

PH30030: QUANTUM MECHANICS

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$$

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Section 1. The concepts and postulates of quantum mechanics

- Set up formal approach to quantum theory, based on a series of postulates
- Discuss wavefunctions, operators, eigenvalues and eigenfunctions
- Show how we can predict the results of measurements of a quantum system
- Discuss the uncertainty principle
- Discuss the time dependence of quantum systems

1.1 Postulate 1

The state of a quantum system is completely defined by its wavefunction ψ . Everything we can know about the system can be derived from ψ .

$$\text{all info} = \Psi$$

One particle in one dimension: $\psi(x, t)$

One particle in three dimensions: $\psi(\underline{r}, t)$

Two particles in three dimensions: $\psi(\underline{r}_1, \underline{r}_2, t)$

In general, ψ is a **complex** function. The probability P of finding a particle at a point in space is proportional to $|\psi|^2 = \Psi^* \Psi$

1 particle in 1-D: $P(x, t)dx = |\psi(x, t)|^2 dx$

1 particle in 3-D: $P(\underline{r}, t)d^3r = |\psi(\underline{r}, t)|^2 d^3r$

Cartesians: $d^3r = dx dy dz$

Spherical polars: $d^3r = r^2 \sin \theta dr d\theta d\phi$

2 prob finding at $x = 1$

Wavefunctions are **normalised**:

1 particle in 1-D: $\int |\psi(x,t)|^2 dx = 1$

1 particle in 3-D: $\iiint |\psi(\underline{r},t)|^2 d^3r = 1$

Integrate over the region of space available to the particle

1.2 Postulate 2

Every measurable quantity (observable) has a corresponding operator.

- **Operators** are mathematical “rules” that act on a function to give another function, e.g.

$$\hat{A} f(x) = g(x)$$

Examples

Let $f(x) = x + x^2$

Differential operator: $\hat{A} = \frac{d}{dx} \rightarrow g(x) = 1 + 2x$

Multiplicative operator: $\hat{A} = x^2 \rightarrow g = x^3 + x^4$

Parity operator: $\hat{A} f(x) = f(-x) \rightarrow g = -x + x^2$

order operator important!

Products of operators are defined as

$$\hat{A}\hat{B} f(x) = \hat{A}(\hat{B}(f(x)))$$

The order of operators is important:

$\hat{A}\hat{B}$ is not necessarily $\hat{B}\hat{A}$

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

In general, \hat{A} and \hat{B} do not commute

Example

Let $f(x) = x + x^2$, $\hat{A} = \frac{d}{dx}$, $\hat{B} = x$

$$\hat{A}\hat{A} f(x) = \hat{A}^2 f(x) = 2$$

$$\hat{A}\hat{B} f(x) = 2x + 3x^2$$

$$\hat{B}\hat{A} f(x) = x + 2x^2$$

$\hat{A}\hat{B} \neq \hat{B}\hat{A}$ in this case

- Operators in quantum mechanics are **linear** and **Hermitian**.

Linear: $\hat{A}(c_1 f_1 + c_2 f_2) = c_1 \hat{A} f_1 + c_2 \hat{A} f_2$

(c_1, c_2 are constants, f_1, f_2 are functions)

Hermitian:

$$\int f_1^*(x) (\hat{A} f_2(x)) dx = \int (\hat{A} f_1(x))^* f_2(x) dx$$

(integrate over region available to the particle)

- Some important operators (Postulate 2A)

Position: $\hat{x} = x$, $\hat{y} = y$, $\hat{z} = z$ ie $\hat{\underline{r}} = \underline{r}$

Momentum:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \quad \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

i.e. $\hat{p} = -i\hbar \nabla$

↑
gradient
operator

- Other operators are derived from these and the classical definitions:

• Kinetic energy, classically $T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$

$$\rightarrow \text{ in QM: } \hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2$$

• Potential energy: $\hat{V}(\underline{r}) = V(\underline{r})$

• Total energy (i.e. Hamiltonian): $\hat{H} = \hat{T} + \hat{V}$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r}) \quad \text{in 3D}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad \text{in 1D}$$

Can's time indep schröd eq't:

Schröd: $\hat{H}\Psi = E\Psi$

Check that these operators are Hermitian

$$\int f_1^*(x) (\hat{A}f_2(x)) dx = \int (\hat{A}f_1(x))^* f_2(x) dx$$

1. Position operator: $\hat{A} \equiv \hat{x} = x$

Multiplicative operator is obviously Hermitian

2. Momentum operator: $\hat{A} \equiv \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

$$\int f_1^*(x) (\hat{p}_x f_2(x)) dx = -i\hbar \int f_1^*(x) \frac{\partial f_2(x)}{\partial x} dx$$

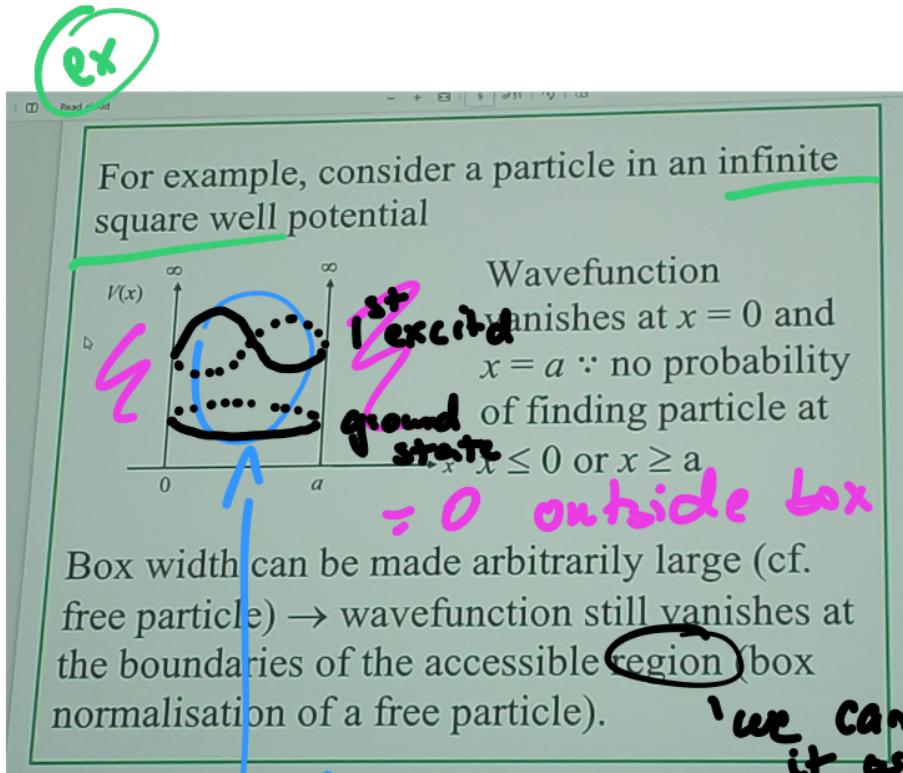
*def by boundaries
occupable reg'*

$$\rightarrow \left[-i\hbar f_1^*(x) f_2(x) \right] + i\hbar \int \frac{\partial f_1^*}{\partial x} f_2(x) dx$$

Assume functions are well behaved at the boundaries of the region

*i.e.
boundary reg' = 0*

$$i\hbar \int \frac{\partial f_1^*}{\partial x} f_2(x) dx = \int (\hat{p}_x f_1)^* f_2(x) dx \therefore \text{Hermitian}$$



particle confined to this area

how I
normalize these
eig's

↑
Same as with momentum

3. For **kinetic energy** see problems sheet

1.3 Postulate 3

The only possible result of a measurement is an eigenvalue of the relevant operator. Whatever the state of the system before the measurement, the state immediately after is the corresponding eigenfunction.

Eigenvalues and eigenfunctions

For a general operator \hat{A} , the equation

$$\hat{A}\phi = \alpha\phi$$

(with relevant boundary conditions) has non-zero solutions only for special values of α . We write these solutions as

$$\hat{A}\phi_n = \alpha_n\phi_n$$

α_n are the **eigenvalues** of \hat{A}

ϕ_n are the **eigenfunctions** of \hat{A}

The label n can be discrete or continuous

Examples

- **Momentum operator in 1D:** $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

$$-i\hbar \frac{\partial}{\partial x} \exp(ikx) = \hbar k \exp(ikx)$$

Eigenvalues: $\hbar k$ (where k is a constant)

Eigenfunctions: $\exp(ikx)$

In this case, the eigenvalues are continuous

Physical interpretation: the wave $\exp(ikx)$ represents a particle moving in the x direction with a momentum $p = \hbar k$

(Consistent with de Broglie relation $\lambda = h/p$)

- If we measure the momentum of a quantum particle we obtain a value $p = \hbar k$ and immediately after the measurement the wavefunction is $\psi = \exp(ikx)$

- **Infinite square well**

Potential energy $V(x) = 0$ for $0 < x < a$ and is infinity elsewhere

Total energy operator in the region available to the particle:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Eigenvalues and eigenfunctions given by:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \sin\left(\frac{n\pi x}{a}\right) = \frac{\hbar^2\pi^2 n^2}{2ma^2} \sin\left(\frac{n\pi x}{a}\right)$$

Eigenvalues: $E_n = \frac{\hbar^2\pi^2 n^2}{2ma^2}$ (n is an integer)

Eigenfunctions: $\phi_n(x) \propto \sin\left(\frac{n\pi x}{a}\right)$

In this case, the eigenvalues are discrete

If we measure the energy of a particle in an infinite square well, the result will be one of the eigenvalues E_n . Immediately after the measurement the wavefunction is $\psi = \phi_n(x)$.

As a result of the measurement, the wavefunction “collapses” into one of the eigenfunctions.

“Quantum Measurement Problem”

1.4 Properties of Hermitian operators

Start with

$$\hat{A}\phi_n = \alpha_n \phi_n$$

Multiply both sides by ϕ_m^* and integrate over relevant range:

$$\int \phi_m^* \hat{A}\phi_n = \alpha_n \int \phi_m^* \phi_n$$

Because \hat{A} is Hermitian, this becomes:

$$\begin{aligned} \int \underbrace{\left(\hat{A}\phi_m \right)^*}_{= \alpha_m^* \phi_m^*} \phi_n &= \alpha_n \int \phi_m^* \phi_n \quad (1) \end{aligned}$$

Taking complex conjugate of $\hat{A}\phi_m = \alpha_m \phi_m$ gives $\left(\hat{A}\phi_m \right)^* = \alpha_m^* \phi_m^*$, so (1) becomes:

$$(\alpha_n - \alpha_m^*) \int \phi_m^* \phi_n = 0$$

- If $n = m$, then $\alpha_n = \alpha_n^*$ so α_n is **real**
- If $n \neq m$, then $\int \phi_m^* \phi_n = 0$ so ϕ 's are **orthogonal**
- If eigenfunctions are normalised we can write

$$\int \phi_m^* \phi_n = \delta_{mn}$$

The eigenvalues of Hermitian operators are real and the eigenfunctions corresponding to different eigenvalues are orthogonal

- The eigenfunctions of Hermitian operators form a **complete set**, so that any function (in the relevant region of space) can be written as a **linear combination**:

$$F = c_1 \phi_1 + c_2 \phi_2 + \dots = \sum_n c_n \phi_n$$

- We have assumed that there is **no degeneracy** (i.e. that all eigenvalues are different). Everything works OK if there are degenerate eigenvalues.

1.5 Postulate 4

Quantum mechanics is not deterministic. We can only predict the probability of the result of a measurement and the average over a series of measurements.

How do we calculate these probabilities?

Assume we make a measurement, where the sets of eigenvalues and eigenfunctions of the corresponding operator \hat{A} are $\{\alpha_n\}$ and $\{\phi_n\}$

At the time of the measurement the normalised wavefunction of the system is ψ

We can write $\psi = \sum_n c_n \phi_n$

The probability of measuring α_m (and collapsing the system into ϕ_m) is $|c_m|^2$

Because ψ and $\{\phi_n\}$ are normalised: $\sum_n |c_n|^2 = 1$

How can we find the coefficients c_m ?

Start with:

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

Multiply both sides by ϕ_m^* and integrate

$$\int \phi_m^* \psi = \sum_n c_n \int \phi_m^* \phi_n$$

Use orthogonality

$$\int \phi_m^* \psi = \sum_n c_n \delta_{mn} = c_m$$

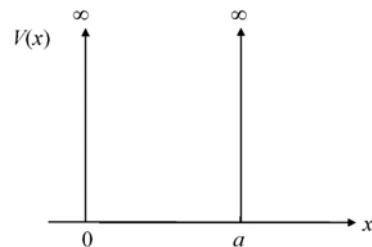
$$c_m = \int \phi_m^* \psi$$

c_m gives the “amount” of ϕ_m contained in ψ

Example: Infinite square well in 1-D

Suppose wavefunction is constant at the time of the measurement

$$\psi(x) = \frac{1}{\sqrt{a}}$$



We measure the total energy of the particle; the corresponding eigenvalues and eigenvectors are

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2} \quad \phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

The coefficients are:

$$c_m = \int \phi_m^* \psi = \frac{\sqrt{2}}{a} \int_0^a \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\rightarrow c_m = \frac{2\sqrt{2}}{m\pi} \text{ for } m \text{ odd}$$

$$c_m = 0 \text{ for } m \text{ even}$$

Probability of measuring $E_1 = \frac{\hbar^2 \pi^2}{2ma^2}$ is $\frac{8}{\pi^2}$

Probability of measuring $E_2 = \frac{4\hbar^2 \pi^2}{2ma^2}$ is 0

Probability of measuring $E_3 = \frac{9\hbar^2 \pi^2}{2ma^2}$ is $\frac{8}{9\pi^2}$

- Expectation values

Suppose we have a large number of identical systems. What would be the average value of a measurement taken on each of these systems?

Average, or **expectation value** of the measurements with corresponding operator \hat{A}

$$\langle \hat{A} \rangle = \sum_n |c_n|^2 \alpha_n$$

- This can be expressed in a more useful form

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi$$

Show that these are equivalent:

$$\langle \hat{A} \rangle = \int \left(\sum c_m^* \phi_m^* \right) \hat{A} \left(\sum c_n \phi_n \right)$$

$$= \int \left(\sum c_m^* \phi_m^* \right) \left(\sum c_n \alpha_n \phi_n \right)$$

$$= \sum_m \sum_n c_m^* c_n \alpha_n \int \phi_m^* \phi_n$$

$$= \sum_n |c_n|^2 \alpha_n$$

Expectation value of position:

$$\langle \hat{x} \rangle = \int \psi^* x \psi \, dx$$

Expectation value of momentum:

$$\langle \hat{p}_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \, dx$$

Schematic summary

- Note that all our analysis has assumed that the eigenvalues are discrete. Everything works OK if the eigenvalues are continuous.

1.6 Commutators and compatibility

- The **commutator** of two operators \hat{A} and \hat{B} is defined by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

If $[\hat{A}, \hat{B}] = 0$ then \hat{A} and \hat{B} commute

If $[\hat{A}, \hat{B}] \neq 0$ then \hat{A} and \hat{B} do not commute and the order of their application matters

Examples

- If $\hat{A} = \hat{p}_x$ and $\hat{B} = \hat{x}$

$$[\hat{p}_x, \hat{x}] \psi = \hat{p}_x \hat{x} \psi - \hat{x} \hat{p}_x \psi$$

$$= -i\hbar \frac{\partial}{\partial x} (x \psi) - x \left(-i\hbar \frac{\partial \psi}{\partial x} \right)$$

$$\begin{aligned} &= -i\hbar \left(x \frac{\partial \psi}{\partial x} + \psi \right) + i\hbar x \frac{\partial \psi}{\partial x} = -i\hbar \psi \\ &\rightarrow [\hat{p}_x, \hat{x}] \psi = -i\hbar \psi \end{aligned}$$

Commutation relation: $[\hat{p}_x, \hat{x}] = -i\hbar$

If $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}_x$ we find $[\hat{x}, \hat{p}_x] = i\hbar$

If $\hat{A} = \hat{p}_x$ and $\hat{B} = \hat{y}$

$$[\hat{p}_x, \hat{y}] \psi = -i\hbar \frac{\partial}{\partial x} (y \psi) - y \left(-i\hbar \frac{\partial \psi}{\partial x} \right)$$

$$= -i\hbar y \frac{\partial \psi}{\partial x} + i\hbar y \frac{\partial \psi}{\partial x} = 0$$

$$\rightarrow [\hat{p}_x, \hat{y}] = 0$$

Why do commutators matter?

Two observables are **compatible** if their corresponding operators have a common set of eigenfunctions, e.g.

$$\hat{A}\phi_n = \alpha_n\phi_n$$

$$\hat{B}\phi_n = \beta_n\phi_n$$

If observable corresponding to \hat{A} is measured the wavefunction will become an eigenfunction eg ϕ_m . If observable corresponding to \hat{B} is then measured, the result will be certain (i.e. β_m).

A set of compatible observables can be known precisely, i.e. measured simultaneously

With non-compatible observables we can only predict the probabilities of the results of measurements. Measuring one observable affects the measurement of the others.

If \hat{A} and \hat{B} commute then their corresponding observables are compatible (and vice versa)

Proof

Consider compatible observables as above:

$$\hat{A}\phi_n = \alpha_n\phi_n \quad \hat{B}\phi_n = \beta_n\phi_n$$

A general wavefunction can be written as

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

Calculate commutator of \hat{A} and \hat{B}

$$\begin{aligned} [\hat{A}, \hat{B}] \psi &= \sum_n c_n (\hat{A} \hat{B} \phi_n - \hat{B} \hat{A} \phi_n) \\ &= \sum_n c_n (\underbrace{\hat{A} \beta_n \phi_n}_{\text{green}} - \underbrace{\hat{B} \alpha_n \phi_n}_{\text{green}}) \\ &= \sum_n c_n (\alpha_n \beta_n \phi_n - \beta_n \alpha_n \phi_n) = 0 \\ \rightarrow [\hat{A}, \hat{B}] &= 0 \end{aligned}$$

If \hat{A} and \hat{B} do not commute then the corresponding observables are not compatible

Example

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

\hat{p}_x and \hat{x} are **not compatible**, so the position and momentum of a particle cannot both be known precisely

- This is closely associated with **Heisenberg's uncertainty principle**

Consider measurements corresponding to an operator \hat{A} on set of systems with wavefunction ψ . The average value will be

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi$$

The quantity

$$\begin{aligned}\Delta A^2 &= \int \psi^* (\hat{A} - \langle \hat{A} \rangle)^2 \psi \\ &= \int \psi^* (\hat{A}^2 - 2\hat{A}\langle \hat{A} \rangle + \langle \hat{A} \rangle^2) \psi \\ &= \langle \hat{A}^2 \rangle - 2\langle \hat{A} \rangle^2 + \langle \hat{A} \rangle^2 \\ &= \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2\end{aligned}$$

gives a measure of the amount of spread (i.e. uncertainty) in the measurements

It can be shown that for measurements corresponding to two operators \hat{A} and \hat{B}

$$\Delta A \Delta B \geq \frac{1}{2} \left| \int \psi^* [\hat{A}, \hat{B}] \psi \right|$$

If \hat{A} and \hat{B} do not commute, there must be “uncertainty” in the measurements of the corresponding observables (i.e. both ΔA and ΔB must be non-zero)

Example: If $\hat{A} = \hat{p}_x$ and $\hat{B} = \hat{x}$, $[\hat{p}_x, \hat{x}] = -i\hbar$
 $\rightarrow \Delta x \Delta p \geq \frac{\hbar}{2}$

1.7 Postulate 5

Between measurements, the evolution of the wavefunction is governed by

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$$

i.e., the **Time-Dependent Schrodinger Equation**

\hat{H} is the total energy (Hamiltonian) operator, so the TDSE can be written

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

Note that knowledge of ψ at one time allows prediction of ψ for all future times

Measurements will disrupt this evolution of ψ . A measurement collapses the wavefunction into an eigenfunction of the relevant operator. ψ is then “reset” and the TDSE takes over again.

1.8 Stationary states

An important case arises if the potential energy $V(\underline{r},t)$ in the TDSE is **not dependent on time t**

The energy eigenvalues and eigenfunctions given by

$$\hat{H}(\underline{r})\phi_n(\underline{r}) = E_n \phi_n(\underline{r})$$

do not depend on time

An arbitrary wavefunction at time t can be expanded as

$$\psi(\underline{r},t) = \sum_n c_n(t) \phi_n(\underline{r})$$

This is substituted into the TDSE to give

$$\begin{aligned} i\hbar \sum_n \frac{dc_n}{dt} \phi_n(\underline{r}) &= \sum_n c_n(t) \hat{H}(\underline{r}) \phi_n(\underline{r}) \\ &= \sum_n c_n(t) E_n \phi_n(\underline{r}) \end{aligned}$$

So

$$\sum_n \left(i\hbar \frac{dc_n}{dt} - E_n c_n(t) \right) \phi_n(\underline{r}) = 0$$

which can be satisfied for a given value of n only if

$$i\hbar \frac{dc_n}{dt} = E_n c_n(t)$$

Solution is

$$c_n(t) = c_n(0) \exp(-iE_n t / \hbar)$$

So, wavefunction is given by

$$\psi(\underline{r}, t) = \sum_n c_n(0) \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

At $t = 0$ we have

$$\psi(\underline{r}, 0) = \sum_n c_n(0) \phi_n(\underline{r})$$

and the coefficients can be found from (see section 1.5)

$$c_m(0) = \int d^3 r \phi_m^*(\underline{r}) \psi(\underline{r}, 0)$$

If the potential energy is not time dependent, then all information about the wavefunction can be derived from the energy eigenvalues and eigenfunctions, i.e. from solutions of

$$\hat{H}(\underline{r}) \phi_n(\underline{r}) = E_n \phi_n(\underline{r})$$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r}) \right) \phi_n(\underline{r}) = E_n \phi_n(\underline{r})$$

Time-Independent Schrodinger Equation

If ψ starts in an energy eigenfunction [e.g. $\phi_m(\underline{r})$] then

$$\psi(\underline{r}, t) = \phi_m(\underline{r}) \exp(-iE_m t / \hbar) \quad (1)$$

i.e. ψ remains in an energy eigenfunction and a later measurement of the energy will give E_m

These energy eigenfunctions (i.e. solutions of the TISE) are called **stationary states**.

[Note that if an eigenfunction is multiplied by an arbitrary phase factor, then it remains an eigenfunction.

Likewise, $\psi(\underline{r}, t)$ can be multiplied by an arbitrary phase factor $e^{i\theta}$, but this does not change the physics e.g. $|\psi|^2$ does not change. Could also multiply $\psi(\underline{r}, t)$ by -1 with the same effect.]

1.9 Spreading of a wave packet

Superposition of plane waves → Gaussian wavepacket representing the localised state of a particle.

Consider a 1D quantum system in free space is described by a Gaussian wavefunction. At $t = 0$,

$$\psi(x,0) = \left(\frac{a}{\pi}\right)^{1/4} \exp\left(-\frac{1}{2}ax^2\right)$$

Calculate $\psi(x,t)$

This example nicely demonstrates several of the concepts and postulates we have looked at so far. It also shows how we handle systems with **continuous eigenvalues**.

Notes on $\psi(x, 0)$:

1. $\psi(x, 0)$ is normalised, because

$$\int_{-\infty}^{\infty} dx \exp(-ax^2) = \left(\frac{\pi}{a}\right)^{1/2}$$

2. Expectation value of \hat{x}

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} dx \psi^*(x,0) x \psi(x,0) = 0$$

3. Expectation value of \hat{x}^2

$$\langle \hat{x}^2 \rangle = \int_{-\infty}^{\infty} dx \psi^*(x,0) x^2 \psi(x,0) = \frac{1}{2a}$$

4. Uncertainty in measurements of x (i.e. width of the “wavepacket”)

$$\Delta x = \sqrt{\langle \hat{x}^2 \rangle} = \sqrt{\frac{1}{2a}}$$

Eigenfunctions

The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

In this case (because $V(x) = 0$) the momentum operator \hat{p}_x commutes with \hat{H}

$$\hat{p}_x = -i\hbar \frac{d}{dx} \Rightarrow [\hat{p}_x, \hat{H}] = 0$$

\hat{p}_x and \hat{H} are **compatible** and therefore have a common set of eigenfunctions: $\exp(ikx)$

$$\hat{p}_x : -i\hbar \frac{d}{dx} \exp(ikx) = \hbar k \exp(ikx)$$

$$\hat{H} : -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \exp(ikx) = \frac{\hbar^2 k^2}{2m} \exp(ikx)$$

Aside

If we measure momentum on the initial wavepacket $\psi(x, 0)$, what is the probability of obtaining a particular value $\hbar k$?

In section 1.5 we saw that any wavefunction can be expanded in eigenfunctions as

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

and the probability of measuring α_m (ie the eigenvalue corresponding to ϕ_m) is $|c_m|^2$. How does this work with continuous eigenvalues?

Use results of **Fourier transforms**

$$f(x) = \int_{-\infty}^{\infty} dk F(k) \exp(ikx)$$

$$F(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx f(x) \exp(-ikx)$$

In our case

$$\psi(x, t=0) = \sum_n c_n(t=0) \phi_n(x)$$

can be re-written as

$$\psi(x, 0) = \int_{-\infty}^{\infty} dk c(k) \exp(ikx)$$

Fourier analysis gives us $c(k)$:

$$\begin{aligned} c(k) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \psi(x, 0) \exp(-ikx) \\ &= \frac{1}{2\pi} \left(\frac{a}{\pi} \right)^{1/4} \int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}ax^2\right) \exp(-ikx) \\ &= \left(\frac{1}{2\pi} \right)^{1/2} \left(\frac{1}{\pi a} \right)^{1/4} \exp\left(-\frac{k^2}{2a}\right) \end{aligned}$$

Probability of measuring momentum $p = \hbar k$ is

$$\propto |c(k)|^2 \propto \exp(-k^2 / a)$$

Uncertainty in measurement of p is

$$\Delta p = \hbar \sqrt{\frac{a}{2}}$$

In this case

$$\Delta x \Delta p = \frac{\hbar}{2}$$

[Back to the problem....](#)

In section 1.8, we saw that the time dependence of a wavefunction is given by

$$\psi(\underline{r}, t) = \sum_n c_n(0) \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

ϕ_n are energy eigenfunctions

$c_n(0)$ are expansion coefficients at $t = 0$

In our case the energy eigenfunctions are the same as the momentum eigenfunctions (ie $\exp(ikx)$), so the coefficients are just the $c(k)$ calculated above

We find

$$\psi(x, t) = \left(\frac{1}{2\pi} \right)^{1/2} \left(\frac{1}{\pi a} \right)^{1/4} \times \int_{-\infty}^{\infty} dk \exp\left(-\frac{k^2}{2a}\right) \exp(ikx) \exp\left(-\frac{i\hbar k^2 t}{2m}\right)$$

Integral can be performed to give

$$\psi(x, t) = \left(\frac{1}{\pi a} \right)^{1/4} (2\pi a')^{1/2} \exp\left(-\frac{1}{2} a' x^2\right)$$

$$\text{where } \frac{1}{a'} = \frac{1}{a} + \frac{i\hbar t}{m}$$

The wavefunction stays Gaussian, with width given by

$$\Delta x(t) = \sqrt{\frac{1}{2a} + \frac{\hbar^2 a t^2}{2m^2}}$$

Note how the wavefunction spreads out over time

1.10 Dirac notation

This is a useful shorthand for writing down the integrals that arise in quantum mechanics

We write

$$\int \psi_1^*(\underline{r}) \psi_2(\underline{r}) d^3r \equiv \langle \psi_1 | \psi_2 \rangle$$

(and similarly for 1D integrals)

$\langle \psi_1 |$ is a “bra”

$|\psi_2 \rangle$ is a “ket”

$\langle \psi_1 | \psi_2 \rangle$ is a bra(c)ket!

Integrals involving operators are written as:

$$\int \psi_1^*(\underline{r}) \hat{A} \psi_2(\underline{r}) d^3r \equiv \langle \psi_1 | \hat{A} | \psi_2 \rangle$$

For example, repeat our analysis in section 1.5.
Expand wavefunction in eigenfunctions

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle$$

“Close” with $\langle \phi_m |$

$$\langle \phi_m | \psi \rangle = \sum_n c_n \langle \phi_m | \phi_n \rangle = \sum_n c_n \delta_{mn} = c_m$$

So we can write

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

So far, we have discussed wavefunctions in space, i.e. $\psi(\underline{r})$. There are other representations of wavefunctions, e.g. a matrix representation. **Dirac notation stays the same in all cases, so it is a more general formulation of quantum mechanics.**

1.11 Matrix representation

This is a rather different way to set up problems in QM. Later, we shall see examples of its use.

Consider an observable with operator \hat{A} . We want to find its eigenfunctions and eigenvalues, i.e. solutions of

$$\hat{A}\phi(\underline{r}) = \alpha\phi(\underline{r}) \quad \text{or} \quad \hat{A}|\phi\rangle = \alpha|\phi\rangle \quad (1)$$

We try to find a solution by expanding ϕ in a set of **orthogonal** and **normalised** functions:

$$\phi(\underline{r}) = \sum_n a_n u_n(\underline{r}) \quad \text{or} \quad |\phi\rangle = \sum_n a_n |u_n\rangle \quad (2)$$

Note that the functions $u_n(\underline{r})$ can be **any complete set of orthogonal functions that “span” the relevant region of space**. They are not the eigenfunctions of \hat{A} .

Substitute (2) into (1) to give (using Dirac notation)

$$\sum_n a_n \hat{A}|u_n\rangle = \alpha \sum_n a_n |u_n\rangle$$

“Close” with $\langle u_m |$ (i.e. multiply both sides by $u_m^*(\underline{r})$ and integrate over space) and use orthogonality property $\langle u_m | u_n \rangle = \delta_{mn}$:-

$$\sum_n \langle u_m | \hat{A} | u_n \rangle a_n = \alpha \sum_n a_n \langle u_m | u_n \rangle$$

$$\Rightarrow \sum_n A_{mn} a_n = \alpha a_m \quad \text{where} \quad A_{mn} = \langle u_m | \hat{A} | u_n \rangle$$

This is a **matrix eigenvalue problem**

$$\begin{pmatrix} A_{11} & A_{12} & \cdots & \cdots \\ A_{21} & A_{22} & \cdots & \cdots \\ \vdots & \vdots & \ddots & \ddots \\ \vdots & \vdots & & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \end{pmatrix} = \alpha \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \end{pmatrix} \quad (3)$$

Notes

- This is not a new problem – it's the same problem in a different representation. All the results we've seen so far have an equivalent in matrix representation.
- There are often infinitely many “basis states” $|u_n\rangle$. Matrix representation is often used in practical QM computations, in which case the basis is truncated to give a finite matrix.

- Dirac notation can also be used in the matrix representation. Equation 3 can be written as

$$\hat{A} |a\rangle = \alpha |a\rangle$$

Operators are now matrices

Kets are now column vectors

Bras are now row vectors

$\langle \quad | \quad \rangle$ now implies matrix multiplication

$$\langle a | b \rangle \equiv \begin{pmatrix} a_1^* & a_2^* & \cdots & \cdots \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ \vdots \end{pmatrix} = a_1^* b_1 + a_2^* b_2 + \cdots$$

$$\langle b|a \rangle^* \equiv (b_1 \quad b_2 \quad \cdots \quad \cdots) \begin{pmatrix} a_1^* \\ a_2^* \\ \vdots \\ \vdots \end{pmatrix} = a_1^* b_1 + a_2^* b_2 + \cdots$$

$$\text{So } \langle a|b \rangle = \langle b|a \rangle^*$$

The **conjugate transpose** (or **Hermitian conjugate**) of a ket is the corresponding bra and vice versa: $|a\rangle^\dagger = \langle a|$, $\langle a|^\dagger = |a\rangle$

Example

The complex conjugate of the ket

$$|a\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \end{pmatrix}$$

is given by

$$|a\rangle^* = \begin{pmatrix} a_1^* \\ a_2^* \\ \vdots \\ \vdots \end{pmatrix}$$

and $|a\rangle^\dagger$ is the matrix transpose of this complex conjugate, i.e.,

$$|a\rangle^\dagger = \langle a| = (a_1^* \quad a_2^* \quad \cdots \quad \cdots)$$

Section 2. Angular momentum

- Important example of the use of operators in quantum mechanics
- Leads to analysis of spin
- Lays the foundation for solutions of the Schrödinger equation in 3D

2.1 Definitions, operators and commutators

- In classical mechanics, the angular momentum of a particle at position \underline{r} and with momentum \underline{p} is:

In quantum mechanics we replace \underline{r} and \underline{p} with the corresponding operators (see section 1.2), so the angular momentum operator becomes:

$$\hat{\underline{L}} = \hat{\underline{r}} \times \hat{\underline{p}}$$

Cartesian components are:

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

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

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

What is the commutator of \hat{L}_x and \hat{L}_y ?

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= \underbrace{\hat{L}_x \hat{L}_y}_{\text{underbrace}} - \underbrace{\hat{L}_y \hat{L}_x}_{\text{underbrace}} \\ &= \underbrace{(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)}_{\text{underbrace}} \underbrace{(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)}_{\text{underbrace}} - \underbrace{(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)}_{\text{underbrace}} \underbrace{(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)}_{\text{underbrace}} \end{aligned}$$

The only non-commuting operators here are \hat{z} and \hat{p}_z , so

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= \hat{y}\hat{p}_x (\hat{p}_z \hat{z} - \hat{z}\hat{p}_z) + \hat{x}\hat{p}_y (\hat{z}\hat{p}_z - \hat{p}_z \hat{z}) \\ &= (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)(\hat{z}\hat{p}_z - \hat{p}_z \hat{z}) \\ &= i\hbar (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar \hat{L}_z \end{aligned}$$

We find

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

- We can also define the square magnitude of the total angular momentum as

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

- What are the commutators of \hat{L}^2 with \hat{L}_x , \hat{L}_y and \hat{L}_z ?

e.g. $[\hat{L}^2, \hat{L}_z] = [\hat{L}_x^2, \hat{L}_z] + [\hat{L}_y^2, \hat{L}_z] + [\hat{L}_z^2, \hat{L}_z]$

We find that the first two commutators on the rhs cancel, and the last commutator is zero, so

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$

- The separate components of angular momentum are **not compatible** and can not be measured simultaneously
- Each component is **compatible** with the total angular momentum

We can therefore look for solutions which are **common eigenfunctions** of \hat{L}^2 and \hat{L}_z

Aside: Spinning top

Uncertainty:

$$\Delta A \Delta B \geq \frac{1}{2} \left| \int \psi^* [\hat{A}, \hat{B}] \psi \right|$$

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

So

$$\begin{aligned}\Delta L_x \Delta L_y &\geq \frac{1}{2} \left| \int \psi^* i\hbar \hat{L}_z \psi \right| \\ &\geq \frac{\hbar}{2} \left| \int \psi^* \hat{L}_z \psi \right| \\ &\geq \frac{\hbar}{2} \left| \langle \hat{L}_z \rangle \right|\end{aligned}$$

Back to the problem: eigenvalues of \hat{L}^2 and \hat{L}_z

- To help in the analysis, we define two more operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y$$

- Properties of \hat{L}_+ and \hat{L}_-

$$\hat{L}_+ \hat{L}_- = (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) \quad (1)$$

$$\begin{aligned} &= \hat{L}_x^2 + \hat{L}_y^2 - i\hat{L}_x\hat{L}_y + i\hat{L}_y\hat{L}_x \\ &= \hat{L}^2 - L_z^2 - i[\hat{L}_x, \hat{L}_y] \\ &= \hat{L}^2 - L_z^2 + \hbar\hat{L}_z \end{aligned}$$

Similarly

$$\hat{L}_- \hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$$

So

$$[\hat{L}_+, \hat{L}_-] = 2\hbar\hat{L}_z$$

$$\begin{aligned} [\hat{L}_z, \hat{L}_+] &= [\hat{L}_z, \hat{L}_x] + i[\hat{L}_z, \hat{L}_y] \\ &= i\hbar(\hat{L}_y - i\hat{L}_x) \end{aligned} \quad (2)$$

So

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

Similarly

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

2.2 Eigenvalues of \hat{L}^2 and \hat{L}_z

Because \hat{L}^2 and \hat{L}_z commute, they must have a **common set of eigenfunctions**. We can write

$$\hat{L}^2 |\phi_n\rangle = \alpha_n |\phi_n\rangle \quad \text{and} \quad \hat{L}_z |\phi_n\rangle = \beta_n |\phi_n\rangle$$

The eigenvalues α_n and β_n can be determined just using operator expressions, together with the condition

$$\alpha_n \geq \beta_n^2$$

The algebra....

$$\hat{L}_z |\phi_n\rangle = \beta_n |\phi_n\rangle$$

$$\hat{L}_+ \hat{L}_z |\phi_n\rangle = \beta_n \hat{L}_+ |\phi_n\rangle$$

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

$$\begin{aligned} \therefore \hat{L}_+ \hat{L}_z |\phi_n\rangle &= (\hat{L}_z \hat{L}_+ - \hbar \hat{L}_+) |\phi_n\rangle \\ &= \hat{L}_z (\hat{L}_+ |\phi_n\rangle) - \hbar (\hat{L}_+ |\phi_n\rangle) \\ &= \beta_n (\hat{L}_+ |\phi_n\rangle) \end{aligned}$$

$$\Rightarrow \hat{L}_z (\hat{L}_+ |\phi_n\rangle) = (\beta_n + \hbar) (\hat{L}_+ |\phi_n\rangle)$$

Similarly, we can show

$$\hat{L}_z (\hat{L}_- |\phi_n\rangle) = (\beta_n - \hbar) (\hat{L}_- |\phi_n\rangle)$$

$\hat{L}_+ |\phi_n\rangle$ is an eigenfunction of \hat{L}_z with eigenvalue $\beta_n + \hbar$ (provided $\hat{L}_+ |\phi_n\rangle \neq 0$)

$\hat{L}_- |\phi_n\rangle$ is an eigenfunction of \hat{L}_z with eigenvalue $\beta_n - \hbar$ (provided $\hat{L}_- |\phi_n\rangle \neq 0$)

More algebra....

$$\hat{L}^2 |\phi_n\rangle = \alpha_n |\phi_n\rangle$$

$$\Rightarrow \hat{L}_+ \hat{L}^2 |\phi_n\rangle = \alpha_n \hat{L}_+ |\phi_n\rangle$$

$$\hat{L}_- \hat{L}^2 |\phi_n\rangle = \alpha_n \hat{L}_- |\phi_n\rangle$$

\hat{L}^2 commutes with \hat{L}_x and \hat{L}_y , so it must commute with \hat{L}_+ and \hat{L}_-

$$\Rightarrow \hat{L}^2 (\hat{L}_+ |\phi_n\rangle) = \alpha_n (\hat{L}_+ |\phi_n\rangle)$$

$$\hat{L}^2 (\hat{L}_- |\phi_n\rangle) = \alpha_n (\hat{L}_- |\phi_n\rangle)$$

$\hat{L}_+ |\phi_n\rangle$ and $\hat{L}_- |\phi_n\rangle$ are eigenfunctions of \hat{L}^2 with eigenvalue α_n

- For each eigenvalue of \hat{L}^2 there are a set of eigenfunctions with different \hat{L}_z eigenvalues. The \hat{L}_+ and \hat{L}_- operators “raise” or “lower” the eigenfunctions within this set.
- \hat{L}_+ and \hat{L}_- are called “ladder operators” or “creation” and “annihilation” operators
- We now use the condition $\alpha_n \geq \beta_n^2$. This implies there is a **maximum and minimum value of β** . Call these β_{\max} and β_{\min} , with corresponding eigenfunctions $|\phi_{\max}\rangle$ and $|\phi_{\min}\rangle$

Yet more algebra....

$$\hat{L}_+ |\phi_{\max}\rangle = 0 \quad \text{so} \quad \hat{L}_- \hat{L}_+ |\phi_{\max}\rangle = 0$$

From above

$$\hat{L}_- \hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z$$

so

$$(\hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z) |\phi_{\max}\rangle = 0$$

i.e.

$$(\alpha - \beta_{\max}^2 - \hbar \beta_{\max}) |\phi_{\max}\rangle = 0$$

$$\therefore \alpha = \beta_{\max} (\beta_{\max} + \hbar)$$

In a similar way, starting from $\hat{L}_- |\phi_{\min}\rangle = 0$ we find

$$\alpha = \beta_{\min} (\beta_{\min} - \hbar)$$

It follows that

$$\beta_{\min} = -\beta_{\max}$$

such that

$$\begin{aligned} \alpha &= \beta_{\min} (\beta_{\min} - \hbar) \\ &= -\beta_{\max} (-\beta_{\max} - \hbar) \\ &= \beta_{\max} (\beta_{\max} + \hbar) \end{aligned}$$

as required

Neighbouring values of β on the \hat{L}_z “ladder” differ by \hbar , so

$$\beta_{\max} - \beta_{\min} = n\hbar \quad (n \text{ integer})$$

$$\text{So } \beta_{\max} - (-\beta_{\max}) = 2\beta_{\max} = n\hbar$$

$$\text{or } \beta_{\max} = n\hbar/2$$

$$\Rightarrow \beta_{\max} = -\beta_{\min} = \frac{n}{2}\hbar \equiv \ell\hbar$$

So

$$\alpha = \beta_{\max} (\beta_{\max} + \hbar) = \ell \hbar (\ell \hbar + \hbar) = \ell (\ell + 1) \hbar^2$$

$$\alpha = \beta_{\min} (\beta_{\min} - \hbar) = \ell \hbar (\ell \hbar + \hbar) = \ell (\ell + 1) \hbar^2$$

Then

$$\hat{L}^2 |\phi\rangle = \alpha |\phi\rangle \text{ with } \alpha = \ell (\ell + 1) \hbar^2$$

$\ell = n/2$ is integer or half integer

Also

$$\hat{L}_z |\phi\rangle = \beta |\phi\rangle \text{ with } \beta_{\min} = -\ell \hbar \text{ and } \beta_{\max} = +\ell \hbar$$

$$\hat{L}_z (\hat{L}_+ |\phi\rangle) = (\beta + \hbar) (\hat{L}_+ |\phi\rangle)$$

$$\hat{L}_z (\hat{L}_- |\phi\rangle) = (\beta - \hbar) (\hat{L}_- |\phi\rangle)$$

Ladder of eigenvalues of \hat{L}_z separated by integer units of \hbar , $\Delta\beta = \pm \hbar$

Finally, we have

Eigenvalues of \hat{L}^2 are $\alpha = \ell (\ell + 1) \hbar^2$, with ℓ an integer or “half integer”

For each value of ℓ , eigenvalues of \hat{L}_z can be written as $\beta = m \hbar$, where m varies in integer steps between $-\ell$ and $+\ell$

- For **orbital** angular momentum (i.e. what we've been talking about so far) only integer values of ℓ matter.
- However, for **more general** angular momentum, the half integer solutions are also relevant.

$$L^2 = \ell(\ell+1)\hbar^2 \Rightarrow L = \sqrt{\ell(\ell+1)}\hbar$$

$$L_z = m\hbar, \quad m = -\ell, -\ell+1, \dots, +\ell$$

For $\ell = 1/2$ see later

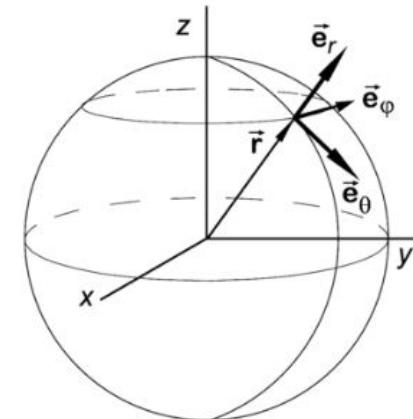
2.3 Eigenfunctions of \hat{L}^2 and \hat{L}_z

These cannot be obtained just from operator algebra – we have to solve the equations. It is most convenient to use **spherical polar coordinates**.

Start from

$$\hat{L} = \hat{\underline{r}} \times \hat{\underline{p}} = -i\hbar \underline{r} \times \nabla$$

Use spherical polars: -



\underline{r} : intercepts sphere at point P

Unit vectors: -

\underline{e}_r : in radial direction at point P

\underline{e}_θ : tangent to sphere through point P with constant longitude

\underline{e}_ϕ : tangent to sphere through point P with constant latitude

In spherical polars

$$\underline{\nabla} = \underline{e}_r \frac{\partial}{\partial r} + \underline{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \underline{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$$

So

$$\begin{aligned}\hat{L} &= -i\hbar \begin{vmatrix} \underline{e}_r & \underline{e}_\theta & \underline{e}_\phi \\ r & 0 & 0 \\ \frac{\partial}{\partial r} & \frac{1}{r} \frac{\partial}{\partial \theta} & \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \end{vmatrix} \\ &= -i\hbar \left(\underline{e}_\phi \frac{\partial}{\partial \theta} - \underline{e}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right)\end{aligned}$$

The relation between Cartesian and spherical polar unit vectors is: -

$$\begin{pmatrix} \underline{e}_x \\ \underline{e}_y \\ \underline{e}_z \end{pmatrix} = \begin{pmatrix} \sin \theta \cos \phi & \cos \theta \cos \phi & -\sin \phi \\ \sin \theta \sin \phi & \cos \theta \sin \phi & \cos \phi \\ \cos \theta & -\sin \theta & 0 \end{pmatrix} \begin{pmatrix} \underline{e}_r \\ \underline{e}_\theta \\ \underline{e}_\phi \end{pmatrix}$$

For \hat{L}^2 we find

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

- We want to solve

$$\hat{L}^2 |Y_{\ell m}(\theta, \phi)\rangle = \ell(\ell+1) \hbar^2 |Y_{\ell m}(\theta, \phi)\rangle$$

$$\hat{L}_z |Y_{\ell m}(\theta, \phi)\rangle = m\hbar |Y_{\ell m}(\theta, \phi)\rangle$$

$Y_{\ell m}(\theta, \phi)$ are the **common eigenfunctions** of \hat{L}^2 and \hat{L}_z with **eigenvalues** $\ell(\ell+1)\hbar^2$ and $m\hbar$ respectively

- The **solutions** $Y_{\ell m}(\theta, \phi)$ **are called spherical harmonics**. Derivations of them can be found in textbooks and in other units.

- The lowest few spherical harmonics are

$$Y_{00} = \sqrt{\frac{1}{4\pi}}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta \exp(\pm i\phi)$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}} (3\cos^2 \theta - 1)$$

$$Y_{2\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \cos \theta \sin \theta \exp(\pm i\phi)$$

$$Y_{2\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta \exp(\pm 2i\phi)$$

Normalisation: $\int_0^{2\pi} \int_0^\pi |Y_{\ell m}(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1$

2.4 Spin angular momentum

- The Stern-Gerlach experiment allows us to measure the z component of angular momentum.
- Orbital angular momentum is insufficient to explain results for atoms
- We therefore postulate that quantum particles have an **intrinsic angular momentum**, or spin
- We postulate **spin operators** \hat{S}_x , \hat{S}_y , \hat{S}_z with the same commutation properties as \hat{L}_x , \hat{L}_y , \hat{L}_z , i.e.

- We can also define

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

All of the previous analysis for angular momentum operators follows through, and we can conclude that:

- Eigenvalues of \hat{S}^2 are $s(s+1)\hbar^2$, with s an integer or “half integer”
- Eigenvalues of \hat{S}_z are $m_s\hbar$, where m_s varies in integer steps between $-s$ and s

For spin, the half integer solutions matter. Atoms with no orbital angular momentum and a single unpaired electron split into two beams in a Stern-Gerlach experiment.

∴ Electrons are spin-half particles, i.e. $s = \frac{1}{2}$

2.5 Pauli spin matrices

What are the eigenfunctions of \hat{S}^2 and \hat{S}_z for a spin-half particle?

These cannot be functions of the particle's position, and so we need a representation that doesn't depend on spatial coordinates

In section 1.11 we discussed the **matrix representation** of quantum mechanics. This turns out to be a natural representation for spin angular momentum

Operators become matrices

Bra/Kets become row/column vectors

- The **Pauli spin matrices** are defined as

- The spin components are

These obey all the commutation relations, e.g.

$$\begin{aligned} [\hat{S}_x, \hat{S}_y] &= \frac{\hbar^2}{4} \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right) \\ &= \frac{\hbar^2}{4} \left(\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \right) \\ &= i\hbar \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\hbar \hat{S}_z \end{aligned}$$

- It is simple to calculate the eigenvalues and eigenfunctions (i.e. eigenvectors) of \hat{S}_x , \hat{S}_y , \hat{S}_z :

Component	Eigenvalue	Eigenvector
\hat{S}_x	$+\frac{\hbar}{2}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$
\hat{S}_x	$-\frac{\hbar}{2}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$
\hat{S}_y	$+\frac{\hbar}{2}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}$
\hat{S}_y	$-\frac{\hbar}{2}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$
\hat{S}_z	$+\frac{\hbar}{2}$	$\begin{pmatrix} 1 \\ 0 \end{pmatrix}$
\hat{S}_z	$-\frac{\hbar}{2}$	$\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

- What about \hat{S}^2 ? We find

$$\hat{S}_x^2 = \hat{S}_y^2 = \hat{S}_z^2 = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

so $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ becomes

$$\hat{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

- As expected, \hat{S}^2 commutes with \hat{S}_x , \hat{S}_y , \hat{S}_z

- All of the above eigenvectors are also eigenvectors of \hat{S}^2 with **eigenvalue** $\frac{3}{4}\hbar^2$, as

expected for $s = \frac{1}{2}$

Section 3. Many particle systems

- As discussed in section 1.8, if the potential energy is not time dependent, then all information about the particle state can be obtained by solving the TISE
- How do we write the TISE for systems containing more than one particle?
- Illustrate with examples of two-particle systems
- Discuss the consequences of the indistinguishability of identical particles
- Fermions and bosons and symmetry of the wavefunction.
- Pauli exclusion principle

3.1 Wavefunction and operators

- Wavefunction for an N particle system (ignoring spin)

where

is the probability that particle 1 is in volume element $d^3 \underline{r}_1$ and particle 2 is in volume element $d^3 \underline{r}_2 \dots$ and particle N is in volume element $d^3 \underline{r}_N$

Normalisation: $\iiint |\Psi|^2 d^3 \underline{r}_1 d^3 \underline{r}_2 \dots d^3 \underline{r}_N = 1$

- Momentum operator for single particle i

$$\hat{p}_i = -i\hbar\nabla_i$$

For all N particles

$$\hat{p} = \sum_{i=1}^N \hat{p}_i$$

- Operators describing single particle observables commute when they refer to different particles e.g.

$$[\hat{p}_{xi}, \hat{x}_j] = -i\hbar\delta_{ij}$$

- The Hamiltonian

$$\hat{H} = -\sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + V(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$$

In general potential energy $V(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$ will depend on (i) interaction between particles and (ii) presence of an external field

3.2 Two interacting particles, no external field

- The potential energy depends only on the separation between the particles

$$V(\underline{r}_1, \underline{r}_2) = V(\underline{r})$$

where $\underline{r} = \underline{r}_1 - \underline{r}_2$. The two particle Hamiltonian becomes

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(\underline{r}_1, \underline{r}_2) \quad (1)$$

- As in classical mechanics, treat the centre-of-mass and relative motion separately

Centre of mass coordinate given by

$$\underline{R} = \frac{m_1 \underline{r}_1 + m_2 \underline{r}_2}{m_1 + m_2} = \frac{m_1}{M} \underline{r}_1 + \frac{m_2}{M} \underline{r}_2$$

where total mass $M = m_1 + m_2$. Velocity of centre of mass

$$\underline{V} = \frac{d\underline{R}}{dt} = \frac{m_1}{M} \underline{v}_1 + \frac{m_2}{M} \underline{v}_2$$

Momentum of centre of mass

$$\underline{P} = M\underline{V} = \underline{p}_1 + \underline{p}_2 \quad (2)$$

For relative motion, particle of

with coordinate $\underline{r} = \underline{r}_1 - \underline{r}_2$ has velocity

$$\underline{v} = \frac{d\underline{r}}{dt} = \underline{v}_1 - \underline{v}_2$$

Momentum

$$\begin{aligned} \underline{p} &= \mu \underline{v} = \frac{m_1 m_2}{M} \underline{v}_1 - \underline{v}_2 \\ &= \frac{m_2 \underline{p}_1 - m_1 \underline{p}_2}{M} \end{aligned} \quad (3)$$

Solving (2) and (3) gives

$$\underline{p}_1 = \underline{p} + \frac{m_1}{M} \underline{P}$$

$$\underline{p}_2 = -\underline{p} + \frac{m_2}{M} \underline{P}$$

- So the Hamiltonian operator in (1) becomes

$$\begin{aligned} \hat{H} &= \frac{m_1 + m_2}{2M^2} \underline{\hat{P}}^2 + \frac{1}{2} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \underline{\hat{p}}^2 + V(\underline{r}) \\ &= \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2\mu} + V(\underline{r}) \end{aligned}$$

Or

$$\hat{H} = \hat{H}_{\text{CM}} + \hat{H}_{\text{rel}}$$

where

$$\hat{H}_{\text{CM}} = -\frac{\hbar^2}{2M} \nabla_{\underline{R}}^2$$

$$\hat{H}_{\text{rel}} = -\frac{\hbar^2}{2\mu} \nabla_{\underline{r}}^2 + V(\underline{r})$$

We have used $\hat{P} = -i\hbar \nabla_{\underline{R}}$ and $\hat{p} = -i\hbar \nabla_{\underline{r}}$ where the gradient operators $\nabla_{\underline{R}}$ and $\nabla_{\underline{r}}$ are with respect to the vectors \underline{R} and \underline{r} , respectively.

- We can use the separation of variables method and write

$$\phi(\underline{R}, \underline{r}) = U(\underline{R})u(\underline{r})$$

The problem separates into 2 TISEs, one for the centre of mass

and one for a particle of reduced mass μ moving in the potential $V(\underline{r})$

where the total energy $E = E_R + E_r$.

Example: Central potentials

- If the potential energy $V(\underline{r})$ depends only on the distance from the origin, then the 3D Schrodinger equation separates nicely in spherical polar coordinates $\underline{r} = (r, \theta, \phi)$
- The TISE becomes

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \phi^2} \right] + V(r) u = E u \quad (1)$$

Potential energy V is a function of r only

- We look for **separable** solutions of the form

(2)

R is a function only of the radial coordinate
 Y is a function only of the angular coordinates.
The use of the symbol Y is not an accident!

Substitute (2) into (1), multiply by r^2 and divide through by u :

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + r^2 V(r) - r^2 E \right] - \frac{\hbar^2}{2\mu} \left[\frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y} \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] = 0$$

- The first bracket depends only on r and the second bracket depends only on θ and ϕ , but

the whole equation holds at every point in space. Therefore, each bracket must be a constant. We call the second bracket $-\lambda$, which gives:

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(V(r) + \frac{\hbar^2 \lambda}{2\mu r^2} \right) R = E R \quad (3)$$

$$-\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = \lambda Y \quad (4)$$

- In section 2.3 we saw that the angular momentum operator \hat{L}^2 in spherical polars is

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (5)$$

and its eigenfunctions are spherical harmonics

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right) R = E R \quad (6)$$

By comparing (4), (5) and (6), we can see that the angular parts of the wavefunction must be spherical harmonics and that $\lambda = \ell(\ell+1)$

The angular momentum quantum numbers ℓ and m characterise the angular parts of the wavefunction

The radial equation (3) becomes

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right) R = E R \quad (7)$$

Notes

- All central potentials have their angular solutions given by spherical harmonics. The radial dependence is found by solving (7)
- The energy eigenvalues are also given by (7). They depend on ℓ but do not depend on m .
- Solutions with a given ℓ value (which fixes the total angular momentum), but different m values (i.e. different L_z components) are degenerate

Case of the Hydrogen atom

For the H atom $V(r)$ is the electrostatic potential energy between an electron and a proton

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

and (7) can be solved to find $R(r)$, which leads to the introduction of a new quantum number n ($= 1, 2, 3\dots$).

$$n, \ell, m \text{ satisfy } n > \ell \text{ and } |m| \leq \ell.$$

The energy eigenvalues

$$E_n = -\frac{1}{n^2} \left(\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \right)$$

depend only on n . The H atom is a special case in this respect. For most central potentials, the energy depends on both n and ℓ .

- For $n=1, \ell=0, m=0$,

$$R(r) \propto \exp(-r/a_0)$$

where

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

Also $Y_{00} = \sqrt{\frac{1}{4\pi}}$

So

$$u_{100}(r, \theta, \phi) = A \exp(-r/a_0)$$

To find the normalisation constant A we require

$$\iiint r^2 \sin \theta dr d\theta d\phi |u(r, \theta, \phi)|^2 = 1$$

Eigenvalue $E_1 = -13.6 \text{ eV}$

- For $n=2, \ell=1, m=-1, 0, 1$

$$R(r) \propto r \exp(-r/2a_0)$$

Also

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta \exp(\pm i\phi)$$

So the degenerate eigenfunctions

$$u_{21-1}(r, \theta, \phi) = A r \exp(-r/2a_0) \sin \theta \exp(-i\phi)$$

$$u_{210}(r, \theta, \phi) = A r \exp(-r/2a_0) \cos \theta$$

$$u_{211}(r, \theta, \phi) = A r \exp(-r/2a_0) \sin \theta \exp(+i\phi)$$

Eigenvalue: $E_2 = -13.6/4 \text{ eV}$

3.3 Two distinguishable non-interacting particles in an external field

- The particles are **independent** because they do not interact. Potential energy

$$V(\underline{r}_1, \underline{r}_2) = V_1(\underline{r}_1) + V_2(\underline{r}_2)$$

- So the Hamiltonian

- Use the separation of variables method and write

$$\phi(\underline{r}_1, \underline{r}_2) = u_a(\underline{r}_1)u_b(\underline{r}_2)$$

- The two particle TISE $\hat{H}\phi = E\phi$ becomes

$$\left[-\frac{\hbar^2}{2m_1} \frac{1}{u_a} \nabla_1^2 u_a + \frac{1}{u_a} V_1(\underline{r}_1) u_a \right] + \left[-\frac{\hbar^2}{2m_2} \frac{1}{u_b} \nabla_2^2 u_b + \frac{1}{u_b} V_2(\underline{r}_2) u_b \right] = E$$

As above, each bracket is a function of only one variable, but the whole equation holds for every point in space. **Therefore each bracket must be a constant, and the sum of these constants must be E .**

The problem separates into 2 separate TISEs

$$\begin{aligned} -\frac{\hbar^2}{2m_1} \nabla_1^2 u_a + V_1(\underline{r}_1) u_a &= E_1 u_a \\ -\frac{\hbar^2}{2m_2} \nabla_2^2 u_b + V_2(\underline{r}_2) u_b &= E_2 u_b \end{aligned}$$

where $E = E_1 + E_2$

3.4 Indistinguishable particles

- **Identical particles** cannot be distinguished in any physical measurement and are therefore **indistinguishable**
- A **Hermitian** operator, representing a physical observable, must remain unchanged if the particle labels are interchanged i.e.

$$\hat{A}(1,2) = \hat{A}(2,1) \quad (1)$$

- Introduce the **particle exchange operator** \hat{P}_{12} .

When \hat{P}_{12} acts on an eigenfunction $\phi(1,2)$ of $\hat{A}(1,2)$, the labels 1 & 2 are interchanged

$$\hat{P}_{12}\phi(1,2) = \phi(2,1)$$

If α is the corresponding eigenvalue

$$\hat{A}(1,2)\phi(1,2) = \alpha\phi(1,2) \quad (2)$$

Swapping labels should have no effect

$$\hat{A}(2,1)\phi(2,1) = \alpha\phi(2,1) \quad (3)$$

Applying \hat{P}_{12} to (2)

$$\begin{aligned} \hat{P}_{12}\hat{A}(1,2)\phi(1,2) &= \alpha\hat{P}_{12}\phi(1,2) \\ &= \alpha\phi(2,1) \\ &= \hat{A}(2,1)\phi(2,1) \quad \text{using (3)} \\ &= \hat{A}(1,2)\hat{P}_{12}\phi(1,2) \quad \text{using (1)} \end{aligned}$$

So

$$\hat{P}_{12}\hat{A}(1,2)\phi(1,2) - \hat{A}(1,2)\hat{P}_{12}\phi(1,2) = 0$$

i.e., the commutation relation

$$[\hat{P}_{12}, \hat{A}(1,2)] = 0 \quad (4)$$

Hence, \hat{P}_{12} is compatible with any Hermitian operator $\hat{A}(1,2)$. An eigenfunction $\phi(1,2)$ of $\hat{A}(1,2)$ must therefore be a solution of the eigenvalue equation

$$\hat{P}_{12}\phi(1,2) = p\phi(1,2) \quad (5)$$

where p is the eigenvalue. So

- From the definition of \hat{P}_{12}

$$\begin{aligned}\phi(1,2) &= \hat{P}_{12}\phi(2,1) \\ &= p\phi(2,1)\end{aligned}$$

Hence

$$\phi(1,2) = \pm\phi(2,1)$$

Eigenfunction is **symmetric** if there is no change of sign on particle interchange (+ sign)

Eigenfunction is **antisymmetric** if there is change of sign on particle interchange (– sign)

- From (4), \hat{P}_{12} and the Hermitian operator $\hat{A}(1,2)$ share a **common set** of eigenfunctions. So, if a system starts in a symmetric (antisymmetric) state, the application of \hat{P}_{12} will not change that state, i.e. it will **remain** symmetric (antisymmetric) for all time

- Turns out that **every particle is described by either a symmetric or antisymmetric wavefunction**. It is an empirical fact that mixed symmetry does not occur

3.5 Two non-interacting indistinguishable particles in an external field

- In section 3.3, we considered the TISE for two non-interacting distinguishable particles in an external field. For particle 1 in state a with eigenfunction $u_a(\underline{r}_1)$ and particle 2 in state b with eigenfunction $u_b(\underline{r}_2)$ we found solutions of the form $u_a(\underline{r}_1)u_b(\underline{r}_2)$
- For two non-interacting **indistinguishable** particles, $m_1 = m_2$ and $V_1(\underline{r}_1) = V_1(\underline{r}_2)$ and $V_2(\underline{r}_2) = V_2(\underline{r}_1)$. The solution to the TISE cannot depend on which particle is in which state
- Need to look for solutions that have the appropriate **symmetry** with respect to particle exchange. These are **linear combinations** of $u_a(\underline{r}_1)u_b(\underline{r}_2)$ and $u_a(\underline{r}_2)u_b(\underline{r}_1)$

$$u_+(1,2) = \frac{1}{\sqrt{2}} [u_a(1)u_b(2) + u_a(2)u_b(1)]$$

and

$$u_-(1,2) = \frac{1}{\sqrt{2}} [u_a(1)u_b(2) - u_a(2)u_b(1)]$$

Note change of notation for simplicity of representation

- As required

$$\begin{aligned} u_+(2,1) &= \frac{1}{\sqrt{2}} [u_a(2)u_b(1) + u_a(1)u_b(2)] \\ &= u_+(1,2) \end{aligned}$$

and

$$\begin{aligned} u_-(2,1) &= \frac{1}{\sqrt{2}} [u_a(2)u_b(1) - u_a(1)u_b(2)] \\ &= -u_-(1,2) \end{aligned}$$

- If two fermions tried to occupy the same state such that $u_a = u_b$

$$\begin{aligned} u_-(1,2) &= \frac{1}{\sqrt{2}} [u_a(1)u_a(2) - u_a(2)u_a(1)] \\ &= 0 \end{aligned}$$

i.e. the state does not exist.

This is the **Pauli exclusion principle: two fermions cannot exist in the same single particle state** (Noble Prize 1945). The principle is the cornerstone of atomic and molecular physics and chemistry

The occupation of a fermion state is either zero or unity – **Fermi-Dirac** statistics

- For bosons, $u_+(1,2) \neq 0$ if $u_a = u_b$, i.e. the state exists. There is **no limit** on the number of particles that can occupy the same quantum state – **Bose-Einstein** statistics

At low temperatures, a system of bosons (e.g. liquid ${}^4\text{He}$) exhibits a tendency for **all particles to occupy the same ground state**. This is the phenomenon of **Bose-Einstein condensation** (Nobel Prize in Physics 2001)

3.6 Two non-interacting indistinguishable spin $\frac{1}{2}$ fermions

- In general, the spin of particles cannot be ignored
- If \hat{S}_i is the operator for a fermion with spin $s_i = 1/2$ ($i = 1, 2$), the operator for the total spin $\hat{S} = \hat{S}_1 + \hat{S}_2$
- Expect that the net spin of the system is either $S = s_1 + s_2 = 1$ (spins parallel $\uparrow\uparrow$) or $S = s_1 - s_2 = 0$ (spins antiparallel $\uparrow\downarrow$)
- If the spin eigenfunctions are denoted by $\chi_{SM_S}(1,2)$, expect that (see Section 2.2)

$$\hat{S}^2 \chi_{SM_S}(1,2) = S(S+1)\hbar^2 \chi_{SM_S}(1,2)$$

$$\hat{S}_z \chi_{SM_S}(1,2) = M_S \hbar \chi_{SM_S}(1,2)$$

where the ‘spin magnetic quantum number’
 $M_s = -S, -S+1, \dots, S$

The total spin operator

$$\begin{aligned}\hat{S}^2 &= (\hat{S}_1 + \hat{S}_2) \bullet (\hat{S}_1 + \hat{S}_2) \\ &= \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \bullet \hat{S}_2\end{aligned}$$

where

$$\hat{S}_1 \bullet \hat{S}_2 = \hat{S}_{x1}\hat{S}_{x2} + \hat{S}_{y1}\hat{S}_{y2} + \hat{S}_{z1}\hat{S}_{z2}$$

The z component of the total spin operator

$$\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$$

- Represent the eigenfunctions for two fermions with spin $s_i = 1/2$ ($i = 1, 2$) by

$$\alpha_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \beta_i = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

such that

$$\hat{S}_{zi}\alpha_i = \frac{\hbar}{2}\alpha_i \quad \text{and} \quad \hat{S}_{zi}\beta_i = -\frac{\hbar}{2}\beta_i$$

Example

For a two-particle state such as $\alpha_1\alpha_2$, the subscripts refer to different electrons. So

$$\hat{S}_{z1}\alpha_1\alpha_2 = (\hat{S}_{z1}\alpha_1)\alpha_2 = \frac{\hbar}{2}\alpha_1\alpha_2$$

and

$$\hat{S}_{z2}\alpha_1\alpha_2 = \alpha_1(\hat{S}_{z2}\alpha_2) = \frac{\hbar}{2}\alpha_1\alpha_2$$

- For $S = 1$, expect three spin eigenfunctions corresponding to $M_s = -1, 0, 1$

These states are given by the symmetric combinations

$$\chi_{11}(1,2) = \alpha_1\alpha_2,$$

$$\chi_{1-1}(1,2) = \beta_1\beta_2,$$

$$\chi_{10}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 + \alpha_2\beta_1]$$

Check: For $\chi_{11}(1,2)$,

$$\begin{aligned}\hat{S}^2\chi_{11}(1,2) &= (\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \bullet \hat{S}_2)\chi_{11}(1,2) \\ &= 2\hbar^2\chi_{11}(1,2) = S(S+1)\hbar^2\chi_{11}(1,2) \\ &\Rightarrow S = 1\end{aligned}$$

$$\begin{aligned}\hat{S}_z\chi_{11}(1,2) &= (\hat{S}_{z1} + \hat{S}_{z2})\chi_{11}(1,2) \\ &= \hbar\chi_{11}(1,2) = M_s\hbar\chi_{11}(1,2) \\ &\Rightarrow M_s = 1\end{aligned}$$

- For $S = 0$, expect one spin eigenfunction corresponding to $M_s = 0$

The state is given by the antisymmetric combination

$$\chi_{00}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \alpha_2\beta_1]$$

Check

$$\begin{aligned}\hat{S}^2\chi_{00}(1,2) &= (\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \bullet \hat{S}_2)\chi_{00}(1,2) \\ &= 0\chi_{00}(1,2) = S(S+1)\hbar^2\chi_{00}(1,2) \\ &\Rightarrow S = 0\end{aligned}$$

$$\begin{aligned}\hat{S}_z\chi_{00}(1,2) &= (\hat{S}_{z1} + \hat{S}_{z2})\chi_{00}(1,2) \\ &= 0\chi_{00}(1,2) = M_s\chi_{00}(1,2) \\ &\Rightarrow M_s = 0\end{aligned}$$

- For a two-particle system of identical spin 1/2 fermions, write the overall space and spin dependent eigenfunctions as

$$\phi(1,2) = u(1,2)\chi(1,2)$$

- There are two ways of generating the antisymmetric eigenfunctions $\phi(1,2)$ required for fermions

- Triplet state $\uparrow\uparrow$

$u(1,2)$ antisymmetric and $\chi(1,2)$ symmetric

$$u_-(1,2) = \frac{1}{\sqrt{2}} [u_a(1)u_b(2) - u_a(2)u_b(1)]$$

with

$$\chi_{11}(1,2) = \alpha_1\alpha_2$$

or

$$\chi_{1-1}(1,2) = \beta_1\beta_2$$

or

$$\chi_{10}(1,2) = \frac{1}{\sqrt{2}} [\alpha_1\beta_2 + \alpha_2\beta_1]$$

If $\underline{r}_1 \approx \underline{r}_2$, then $u_a(1)u_b(2) \approx u_a(2)u_b(1)$ such that $u_-(1,2) \approx 0$ and $\phi(1,2) \approx 0 \Rightarrow$ fermions with aligned spins have a small probability of being found in the same region of space

- Singlet state $\uparrow\downarrow$

$u(1,2)$ symmetric and $\chi(1,2)$ antisymmetric

$$u_+(1,2) = \frac{1}{\sqrt{2}} [u_a(1)u_b(2) + u_a(2)u_b(1)]$$

with

$$\chi_{00}(1,2) = \frac{1}{\sqrt{2}} [\alpha_1\beta_2 - \alpha_2\beta_1]$$

If $\underline{r}_1 \approx \underline{r}_2$, $\phi(1,2) \neq 0 \Rightarrow$ fermions with anti-parallel spins have a larger probability of being found in the same region of space

- Two spin $\frac{1}{2}$ fermions in a triplet state act as if they repel each other at short separations. This is not e.g. the Coulomb repulsion because we have assumed that the fermions do not interact. It is a property of the anti-symmetric space eigenfunctions

- Two spin $\frac{1}{2}$ fermions in a singlet state act as if they attract each other at short separations
- So the spin $\frac{1}{2}$ fermions move under the influence of a force whose sign (repulsive or attractive) depends on the relative orientation of their spins. This is the exchange force
- He atom provides the simplest realistic system where the question of particle identity plays an important role

Example

Consider two non-interacting spin $1/2$ fermions in a 1D infinite square well potential.

If the spins are parallel, the total spin $S = 1$.

The space and spin dependent eigenfunction

$$\phi(1,2) = u_-(1,2)\chi_{1M_S}(1,2)$$

where

$$u_-(1,2) = \frac{1}{\sqrt{2}}[u_a(1)u_b(2) - u_a(2)u_b(1)].$$

If the fermions try to occupy the **same** state with $a = b$, then $u_-(1,2) = 0$. The ground state does not correspond $a = b = 1$ because this state does not exist.

If the spins are antiparallel, the total spin $S = 0$.

The space and spin eigenfunction for the ground state

$$\phi(1,2) = u_+(1,2)\chi_{00}(1,2)$$

with $a = b = 1$

$$\begin{aligned} u_+(1,2) &= \frac{1}{2}[u_1(x_1)u_1(x_2) + u_1(x_2)u_1(x_1)] \\ &= u_1(x_1)u_1(x_2) \end{aligned}$$

i.e. the state exists. The Hamiltonian

$$\hat{H} = \hat{T}_1 + \hat{T}_2$$

where

$$\hat{T}_i = -\frac{\hbar^2}{2m} \frac{d^2}{dx_i^2}$$

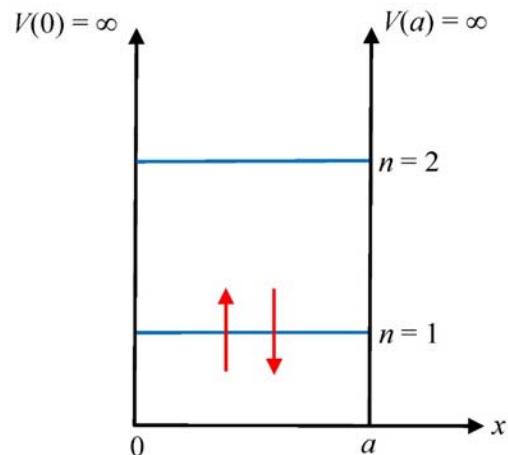
and

$$\hat{T}_i u_1(x_i) = E_1 u_1(x_i)$$

TISE for the two-particle system

$$\begin{aligned}
\hat{H}\phi(1,2) &= (\hat{T}_1 + \hat{T}_2)\phi(1,2) \\
&= \chi_{00} \left\{ [\hat{T}_1 u_1(x_1)] u_1(x_2) + u_1(x_1) [\hat{T}_2 u_1(x_2)] \right\} \\
&= 2E_1 \chi_{00} u_1(x_1) u_1(x_2) \\
&= 2E_1 \phi(1,2)
\end{aligned}$$

So, the ground state corresponds to $a = b = 1$,
and the ground state energy is $2E_1$

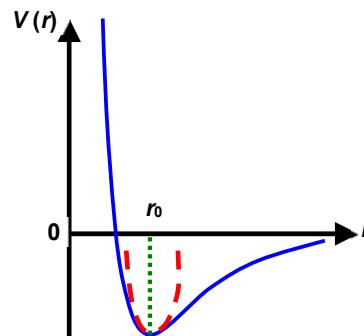


Section 4. Approximate methods for stationary states

In this course and the year 2 course we have looked at examples where the TISE in 1D or 3D has exact solutions (infinite square well, finite square well, harmonic oscillator, H atom, etc).

- Introduce methods for cases where exact solutions cannot be found, in particular where the system is “close to” an exactly solvable case
- Non-degenerate perturbation theory
- Degenerate perturbation theory

Example Harmonic oscillator



4.1 Non-degenerate perturbation theory

- Consider the case where the total energy (Hamiltonian) operator can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

- \hat{H}_0 is the Hamiltonian of the “unperturbed” system, and we assume that we know its eigenvalues and eigenfunctions, i.e. solutions of

$$\hat{H}_0 |\phi_{0n}\rangle = E_{0n} |\phi_{0n}\rangle \quad (1)$$

- \hat{H}' represents an additional energy term that acts as a “perturbation” on the system described by \hat{H}_0 . We **assume that it is small in comparison to \hat{H}_0** .

Example: \hat{H}_0 could be the Hamiltonian for the H atom, and \hat{H}' could be the effect of a weak electric field

- What is the effect of \hat{H}' on the eigenvalues and eigenfunctions of \hat{H}_0 (i.e on E_{0n} and $|\phi_{0n}\rangle$)?

In this sub-section, we assume that $|\phi_{0n}\rangle$ is not degenerate, so E_{0n} is unique

We build up the solution in powers of \hat{H}' . To do this, it's helpful to write

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \quad (2)$$

We look for solutions of

$$\hat{H} |\phi_n\rangle = E_n |\phi_n\rangle \quad (3)$$

in the form

$$E_n = E_{0n} + \lambda E_{1n} + \lambda^2 E_{2n} + \dots \quad (4)$$

$$|\phi_n\rangle = |\phi_{0n}\rangle + \lambda |\phi_{1n}\rangle + \lambda^2 |\phi_{2n}\rangle + \dots \quad (5)$$

- Substitute (4) and (5) into (3) and equate the terms with different powers of λ

$$\hat{H}_0 |\phi_{0n}\rangle = E_{0n} |\phi_{0n}\rangle \quad (6)$$

$$\hat{H}' |\phi_{0n}\rangle + \hat{H}_0 |\phi_{1n}\rangle = E_{0n} |\phi_{1n}\rangle + E_{1n} |\phi_{0n}\rangle \quad (7)$$

$$\hat{H}' |\phi_{1n}\rangle + \hat{H}_0 |\phi_{2n}\rangle = E_{0n} |\phi_{2n}\rangle + E_{1n} |\phi_{1n}\rangle + E_{2n} |\phi_{0n}\rangle \quad (8)$$

Write the first order correction $|\phi_{1n}\rangle$ as

$$|\phi_{1n}\rangle = \sum_k a_{nk} |\phi_{0k}\rangle \quad (9)$$

[This is an eigenfunction expansion, as in section 1.5. The coefficient a_{nk} gives the “amount” of $|\phi_{0k}\rangle$ in $|\phi_{1n}\rangle$.]

- Substitute (9) into (7) and use (6) to get

$$(\hat{H}' - E_{1n})|\phi_{0n}\rangle = \sum_k a_{nk} (E_{0n} - E_{0k}) |\phi_{0k}\rangle$$

- “Close” both sides with $\langle\phi_{0n}|$. Because of orthogonality, $\langle\phi_{0n}|\phi_{0k}\rangle = \delta_{nk}$, and the r.h.s. is zero. The l.h.s. gives

$$E_{1n} = \langle\phi_{0n}|\hat{H}'|\phi_{0n}\rangle \quad (10)$$

In 1D this becomes

$$E_{1n} = \int \phi_{0n}^*(x) \hat{H}'(x) \phi_{0n}(x) dx$$

In 3D this becomes

$$E_{1n} = \iiint \phi_{0n}^*(\underline{r}) \hat{H}'(\underline{r}) \phi_{0n}(\underline{r}) d^3r$$

This process can be continued. We eventually find

$$\begin{aligned} E_n &= E_{0n} + \langle\phi_{0n}|\hat{H}'|\phi_{0n}\rangle \\ &\quad + \sum_{k \neq n} \frac{\langle\phi_{0n}|\hat{H}'|\phi_{0k}\rangle \langle\phi_{0k}|\hat{H}'|\phi_{0n}\rangle}{E_{0n} - E_{0k}} + \dots \end{aligned} \quad (11)$$

$$|\phi_n\rangle = |\phi_{0n}\rangle + \sum_{k \neq n} \frac{\langle\phi_{0k}|\hat{H}'|\phi_{0n}\rangle}{E_{0n} - E_{0k}} |\phi_{0k}\rangle + \dots \quad (12)$$

Example

An infinite square well in 1D of width a has a potential “bump” at its centre, of height V' and covering one fifth of the width of the well.

What is the first order effect on the eigenvalues?

$$\therefore E_{1n} = V' \left(0.2 - \frac{\sin(1.2n\pi) - \sin(0.8n\pi)}{2n\pi} \right)$$

Energy of perturbed system (to first order)

Unperturbed system:

$$\phi_{0n}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad E_{0n} = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

First order perturbation:

$$E_{1n} = \frac{2}{a} \int_{0.4a}^{0.6a} \sin\left(\frac{n\pi x}{a}\right) V' \sin\left(\frac{n\pi x}{a}\right) dx$$

4.2 Degenerate perturbation theory

- If we look at equations (11) and (12) of section 4.1, we can see that problems will arise if the separation of unperturbed energy levels $E_{0n} - E_{0k}$ becomes smaller than $\langle \phi_{0k} | \hat{H}' | \phi_{0n} \rangle$.
- In particular, if two unperturbed eigenvalues are degenerate, the theory of section 4.1 fails completely.
- What effect does a perturbation have on two (or more) degenerate states?

- Consider the case of two degenerate states $|\phi_{01}\rangle$ and $|\phi_{02}\rangle$. These obey

$$\hat{H}_0 |\phi_{01}\rangle = E_0 |\phi_{01}\rangle \quad \text{and} \quad \hat{H}_0 |\phi_{02}\rangle = E_0 |\phi_{02}\rangle \quad (1)$$

- We look for solutions of

$$(\hat{H}_0 + \hat{H}') |\phi\rangle = E |\phi\rangle \quad (2)$$

in the form

$$|\phi\rangle = a_1 |\phi_{01}\rangle + a_2 |\phi_{02}\rangle \quad (3)$$

- Substitute (3) into (2) and use (1) to give

$$(E_0 - E) a_1 |\phi_{01}\rangle + (E_0 - E) a_2 |\phi_{02}\rangle + a_1 \hat{H}' |\phi_{01}\rangle + a_2 \hat{H}' |\phi_{02}\rangle = 0 \quad (4)$$

Note that $|\phi_{01}\rangle$ and $|\phi_{02}\rangle$ are orthogonal and normalised, so $\langle \phi_{01} | \phi_{01} \rangle = 1$, $\langle \phi_{01} | \phi_{02} \rangle = 0$, etc

- Close (4) with $\langle \phi_{01} |$ and then $\langle \phi_{02} |$ to give

$$(E_0 + H'_{11} - E)a_1 + H'_{12}a_2 = 0 \quad (5)$$

$$H'_{21}a_1 + (E_0 + H'_{22} - E)a_2 = 0 \quad (6)$$

where $H'_{\alpha\beta} = \langle \phi_{0\alpha} | \hat{H}' | \phi_{0\beta} \rangle \quad (7)$

- (5) and (6) can be expressed in matrix form as

$$\begin{pmatrix} (E_0 + H'_{11}) - E & H'_{12} \\ H'_{21} & (E_0 + H'_{22}) - E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$$

- Note that

$$H'_{21} = (H'_{12})^* \quad (\hat{H}' \text{ is a Hermitian operator})$$

This is a standard matrix eigenvalue problem. The eigenvalues E are determined by the condition

$$\begin{vmatrix} (E_0 + H'_{11}) - E & H'_{12} \\ H'_{21} & (E_0 + H'_{22}) - E \end{vmatrix} = 0 \quad (9)$$

In the simple case where $H'_{11} = H'_{22}$ we get

$$((E_0 + H'_{11}) - E)^2 - |H'_{12}|^2 = 0$$

so

$$E = E_0 + H'_{11} \pm |H'_{12}| \quad (10)$$

The perturbation breaks the degeneracy of $|\phi_{01}\rangle$ and $|\phi_{02}\rangle$

The same method can be applied if there are M degenerate unperturbed states

Equation (3) is generalised to

$$|\phi\rangle = \sum_{m=1}^M a_m |\phi_{0m}\rangle$$

Equation (9) becomes

$$\begin{vmatrix} H'_{11} - \Delta E & H'_{12} & \cdots & H'_{1M} \\ H'_{21} & H'_{22} - \Delta E & & \vdots \\ \vdots & & \ddots & \\ H'_{M1} & \cdots & & H'_{MM} - \Delta E \end{vmatrix} = 0 \quad (11)$$

where

$$H'_{\alpha\beta} = \langle \phi_{0\alpha} | \hat{H}' | \phi_{0\beta} \rangle$$

and

$$\Delta E = E - E_0$$

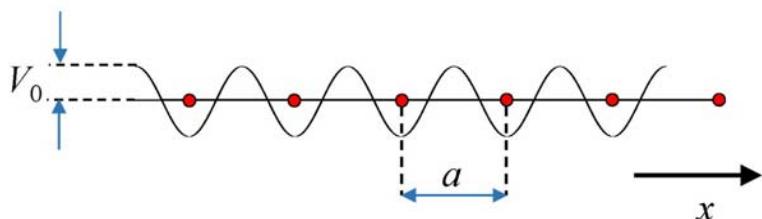
Example: One dimensional “solid”

The unperturbed states will be **free electron states** in 1D:

$$|\phi_{0k}\rangle = \sqrt{\frac{1}{L}} \exp(ikx) \quad E_{0k} = \frac{\hbar^2 k^2}{2m}$$

The perturbation is a weak periodic potential:

$$\hat{H}' = V_0 \cos\left(\frac{2\pi x}{a}\right)$$



What happens to the eigenvalues?

First calculate $H'_{\alpha\beta}$

$$H'_{kk} = H'_{k'k'} = \frac{V_0}{L} \int_0^L \cos\left(\frac{2\pi x}{a}\right) dx = 0 \quad (12)$$

$$H'_{kk'} = \frac{1}{L} \int_0^L \exp(-ikx) V_0 \cos\left(\frac{2\pi x}{a}\right) \exp(ik'x) dx$$

$$\begin{aligned} &= \frac{V_0}{2} \quad \text{if } k - k' = \pm \frac{2\pi}{a} \\ &= 0 \quad \text{otherwise} \end{aligned} \quad (13)$$

$E_{0k} = \frac{\hbar^2 k^2}{2m}$ so the unperturbed state with $k = \frac{\pi}{a}$ is exactly degenerate with the state with $k' = -\frac{\pi}{a}$.

For these states, $k - k' = \frac{2\pi}{a}$ i.e. $H'_{kk'} = H'_{k'k} = \frac{V_0}{2}$

Equation (9) becomes

$$\begin{vmatrix} E_0 - E & V_0/2 \\ V_0/2 & E_0 - E \end{vmatrix} = 0$$

The solution is

$$E = E_0 \pm V_0/2$$

So the **perturbation lifts the degeneracy of the electrons with $|k| = \frac{\pi}{a}$**

We can extend our theory to nearly degenerate states, and consider unperturbed states with

$$k = \frac{\pi}{a} + \delta k \quad \text{call this } |\phi_{01}\rangle$$

$$k' = -\frac{\pi}{a} + \delta k \quad \text{call this } |\phi_{02}\rangle$$

The unperturbed energies of these states are

$$E_{01} = \frac{\hbar^2}{2m} \left(\left(\frac{\pi}{a} \right)^2 + \delta k^2 + \frac{2\pi\delta k}{a} \right)$$

$$E_{02} = \frac{\hbar^2}{2m} \left(\left(\frac{\pi}{a} \right)^2 + \delta k^2 - \frac{2\pi\delta k}{a} \right)$$

Write these as

$$E_{01} = \bar{E}_0 + \frac{\hbar^2\pi\delta k}{ma} \quad \text{and} \quad E_{02} = \bar{E}_0 - \frac{\hbar^2\pi\delta k}{ma}$$

From (12) and (13) we have

$$H'_{11} = H'_{22} = 0 \quad \text{and} \quad H'_{12} = H'_{21} = \frac{V_0}{2}$$

All the previous analysis goes through, and equation (9) becomes

$$\begin{vmatrix} (E_{01} + H'_{kk}) - E & H'_{kk'} \\ H'_{k'k} & (E_{02} + H'_{k'k'}) - E \end{vmatrix} = 0$$

or

$$\begin{vmatrix} \frac{\hbar^2\pi\delta k}{ma} - (E - \bar{E}_0) & \frac{V_0}{2} \\ \frac{V_0}{2} & -\frac{\hbar^2\pi\delta k}{ma} - (E - \bar{E}_0) \end{vmatrix} = 0$$

The perturbation affects states over a range of δk values where $\frac{\hbar^2\pi\delta k}{ma}$ is small compared to

$\frac{V_0}{2}$ i.e. perturbation has a negligible effect on

states that are not close to $k = \pm \frac{\pi}{a}$ - see Rae

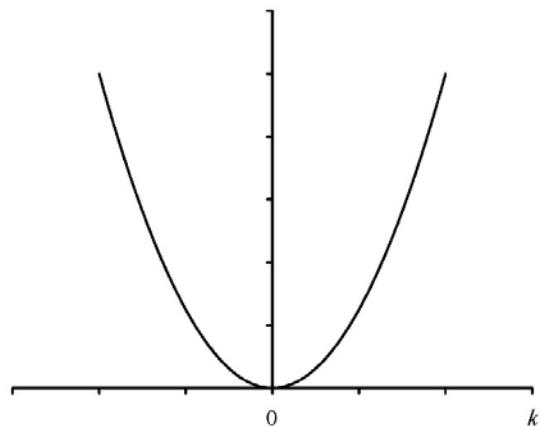
When $\delta k = 0$ there is a “band gap” of size V_0

Solving this gives

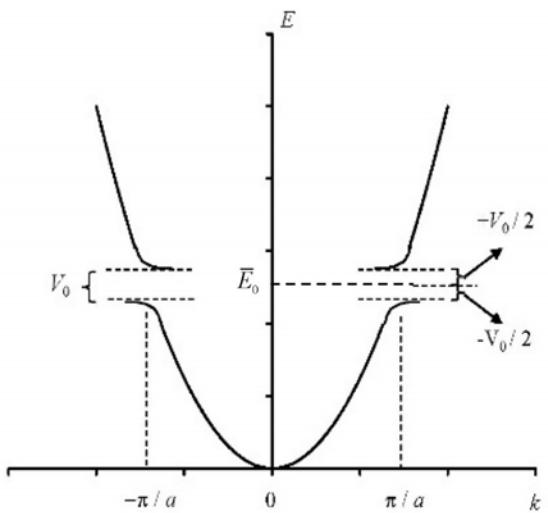
$$E = \bar{E}_0 \pm \sqrt{\left(\frac{\hbar^2\pi\delta k}{ma}\right)^2 + \frac{V_0^2}{4}}$$

Unperturbed system: -

$$E_{0k} = \frac{\hbar^2 k^2}{2m}$$



Perturbed system: -



Section 5. Variational Method

- First-order perturbation theory can be insufficiently accurate to solve stationary state problems
- Another approximate method, the **variational method**, can be helpful
- It does not presuppose knowledge of the solutions of a simpler problem
- Particularly useful for calculating the **ground state energy**

- Start with solutions of the TISE

$$\hat{H}\phi_n = E_n\phi_n$$

with $E_1 < E_2 < \dots$

Write any state ψ of the system as

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

- Normalisation:

$$\begin{aligned} \langle \psi | \psi \rangle &= \left\langle \sum_m c_m \phi_m \middle| \sum_n c_n \phi_n \right\rangle \\ &= \sum_m \sum_n c_m^* c_n \langle \phi_m | \phi_n \rangle \\ &= \sum_n |c_n|^2 = 1 \end{aligned}$$

- Expectation value:

$$\begin{aligned}
 \langle \hat{H} \rangle &= \langle \psi | \hat{H} | \psi \rangle \\
 &= \left\langle \sum_m c_m \phi_m \middle| \hat{H} \sum_n c_n \phi_n \right\rangle \\
 &= \sum_m \sum_n c_m^* c_n E_n \langle \phi_m | \phi_n \rangle \\
 &= \sum_n |c_n|^2 E_n \\
 &\geq E_1 \sum_n |c_n|^2 = E_1
 \end{aligned}$$

So

$$\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle \geq E_1$$

If ψ has adjustable parameters, change them to
minimise $\langle \hat{H} \rangle$ to get best approximation to E_1

Example: Ground state of hydrogen atom

Let's suppose that the ground state corresponds to $\ell = 0$ so that the wavefunction depends only on the radial coordinate $\psi = \psi(r)$ with $\psi(r) \neq 0$. At large distances, the wavefunction must vanish

Trial wavefunction satisfying these boundary conditions is

$$\psi = Ce^{-\alpha r}$$

$$\text{Normalisation: } \langle \psi | \psi \rangle = C^2 \int_0^\infty e^{-2\alpha r} 4\pi r^2 dr = 1$$

So

$$C = \left(\frac{\alpha^3}{\pi} \right)^{\frac{1}{2}}$$

For the hydrogen atom, the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

The expectation value for the potential energy

$$\begin{aligned} \langle \psi | V | \psi \rangle &= -C^2 \int_0^\infty e^{-\alpha r} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} e^{-\alpha r} 4\pi r^2 dr \\ &= -\frac{\alpha^3}{\pi} \frac{e^2}{\epsilon_0} \int_0^\infty r e^{-2\alpha r} dr \\ &= -\frac{e^2}{4\pi\epsilon_0} \alpha \end{aligned}$$

In spherical polars

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

The trial wavefunction has no angular dependence, so take $d^3r = 4\pi r^2 dr$. So, the expectation value for the kinetic energy

$$\begin{aligned}\langle \psi | \hat{T} | \psi \rangle &= -\frac{\hbar^2}{2\mu} C^2 4\pi \int_0^\infty dr e^{-\alpha r} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) e^{-\alpha r} \\ &= \frac{\hbar^2}{2\mu} \alpha^2\end{aligned}$$

Hence

$$\langle \psi | \hat{H} | \psi \rangle = \frac{\hbar^2}{2\mu} \alpha^2 - \frac{e^2}{4\pi\epsilon_0} \alpha \quad (1)$$

Minimise wrt α :

$$\frac{d}{d\alpha} \langle \psi | \hat{H} | \psi \rangle = 0$$

$$\Rightarrow \alpha = \frac{e^2 \mu}{4\pi\epsilon_0 \hbar^2}$$

Substitute into (1) to get upper bound for ground state energy

$$E_1 = -\frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{\mu}{\hbar^2} = -13.6 \text{ eV}$$

This is the actual ground state energy because our trial wavefunction is exact: it is $u_{100}(r)$

In a similar way, the variational method can be used to estimate the ground state energy for the He atom using as a trial function the hydrogen-like wavefunction for the 1s orbital

$$\psi(\underline{r}_1, \underline{r}_2) = u_{100}(\underline{r}_1) u_{100}(\underline{r}_2)$$

– see the textbooks for details

Section 6. Time dependent perturbations

- Show how time dependence in quantum mechanics leads to transitions between energy levels
- Absorption and emission of radiation by atoms

6.1 Time-dependent perturbation theory

- We aim to solve the time-dependent Schrodinger equation

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$$

where

$$\hat{H}(\underline{r},t) = \hat{H}_0(\underline{r}) + \hat{H}'(\underline{r},t)$$

- As in section 4, \hat{H}_0 is the Hamiltonian of the unperturbed system, and **does not depend on time**. We assume we know its eigenvalues and eigenfunctions, i.e. solutions of

$$\hat{H}_0 |\phi_n\rangle = E_n |\phi_n\rangle$$

The difference now is that the perturbation \hat{H}' depends on time

- We expand the wavefunction $\psi(\underline{r}, t)$ in terms of the eigenfunctions of \hat{H}_0

$$\psi(\underline{r}, t) = \sum_n c_n(t) \phi_n(\underline{r}) \exp(-iE_n t / \hbar) \quad (1)$$

Note that the **coefficients** c_n **depend on time**

$\hat{H}\psi$ becomes

$$\sum_n c_n(t) (E_n + \hat{H}') \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

$i\hbar \frac{\partial \psi}{\partial t}$ becomes

$$i\hbar \sum_n \left(-\frac{ic_n E_n}{\hbar} + \frac{dc_n}{dt} \right) \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

- Equating these and simplifying gives

$$i\hbar \sum_n \frac{dc_n}{dt} \phi_n(\underline{r}) \exp(-iE_n t / \hbar) = \\ \sum_n c_n(t) \hat{H}' \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

Multiply both sides by $\phi_m^*(\underline{r})$, integrate over $d^3 r$, and use orthogonality:

$$i\hbar \sum_n \frac{dc_n}{dt} \exp(-iE_n t / \hbar) \int \phi_m^*(\underline{r}) \phi_n(\underline{r}) d^3 r = \\ \sum_n c_n(t) \exp(-iE_n t / \hbar) \int \phi_m^*(\underline{r}) \hat{H}' \phi_n(\underline{r}) d^3 r$$

So

$$\frac{dc_m}{dt} = \frac{1}{i\hbar} \sum_n c_n(t) H'_{mn}(t) \exp(i\omega_{mn} t) \quad (2)$$

where

$$H'_{mn}(t) = \iiint \phi_m^*(\underline{r}) \hat{H}'(\underline{r}, t) \phi_n(\underline{r}) d^3 r \quad (3)$$

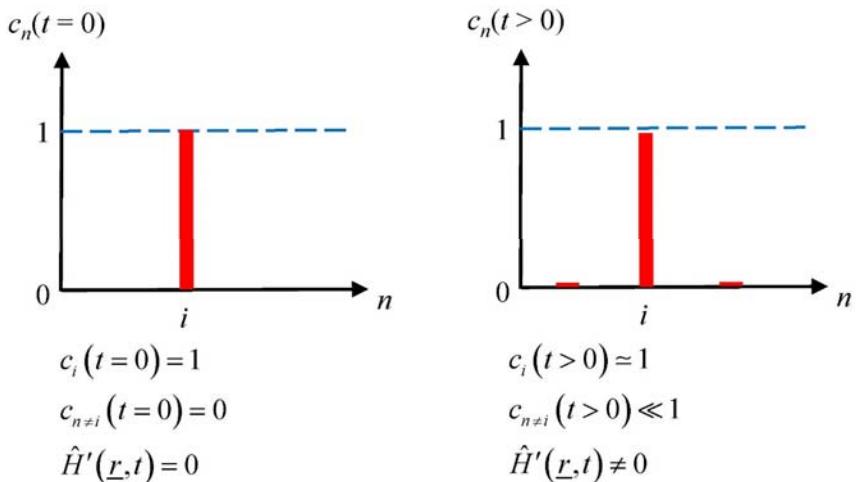
and

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \quad (4)$$

- We want to solve (2) for the coefficients $c_m(t)$. We assume that the perturbation is switched on at time $t = 0$, and that the system is in the eigenfunction $\phi_i(\underline{r})$ at that time, i.e.

$$c_i(t=0) = 1, \quad c_n(t=0) = 0 \text{ for all } n \neq i \quad (5)$$

- If the perturbation \hat{H}' is weak, we can assume that all the c_n for $n \neq i$ are small, and that c_i remains at 1.



Equation (2) becomes

$$\begin{aligned}\frac{dc_m}{dt} &= \frac{1}{i\hbar} \sum_n c_n(t) H'_{mn}(t) \exp(i\omega_{mn} t) \\ &\simeq \frac{1}{i\hbar} H'_{mi}(t) \exp(i\omega_{mi} t)\end{aligned}$$

which has the solution

$$c_m(t) = \frac{1}{i\hbar} \int_0^t H'_{mi}(t') \exp(i\omega_{mi} t') dt' \quad (6)$$

- What will a measurement of the energy of the system give?

At $t = 0$, the wavefunction of the system is the eigenfunction $\phi_i(\underline{r})$ and so the energy is E_i

Equations (1) and (6) show how the wavefunction evolves in time

At any time t the probability of measuring the energy as E_m is $|c_m(t)|^2$

We can see that the time-dependent perturbation causes transitions between the quantum states

6.2 Periodic perturbations

- Consider a sinusoidal perturbation of angular frequency ω :

$$\begin{aligned}\hat{H}'(\underline{r}, t) &= \hat{H}'(\underline{r}) \cos \omega t \\ &= \frac{1}{2} \hat{H}'(\underline{r}) [\exp(i\omega t) + \exp(-i\omega t)] \quad (7)\end{aligned}$$

Equation (3) becomes

$$\begin{aligned}H'_{fi}(t) &= \iiint d^3 r \phi_f^*(\underline{r}) \hat{H}'(\underline{r}, t) \phi_i(\underline{r}) \\ &= \frac{1}{2} \iiint d^3 r \phi_f^*(\underline{r}) \hat{H}'(\underline{r}) \phi_i(\underline{r}) [e^{i\omega t} + e^{-i\omega t}] \\ &\equiv \frac{1}{2} H'_{fi} [e^{i\omega t} + e^{-i\omega t}]\end{aligned}$$

with

$$H'_{fi} = \iiint \phi_f^*(\underline{r}) \hat{H}'(\underline{r}) \phi_i(\underline{r}) d^3 r \quad (8)$$

Equation (6) becomes

$$c_f(t) = \frac{H'_{fi}}{2i\hbar} \left[\int_0^t \exp(i(-\omega + \omega_{fi})t') dt' + \int_0^t \exp(i(\omega + \omega_{fi})t') dt' \right] \quad (9)$$

with

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} \quad (10)$$

- Doing the integrals gives

$$c_f(t) = -\frac{H'_{fi}}{2\hbar} \left[\frac{\exp(i(-\omega + \omega_{fi})t) - 1}{-\omega + \omega_{fi}} + \frac{\exp(i(\omega + \omega_{fi})t) - 1}{\omega + \omega_{fi}} \right] \quad (11)$$

- The first term is peaked for $\omega = \omega_{fi}$ and the second is peaked for $\omega = -\omega_{fi}$.

- In an experiment we can set the apparatus to measure either energy gain or energy loss. If we choose to look at energy gain, only the first term will be significant.

Consider only the first term and let

$$W = -\omega + \omega_{fi}$$

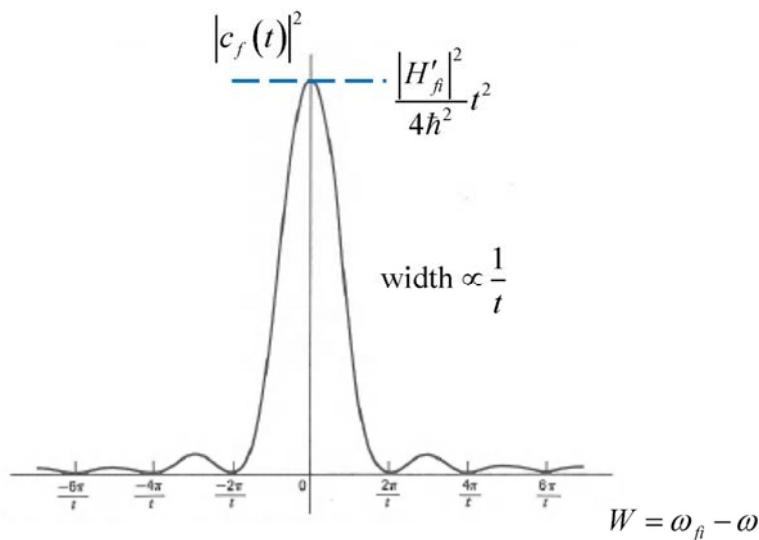
The probability of finding the system in state $\phi_f(r)$ is $|c_f(t)|^2$

$$\begin{aligned} |c_f(t)|^2 &= \frac{|H'_{fi}|^2}{4\hbar^2} \left| \frac{e^{iWt} - 1}{W} \right|^2 \\ &= \frac{|H'_{fi}|^2}{4\hbar^2} \frac{1}{W^2} (e^{iWt} - 1)(e^{-iWt} - 1) \\ &= \frac{|H'_{fi}|^2}{4\hbar^2} \frac{1}{W^2} 2(1 - \cos Wt) \\ &= \frac{|H'_{fi}|^2}{4\hbar^2} \frac{\sin^2(Wt/2)}{(W/2)^2} \quad (12) \end{aligned}$$

As $W \rightarrow 0$, $\sin(Wt/2) \rightarrow Wt/2$

For $W = 2\pi/t$, $\sin(Wt/2) = \sin \pi = 0$

So, as t increases, $|c_f(t)|^2$ becomes very strongly peaked for $W = \omega_{fi} - \omega = 0$ i.e. when $\hbar\omega = E_f - E_i$



- There is a high probability of causing a transition from initial state i to final state f only if the frequency of the perturbation matches the energy difference between the states

- If the perturbation is caused by an electromagnetic wave of angular frequency ω , this corresponds to **excitation** of the quantum system
- Substituting $W = -\omega + \omega_{fi}$ into equation (12) gives

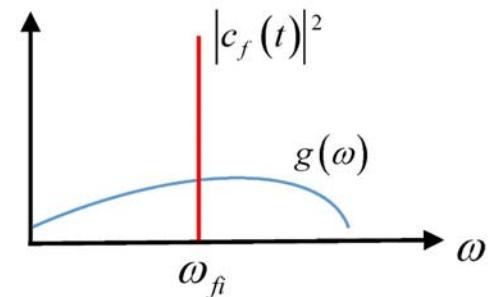
$$|c_f(t)|^2 = \frac{|H'_{fi}|^2}{4\hbar^2} \left(\frac{\sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right)^2 \quad (13)$$

- Everything works similarly if we look at the $\omega = -\omega_{fi}$ peak. This would correspond to **stimulated emission** of an excited state

- In practice, you don't get a perturbation that is purely sinusoidal for all time. We can treat this by saying that the perturbation includes a range of frequencies, where the “density” of frequencies between ω and $\omega + d\omega$ is $g(\omega)d\omega$
- The total probability of excitation from i to f after time t is then

$$\begin{aligned} P(t) &= \frac{|H'_{fi}|^2}{4\hbar^2} \int_0^\infty \left(\frac{\sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right)^2 g(\omega) d\omega \\ &= \frac{|H'_{fi}|^2}{4\hbar^2} t^2 \int_0^\infty \text{sinc}^2[(\omega_{fi} - \omega)t/2] g(\omega) d\omega \end{aligned} \quad (14)$$

If $g(\omega)$ is slowly varying with respect to the sinc-squared function,



the only contribution to equation (14) will come from $\omega = \omega_{fi}$, so

$$P(t) = \frac{\pi |H'_{fi}|^2}{2\hbar^2} g(\omega_{fi}) t \quad (15)$$

- The **transition rate** (transition probability per unit time) is then

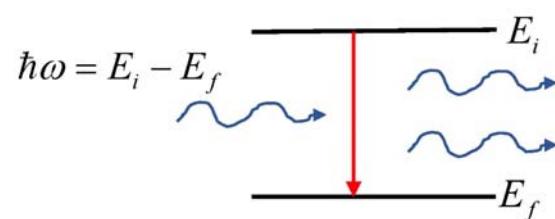
$$W = \frac{\pi |H'_{fi}|^2}{2\hbar^2} g(\omega_{fi})$$

This is called “**Fermi’s golden rule**”

6.3 Atomic transitions

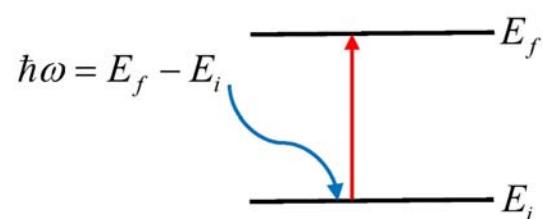
- Atoms can absorb and emit radiation by electrons undergoing transitions between energy levels
- This can be understood in terms of time-dependent perturbation theory, where the basic system is the atom and the perturbation is due to the electromagnetic field of the radiation
- We will use the theory of the previous section, even though there is no reference to the quantisation of radiation, i.e. photons
- This “**semi-classical**” approximation is OK for absorption and stimulated emission – for spontaneous emission we need a proper quantisation of the electromagnetic fields

Stimulated emission:

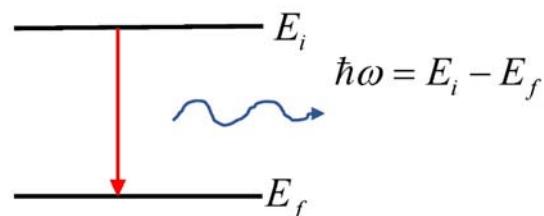


Emitted photons have same energy as incident photon

Absorption:



Spontaneous emission:



Transition is spontaneous – not stimulated by another photon

- The main effect is from the **electric field** of the radiation:

$$\underline{\varepsilon} = \underline{\varepsilon}_0 \cos(\underline{k} \cdot \underline{r} - \omega t)$$

$\underline{\varepsilon}$ time and space varying electric field

$\underline{\varepsilon}_0$ electric field amplitude (a vector)

\underline{k} wavevector of the radiation

ω angular frequency of the radiation, $\omega = c|\underline{k}|$

- We assume that the atom is at $\underline{r} = 0$. An atom is of size $\sim 1 \text{ \AA}$ whereas the wavelength of visible light $\lambda = 3900 - 7000 \text{ \AA}$. So $\underline{k} \cdot \underline{r}$ is very small. Hence, $\cos(\underline{k} \cdot \underline{r}) \approx 1$, $\sin(\underline{k} \cdot \underline{r}) \approx 0$ and

$$\underline{\varepsilon} = \underline{\varepsilon}_0 \cos(\underline{k} \cdot \underline{r} - \omega t)$$

$$= \underline{\varepsilon}_0 [\cos(\underline{k} \cdot \underline{r}) \cos(-\omega t) + \sin(\underline{k} \cdot \underline{r}) \sin(-\omega t)] \\ \approx \underline{\varepsilon}_0 \cos(\omega t)$$

If $\underline{\varepsilon}$ is in the z direction, the work done in moving an electron by a distance z is given by

$$\text{work done} = e\varepsilon z$$

$$= e\varepsilon_0 z \cos(\omega t)$$

So the perturbation becomes

$$\begin{aligned}\hat{H}'(\underline{r}, t) &= \hat{H}'(\underline{r}) \cos \omega t \\ &= e\varepsilon_0 z \cos \omega t\end{aligned}$$

- As in section 6.2, transitions will occur only if $\hbar\omega$ matches the difference between atomic energy levels

- The transition probability is

$$W = \frac{\pi |H'_{fi}|^2}{2\hbar^2} g(\omega_{fi})$$

where

$$H'_{fi} = e\varepsilon_0 \iiint \phi_f^*(\underline{r}) z \phi_i(\underline{r}) d^3 r$$

We find that the rate of spontaneous emission is also proportional to $|H'_{fi}|^2$

- For the hydrogen atom, the states $\phi_i(\underline{r})$ and $\phi_f(\underline{r})$ can be written as

$$\phi_i(\underline{r}) = R_{n_i \ell_i}(r) Y_{\ell_i m_i}(\theta, \phi)$$

$$\phi_f(\underline{r}) = R_{n_f \ell_f}(r) Y_{\ell_f m_f}(\theta, \phi)$$

and in spherical polars $z = r \cos \theta$.

H'_{fi} becomes

$$H'_{fi} = e \epsilon_0 \int_0^\infty dr r^3 R_{n_f \ell_f}^*(r) R_{n_i \ell_i}(r) \times \\ \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \cos \theta Y_{\ell_f m_f}^*(\theta, \phi) Y_{\ell_i m_i}(\theta, \phi)$$

and this determines the “strength” of spectral lines

- In particular, the θ and ϕ integrals are zero for many combinations of the ℓ and m quantum numbers. This gives rise to “**selection rules**” that determine which lines are observed in atomic spectra

- For H'_{fi} to be non-zero we require $\ell_f = \ell_i \pm 1$ with $m_i = m_f$

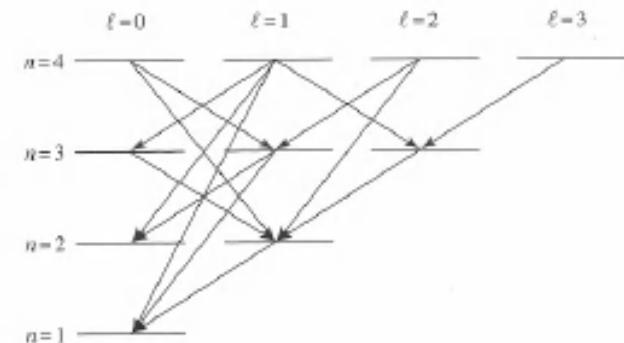


Figure 11.9: Allowed decays for the first four Bohr levels in hydrogen.

- Above corresponds to the field polarised in the z direction. If the field was polarised in the x direction

$$\begin{aligned}\hat{H}'(\underline{r}) &= e\epsilon_0 x \\ &= e\epsilon_0 r \sin \theta \cos \phi\end{aligned}$$

Can then show (see e.g. Rae) that $H'_{fi} = 0$
unless $m_f = m_i \pm 1$.

- So, for an electromagnetic wave of arbitrary polarisation, the selection rules for the allowed transitions are

$$\ell_f = \ell_i \pm 1 \Rightarrow \Delta\ell = \pm 1$$

$$m_f = m_i \text{ or } m_f = m_i \pm 1 \Rightarrow \Delta m = 0 \text{ or } \pm 1$$

- Transitions will not take place unless the selection rules are obeyed
- Selection rules are important in the study of atoms, molecules, nuclei and solids

