{2m} + \frac{L^2}{2mr^2} + V(r) = \frac{p_R^2}{2m} + V'(r)$$

where we define an effective potential

$$V'(r) = V(r) + \frac{L^2}{2mr^2}.$$

## 23.2 3D energy eigenstates

The TISE is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right] u(\mathbf{r}) = Eu(\mathbf{r}).$$

The Laplacian is

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

where the angular term can be written in terms of $\hat{L}^2$ as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left(-\frac{1}{\hbar^2}\hat{L}^2\right) = \nabla_R^2 - \frac{1}{r^2\hbar^2}\hat{L}^2.$$

Hence we get for the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla_R^2 + \frac{1}{2mr^2}\hat{L}^2 + V(\mathbf{r}),$$

so we get a term similar to the classical case.

As $\hat{L}^2$ only operates on $\theta$ and $\phi$, it is conserved if it commutes with $V(\mathbf{r})$ which suggests that $V$ must be a central potential.

## 23.3 The radial equation

We look for solutions of the form

$$u(\mathbf{r}) = R(r)Y_{l,m_l}(\theta, \phi)$$

as we know for central potentials $\hat{L}^2$ commutes with the Hamiltonian. Hence, we have

$$-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{l(l+1)\hbar^2}{2mr^2}R + V(r)R = ER.$$

By the substitution $\chi(r) = rR(r)$ we can rewrite this as

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

which is simply a one dimensional TISE with an effective potential

$$V'(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}.$$

As expected, the radial equation does not depend on $m_l$ as the potential is central so it is isotropic.

## 23.4 Coulomb potential

We have for a single electron orbiting a charged nucleus

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}.$$

The radial functions are often expressed in terms of the *Bohr radius*

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.3 \times 10^{-11}\text{m}.$$

The solutions have the form

$$R_{nl}(r) = f_{nl}(r)\exp\left(-\frac{Zr}{na_0}\right)$$

where $n$ is an integer $n > l$ and is called the principal quantum number, $l$ is the angular momentum quantum number and $f_{nl}(r)$ is a polynomial with terms up to $r^{n-1}$.

The energy eigenvalues are

$$E_n = -\frac{me^4}{2\left(4\pi\epsilon_0\right)^2\hbar^2 n^2} = -\frac{e^2}{4\pi\epsilon_0 a_0}\frac{1}{2n^2} = -\frac{13.6}{n^2}\text{eV}.$$

It turns out that for the particular case of the Coulomb potential, the energy eigenvalues are independent of $l$ and only depend on $n$; this is surprising given what we found before and is not a general result for central potentials. It is a so-called "accidental degeneracy". Because of this, there is generally a high degree of degeneracy for each energy state. Generally there are $n^2$ degenerate states for energy $E_n$

# 24 Measuring Angular Momentum

## 24.1 Classical magnetic dipoles

By considering an electron's orbit, we can obtain an expression for its magnetic dipole moment as

$$\boldsymbol{\mu} = -\frac{e}{2m_e}\mathbf{L}.$$

This dipole moment interacts with external magnetic fields. If the field is *uniform*, then the dipole feels a torque

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B}$$

This can be described by a potential energy term

$$V_\mu = -\boldsymbol{\mu} \cdot \mathbf{B}.$$

In a non-uniform field, there will also be a net force on the dipole given by

$$\mathbf{F} = -\nabla V_\mu = \nabla(\boldsymbol{\mu} \cdot \mathbf{B}).$$

## 24.2 The Zeeman effect

Energy shifts in the atomic spectra can be measured when a uniform magnetic field is applied. This can be used to measure the magnetic dipole moment and hence the angular momentum.

We need to know the effect of the change to the potential on the atomic energy eigenvalues. This can be determined using perturbation theory. The extra part of the Hamiltonian is

$$\hat{\Delta} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B},$$

defining the $z$ axis to point along the magnetic field we have

$$\hat{\Delta} = \frac{eB}{2m_e}\hat{L}_z = \frac{\mu_B B}{\hbar}\hat{L})_z$$

where $\mu_B = e\hbar/2m_e$ is the *Bohr magneton*.

The first order perturbation is

$$E^{(1)} = \langle\hat{\Delta}\rangle = \frac{\mu_B B}{\hbar}\langle\hat{L}_z\rangle.$$

Hence, different $\hat{L}_z$ states will split into different energy levels depending on their $m_l$ values. The magnetic field breaks the isotropy, so the states are no longer degenerate. We therefore expect to see each set of degenerate $\hat{L}^2$ states split into the $2l+1$ separate $\hat{L}_z$ states, in energy steps of $\mu_B B$.

The ground state of hydrogen has only $l = 0$ so we expect no shift to the energy levels there. The first excited state has $l = 0$ or 1 and so we would expect the $l = 0$ and $l = 1$, $m_l = 0$ states to not be shifted, while the $l = 1$, $m_l = \pm 1$ states will move up or down in energy, respectively. However, this was *not* observed; the ground state actually split into two energies, moving $\pm\mu_B B$ while the first excited state split into four energies. This was known as the *anomalous Zeeman effect*.

## 24.3 The Stern-Gerlach experiment

Using a non-uniform magnetic field, a force can be applied to atoms that depends on their angular momentum orientation. This force will therefore deflect a beam of atoms depending on the value of $m_l$. Classically, for a fixed $\mu$ magnitude, we would expect a continuous range

of $\mu_z$ values as the atoms would generally have random orientations to the $z$ axis and hence a continuous range of deflections. However, the experiment first done by Stern and Gerlach showed only particular deflections were found; this is a direct manifestation of the quantisation of angular momentum. Again, we would expect hydrogen atoms not to be deflected in their ground state, as $l = 0$, and the first excited state to be split, with $m_l = \pm 1$ being deflected in different directions while the two $m_l = 0$ states are not deflected at all. However, it was found that the ground state gave two lines, corresponding to the deflections expected for $m_l = \pm 1$. The initial conclusion was that they were somehow seeing the $m_l = \pm 1$ states and the $m_l = 0$ states were "missing" in some undefined way.

### 24.4 Spin

These effect can be explained by electrons having some intrinsic angular momentum - called spin. Then we have two sources of magnetic dipole, one corresponding to the electron's orbit and hence its angular momentum, and the other being an intrinsic property. We have

$$\boldsymbol{\mu}_S = -\frac{ge}{2m_e}\mathbf{S},$$

where $g$ is some proportionality constant called the "gyromagnetic ratio". It turns out that $g = 2$, so we take

$$\boldsymbol{\mu}_S = -\frac{e}{m_e}\mathbf{S}.$$

The electron is said to have "spin-half", with $s = 1/2$ and $m_s = \pm 1/2$.

## 25 Spin Eigenvalues and Eigenstates

### 25.1 Spin in QM

We cannot construct $\hat{S}_i$ from spatial and momentum operators. Since we need to add it to orbital angular momentum, we want it to act like orbital angular momentum.

**Proposition.** *The commutator rules for spin operators are the same as for $\hat{L}_i$, e.g. $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$.*

We can deduce the eigenvalues via ladder operators, so we have

$$\hat{S}^2\chi = s(s+1)\hbar^2\chi, \quad \hat{S}_z\chi = m_s\hbar\chi.$$

As we are restricted to a single $s$ value, $s = 1/2$, and two $m_s$ values we need to have $\chi$ to be discrete. For only two $m_s$ values, we need something which only takes two values. We can write it as a vector

$$\chi = \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}.$$

Then, we use matrices to represent spin operators. In order to include the spin in the wavefunction, we then have

$$\psi(x, y, z, w) = \begin{bmatrix} \psi_1(x, y, z) \\ \psi_2(x, y, z) \end{bmatrix}$$

where $w \in \{1, 2\}$.

## 25.2 Spin z

We take

$$\hat{S}_z = \begin{pmatrix} \hbar/2 & 0 \\ 0 & -\hbar/2 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

so it can be deduced that

$$\alpha_z = \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$\beta_z = \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

It is easy to see that these vectors form a complete orthonormal set.

## 25.3 Other spin operators

The raising and lowering operators can be deduced as

$$\hat{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \hat{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

Using the raising and lowering operators, we can then find $\hat{S}_x$ and $\hat{S}_-$. These are

$$\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

We can define Pauli matrices as

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

## 25.4 Spin magnitude

We define $\hat{S}^2$ as

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{\hbar^2}{4} I + \frac{\hbar^2}{4} I + \frac{\hbar^2}{4} I = \frac{3\hbar^2}{4} I.$$

Hence the operator is the identity, so any vector is an eigenvector with an eigenvalue $3\hbar^2/4$.

## 25.5 Eigenvectors of $\hat{S}_x$ and $\hat{S}_y$

It is straightforward to show that

$$\alpha_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \beta_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

and similarly

$$\alpha_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}, \quad \beta_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

# 26 Spin in Magnetic Fields

## 26.1 The wavefunction with spin

With spin, the general Hamiltonian will be

$$\hat{H}(\mathbf{r}, \mathbf{p}, \hat{\mathbf{S}}).$$

The eigenstates will generally be

$$\psi = \begin{pmatrix} \psi_1(\mathbf{r}, t) \\ \psi_2(\mathbf{r}, t) \end{pmatrix}$$

so in general we have two coupled differential equations to solve, one for $\psi_1$ and one for $\psi_2$.

If the spatial and spin components of the Hamiltonian are separate terms, such that

$$\hat{H} = \hat{H}_r(\hat{\mathbf{r}}, \hat{\mathbf{p}}) + \hat{H}_s(\hat{\mathbf{S}})$$

then we have a separable solution of the form

$$\psi = \psi_r(\mathbf{r}, t)\chi_s(t)$$

Then we have two separate TDSEs

$$i\hbar \frac{\partial \psi_r}{\partial t} = \hat{H}_r \psi_r$$
$$i\hbar \frac{d\chi_s}{dt} = \hat{H}_s \chi_s$$

To clarify the form of $\hat{H}_S$ we can write

$$i\hbar \frac{d}{dt} \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \hat{H}_S \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}$$

so it is clear that $\hat{H}_S$ has to be a $2 \times 2$ matrix.

## 26.2 Spin in a uniform magnetic field

If the magnetic field is uniform, $\mathbf{B} \neq \mathbf{B}(\mathbf{r})$, then the potential due to the dipole is a separate term. This means we can separate the spin component of the Hamiltonian such that

$$\hat{H}_S = -\boldsymbol{\mu}_S \cdot \mathbf{B} = \frac{e}{m_e} \mathbf{S} \cdot \mathbf{B}.$$

Defining the $z$ axis to be along the magnetic field, we have

$$\hat{H}_s = \frac{eB}{m_e} \hat{S}_z = \frac{e\hbar B}{2m_e} \sigma_z = \mu_B B \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

in terms of the Bohr magneton $\mu_B$. We have two eigenstates that are also $\hat{S}_z$ eigenstates, with energies $\pm \mu_B B$.

## 26.3 Larmor precession

*Larmor precession* concerns the motion of the spin vector in a magnetic field. We can solve the TDSE

$$i\hbar \frac{d}{dt} \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \mu_B B \begin{pmatrix} \chi_1 \\ -\chi_2 \end{pmatrix}$$

so that

$$\chi_1 = a_1 e^{-iE_1 t/\hbar} = a_1 e^{-i\mu_B Bt/\hbar}, \quad \chi_2 = a_2 e^{-iE_2 t/\hbar} = a_2 e^{i\mu_B Bt/\hbar}.$$

The spin vector is then given by

$$\chi_s = a_1 u_1 \mathrm{e}^{-i\mu_B Bt/\hbar} + a_2 u_2 \mathrm{e}^{i\mu_B Bt/\hbar}$$

We can calculate the expectation values as

$$\langle S_i \rangle(t) = \chi_s^\dagger \hat{S}_i \chi_s$$

Putting in the three matrices gives

$$\begin{aligned}
\langle S_x \rangle &= \hbar a_1 a_2 \cos\left(2\mu_B Bt/\hbar\right) \\
\langle S_y \rangle &= \hbar a_1 a_2 \sin\left(2\mu_B Bt/\hbar\right) \\
\langle S_z \rangle &= \frac{\hbar}{2}\left(a_1^2 - a_2^2\right)
\end{aligned}$$

Hence, the expectation value of $S_z$ is constant with time, as would be expected since the energy eigenstates are also $\hat{S}_z$ eigenstates. However, the $S_x$ and $S_y$ expectation values precess around the magnetic field direction with an angular frequency $2\mu_b B/\hbar = eB/m_e$.