

Quantum Theory

PH3210

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1 Books and Further reading

1.1 Books

- **Bransden and Joachain: Quantum Mechanics, Longman, 2nd edition 2000. (530.12.BRA)[†]**
- C Cohen-Tannoudji, B Diu, F Laloe, Quantum Mechanics, vols 1 and 2, John Wiley 1977. (530.12 COH)
- S Gasiorowicz, Quantum Mechanics, John Wiley, 2003. (530.12 Gas)
- F Mandl, Quantum Mechanics, John Wiley, 1992. (530.12 Man)
- Many other good books...

1.2 Other Resources

- Advanced but excellent notes/book can be found at <http://www-thphys.physics.ox.ac.uk/people/JamesBinney/QBhome.htm>

[†]This is the main book for the course.

2 Introduction to Wavefunctions

2.1 Schrödinger formulation

- De Broglie postulated that we associate a wave with every particle.

$$\lambda = \frac{h}{p} \quad \text{or} \quad \lambda = \frac{\hbar}{p}$$

where $\hbar = h/2\pi$ and $\lambda = \lambda/2\pi$.

- Schrödinger introduced the wavefunction

$$\text{“Wavefunction”}: \quad \psi(x, t)$$

and took $\psi(x, t)$ to satisfy partial differential equation

$$\hat{H}\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad \text{“Schrödinger equation”}$$

- \hat{H} is the “Hamiltonian” - partial differential operator for the total energy
- For a particle moving in 1D

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x)$$

where m is the mass of the particle and V is the potential.

- In QM the momentum operator

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}$$

- 1DSE then reads

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = i\hbar \frac{\partial \psi}{\partial t}$$

- Solution using separation of variables

$$\psi(x, t) = \phi(x)T(t)$$

so

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2 \phi(x)}{\partial x^2} + V(x)\phi(x) \right] T(t) = \left[i\hbar \frac{\partial T(t)}{\partial t} \right] \phi(x)$$

divide both sides by $\psi = \phi T$

$$\frac{1}{\phi} \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \phi(x)}{\partial x^2} + V(x)\phi(x) \right] = \frac{i\hbar}{T} \frac{\partial T(t)}{\partial t}$$

- LHS is $f(x)$ and RHS is a $g(t)$. Only way they can be equal is if both equal to a constant (call it E).
- We get two equations

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + V(x)\phi = E\phi \quad (2.1)$$

$$i\hbar \frac{\partial T(t)}{\partial t} = ET \quad (2.2)$$

- Eq.(2.2) easy to solve

$$T(t) = e^{-iEt/\hbar} \times \text{constant.}$$

- Eq.(2.1) is the **“Time Independent Schrödinger Equation—** or **TISE**, can be hard to solve, depends on V .
- Choose easy example - **free particle**, $V(x) = 0$. TISE becomes

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

with solutions

$$\phi \sim e^{ikx}, e^{-ikx}$$

where

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

- Putting it all together

$\psi(x, t) \sim e^{i(kx - Et/\hbar)}$	Wave moving in +ve x direction
$\psi(x, t) \sim e^{-i(kx + Et/\hbar)}$	Wave moving in -ve x direction

- So we find the angular frequency $\omega = E/\hbar$

$$E = \hbar\omega = h\nu$$

where ν is frequency and we see that the solutions automatically incorporate **Einstein relation**.

- Also for classical free particle $E = p^2/2m$, so we get

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

$$\rightarrow p = \hbar k = \hbar \frac{2\pi}{\lambda} = \frac{h}{\lambda}$$

automatically incorporates **De Broglie “matter wave” relation**.

But what does $\psi(x, t)$ mean?

- $\psi(x, t)$ cannot be a physical wave like an oscillating string, or EM wave of Maxwell theory
- TDSE is complex eqn, solutions are inherently complex (real and imag parts of ψ do not separately solve eqn)
- **Something that is complex cannot be directly measured.**
- So what is this wavefunction?

2.2 $\psi(x, t)$ and Probability

- To understand $\psi(x, t)$ must introduce

$$\text{Probability Density: } P(x, t)$$

- Basic idea is that can no longer be certain of exact position of particle

- Only that Probability of measuring it between x and $x + \delta x$ is

$$\text{Prob(in } x \text{ to } x + \delta x) = P(x, t)\delta x$$

and a postulate of QM is that

$$P(x, t) = \psi(x, t)^* \psi(x, t) = |\psi(x, t)|^2$$

- We can use this to find averages or expectation values

$$\langle x \rangle \equiv \int_{-\infty}^{\infty} x P(x, t) dx = \int_{-\infty}^{\infty} x |\psi(x, t)|^2 dx$$

similarly

$$\langle x^2 \rangle \equiv \int_{-\infty}^{\infty} x^2 P(x, t) dx = \int_{-\infty}^{\infty} x^2 |\psi(x, t)|^2 dx$$

- Total probability of finding particle anywhere must be 1, so

$$1 = \int_{-\infty}^{\infty} P(x, t) dx = \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx$$

which the normalisation condition on $\psi(x, t)$.

- This must be imposed on $\psi(x, t)$ as SE is linear in ψ .
- If ψ is a solution then so is $\psi \times \text{constant}$
- Constant is then fixed by the normalisation condition
- Complication for plane waves

$$\psi(x, t) = G e^{\frac{i}{\hbar}(px - Et)}$$

so

$$\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = \int_{-\infty}^{\infty} |G|^2 dx \rightarrow \infty$$

\Rightarrow Plane wave is not normalisable!

- Reason: Plane waves are not physically realisable.
They exist for all time and are spread over all space
- More physical situation is a “plane wave” confined to some finite region, (e.g. experimental apparatus), then

$$\int_{-L}^L |G|^2 dx = 1$$

$$\Rightarrow G = \frac{1}{\sqrt{2L}}$$

Look at an old example, the infinite square well

- Solving the Schrödinger equation for a number of examples should be familiar from PH2210
- Quick look at the infinite square well, with potential as depicted in Fig 2.1

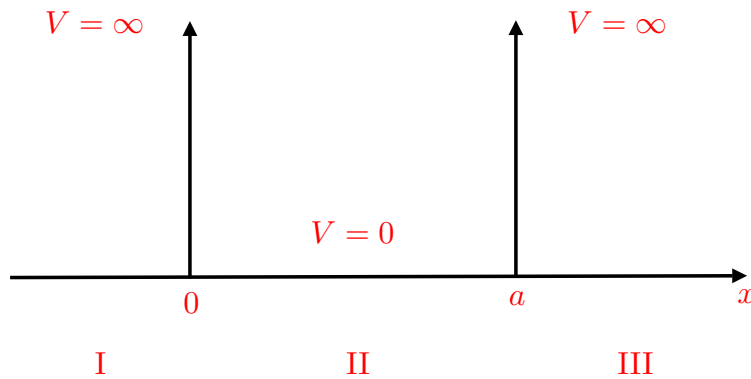


Figure 2.1: Infinite Square Well

- Since $V \neq v(t)$ solutions of form

$$\psi(x, t) = \phi(x)e^{-itE/\hbar}$$

where

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + V(x)\phi = E\phi$$

- In regions where $V = \infty$, ϕ must be zero for finite E solution (as $K.E \geq 0$)
- Inside well

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} = E\phi \quad \text{as } V=0$$

so

$$\phi = Ae^{ikx} + Be^{-ikx} \quad \text{with} \quad \frac{\hbar^2 k^2}{2m} = E$$

- Now have to match inside to outside solutions via **boundary conditions**

ϕ must be continuous

$$\begin{aligned} \text{At } x = 0, \quad 0 &= A + B \\ \text{At } x = a, \quad 0 &= Ae^{ika} + Be^{-ika} = 2iA \sin ka \end{aligned}$$

- Either $A = 0$ (reject this) or

$$\sin ka = 0, \Rightarrow k = \frac{n\pi}{a}, \quad n = 1, 2, 3, \dots$$

- Substitute back in to expression for energy

$$E = \frac{\hbar^2 \pi^2}{2m a^2} n^2, \quad n = 1, 2, 3, \dots$$

- Possible energies of particle are **quantised**
- Typical for particles bound in a potential well (atoms, ...)
- Also **have to normalise solution**

$$\phi_n(x) = A \sin \frac{n\pi x}{a}$$

- so we have

$$1 = \int_{-\infty}^{\infty} |\phi_n(x)|^2 dx = A^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = A^2 \frac{a}{2}$$

$$\Rightarrow A = \sqrt{\frac{2}{a}}$$

- Putting it all together the spacial part of the wavefunction reads

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

- Note that ϕ_n are **orthogonal**

$$\int_{-\infty}^{\infty} \phi_n^*(x)\phi_m(x)dx = \frac{2}{a} \int_0^a \sin \frac{n\pi x}{a} \sin \frac{m\pi x}{a} dx$$

$$= \begin{cases} 1 & : n = m \\ 0 & : n \neq m \end{cases}$$

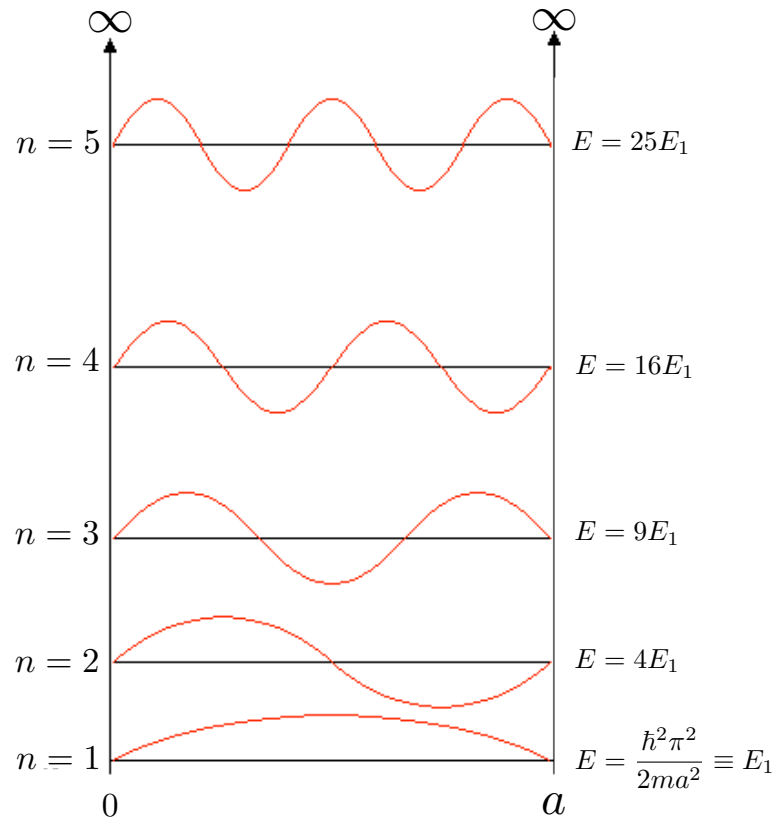


Figure 2.2: Wavefunctions for Infinite Square Well

- From Fig. 2.2 we see that the **ground state, $n = 1$** has no nodes

- First excited state, $n = 2$ has one node
- It should be clear that the physics of low n states is very different from the classical expectation
- Classically: consider a ball bouncing back and forward in the well

$$P(x) = \frac{1}{a}$$

just a uniform distribution. So

$$\begin{aligned}\langle x \rangle &= \int_0^a xP(x) dx = \frac{1}{a} \int_0^a x dx = \frac{a}{2} \\ \langle x^2 \rangle &= \int_0^a x^2P(x) dx = \frac{a^2}{3}\end{aligned}$$

- But quantum

$$\begin{aligned}\langle x \rangle_1 &= \frac{a}{2} \quad \text{same} \\ \langle x^2 \rangle_1 &= \frac{a^2}{3} - \frac{a^2}{2\pi^2} \quad \text{different from classical}\end{aligned}$$

where the subscript 1 means we are using the $n = 1$ state.

- As $n \rightarrow \infty$ find that $\langle x^2 \rangle \rightarrow$ classical result The probability distribution becomes more spread out
- This is an example of the general behaviour

2.3 Energy eigenstates and superposition

- Wavefunction of the form

$$\psi_n(x, t) = \phi_n(x) e^{-iE_n t/\hbar}$$

is special, it is an Energy Eigenstate or Stationary State (same thing)

- Equivalently:

$$\begin{aligned}\hat{H}\psi_n(x, t) &= \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \phi(x)}{\partial x^2} + V(x)\phi(x) \right] \psi_n(x, t) \\ &= i\hbar \frac{\partial}{\partial t} \psi_n(x, t) = E_n \psi_n(x, t) \quad \text{by TDSE}\end{aligned}$$

So $\psi_n(x, t)$ is an Eigenfunction of \hat{H} with Eigenvalue E_n

- Physically:

Energy Eigenstate \Leftrightarrow Particle is in state of definite energy (here E_n)
 \Leftrightarrow If energy is measured, guaranteed result E_n

Superpositions

$$\psi_n(x, t) = \phi_n(x)e^{-iE_n t/\hbar}$$

is not the most general solution to TDSE.

- Since TDSE is linear equation, general solution is sum of above

$$\psi(x, t) = \sum_n a_n \phi_n(x) e^{-iE_n t/\hbar}$$

where a_n are arbitrary complex coefficients.

Example: Superposition of 2 energy eigenstates

$$\psi(x, t) = a_1 \phi_1(x) e^{-iE_1 t/\hbar} + a_2 \phi_2(x) e^{-iE_2 t/\hbar}$$

act with energy operator

$$\hat{H}\psi(x, t) = a_1 E_1 \phi_1(x) e^{-iE_1 t/\hbar} + a_2 E_2 \phi_2(x) e^{-iE_2 t/\hbar} \neq \text{const} \times \psi(x, t)$$

- But ψ is a solution of the TDSE, just not an energy eigenstate as $E_1 \neq E_2$
- What is the physical significance of this?
- For ψ to be valid wavefunction it must be normalised

$$\begin{aligned} 1 &= \int |\psi|^2 dx = \int_0^a dx [a_1^* \phi_1 e^{iE_1 t/\hbar} + a_2^* \phi_2 e^{iE_2 t/\hbar}] [a_1 \phi_1 e^{-iE_1 t/\hbar} + a_2 \phi_2 e^{-iE_2 t/\hbar}] \\ &= \int_0^a dx [|a_1|^2 \phi_1^2 + |a_2|^2 \phi_2^2 + a_1 a_2^* \phi_1 \phi_2 e^{i(E_2 - E_1)t/\hbar} + a_1^* a_2 \phi_1 \phi_2 e^{i(E_1 - E_2)t/\hbar}] \end{aligned}$$

but ϕ_1 and ϕ_2 are orthogonal and are normalised so find

$$1 = |a_1|^2 + |a_2|^2$$

looks like a **sum of probabilities**, thus: **interpretation of superposition**

- If **measurement made of energy** of particle with this wavefunction will get the following result:

E_1	with amplitude a_1 , probability $ a_1 ^2$
E_2	with amplitude a_2 , probability $ a_2 ^2$

- The expectation value of energy should be

$$\langle \hat{H} \rangle = E_1 |a_1|^2 + E_2 |a_2|^2$$

we can check this by doing the calculation directly.

$\langle \hat{H} \rangle = \int_0^a dx \psi^* \hat{H} \psi$

which is the definition of $\langle \hat{H} \rangle$ in state ψ

$$\begin{aligned} \langle \hat{H} \rangle &= \int_0^a dx [a_1^* \phi_1 e^{iE_1 t/\hbar} + a_2^* \phi_2 e^{iE_2 t/\hbar}] [a_1 E_1 \phi_1 e^{-iE_1 t/\hbar} + a_2 E_2 \phi_2 e^{-iE_2 t/\hbar}] \\ &= E_1 |a_1|^2 + E_2 |a_2|^2 \end{aligned}$$

using orthogonality of ϕ s. This is the result we expected.

- Note that $\langle \hat{H} \rangle$ is time independent
- Not all expectation values are time independent for energy superpositions, e.g.

$$\begin{aligned} \langle \hat{p} \rangle &= \int_0^a dx \psi^* \hat{p} \psi = \int_0^a dx \psi^* \left(-i\hbar \frac{\partial}{\partial x} \psi \right) \\ &= -\frac{2i\hbar}{a} \int_0^a dx \left[a_1^* \sin \frac{\pi x}{a} e^{iE_1 t/\hbar} + a_2^* \sin \frac{2\pi x}{a} e^{iE_2 t/\hbar} \right] \left[a_1 \frac{\pi}{a} \cos \frac{\pi x}{a} e^{-iE_1 t/\hbar} + a_2 \frac{2\pi}{a} \cos \frac{2\pi x}{a} e^{-iE_2 t/\hbar} \right] \end{aligned}$$

where we have used the spatial wavefunctions for the infinite square well as our example.

- Using the following useful identities

$$\int_0^a dx \sin \frac{\pi x}{a} \cos \frac{\pi x}{a} = 0 = \int_0^a dx \sin \frac{2\pi x}{a} \cos \frac{2\pi x}{a}$$

and for $m \neq n$

$$\int_0^a dx \sin \frac{m\pi x}{a} \cos \frac{n\pi x}{a} = \frac{am}{\pi(m^2 - n^2)} [1 - (-1)^{m+n}] = \frac{2am}{\pi(m^2 - n^2)} \quad m+n \neq \text{even} \quad (2.3)$$

we arrive at the result

$$\langle \hat{p} \rangle = -\frac{i\hbar 8}{3a} [a_1 a_2^* e^{i(E_2 - E_1)t/\hbar} - \text{c.c.}]$$

where c.c. is the complex conjugate expression. Taking a simplified case where the coefficients are both real ($a_1, a_2 \in \mathcal{R}$)

$$\langle \hat{p} \rangle = \frac{16\hbar}{3a} a_1 a_2 \sin \frac{(E_2 - E_1)t}{\hbar}$$

Momentum oscillates in time!!!!

2.4 Practice Exercises

- (1) Show that in the case of the infinite square well presented in the notes

$$\begin{aligned} \langle x \rangle_1 &= \frac{a}{2} \\ \langle x^2 \rangle_1 &= \frac{a^2}{3} - \frac{a^2}{2\pi^2} \end{aligned}$$

What are these values for the n th state? That is $\langle x \rangle_n$ and $\langle x^2 \rangle_n$. Do these values get closer to the classical values as we increase n ? Is this what we expect?

- (2) Using Eq. (2.3) show that

$$\langle \hat{p} \rangle = \frac{16\hbar}{3a} a_1 a_2 \sin \frac{(E_2 - E_1)t}{\hbar}$$

for the wavefunction $\psi(x, t) = a_1 \phi_1(x) e^{-iE_1 t/\hbar} + a_2 \phi_2(x) e^{-iE_2 t/\hbar}$ where $\phi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$. (Try and prove Eq. (2.3))

3 Operators and Observables

- Numerical values of classical quantities (e.g. Momentum and energy) become differential operators in QM

$$\text{x- momentum : } \hat{p} = -i\hbar \frac{\partial}{\partial x}$$

$$\text{energy : } \hat{H} = \frac{\hat{p}^2}{2m} + V(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

- This is a general principle of QM

Every physical observable corresponds to an operator, \hat{Q}

- Measured numbers in experiments are related to operators via eigenvalue equations
- In general we have

$$\begin{array}{lcl} \hat{Q} \chi_n(x) & = & q_n \chi_n(x) \\ \text{Eigenfunction } \chi_n(x) & & \text{labelled by } n \\ \text{Eigenvalue } q_n(x) & & \text{labelled by } n \end{array}$$

- The set of all q_n is called the spectrum
- Example of energy

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

- Eigenvalue E_n , Eigenfunction ϕ_n
- General principle of QM is

Measurements of a physical observable always give a result which is one of the eigenvalues of corresponding operator \hat{Q}

3.1 Hermitian Operators

- We know that experiments only return real measurements, this means that the class of **QM operators** must have **real eigenvalues**
- This class of operator are called **Hermitian operators**
- So

Every operator representing a physical observable
must be a Hermitian operator

- **Definition** of Hermitian operator; for 1d QM an operator \hat{Q} is Hermitian if

$$\int_{-\infty}^{\infty} \chi^* \hat{Q} \psi dx = \int_{-\infty}^{\infty} (\hat{Q} \chi)^* \psi dx$$

for **any** functions $\chi(x)$, $\psi(x)$ which are **normalisable** and **vanish** at $x = \pm\infty$

What kinds of operators are Hermitian?

- i) The Position operator x

$$\int_{-\infty}^{\infty} \chi^* x \psi dx = \int_{-\infty}^{\infty} (x^* \chi)^* \psi dx = \int_{-\infty}^{\infty} (x \chi)^* \psi dx$$

so since x is a real number

$$x^\dagger = x$$

where the dagger is notation for Hermitian conjugate.

- ii) The potential energy $V(x)$

$$\int_{-\infty}^{\infty} \chi^* V(x) \psi dx = \int_{-\infty}^{\infty} (V(x)^* \chi)^* \psi dx$$

so as long as coefficients in $V(x)$ are real we have

$$V(x)^\dagger = V(x)$$

which is what we expect as a complex potential does not make sense.

- iii) Momentum operator

$$\int_{-\infty}^{\infty} \chi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi dx = -i\hbar \int_{-\infty}^{\infty} \chi^* \frac{\partial \psi}{\partial x} dx$$

we need to get the operator acting on χ , so integrate by parts

$$\text{RHS} = -i\hbar \left\{ [\chi^* \psi]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \chi^*}{\partial x} \psi dx \right\}$$

Since x is real, so $\frac{\partial}{\partial x}$ is also real and

$$\frac{\partial \chi^*}{\partial x} = \left(\frac{\partial \chi}{\partial x} \right)^*$$

so

$$\text{RHS} = \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial \chi}{\partial x} \right)^* \psi dx \quad \checkmark$$

Thus \hat{p} is hermitian. Note that the “i” in the definition of \hat{p} is crucial

- iv) Kinetic energy operator

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

is hermitian. Proof by integration by parts twice.

- v) Hamiltonian operator Since $H = T + V$ and both T and V are Hermitian, $H^\dagger = H$ also. Sums of Hermitian operators are Hermitian.

Proof of the reality of eigenvalues

Let $\hat{Q}\chi_n = q_n\chi_n$, thus

$$\int_{-\infty}^{\infty} \chi_m^* \hat{Q}\chi_n dx = \int_{-\infty}^{\infty} \chi_m^* q_n \chi_n dx$$

but \hat{Q} is hermitian so

$$\text{LHS} = \int_{-\infty}^{\infty} (\hat{Q}\chi_m)^* \chi_n dx = \int_{-\infty}^{\infty} (q_m \chi_m)^* \chi_n dx = \int_{-\infty}^{\infty} q_m^* \chi_m^* \chi_n dx$$

Putting the LHS side and the RHS of Eq. (3.1) together

$$0 = (q_n - q_m^*) \int_{-\infty}^{\infty} \chi_m^* \chi_n dx$$

now chose $m = n$

$$0 = (q_n - q_n^*) \int_{-\infty}^{\infty} |\chi_n|^2 dx = (q_n - q_n^*)$$

$$\Rightarrow q_n = q_n^* \quad q_n \text{ is real}$$

But there is more...choose $n \neq m$ and use reality of q s

$$0 = (q_n - q_m) \int_{-\infty}^{\infty} \chi_m^* \chi_n dx$$

Thus χ_m and χ_n are orthogonal functions. This should be familiar from our infinite square well example where the wavefunctions had the forms

$$\phi_n = \sqrt{\frac{2}{a}} \sin \frac{\pi n x}{a}$$

We know from direct calculation that

$$\int_{-\infty}^{\infty} \phi_n^* \phi_m dx = 0$$

- But yet more..
- For ϕ_m s that have fourier series any function can be expanded as

$$f(x) = \sum_{n=1}^{\infty} a_n \phi_n(x)$$

This is true in general using eigenfunctions of Hermitian operators.

Theorem:

Let $\chi_n(x)$ be the eigenfunction of any hermitian operator
Then any normalisable function $f(x)$ can be written as

$$f(x) = \sum_{n=1}^{\infty} a_n \chi_n(x)$$

- We say that the $\chi_n(x)$ s form a complete set of functions (or states).
- It is this expansion theorem that enables a connection between operators and probabilities
- Let's see how...
- Suppose at a given time (choose $t = 0$) we have a wavefunction $\psi(x, 0)$ and we measure Q
- Can expand $\psi(x, 0)$ in eigenfunctions of Q

$$\psi(x, 0) = \sum_n a_n \chi_n(x)$$

finding a_n s is simple: multiply Eq. (3.1) by $\chi_m^*(x)$ and integrate

$$\text{RHS} = \int_{-\infty}^{\infty} \sum_n \chi_m^* a_n \chi_n dx = \sum_n \int_{-\infty}^{\infty} a_n \chi_m^* \chi_n dx = \sum_n a_n \delta_{nm} = a_m$$

$$\text{LHS} = \int_{-\infty}^{\infty} \sum_n \chi_m^* \psi(x, 0) dx$$

so

$$a_m = \int_{-\infty}^{\infty} \sum_n \chi_m^* \psi(x, 0) dx$$

Now substitute expanded $\psi(x, 0)$ in equation for $\langle \hat{Q} \rangle$

$$\begin{aligned} \langle \hat{Q} \rangle_{\psi} &= \int (\psi(x, 0))^* \hat{Q} \psi(x, 0) dx = \int \left(\sum_n a_n \chi_n(x) \right)^* \hat{Q} \left(\sum_m a_m \chi_m(x) \right) \\ &= \int \left(\sum_n a_n \chi_n(x) \right)^* \sum_m a_m q_m \chi_m(x) \\ &= \sum_{n,m} a_n^* a_m q_m \underbrace{\int \chi_n^* \chi_m dx}_{\delta_{mn}} \\ &= \sum_n |a_n|^2 q_n \end{aligned}$$

Remember that $|a_n|^2$ is the probability that result of a single measurement of Q gives q_n . q_n s are the possible results of single measurements of Q .

- **Example:** Back to the infinite square well. We know $H\phi_n = E_n\phi_n$ with

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

Note that these are **not** momentum eigenfunctions

$$\hat{p}\phi_n = -i\hbar \frac{\partial \phi_n}{\partial x} = -i\hbar \sqrt{\frac{2}{a}} \frac{n\pi}{a} \cos \frac{\pi n x}{a} \neq \text{const} \times \phi_n$$

- Easy to find the momentum eigenfunctions though

$$\tilde{\phi}_{p_n} = \frac{1}{\sqrt{a}} e^{ip_n x/\hbar} \text{ satisfies } -i\hbar \frac{\partial \tilde{\phi}_{p_n}}{\partial x} = p_n \tilde{\phi}_{p_n}$$

Now write the energy eigenfunctions in terms of $\tilde{\phi}_{p_n}$

$$\begin{aligned} \phi_n &= \sqrt{\frac{2}{a}} \frac{1}{2i} (e^{in\pi x \hbar / a \hbar} - e^{-in\pi x \hbar / a \hbar}) \\ &= \frac{1}{i\sqrt{2}} \tilde{\phi}_{p_n} - \frac{1}{i\sqrt{2}} \tilde{\phi}_{-p_n} \end{aligned}$$

where $p_n = \frac{n\pi\hbar}{a}$.

- So if a particle is in **energy eigenstate** ϕ_n and we **measure its momentum** we find

$$\begin{aligned} +p_n \text{ with probability} &= \left| \frac{1}{i\sqrt{2}} \right|^2 = \frac{1}{2} \\ -p_n \text{ with probability} &= \left| \frac{-1}{i\sqrt{2}} \right|^2 = \frac{1}{2} \end{aligned}$$

3.2 Practice Exercises

- (1) Prove that the kinematic operator

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

is Hermitian.

4 Dirac (Bra-Ket) notation

- More powerful and more general than wavefunctions
- Wavefunctions can be linearly **superposed** with complex coefficients
- Mathematical structure is a **complex linear vector space**

Basic object is “state ket” $|\psi\rangle$

which represents the state of the system

- A particular set of states are energy eigenstates

$$\hat{H} |n\rangle = E_n |n\rangle$$

- We also have complex conjugates of wavefunctions and eigenstates.
- Represent these by “state Bras”

$\langle\psi|$ or $\langle n|$

- The **overlap** of wavefunctions

$$\int dx \phi(x)^* \psi(x)$$

generalises to the unitary inner product for bras and kets

inner product = $\langle\phi|\psi\rangle$

- It is clear from this generalisation that

$$\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$$

- A Ket is normalised if

$$\langle\psi|\psi\rangle = 1$$

and $|\psi\rangle$ and $|\phi\rangle$ are orthogonal if

$$\langle\psi|\phi\rangle = \langle\phi|\psi\rangle = 0$$

- The complex vector space possessing the structure of an inner product, which describes the possible states of the system is called the

Hilbert Space

of the system. Sometimes denoted by \mathcal{H} .

- Like all linear spaces \mathcal{H} has a dimension determined by maximal number of linearly independent vectors

$$c_1 |u_1\rangle + c_2 |u_2\rangle + \dots + c_N |u_N\rangle = 0$$

satisfied only if $c_1 = c_2 = \dots = c_N = 0$.

- A difference with vector spaces is that

Dimension of \mathcal{H} is typically ∞

E.g. we know particle in 1D infinite square well has ∞ number of energy eigenstates

$$\phi_n(x) \leftrightarrow |n\rangle$$

which are linearly independent.

- However, later we will meet very important physical systems where \mathcal{H} is **finite dimensional** (spin, ...) and cannot be described by wavefunctions
- Existence of inner product $\langle | \rangle$ allows us to construct complete sets of orthonormal kets (a basis for \mathcal{H}) via Schmidt procedure.

Aside on Schmidt procedure

- Given a set of α linearly independent, normalisable functions (call them ψ_α) we can always construct a new set of α mutually **orthogonal** functions (call them ϕ_α) via the Schmidt procedure.
- Start with the function ψ_1 we write the following series

$$\begin{aligned} \phi_1 &= \psi_1 \\ \phi_2 &= a_{21}\phi_1 + \psi_2 \\ \phi_3 &= a_{31}\phi_1 + a_{32}\phi_2 + \psi_3 \\ &\vdots \\ \phi_\alpha &= a_{\alpha 1}\phi_1 + a_{\alpha 2}\phi_2 + \dots + a_{\alpha, \alpha-1}\phi_{\alpha-1} + \psi_\alpha \end{aligned}$$

We need to find the forms of the a coefficients. Starting with a_{21} , we multiply ϕ_2 by ϕ_1^* and integrate over all space

$$\int \phi_1^* \phi_2 dV = a_{21} \int \phi_1^* \phi_1 dV + \int \phi_1^* \psi_2 dV$$

but by definition the ϕ states are orthogonal and as $\phi_1 = \psi_1$ and the ψ are normalised we are left with

$$0 = a_{21} + \int \phi_1^* \psi_2 dV$$

giving

$$a_{21} = - \int \phi_1^* \psi_2 dV.$$

This leads to the full expression for ϕ_2 as

$$\phi_2 = - \left[\int \phi_1^* \psi_2 dV \right] \phi_1 + \psi_2$$

which is easily shown to be orthogonal to ϕ_1 as desired. Next, we wish to find the form for ϕ_3 . To do so we first multiply the expression for ϕ_3 above by ϕ_1 and integrate over all space to get

$$0 = a_{31} \int \phi_1^* \phi_1 dV + a_{32} \int \phi_1^* \phi_2 dV + \int \phi_1^* \psi_3 dV.$$

Again the ϕ are orthogonal and ϕ_1 is normalised (the other ϕ s are not) and we find

$$a_{31} = - \int \phi_1^* \psi_3 dV.$$

To find a_{32} we follow a similar procedure but multiply by ϕ_2^* . In this case we have

$$a_{32} = - \frac{\int \phi_2^* \psi_3 dV}{\int \phi_2^* \phi_2 dV}.$$

We can now write

$$\phi_3 = - \left[\int \phi_1^* \psi_3 dV \right] \phi_1 - \frac{\int \phi_2^* \psi_3 dV}{\int \phi_2^* \phi_2 dV} \phi_2 + \psi_3$$

We repeat this procedure until we reach the final state ϕ_α which has the form

$$\phi_\alpha = - \sum_{i=1}^{\alpha-1} \frac{\int \phi_i^* \psi_\alpha dV}{\int \phi_i^* \phi_i dV} + \psi_\alpha.$$

- We can redo this exercise using Dirac notation, write the series out again

$$\begin{aligned}
|\phi_1\rangle &= |\psi_1\rangle \\
|\phi_2\rangle &= a_{21} |\phi_1\rangle + |\psi_2\rangle \\
|\phi_3\rangle &= a_{31} |\phi_1\rangle + a_{32} |\phi_2\rangle + |\psi_3\rangle \\
&\vdots \\
|\phi_\alpha\rangle &= a_{\alpha 1} |\phi_1\rangle + a_{\alpha 2} |\phi_2\rangle + \dots + |\psi_\alpha\rangle
\end{aligned}$$

Following the same procedure as above to find a_{21} we find in Dirac notation

$$\langle \phi_1 | \phi_2 \rangle = a_{21} \langle \phi_1 | \phi_1 \rangle + \langle \phi_1 | \psi_2 \rangle.$$

Due to orthogonality $\langle \phi_1 | \phi_2 \rangle = 0$ and ϕ_1 is already normalised we can rearrange and

$$a_{21} = - \langle \phi_1 | \psi_2 \rangle.$$

then

$$|\phi_2\rangle = - |\phi_1\rangle \langle \phi_1 | \psi_2 \rangle + |\psi_2\rangle.$$

Similarly we find

$$|\phi_3\rangle = - |\phi_1\rangle \langle \phi_1 | \psi_3 \rangle - |\phi_2\rangle \frac{\langle \phi_2 | \psi_3 \rangle}{\langle \phi_2 | \phi_2 \rangle} + |\psi_3\rangle.$$

The final state is then given by

$$|\phi_\alpha\rangle = - \sum_{i=1}^{\alpha-1} |\phi_i\rangle \frac{\langle \phi_i | \psi_\alpha \rangle}{\langle \phi_i | \phi_i \rangle} + |\psi_\alpha\rangle$$

To have an orthonormal set we need to normalise these states. This is simply done and the result for the normalised states $|U_m\rangle$ as

$$|U_m\rangle = \frac{|\phi_m\rangle}{\sqrt{\langle \phi_m | \psi_m \rangle}}$$

Now we have a complete set of orthonormal kets (a basis for \mathcal{H}) with

$$|U_m\rangle \quad \text{with} \quad \langle U_n | U_m \rangle = \delta_{nm}$$

- If we have such a basis then any state $|\psi\rangle$ of system can be expanded

$$|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} c_n |U_n\rangle$$

The c_n s determined by taking inner product of this equation with $\langle U_m|$

$$\langle U_m|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} c_n \langle U_m|U_n\rangle = c_m.$$

Thus the expansion for $|\psi\rangle$ is

$$|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} |U_n\rangle \langle U_n|\psi\rangle$$

- The **bras and kets are related by taking the adjoint** (complex conjugate transpose for usual vectors) so

$$|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} c_n |U_n\rangle$$

$$(|\psi\rangle)^\dagger = \left(\sum_{n=1}^{\dim \mathcal{H}} c_n |U_n\rangle \right)^\dagger$$

$$\langle\psi| = \sum_{n=1}^{\dim \mathcal{H}} c_n^* \langle U_n|$$

The normalisation implies

$$1 = \langle\psi|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} c_n^* \langle U_n| \sum_{m=1}^{\dim \mathcal{H}} |U_m\rangle c_m = \sum_{n,m} c_n^* c_m \langle U_n|U_m\rangle = \sum_{n,m} c_n^* c_m \delta_{mn} = \sum_n |c_n|^2$$

- In QM also have (hermitian) operators which represent observables
- **Key principle of QM is that all operators are linear**, i.e. if

$$|\psi\rangle = c_1 |U_1\rangle + c_2 |U_2\rangle$$

then

$$\hat{O}|\psi\rangle = c_1(\hat{O}|U_1\rangle) + c_2(\hat{O}|U_2\rangle)$$

- One exception to this, the “time-reversal” operator \hat{T} which is anti-linear - this is an advanced (and interesting) topic...
- Operators also act on vector space of bras linearly (\hat{O} can act “left” or “right”)

$$\langle \psi | \hat{O} = (c_1^* \langle U_1 | + c_2^* \langle U_2 |) \hat{O} = c_1^* (\langle U_1 | \hat{O}) + c_2^* (\langle U_2 | \hat{O})$$

- Since bras and kets are exchanged by taking adjoint, useful to define action of adjoint on operators

Adjoint \hat{O}^\dagger of operator \hat{O} defined by

$$\langle \psi | \hat{O}^\dagger | \phi \rangle \equiv \langle \phi | \hat{O} | \psi \rangle^*$$

- Hermitian (or “self-adjoint”) operators satisfy

$$\hat{O}^\dagger = \hat{O}$$

- For hermitian ops (only)

$$\langle \psi | \hat{O} | \phi \rangle \equiv \langle \phi | \hat{O} | \psi \rangle^*$$

The quantity $\langle \phi | \hat{O} | \psi \rangle$ is called the “matrix element” of \hat{O} between states $|\phi\rangle$ and $|\psi\rangle$

- If $|U_n\rangle$ is an orthonormal basis then

$$\langle U_m | \hat{O} | U_n \rangle$$

is a matrix element in the conventional sense.

- A surprisingly useful operator secretly appears in the expansion of general $|\psi\rangle$

$$|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} |U_n\rangle \langle U_n | \psi \rangle$$

- Since this holds for any ket $|\psi\rangle$ we find

$$\hat{I} = \sum_{n=1}^{\dim \mathcal{H}} |U_n\rangle \langle U_n|$$

where \hat{I} is the “identity operator”

which leaves all states unchanged

$$\hat{I} |\phi\rangle = \sum_{n=1}^{\dim \mathcal{H}} |U_n\rangle \langle U_n | \phi\rangle = |\phi\rangle$$

by expansion theorem for $|\phi\rangle$.

- The matrix element of \hat{I} is (in some a basis)

$$\langle U_p | \hat{I} | U_q \rangle = \sum_{n=1}^{\dim \mathcal{H}} \langle U_p | U_n \rangle \langle U_n | U_q \rangle = \sum_{n=1}^{\dim \mathcal{H}} \delta_{pn} \delta_{nq} = \delta_{pq}$$

- Thus written explicitly as a matrix \hat{I} is represented as

$$\hat{I} \leftrightarrow \underbrace{\begin{pmatrix} 1 & 0 & 0 & 0 & \dots \\ 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & 1 & 0 & \dots \\ 0 & 0 & 0 & 1 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}}_{\dim \mathcal{H}} \Bigg\} \dim \mathcal{H}$$

The **unit matrix**.

- Another important example is the matrix element of a product of operators

$$\langle U_p | \hat{A} \hat{B} | U_q \rangle = \underbrace{\langle U_p | \hat{A} \hat{B} | U_q \rangle}_{\text{can always insert } \hat{I}} = \sum_n \langle U_p | \hat{A} | U_n \rangle \langle U_n | \hat{B} | U_q \rangle = \sum_n A_{pn} B_{nq}$$

just usual matrix multiplication of matrices representing \hat{A} and \hat{B} .

- Check that our earlier definition of \hat{O}^\dagger agrees with adjoint of matrix

$$(\hat{O}^\dagger)_{mn} \equiv \langle U_m | \hat{O}^\dagger | U_n \rangle = \langle U_n | \hat{O} | U_m \rangle^* = (\hat{O})_{nm}^* = (\hat{O}_{mn})^{*T}$$

Summary so far...Fundamental Postulates of QM

- I) States of a system are represented by **normalised** kets $|\psi\rangle$ or bras $\langle\phi|$ in a Hilbert space (which varies from system to system)
- II) Observables are represented by **linear hermitian operators** acting on kets and bras
- III) Such hermitian operators \hat{A} are assumed to possess a **complete set of orthonormal eigenstates**, e.g.

$$\begin{array}{lll} |1\rangle & \text{with eigenvalue} & a_1 \\ |2\rangle & \text{with eigenvalue} & a_2 \\ |3\rangle & \text{with eigenvalue} & a_3 \\ \vdots & \vdots & \vdots \end{array}$$

“Complete set” means that $|1\rangle, |2\rangle, \dots$ forms a basis for the space, so any $|\psi\rangle$ can be **expanded in eigenstates** of \hat{A} (and for any \hat{A})

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

- IV) The **fundamental probability postulate for measurement** is
 - 1) Possible results of measurement of A are eigenvalues of \hat{A} only.
 - 2) $\text{Prob}(A = a_n) = |\langle n|\psi\rangle|^2$
 - 3) **After measurement** of \hat{A} with result a_n the state $|\psi\rangle$ is **reduced** to (“collapsed to”)

$$|\psi_{\text{after}}\rangle = |n\rangle$$

coefficient in front of $|n\rangle$ is changed to 1 where $|n\rangle$ is an eigenket of \hat{A} with $\hat{A}|n\rangle = a_n|n\rangle$.

Subsequent measurements of same \hat{A} on $|\psi_{\text{after}}\rangle = |n\rangle$ return a_n with probability =1. As long as no measurements of other operators \hat{B} are made at intermediate times...more later.

(Note: if a_n is a degenerate eigenvalue (i.e. if more than one linearly independent ket has same a_n eigenvalues, the procedure of reduction is slightly more involved - advanced topic)

- V) In the absence of a measurement the time evolution of the $|\psi(t)\rangle$ describing the state of the system at time t changes smoothly in time according to the TDSE

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H} |\psi(t)\rangle$$

Notes

- 1) The TDSE is a linear eqn, which is also deterministic, i.e. given the state at $t = 0$, $|\psi(0)\rangle$. The state at a later time t is uniquely determined as long as no measurements are performed.
- 2) Thus the probabilistic, non-deterministic aspects of QM are purely due to the collapse of the state upon measurement.
- 3) \hat{H} is the Hamiltonian - the operator corresponding to the energy of the system
- 4) We can formally integrate the TDSE ($\hat{H}|\psi\rangle = i\hbar\frac{\partial|\psi\rangle}{\partial t}$) from time = t_0 to t_f

$$|\psi(t_f)\rangle = e^{-i\hat{H}(t_f-t_0)/\hbar}|\psi(t_0)\rangle$$

where the exponential is defined by its power series, e.g.

$$e^{\hat{O}} = 1 + \hat{O} + \frac{\hat{O}^2}{2!} + \dots$$

since $\hat{H} = \hat{H}^\dagger$ (hermitian) the operator

$$U \equiv e^{-i\hat{H}(t_f-t_0)/\hbar}$$

is unitary,

$$U^\dagger U = e^{i\hbar\hat{H}^\dagger(t_f-t_0)/\hbar}e^{-i\hbar\hat{H}(t_f-t_0)/\hbar} = 1$$

so the time evolution is “unitary evolution”.

4.1 Recovering Wavefunctions

- How do we recover wavefunctions?
- Consider position operator \hat{x} . This has a continuous spectrum of eigenvalues

$$\hat{x}|x\rangle = x|x\rangle$$

- The eigenkets $|x\rangle$ are normalised as

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

$\delta(x-x')$ is the analogue of $\langle n|m\rangle = \delta_{nm}$ in the discrete case. Some useful identities with delta functions are

$$\int_{-\infty}^{\infty} e^{ikx} dk = 2\pi\delta(x)$$

This should be used inside integral as

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)dx = f(a)$$

In 3-d this becomes

$$\int_{-\infty}^{\infty} e^{i\mathbf{k}\cdot\mathbf{x}} d^3k = (2\pi)^3 \delta^3(\mathbf{x})$$

- The expansion of a normalised state $|\psi\rangle$ of the particle in terms of position eigenkets reads

$$|\psi\rangle = \int dx |x\rangle \langle x|\psi\rangle$$

which is the analogue of $|\psi\rangle = \sum_n |n\rangle \langle n|\psi\rangle$

- General rules of the Dirac formalism tell us the interpretation of $\langle x|\psi\rangle$

$\langle x|\psi\rangle$ = probability amplitude that a particle
in state $|\psi\rangle$ is located at x

- I.e. $\langle x|\psi\rangle$ is precisely what we **previously** called **the wavefunction**
- The description of states by wavefunctions is called the **“x-representation”** (or coordinate representation)
- Schrödinger’s wave mechanics is the form QM takes if the coordinates of a particle are all one cares about. (E.g. if no spin, no antiparticle creation, ...)
- All aspects of wave mechanics can be derived from Dirac description, e.g. overlap

$$\begin{aligned} \langle \psi|\phi\rangle &= \langle \psi| \underbrace{\int dx |x\rangle \langle x|}_{\text{inserting } \hat{I} \text{ in x-rep}} |\phi\rangle \\ &= \int dx \langle \psi|x\rangle \langle x|\phi\rangle \\ &= \int dx \langle x|\psi\rangle^* \langle x|\phi\rangle = \int dx \psi^*(x) \phi(x) \quad \checkmark \end{aligned}$$

4.1.1 Manipulation with the momentum Operator

- Momentum operator \hat{p} acting on some eigenstate of momentum (look at one dimension example)

$$\hat{p}|p\rangle = \underline{p}|p\rangle$$

We also have that

$$\langle r|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ipr/\hbar}$$

Can check the normalisation by using the fact that $\langle p|p'\rangle = \delta(p - p')$ and

$$\langle p|p'\rangle = \int dr \langle p|r\rangle \langle r|p'\rangle = \int dr \frac{1}{2\pi\hbar} e^{ipr/\hbar} e^{-ip'r/\hbar} = \delta(p - p')$$

Also we can rewrite the following

$$\begin{aligned} \langle r|\hat{p}|\psi\rangle &= \int dp \langle r|p\rangle \langle p|\hat{p}|\psi\rangle = \int dp \langle r|p\rangle \underline{p} \langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int dr e^{ipr/\hbar} \underline{p} \langle p|\psi\rangle \\ &= -i\hbar \frac{\partial}{\partial r} \int dr \langle r|p\rangle \langle p|\psi\rangle = -i\hbar \frac{\partial}{\partial r} \langle r|\psi\rangle \end{aligned}$$

Therefore

$$\langle r|\hat{p}|\psi\rangle = -i\hbar \frac{\partial}{\partial r} \psi(r)$$

Similarly

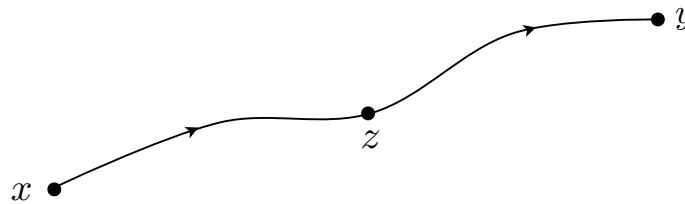
$$\langle r|\frac{\hat{p}^2}{2m}|\psi\rangle = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(r)}{\partial r^2}$$

4.2 Rules for Amplitudes

- In the x-representation (i.e. usual wavefunctions) the amplitudes are found by solving the TDSE with appropriate boundary conditions
- Now we come to **very general rules** for probability amplitudes that can be derived from the Dirac formulation
- Define “**an event**” in an experiment to be a situation in which **all the initial and final** conditions of the experiment are **completely specified**. I.e. all positions, angular momenta,... if all particles specified.

Rules

- **Rule 1:** When an event can occur **several alternative ways** the **amplitude** is the **sum** of the amplitudes for each way considered separately (**so we get interference**)
- **Rule 2:** The **amplitude for each separate way** an event can occur can be written as the **product** of the amplitude for part of the event occurring that way with the amplitude of the remaining part e.g. Amp(particle $x \rightarrow y$)



$$\text{Amp}(x \rightarrow y) = \text{Amp}(x \rightarrow z) \cdot \text{Amp}(z \rightarrow y)$$

or

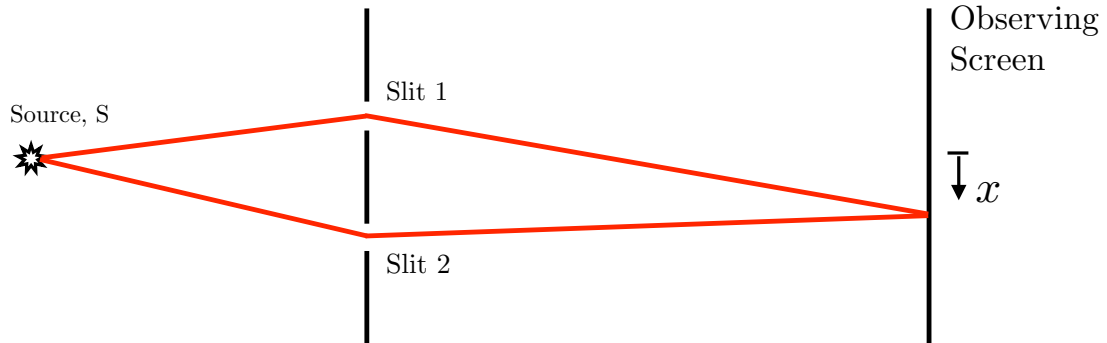
$$\langle y|x \rangle = \langle y|z \rangle \langle z|x \rangle$$

- **Rule 3:** If an experiment is performed which is **capable in principle** of **determining which of the alternative ways** is actually taken (so in fact not all final conditions are the same) Then total **probability** (not amplitude) is **sum of probabilities for each alternative**

$$P_{tot} = P_1 + P_2 + \dots$$

⇒ interference is lost. NOTE: “capable in principle” doesn’t mean that its necessary for a human (or other scientific being) to check that all final conditions are the same. (its enough for the state of one atom to be different whether we are aware or not)

- Useful to manipulate amplitudes even when we don’t know (yet) exactly their value E.g. two slit interference



$$\langle 1|S \rangle = \text{Amplitude for particle to go from } S \text{ to slit 1}$$

$$\langle x|1 \rangle = \text{Amplitude for particle to go from 1 to slit } x$$

similar for $\langle 2|S \rangle$ and $\langle x|2 \rangle$. So the total amplitude from source S to x

$$\text{Amp}_{1+2} = \langle x|1 \rangle \langle 1|S \rangle + \langle x|2 \rangle \langle 2|S \rangle$$

where we multiply amplitudes along the route and add the different routes. This leads to

$$\text{Prob}(S \rightarrow x) = |\text{Amp}_{1+2}|^2$$

and because of the interference term this is not simply equal to $|\langle x|1 \rangle \langle 1|S \rangle|^2 + |\langle x|2 \rangle \langle 2|S \rangle|^2$.

5 Conserved Quantities

- In classical physics many conserved quantities (e.g. Energy, Momentum, Angular momentum) What about in QM?
- Consider expectation value of some operator Q which does not have any explicit time-dependence (e.g. x or $-i\hbar\partial/\partial x$)

$$\langle Q \rangle_\psi = \int_{-\infty}^{\infty} \psi^*(x, t) Q \psi(x, t) dx$$

- Due to the fact that ψ is a function of t we will find that, in general, $\langle Q \rangle_\psi$ is also a function of $t...$

$$\frac{d\langle Q \rangle_\psi}{dt} = \int_{-\infty}^{\infty} \left\{ \frac{\partial \psi^*}{\partial t} Q \psi + \psi^* Q \frac{\partial \psi}{\partial t} \right\} dx$$

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

$$\begin{aligned} \frac{d\langle Q \rangle_\psi}{dt} &= \int_{-\infty}^{\infty} \left\{ \left(\frac{H\psi}{i\hbar} \right)^* Q \psi + \psi^* Q \left(\frac{H\psi}{i\hbar} \right) \right\} dx \\ &= \frac{1}{i\hbar} \int_{-\infty}^{\infty} \{ -\psi^* H Q \psi + \psi^* Q H \psi \} dx \end{aligned}$$

using the fact that H is hermitian.

$$\frac{d\langle Q \rangle_\psi}{dt} = \frac{i}{\hbar} \int_{-\infty}^{\infty} \psi^* (H Q - Q H) \psi dx = \frac{i}{\hbar} \langle (H Q - Q H) \rangle_\psi$$

- q is a conserved quantity if

$$\frac{d\langle Q \rangle_\psi}{dt} = 0$$

no matter what state ψ the particle is in.

- Only can happen if

$$(H Q - Q H) \psi \equiv [H, Q] \psi = 0$$

for any normalisable function, ψ . The object $[H, Q]$ is the commutator of H and Q .

Example

Simplest case is $Q = 1$.

$$\frac{d}{dt} \langle \psi | \psi \rangle = \frac{i}{\hbar} \langle \psi | [H, 1] | \psi \rangle = 0$$

as $[H, 1] = 0$ for any operator A .

- Namely, **the probability is conserved** independent of time, i.e. $\langle \psi | \psi \rangle = 1$

Aside on Probability Current

- $\rho = \psi^* \psi$ is the probability density

$$\frac{\partial \rho}{\partial t} = \frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \tag{5.1}$$

but TDSE says for 1D QM

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

Using this in Eq. (5.1) we have

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{i}{\hbar} \left\{ \left(-\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* \right) \psi - \psi^* \left(\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \right) \right\} \\ &= -\frac{i\hbar}{2m} \nabla \cdot (\psi \nabla \psi^* - \psi^* \nabla \psi) \end{aligned}$$

Defining

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

and we finally have the conservation equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

Return to basic conservation equation

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

- So far looked at case of $Q = 1$
- Now explore more generally, with $H = \frac{p^2}{2m} + V(x)$
- i) Total energy is conserved because

$$[H, H] = HH - HH = 0$$

so

$$\frac{d}{dt} \langle \psi | H | \psi \rangle = 0 \quad \forall |\psi\rangle$$

- ii) Now consider momentum p

$$\begin{aligned} [H, p] &= \left[\frac{p^2}{2m} + V(x), p \right] = \left[\frac{p^2}{2m}, p \right] + [V(x), p] \\ &= \frac{1}{2m} \underbrace{(p^2 p - p p^2)}_{=0} + [V(x), p] = [V(x), p] \end{aligned}$$

but $[V(x), p] = [V(x), -i\hbar \frac{\partial}{\partial x}]$. To work this out *we must put arbitrary function on RHS and we find*

$$[V(x), p] f(x) = i\hbar \frac{\partial V(x)}{\partial x} f(x)$$

So...

$$[V(x), p] = i\hbar \frac{\partial V(x)}{\partial x}$$

Not Zero!

Therefore $[H, p] = i\hbar \frac{\partial V(x)}{\partial x}$ and

$$\frac{\partial \langle p \rangle}{\partial t} = - \left\langle \frac{\partial V(x)}{\partial x} \right\rangle$$

Note the similarity of this result to classical equation of motion.

- This shows that $d\langle p \rangle / dt$ cannot be zero **unless** $\partial V(x) / \partial x = 0$. But this means that $V = \text{Const}$ and we find linear momentum conservation only when H is independent of position (system is independent of position)
- iii) Now take $Q = X$

$$[H, x] = \left[\frac{p^2}{2m} + V(x), x \right] = \left[\frac{p^2}{2m}, x \right] + \underbrace{[V(x), x]}_{=0}$$

A useful identity is

$$[A^2, B] = A[A, B] + [A, B]A$$

Applying this we have

$$[H, x] = \frac{1}{2m} \{p[p, x] + [p, x]p\}$$

Finally we need $[p, x]$

$$[p, x]f(x) = \left(-i\hbar \frac{\partial}{\partial x} x + x i\hbar \frac{\partial}{\partial x} \right) f(x) = -i\hbar \left\{ \frac{\partial x}{\partial x} f(x) + x \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial x} \right\} = -i\hbar f(x)$$

This is a fundamental property of x and p operators.

Hence,

$$[H, x] = \frac{1}{2m} \{p(-i\hbar) + (-i\hbar)p\} = -i\hbar \frac{p}{m}$$

Thus

$$\boxed{\frac{\partial \langle x \rangle}{\partial t} = \frac{\langle p \rangle}{m}}$$

- And position is not conserved unless in special case with $\langle p \rangle = 0$.
- Note: the above equation is analogue to classical $\dot{x} = p/m$
- From both the above equation and $\frac{\partial \langle p \rangle}{\partial t} = - \left\langle \frac{\partial V(x)}{\partial x} \right\rangle$ we see that the classical equations of motion are obeyed **on the average in QM** - - **EHRENFEST THEOREM**
More on commutators
- We have seen that $[H, Q] = 0$ implies $\frac{d\langle Q \rangle}{dt} = 0$
- So far we have been working with expectation values

- We now would like to ask, does $[H, Q] = 0$ have special consequences for **individual measurements**...Answer is yes...
- We know eigenstates of h satisfy

$$H\phi_n = E_n\phi_n$$

Recall that this means that if

$$\psi(x, t) = \underbrace{e^{-iE_n t/\hbar}\phi_n(x)}_{\text{not a superposition}}$$

then when we measure energy we will get E_n (with probability =1).

- Now suppose the same functions ϕ_n are also **eigenstates of another operator Q**

$$Q\phi_n = q_n\phi_n$$

- This means that if the particle is described by ϕ_n **then it also has a definite value of Q given by q_n**

$$\text{Prob}(Q = q_n) = 1$$

- What is the condition that this is possible?
- Act on $H\phi_n = E_n\phi_n$ with Q

$$QH\phi_n = E_nQ\phi_n = E_nq_n\phi_n$$

- Alternatively act on $Q\phi_n = q_n\phi_n$ with H

$$HQ\phi_n = q_nH\phi_n = q_nE_n\phi_n$$

- This is the same result. Subtracting these two equations

$$(HQ - QH)\phi_n = 0$$

Since, by assumption, this is true for all ϕ_n

$$\boxed{[H, Q] = 0}$$

Thus

If $[H, Q] = 0$ it is possible for the particle to be in state of definite energy a “stationary state” in which the value of Q is also definite

- What happens if $\psi(x, t)$ is **not** an eigenstate? E.g. a superposition of 2 eigenstates

$$\psi(x, t) = a_1\phi_1(x)e^{-iE_1t/\hbar} + a_2\phi_2(x)e^{-iE_2t/\hbar}$$

with

$$1 = |a_1|^2 + |a_2|^2$$

so

$$\text{Prob}(E = E_1) = |a_1|^2$$

$$\text{Prob}(E = E_2) = |a_2|^2$$

Let us compute $\langle Q \rangle$

$$\begin{aligned} \langle Q \rangle &= \int \psi^* Q \psi \, dx \\ &= \int (a_1^* \phi_1 e^{iE_1 t/\hbar} + a_2^* \phi_2 e^{iE_2 t/\hbar}) (a_1 \phi_1 e^{-iE_1 t/\hbar} + a_2 \phi_2 e^{-iE_2 t/\hbar}) \\ &= q_1 |a_1|^2 + q_2 |a_2|^2 \end{aligned}$$

This is just

$$\langle Q \rangle = q_1 \times (\text{Prob in state 1}) + q_2 \times (\text{Prob in state 2})$$

So if we make a measurement of **both H and Q** we find

$$\begin{aligned} (E_1, q_1) &\text{ with prob} = |a_1|^2 \\ (E_2, q_2) &\text{ with prob} = |a_2|^2 \end{aligned}$$

Fundamental point is the following:

If $[H, Q] = 0$ then can measure both quantities and simultaneously find precise values of both H and Q

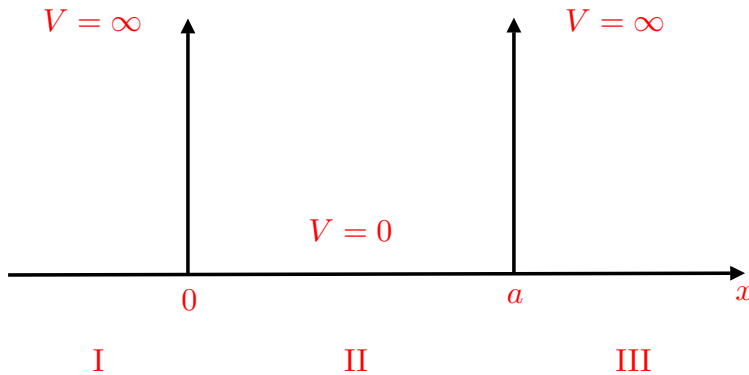


Figure 5.1: Infinite Square Well

What happens if $[H, Q] \neq 0$?

We have already studied this when we looked at $Q = P$ in the case of the infinite square well.

$$[H, P] = i\hbar \frac{\partial V}{\partial x} \neq 0$$

Since

$$\begin{aligned} \text{at } x = 0 \quad \frac{\partial V}{\partial x} &\rightarrow -\infty \\ \text{and at } x = a \quad \frac{\partial V}{\partial x} &\rightarrow \infty \end{aligned}$$

- In this case we saw that **If** particle has **definite energy**

$$\psi(x, t) = e^{-iE_n t/\hbar} \phi_n(x)$$

then

ψ is a superposition of states with **different momenta**

- Equivalent:

We cannot know both E and P for sure since $[H, P] \neq 0$

- General result in QM

If A and B are physical (hermitian) ops. with $[A, B] \neq 0$ then cannot in general simultaneously know values A and B .

5.1 Complete sets of Quantum Numbers

- Suppose we have two operators Q_1, Q_2 satisfying

$$[H, Q_1] = 0, \text{ and } [H, Q_2] = 0$$

then

$$\frac{d\langle Q_1 \rangle}{dt} \text{ and } \frac{d\langle Q_2 \rangle}{dt}$$

and both observables are conserved.

- **However** if $[Q_1, Q_2] \neq 0$ then will not be able to make a definite measurement of both
- If $[Q_1, Q_2] = 0$ then always **possible** to find simultaneous eigenstates of Q_1 and Q_2 and H . In this case the wavefunction

$$\psi(x, t) = e^{-iE_n t/\hbar} \phi_n(x)$$

which has

Definite energy	E_n
Definite Q_1	q_1
Definite Q_2	q_2

These are the quantum numbers of the state ψ . In this case $[Q_1, Q_2] = 0$, Q_1 and Q_2 are “compatible”.

- In the case $[Q_1, Q_2] \neq 0$, Q_1 and Q_2 are “incompatible” and it is possible for us to have state

$$\psi(x, t) = e^{-iEt/\hbar} \phi(x)$$

with either a

Definite energy	E_n
Definite Q_1	q_1

or

$$\begin{array}{ll} \text{Definite energy} & E_n \\ \text{Definite } Q_2 & q_1 \end{array}$$

But not both

- E.g. Since $[p, x] = i\hbar$ we can never have a state in which both p and x have definite values
- We say that E, \dots form a complete set of Quantum numbers if maximal number of simultaneous eigenvalues are specified

5.2 The Uncertainty Principle

- We now want to know what happens when we make measurements on some general superposition
- Consider, e.g. energy superposition

$$\psi(x, t) = a_1\phi_1e^{-iE_1t/\hbar} + a_2\phi_2e^{-iE_2t/\hbar}$$

- Suppose measurement of energy at $t = t_0$ gives result E_1
 - Means we know for sure that energy is E_1
 - But this implies that now (for $t \geq t_0$) system must be in energy eigenstate

$$\psi(x, t > t_0) = \phi_1e^{-iE_1t/\hbar}$$

Thus

- (1) Part of original ψ which has different energy to the one measured disappears
- (2) Remaining part has its coeff changed so that new wavefunction is correctly normalised

- Procedure is the so-called “collapse of the wavefunction”
- Applies when any quantity (not just energy) is measured
- “Collapse of the wavefunction” also know as “Projection Postulate”
- Radical proposals such as “many worlds” which tries to explain why we experience collapse.
- In any case important to stress

Every experiment ever performed leads to results consistent with the simple “collapse” postulate and so we don’t need anything more fancy

- Let’s see what happens in an **example of a series of measurements**

- (1) Start with infinite square well

$$\psi(x, t) = \phi_n(x)e^{-iE_n t/\hbar}, \quad E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}, \quad \phi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

- (2) measure energy: Result: E_1 , **so wavefunction collapses to**

$$\psi(x, t)_a = \phi_1(x)e^{-iE_1 t/\hbar},$$

- (3) Now measure momentum. To work out possible results must **rewrite ψ_a as a sum of momentum eigenstates**

$$\psi_a = e^{-iE_1 t/\hbar} \sqrt{\frac{2}{a}} \frac{1}{2i} (e^{i\pi x/a} - e^{-i\pi x/a}).$$

This is a **superposition of two momentum states one with $\frac{\pi\hbar}{a}$ and $-\frac{\pi\hbar}{a}$.**

- Suppose we now measure momentum $\pi\hbar/a \Rightarrow$ Wavefunction **collapses to**

$$\psi_b = e^{-iE_1 t/\hbar} \frac{e^{i\pi x/a}}{\sqrt{a}}$$

- (4) Now measure energy again. To work out possible results **must rewrite ψ_a as a sum of energy eigenstates**

$$\frac{e^{i\pi x/a}}{\sqrt{a}} = \frac{1}{\sqrt{a}} \left(\cos \frac{\pi x}{a} + i \sin \frac{\pi x}{a} \right)$$

$\sin \frac{\pi x}{a}$ is already an energy eigenstate but we must expand $\cos \frac{\pi x}{a}$ in terms of a Fourier series

$$\frac{1}{\sqrt{a}} \cos \frac{\pi x}{a} = \sum_{n=1}^{\infty} a_n \underbrace{\left(\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right)}$$

remember this is an energy eigenfunction

where

$$a_n = \frac{1}{\sqrt{a}} \int_0^a \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \cos \frac{n\pi x}{a} dx = \begin{cases} 0 & \text{if } n = \text{odd} \\ \frac{2\sqrt{2}n}{\pi(n^2-1)} & \text{if } n = \text{even} \end{cases}$$

Thus

$$\frac{e^{i\pi x/a}}{\sqrt{a}} = \frac{i}{\sqrt{a}} (\phi_1(x)) + \sum_{n \text{ even}} \frac{2\sqrt{2}n}{\pi(n^2-1)} (\phi_n(x))$$

So when we measure energy we get

$$\begin{array}{lll} E_1 & \text{with prob.} & P(E_1) = \frac{1}{2} \\ E_2 & \text{with prob.} & P(E_2) = \frac{32}{9\pi^2} \\ E_4 & \text{with prob.} & P(E_4) = \frac{128}{225\pi^2} \\ \vdots & \vdots & \vdots \\ E_n & \text{with prob.} & P(E_n) = \frac{8n^2}{(n^2-1)^2\pi^2} \end{array}$$

- Thus even though we started with an energy eigenstate, **by making a measurement of momentum** (an operator incompatible with H) we have **left a particle in a state of very indefinite energy!**
- These considerations lead Heisenberg to his famous **uncertainty principle**
- Uncertainty principle not separate axiom of QM it is a consequence of rules already stated.
- When there is uncertainty in the outcome of measurement useful to quantify: **Define Uncertainty** as

$$(\Delta q)^2 \equiv \langle q^2 \rangle - \langle q \rangle^2$$

$\Delta q = 0$ if q takes a single value.

Heisenberg's Uncertainty principle considers x and p (remember $[x, p] = i\hbar$) and states

$$\Delta x \Delta p \geq \hbar/2$$

But what does this mean?

- It says that is we prepare a particle in a state whereby its location x is know to within Δx , then the uncertainty in its momentum is at **least $\hbar/2\Delta x$**

Example:

- Suppose we have a **Gaussian** wavefunction

$$\phi(x) = \frac{1}{a^{1/2}\pi^{1/4}} e^{-x^2/2a^2}$$

clearly

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\phi(x)|^2 dx = 0$$

also

$$\langle x^2 \rangle = \frac{1}{a\pi^{1/2}} \int_{-\infty}^{\infty} x^2 e^{-x^2/a^2} dx = \frac{a^2}{2}$$

so that

$$\Rightarrow \Delta x = [\langle x^2 \rangle - \langle x \rangle^2]^{1/2} = \frac{a}{\sqrt{2}}$$

Now for the momentum p

$$\langle p \rangle = -\frac{i\hbar}{a\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-x^2/2a^2} \frac{\partial}{\partial x} e^{-x^2/2a^2} dx = 0$$

and

$$\langle p^2 \rangle = -\frac{\hbar^2}{a\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-x^2/2a^2} \frac{\partial^2}{\partial x^2} e^{-x^2/2a^2} dx = -\frac{\hbar^2}{a\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-x^2/a^2} \left(\frac{x^2}{a^4} - \frac{1}{a^2} \right) dx = \frac{\hbar^2}{2a^2}$$

using the useful integral

$$\int_{-\infty}^{\infty} e^{-x^2/a^2} dx = a\sqrt{\pi}$$

Finally we get

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

Putting this all together

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

Exactly the saturation of Heisenberg's uncertainty principle bound. In fact, a Gaussian wavefunction gives the least possible value for $\Delta p \Delta x$.

- Since $\Delta p \neq 0$ interesting to ask what the momentum distribution is.

- We know x-space wavefunction

$$\phi(x) = \frac{1}{a^{1/2}\pi^{1/4}} e^{-x^2/2a^2}$$

In Dirac notation this is $\langle x|\phi\rangle$ - “Amplitude for particle in state ϕ to be found at x .”

- We want $\langle p|\phi\rangle$ - “Amplitude for particle in state ϕ to be measured with momentum p . This is just the Fourier transform of $\phi(x)$ ”

$$\tilde{\phi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ipx/\hbar} \phi(x) dx$$

Factor in front of the integral is there so $\int_{-\infty}^{\infty} dp |\tilde{\phi}|^2 = 1$

Or in Dirac notation

$$\langle p|\phi\rangle = \sum_{\text{all values of } x} \langle p|x\rangle \langle x|\phi\rangle$$

where

$$\langle p|x\rangle = \langle x|p\rangle^* = \left(\frac{e^{-ipx/\hbar}}{\sqrt{2\pi\hbar}} \right)^* = \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}$$

- Integral for $\tilde{\phi}(p)$ can be done by completing the square

$$\tilde{\phi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx e^{-\frac{1}{2a^2} \{ (x-ipa^2/\hbar)^2 + p^2 a^4/\hbar^2 \}} = \sqrt{\frac{a}{\hbar\pi^{1/2}}} e^{-p^2 a^2/2\hbar^2}$$

Another Gaussian!

6 Simple Harmonic Oscillator (SHO)

- Many systems to leading approximation are the SHO (or many weakly coupled SHOs), so this is an important case
- Potential energy is

$$V(x) = \frac{1}{2}kx^2$$

so TISE

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} + \frac{1}{2}kx^2 = E\phi$$

convenient to rescale the x variable by $x = \alpha y$

$$-\frac{\hbar^2}{2m\alpha^2} \frac{d^2\phi}{dy^2} + \frac{1}{2}\alpha^2 ky^2 = E\phi$$

and insist that coefficients of K.E. and P.E. are the same

$$\frac{\hbar^2}{2m\alpha^2} = \frac{1}{2}k\alpha^2$$

$$\Rightarrow \alpha^2 = \frac{\hbar}{\sqrt{mk}}$$

Then we have

$$\hbar\sqrt{\frac{k}{m}} \frac{1}{2} \left(-\frac{d^2\phi}{dy^2} + y^2\phi \right) = E\phi$$

Now set $\sqrt{k/m} = \omega$ the classical angular frequency, so let

$$\epsilon = \frac{E}{\left(\frac{\hbar\omega}{2}\right)}$$

i.e., ϵ is the energy in units of $\hbar\omega/2$. Thus our TISE becomes

$$-\frac{d^2\phi}{dy^2} + y^2\phi = \epsilon\phi$$

It is easy to check that

$$\phi_0 = e^{-y^2/2}$$

is a solution (and is normalisable), let plug it in...

$$\begin{aligned}\phi_0' &= -ye^{-y^2/2} \\ \phi_0'' &= -y^2e^{-y^2/2} - e^{-y^2/2}\end{aligned}$$

So TISE reads

$$-(y^2e^{-y^2/2} - e^{-y^2/2}) + y^2e^{-y^2/2} = \epsilon e^{-y^2/2}$$

\Rightarrow Solution if $\epsilon = 1 \Rightarrow$ The energy eigenvalue.

We will soon see that this is the ground state

$$E_0 = \frac{\hbar\omega}{2} > 0$$

- What about the other energy eigenstates? - There are two ways of getting rest...
- (I) Try

$$\phi = H(y)e^{-y^2/2}$$

Putting this into the TISE we find

$$H'' - 2yH' + H(\epsilon - 1) = 0$$

This is called **Hermite's equation**, and can be solved by Frobenius series method. See second year notes for details.

- There are normalisable solutions for $\epsilon = 2n + 1$; $H_n(y)$ is a Hermite polynomial

6.1 Operator Method.

- (II): A much more instructive method which generalises to many other problems In y coords our Hamiltonian operator is

$$H = -\frac{\partial^2}{\partial y^2} + y^2$$

Let's try to "factorise" this **Define Operators**

$$a_+ = -\frac{\partial}{\partial y} + y \quad a_- = \frac{\partial}{\partial y} + y$$

Acting on arbitrary $f(y)$

$$\begin{aligned} a_+ a_- f(y) &= \left(-\frac{\partial}{\partial y} + y \right) \left(\frac{\partial}{\partial y} + y \right) f(y) \\ &= -\frac{d^2 f}{dy^2} + y^2 f - f \end{aligned}$$

Similarly

$$a_- a_+ f(y) = -\frac{d^2 f}{dy^2} + y^2 f + f$$

So we learn

- i)

$$[a_+, a_-] = -2$$

(6.1)

- ii) We can write TISE as

$$(a_+ a_- + 1)\phi = \epsilon\phi$$

(6.2)

- iii) Apply a_- to ground state wavefunction:

$$a_- \phi_0 = \left(\frac{\partial}{\partial y} + y \right) e^{-y^2/2} = 0$$

Thus

$$(a_+ a_- + 1)\phi_0 = 1 \cdot \phi_0$$

and again we have found $\epsilon_0 = 1$.

- iv) Now act on TISE (the energy eigenvalue eqn, 6.2) with a_+ and use commutator $[a_+, a_-]$

$$\begin{aligned} a_+ (a_+ a_- + 1)\phi &= \epsilon a_+ \phi \\ a_+ (a_- a_+ - 2 + 1)\phi &= \epsilon a_+ \phi \\ [a_+ a_- a_+ + (-2 + 1)a_+] \phi &= \epsilon a_+ \phi \\ \Rightarrow (a_+ a_- + 1)(a_+ \phi) &= (\epsilon + 2)(a_+ \phi) \end{aligned}$$

So we have learnt

If ϕ has eigenvalue ϵ
 $a_+ \phi$ has eigenvalue $\epsilon + 2$

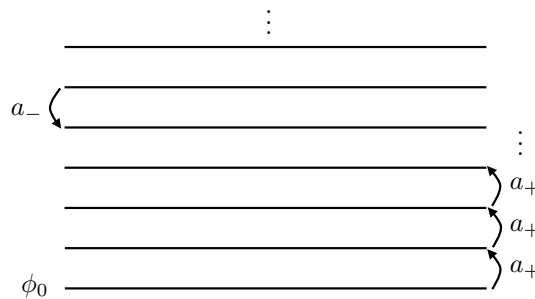
- v) Similarly easy to show that

If ϕ has eigenvalue ϵ
 $a_-\phi$ has eigenvalue $\epsilon - 2$

- Since $a_-\phi_0 = 0$, we say that

“ a_- annihilates ϕ_0 ”

- There is no state with lower energy than $\phi_0 \Rightarrow \phi_0$ is indeed ground state, with $\epsilon = 1$
- vi) **By repeated application of a_+ on ϕ_0 we generate entire spectrum**
 a_+ and a_- as “raising and lowering” or “ladder” or “creation and annihilation” operators.



- Thus spectrum of SHO is

$$\begin{array}{lll}
 \epsilon_0 = 1 & E_0 = \frac{\hbar\omega}{2} & \phi_0 = e^{-y^2/2} \\
 \epsilon_1 = 3 & E_1 = (1 + \frac{1}{2})\hbar\omega & \phi_1 = \left(-\frac{\partial}{\partial y} + y\right) \phi_0 = 2ye^{-y^2/2} \\
 \epsilon_2 = 5 & E_2 = (2 + \frac{1}{2})\hbar\omega & \phi_2 = \left(-\frac{\partial}{\partial y} + y\right) \phi_1 = 2(2y^2 - 1)e^{-y^2/2} \\
 \vdots & \vdots & \vdots
 \end{array}$$

leading to, for general n

$$\epsilon_n = 2n + 1 \quad E_n = (n + \frac{1}{2})\hbar\omega \quad \phi_n = \left(-\frac{\partial}{\partial y} + y\right)^n \phi_0 = H_n(y)e^{-y^2/2}$$

This is a complete solution of the problem!

- So far we have not normalised the wavefunctions, e.g. $\phi_0(x) = ce^{-x^2/2\alpha^2}$ (note: must convert back to x)

$$1 = \int_{-\infty}^{\infty} dx |\phi_0|^2 = c^2 \int_{-\infty}^{\infty} dx e^{-x^2/\alpha^2} = c^2 \pi^{1/2} \alpha$$

$$\Rightarrow C = \frac{1}{\alpha^{1/2} \pi^{1/4}} \quad \text{recall } \alpha^2 = \frac{\hbar}{\sqrt{mk}}$$

- Similarly can normalise higher $\phi_n(x)$ s...
- Just as important our wavefunctions are also **orthogonal**

$$\int_{-\infty}^{\infty} \phi_n(x) \phi_m(x) dx = 0 \quad n \neq m$$

- This **must be true**: they are eigenfunctions of hermitian operator H with different eigenvalues ϵ_n and ϵ_m .
- Note that the $\phi_n(x)$ go **even-odd-even** and just like the infinite square well, **the n th excited state has n nodes**.
- Features of the ground-state

$$\phi(x)_0 = \frac{1}{\alpha^{1/2} \pi^{1/4}} e^{-\frac{x^2}{2\alpha^2}}, \quad E_0 = \frac{\hbar\omega}{2}, \quad \alpha^2 = \frac{\hbar}{\sqrt{mk}}$$

- A classical particle of total energy $\hbar\omega/2$ would be confined to a region where

$$V(x) \leq E_0, \quad \frac{1}{2} kx^2 \leq \frac{\hbar\omega}{2} \Rightarrow x^2 \leq \frac{\hbar\omega}{k} = \frac{\hbar}{k} \sqrt{\frac{k}{m}} = \frac{k}{\sqrt{mk}} = \alpha^2$$

- i.e. **$-\alpha \leq x \leq \alpha$**
- If we go back to TISE

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} + \frac{1}{2} kx^2 \phi = E\phi$$

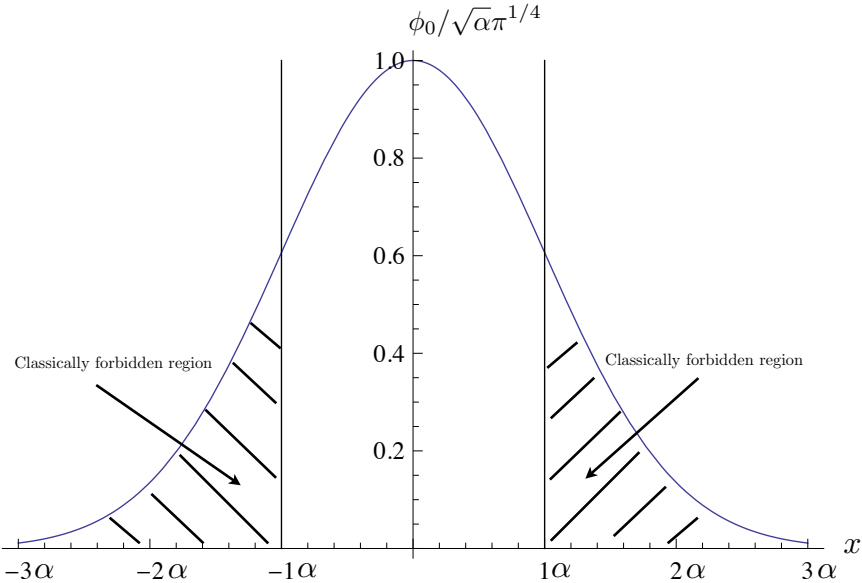
at the point where $E = V(x)$ (The limit of the classical motion) we see that

$$\frac{d^2\phi}{dx^2} = 0$$

this is a point of inflexion for ϕ . We can calculate the probability of being outside of the classical region. Quantum effects most significant for low E states.

Prob outside classical region	n
0.157	0
0.116	1
0.095	2

Below is a plot of the $n = 0$ case.



7 The Periodic Potential

- Final example of 1-d problems, consider the motion of a particle in a periodic potential of period, l , so that

$$V(x + l) = V(x) \quad (7.1)$$

An example of such a potential is shown in Figure 7.1. This type of potential can be used to model the interactions to which an electron is subjected in a crystal lattice consisting of a regular array of single atoms separated by the distance l .

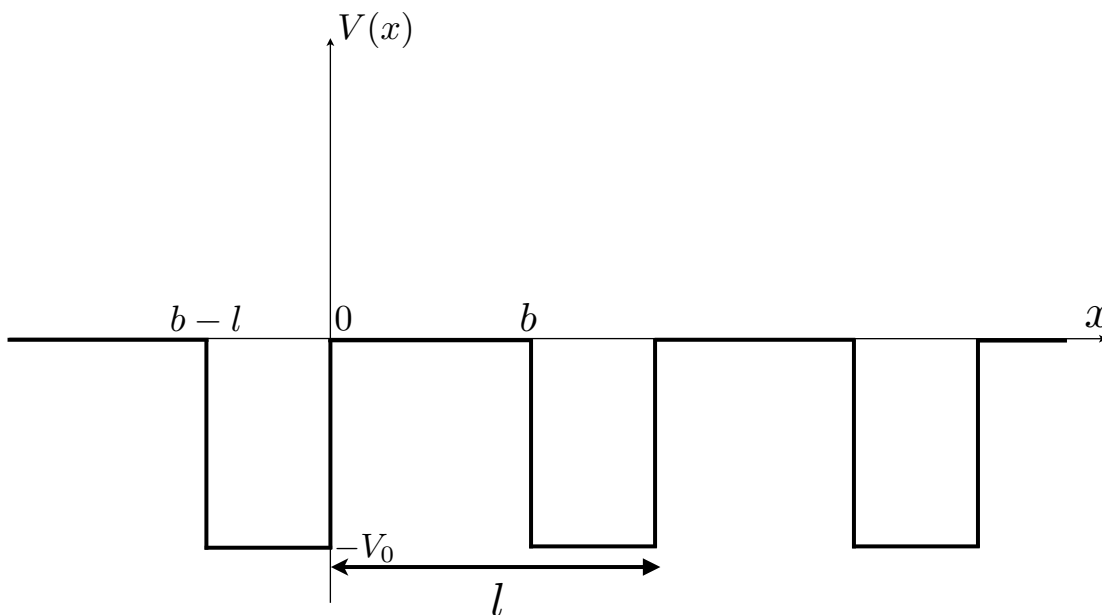


Figure 7.1: Periodic potential with rectangle sections, called the Konig-Penny potential.

7.1 Bloch Waves.

- Although a real crystal is of finite length, assume here that Eq. (7.1) is true for all x .
- Thus, if $\psi(x)$ is a solution of the Schrödinger equation corresponding to energy E , then so is $\psi(x + l)$.

- As SE is a linear equation, any solution $\psi(x)$ can be represented as a linear combination of two linearly independent solutions $\psi_1(x)$ and $\psi_2(x)$

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x).$$

- Now $\psi_1(x+l)$ and $\psi_2(x+l)$ are also solutions and can be represented as linear combinations of $\psi_1(x)$ and $\psi_2(x)$

$$\psi_1(x+l) = a_{11}\psi_1(x) + a_{12}\psi_2(x)$$

$$\psi_2(x+l) = a_{21}\psi_1(x) + a_{22}\psi_2(x)$$

Thus we can write $\psi(x+l)$ as

$$\psi_1(x+l) = (c_1a_{11} + c_2a_{21})\psi_1(x) + (c_1a_{12} + c_2a_{22})\psi_2(x) = d_1\psi_1(x) + d_2\psi_2(x)$$

- The relationship between the coefficients (c_1, c_2) and (d_1, d_2) clearly involves the matrix multiplication

$$\begin{pmatrix} d_1 \\ d_2 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{21} \\ a_{12} & a_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

- Let us see what happens if we diagonalise the 2×2 matrix in this equation. We must then solve the equation

$$\begin{vmatrix} a_{11} - \lambda & a_{21} \\ a_{12} & a_{22} - \lambda \end{vmatrix} = 0$$

- This generates a quadratic equation for λ , with two solutions λ_1 and λ_2 . If (c_1, c_2) is an eigenvector corresponding to one of the eigenvalues λ , we have $d_1 = \lambda c_1$ and $d_2 = \lambda c_2$.
- Thus among the solutions there are two having the property

$$\psi(x+l) = \lambda\psi(x)$$

where λ is a constant factor. This result is known as “Floquet’s Theorem”.

- We see immediately that

$$\psi(x+nl) = \lambda^n\psi(x), \quad n = 0, \pm 1, \pm 2, \dots$$

Now let ψ_{λ_1} and ψ_{λ_2} be two solutions of the SE corresponding to the energy E , which satisfy $\psi(x+l) = \lambda\psi(x)$, and correspond respectively to the eigenvalues λ_1 and λ_2 of Eq. (7.2). Let ψ'_{λ_1} and ψ'_{λ_2} are their derivatives

$$W = \begin{vmatrix} \psi_{\lambda_1} & \psi_{\lambda_2} \\ \psi'_{\lambda_1} & \psi'_{\lambda_2} \end{vmatrix}$$

denotes something called the Wronskian determinant of ψ_{λ_1} and ψ_{λ_2} , we have, using $\psi(x+l) = \lambda\psi(x)$,

$$W(x+l) = \lambda_1\lambda_2W(x).$$

Turns out that Wronskian determinant of two solutions of the SE equation corresponding to the same energy eigenvalue E is a constant, from this we deduce

$$\lambda_1\lambda_2 = 1.$$

- Returning to Eq. (7.2). If $|\lambda| > 1$, it is clear that for $x \rightarrow \infty$ ψ grows and grows, if $\lambda < 1$ for $x \rightarrow -\infty$ ψ also grows and grows. Therefore, must have $|\lambda| = 1$. Given this,

$$\lambda_1 = e^{iKl}, \quad \lambda_2 = e^{-iKl}.$$

where K is a real number. We get a full range of values for the λ s by restricting the value of K to the interval

$$-\frac{\pi}{l} \leq K \leq \frac{\pi}{l}.$$

Therefore, all physically admissible solutions must satisfy the relation

$$\psi(x+nl) = e^{inKl}\psi(x), \quad n = 0, \pm 1, \pm 2, \dots$$

which is the **Bloch Condition**. If we rewrite this by letting

$$\psi(x+nl) = e^{iKx}u_K(x)$$

then it follows that

$$u_K(x+l) = u_K(x)$$

which is called **Bloch's Theorem**. Then we see that the **Bloch wave function**, $\psi(x+nl) = e^{iKx}u_K(x)$ represents a travelling wave of wavelength $2\pi/K$, whose amplitude $u_K(x)$ is periodic with the same period l as the crystal lattice.

8 Angular Momentum

Throughout this section we will work in 3-D.

- Classically angular momentum is given by $\underline{L} = \underline{r} \times \underline{p}$ so in QM we have the operator

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

where $\underline{\nabla} = \underline{i} \frac{\partial}{\partial x} + \underline{j} \frac{\partial}{\partial y} + \underline{k} \frac{\partial}{\partial z}$. From this we find the individual components as

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

and using $p_i = -i\hbar \frac{\partial}{\partial x_i}$

$$L_x = -i\hbar \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right]$$

$$L_y = -i\hbar \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right]$$

$$L_z = -i\hbar \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right]$$

with total angular momentum

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

How many angular momentum quantum numbers are there?

- In classical case all L_i and L^2 are all defined, and specifying any 3 completely determines the angular momentum
- **This is not the case in QM**, indeed L_x, L_y, L_z and L^2 do not all commute with each other.
- In fact we have

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

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

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

so no 2 operators out of L_x, L_y, L_z commute. We can write this compactly as

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$$

where

$$\epsilon_{ijk} = \begin{cases} +1 & \text{if } (i, j, k) \text{ is } (1, 2, 3), (3, 1, 2) \text{ or } (2, 3, 1) \\ -1 & \text{if } (i, j, k) \text{ is } (1, 3, 2), (3, 2, 1) \text{ or } (2, 1, 3) \\ 0 & \text{otherwise: } i = j \text{ or } j = k \text{ or } k = i \end{cases}$$

- So out of L_x, L_y, L_z we can at most have 1 operator which leads to a quantum number.
- Conventional to choose L_z , however, this is not yet the maximal set.
- Easy to show that

$$[L_x, L^2] = 0$$

Thus, maximal set of commuting ops is L^2 and L_z

Can easily show that both L_x and L_y commute with L^2 and so we could use an alternative set of commuting operators L^2, L_x or L^2, L_y .

8.1 Angular Momentum Eigenvalues and Eigenfunctions

- We will not derive the eigenfunctions and eigenvalues of angular momentum here as they were covered in detail in 2nd year course but you should be familiar with the derivation - see second year notes
- The eigenfunctions and eigenvalues are

$$L^2 Y_{l,m} = \hbar^2 \ell(\ell + 1) Y_{l,m}, \quad L_x Y_{l,m} = \hbar m Y_{l,m}$$

where $\ell = 0, 1, 2, 3, \dots$ and for a fixed ℓ , $m = -\ell, -\ell + 1, \dots, \ell - 1, \ell$. The eigenfunctions $Y_{l,m}$ are called the spherical harmonics and are functions of (θ, ϕ) and normalised via

$$\int Y_{l,m}^*(\theta, \phi) Y_{l',m'}(\theta, \phi) d\Omega = \delta_{\ell\ell'} \delta_{mm'}$$

where θ and ϕ are defined in terms of spherical polar coordinates as

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta.$$

- The first few spherical harmonics are

$$\begin{aligned}
 Y_{0,0}(\theta, \phi) &= \sqrt{\frac{1}{4\pi}} \\
 Y_{1,0}(\theta, \phi) &= \sqrt{\frac{3}{4\pi}} \cos \theta \\
 Y_{1,\pm 1}(\theta, \phi) &= \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}
 \end{aligned}$$

8.2 Angular Momentum: A better method.

- Recall for the SHO we had two ways of getting eigenvalues/eigenvectors
 - Differential Equations
 - “Algebraic” using a_+ , a_- ops
- We can do similar thing for angular momentum.
- We can introduce “step” or “ladder” operators and solve for eigenvalues of L^2 and L_z algebraically
- Big difference though: algebraic method shows there are more possible eigenvalues of L^2 and L_z than what is found using differential ops.
- How can this happen? Start from the beginning and propose eigenvalue equations

$$L^2\psi = \hbar^2 K^2\psi, \quad L_z\psi = \hbar k\psi$$

- To find out what K^2 and k are consider

$$L_+ = L_x + iL_y, \quad L_- = L_x - iL_y$$

these are the angular momentum “step” operators. Note that

$$[L_{\pm}, L_z] = [L_x \pm iL_y, L_z] = \mp \hbar L_{\pm}$$

- Now consider a ψ_k which satisfies

$$L_z\psi_k = \hbar k\psi_k$$

and define a new function $\psi' = L_+\psi_k$ (if it exists - it might be zero - come back to this).

- What L_z value does ψ' have, i.e. $L_z(L_+\psi_k) = ?$
- Use commutation relation

$$[L_z, L_+] = \hbar L_+ \Rightarrow L_z L_+ = \hbar L_+ + L_+ L_z$$

- Thus

$$L_z(L_+\psi_k) = (\hbar L_+ + L_+ L_z)\psi_k = \hbar\psi' + L_+\hbar k\psi_k = \hbar(k+1)\psi'$$

- So the state ψ' must be proportional to a state with L_z eigenvalue $\hbar(k+1)$

$$L_+\psi_k = \underbrace{c_+(k)}_{\text{Normalisation}} \psi_{k+1}$$

similarly easy to show that $L_-\psi_k$ satisfies

$$L_z(L_-\psi_k) = \hbar(k-1)(L_-\psi_k)$$

so similarly we have

$$L_-\psi_k = c_-(k)\psi_{k-1}$$

L_+ and L_- step up and down tower of L_z eigenvalues by one \hbar unit

- What do L_+ , L_- do to L^2 eigenvalues
- Since, L^2 commutes with L_x and L_y and $L_\pm = L_x \pm L_y$ obvious that

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

- This means that if ψ_k satisfies $L^2\psi_k = \hbar^2 K^2\psi_k$ (so label as ψ_{k,K^2}) then

$$L^2(L_+\psi_{k,K^2}) = L_+L^2\psi_{k,K^2} = L_+\hbar^2 K^2\psi_{k,K^2} = \hbar^2 K^2(L_+\psi_{k,K^2})$$

and similarly for $L_-\psi_{k,K^2}$.

Thus L_+ , L_- do not change L^2 eigenvalue

- But this implies that we have a tower of L_z eigenstates with eigenvalues

$$\dots \hbar(k-2), \hbar(k-1), \hbar k, \hbar(k+1) \dots$$

generated by L_+ or L_- repeatedly acting on ψ_k . **This must be terminated at both ends**

- To see this, note that

$$L^2 - L_z^2 = L_x^2 + L_y^2 + L_z^2 - L_z^2 = L_x^2 + L_y^2$$

- Now consider an arbitrary member of the tower (say ψ_{k', K^2}) and take expectation values of both sides of $L^2 - L_z^2 = L_x^2 + L_y^2$

$$LHS = \langle k', K^2 | (L^2 - L_z^2) | k', K^2 \rangle = ((\hbar K)^2 - (\hbar k')^2) \langle k', K^2 | k', K^2 \rangle = \hbar^2(K^2 - k'^2)$$

BUT

$$RHS = \langle k', K^2 | (L_x^2 + L_y^2) | k', K^2 \rangle \geq 0$$

since the sum of expectation values of squares of Hermitian operators is always positive.

$$\Rightarrow \hbar^2(K^2 - k'^2) \geq 0$$

$$\Rightarrow k'^2 \leq K^2$$

I.e. L_z eigenvalue is bounded.

- Since k'^2 is bounded by K^2 there must exist a state with **highest L_z** , call this

$$\psi_{k_{\max}, K^2}$$

label this as $|k_{\max}, K^2\rangle$ in Dirac notation and a state with **lowest L_z**

$$\psi_{k_{\min}, K^2}$$

label this as $|k_{\min}, K^2\rangle$ in Dirac notation.

- The only way this can be consistent with action of L_+ and L_- is if

$$L_+ |k_{\max}, K^2\rangle = 0 \quad \text{i.e. } c_+(k_{\max}) = 0$$

and

$$L_- |k_{\min}, K^2\rangle = 0 \quad \text{i.e. } c_-(k_{\min}) = 0$$

- In fact there is a connection between values k_{\max} and K^2 (or k_{\min} and K^2)
- To see this need to manipulate operators

$$L_-L_+, \quad L_+L_-$$

$$\begin{aligned} L_-L_+ &= (L_x - iL_y)(L_x + iL_y) = L_x^2 + L_y^2 + i[L_x, L_y] \\ L_-L_+ &= L^2 - L_z^2 - \hbar L_z \end{aligned}$$

Similarly

$$L_+L_- = L^2 - L_z^2 + \hbar L_z$$

Now act on $L_+|k_{\max}, K^2\rangle = 0$ with L_- and use $L_-L_+ = L^2 - L_z^2 - \hbar L_z$ to show

$$\begin{aligned} (L^2 - L_z^2 - \hbar L_z) |k_{\max}, K^2\rangle &= 0 \\ \Rightarrow \hbar^2(K^2 - k_{\max}^2 - k_{\max}) |k_{\max}, K^2\rangle &= 0 \end{aligned}$$

$$\Rightarrow K^2 = k_{\max}(k_{\max} + 1)$$

- Imagine starting from the top of the tower $|k_{\max}, K^2\rangle$ and acting q times with L_- until we reach $|k_{\min}, K^2\rangle$
- But, $|k_{\min}, K^2\rangle$ satisfies $L_-|k_{\min}, K^2\rangle = 0$ and acting with L_+ on this and using $L_+L_- = L^2 - L_z^2 + \hbar L_z$ gives

$$\begin{aligned} (L^2 - L_z^2 + \hbar L_z) |k_{\min}, K^2\rangle &= 0 \\ \Rightarrow \hbar(K^2 - k_{\min}^2 + k_{\min}) |k_{\min}, K^2\rangle &= 0 \end{aligned}$$

then

$$\Rightarrow K^2 = k_{\min}(k_{\min} + 1)$$

Comparing this with $K^2 = k_{\max}(k_{\max} + 1)$ we find that

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

Moreover, as we get from k_{\max} to k_{\min} in q steps (using L_-) must have

$$\begin{aligned} k_{\max} - k_{\min} &= 2k_{\max} = q \\ \Rightarrow k_{\max} &= \frac{q}{2} \quad q = 0, 1, 2, 3, \dots \end{aligned}$$

- Conventional to refer to $q/2 = j$ where $j = 0, 1/2, 1, 3/2, \dots$ as the angular momentum of state ($j = k_{\max}$)
- Finally $K^2 = k_{\max}(k_{\max} + 1) = j(j + 1)$
- Thus we have learnt

$$\begin{aligned}
 J^2 |j, m\rangle &= \hbar^2 j(j + 1) |j, m\rangle & J_z |j, m\rangle &= \hbar m |j, m\rangle \\
 j &= 0, 1/2, 1, 3/2, \dots \\
 m &= -j, -j + 1, -j + 2, \dots, j - 1, j
 \end{aligned}$$

- It is also easy to see that there are $2j + 1$ possible states of the same j but with different m (that is there are $2j + 1$ different values for m).

8.3 Meaning of Angular Momentum Operator Results

- We have shown that we get both integer and half integer results for angular momentum j .
- But in the second year course it was shown that the solutions to the associated Legendre equation are only normalisable when $K^2 = j(j + 1)$ where j is integer only.

What is going in?

- The extra half-integer eigenvalues arose because we have in fact solved a more general problem than that of L_x, L_y, L_z, L^2 (although we did not know we were!
 - Nowhere did we use explicit differential representation for L_z, L^2 , etc
 - We just used the commutation relations

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k$$

which reflects the law of the combination of rotations in 3-dimensions and which must be satisfied **whatever be the nature of the wave functions they rotate**

- What we have discovered is **“spin” which can take on both integral and odd-half-integral values**

E.g. photon: $j = 1$, pion: $j = 0$, Higgs: $j = 0$, Many Nuclei: $j = 0, 1, \dots$, Electron: $j = 1/2$, Proton: $j = 1/2$, Many Nuclei: $j = 1/2, 3/2, \dots$

- Spin Wavefunctions are not functions of angular coords θ, ϕ but must instead be represented as

$$\begin{array}{l}
 2 - \text{state vectors} \quad \begin{pmatrix} \cdot \\ \cdot \end{pmatrix} \quad \text{for } j = 1/2 \\
 3 - \text{state vectors} \quad \begin{pmatrix} \cdot \\ \cdot \\ \cdot \end{pmatrix} \quad \text{for } j = 1 \\
 4 - \text{state vectors} \quad \begin{pmatrix} \cdot \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} \quad \text{for } j = 3/2 \dots
 \end{array}$$

then the L_x, L_y, L_z, L^2 act as matrices on these vectors and “re-shuffle” their components.

- Spin has forced us to use “Heisenberg’s formulation of QM (“matrix Mechanics”) which is more general, though more abstract than Schrödinger’s. Heisenberg thought of all operators as matrices
- On the other hand, normal “orbital” angular momentum is always integral and therefore can always be represented by $Y_{lm}(\theta, \phi)$ and differential operators.
- It is conventional to have a notation which distinguishes “orbital” from “spin” (or intrinsic) angular momentum. We write

$$J_i = L_i + S_i$$

where $i = x, y, z$. J_i is the total angular momentum ($j = 0, 1/2, 1, 3/2, \dots$), L_i is orbital angular momentum ($l = 0, 1, 2 \dots$ only) and S_i is spin ($s = 0, 1/2, 1, 3/2, \dots$)

- The operators S_i obey the same commutation relations

$$[S_x, S_y] = i\hbar S_z \text{ etc}$$

Thus so do the J_s

$$[J_x, J_y] = i\hbar J_z \text{ etc}$$

In summary, the eigenvalue equations are

$$\text{Total} \quad \begin{cases} J^2 |j, j_z\rangle = \hbar^2 j(j+1) |j, j_z\rangle & j = 0, \frac{1}{2}, 1, \dots \\ J_z |j, j_z\rangle = \hbar j_z |j, j_z\rangle & j_z = -j, -j+1, \dots, j-1, j \end{cases}$$

$$\begin{array}{l} \text{Orbital} \\ \text{Spin} \end{array} \left\{ \begin{array}{ll} L^2 |l, m\rangle = \hbar^2 l(l+1) |l, l_z\rangle & l = 0, 1, 2, \dots \\ L_z |l, l_z\rangle = \hbar l_z |l, l_z\rangle & m = -l, -l+1, \dots, l-1, l \\ S^2 |s, s_z\rangle = \hbar^2 s(s+1) |s, s_z\rangle & s = 0, \frac{1}{2}, 1, \dots \\ S_z |s, s_z\rangle = \hbar l_z |s, s_z\rangle & s_z = -s, -s+1, \dots, s-1, s \end{array} \right.$$

and as $J_i = L_i + S_i$ we have $J_z = L_z + S_z$ so

$$j_z = m + s_z.$$

8.4 A close look at Spin

- Let us look at spin 1/2 example. We showed that:

$$\begin{aligned} J^2 |j, j_z\rangle &= J^2 \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle = \hbar^2 j(j+1) \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle = \frac{3\hbar^2}{2} \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle \\ J_z \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle &= \pm \hbar \frac{1}{2} \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle \end{aligned}$$

- As we have seen, these do not turn up when we solve the Schrödinger, but requires the use of **matrix** formulation of Q.M.
- The spin 1/2 case is particularly important as electrons, protons, neutrons, quarks,... all have spin 1/2
- Since for $j = 1/2$ it is not possible to represent angular momentum operators as differential operators
- Consider the matrices:

$$S_x = \frac{\hbar}{2} \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\sigma_x} \quad S_y = \frac{\hbar}{2} \underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\sigma_y} \quad S_z = \frac{\hbar}{2} \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{\sigma_z}$$

where $\sigma_x, \sigma_y, \sigma_z$ are the Pauli matrices. These are Hermitian as

$$S_x^\dagger = S_x, \quad S_y^\dagger = S_y, \quad S_z^\dagger = S_z$$

So these have real eigenvalues.

- Now calculate commutator of S_x and S_y :

$$[S_x, S_y] = \left(\frac{\hbar}{2}\right)^2 \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right) = i\hbar S_z$$

Exactly the angular momentum commutation relation. In general therefore we have $[S_i, S_j] = i\hbar\epsilon_{ijk}S_k$.

- We can also calculate the matrix for S^2

$$S^2 = S_x^2 + S_y^2 + S_z^2 = \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1\right) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1\right) I$$

- Exactly what we want for S^2 so that we can act on a two component vector which is an eigenvector of S^2 with eigenvalue $\hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1\right)$.

- Let's also look at $S_z = \hbar/2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, what are its eigenvalues?

- Since S_z is diagonal, obvious that

$$S_z \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ is state with } S_z = \frac{\hbar}{2}$$

$$\text{Similarly } \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{ is state with } s_z = -\frac{\hbar}{2}$$

- We can also find eigenvalues and eigenvectors of S_x as well

$$\det \begin{pmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{pmatrix} = 0, \quad \Rightarrow \lambda^2 - (\hbar/2)^2 = 0$$

$$\Rightarrow \lambda = \pm \hbar/2$$

This time the eigenvectors are

$$\left. \begin{array}{l} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ for } \lambda = +\hbar/2 \\ \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ for } \lambda = -\hbar/2 \end{array} \right\} S_x$$

Similarly for S_y

$$\left. \begin{array}{l} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad \text{for } \lambda = +\hbar/2 \\ \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \quad \text{for } \lambda = -\hbar/2 \end{array} \right\} S_y$$

8.5 Stern-Gerlach experiment

- How do we know that the electron has spin 1/2?
- Classically a charged object with angular momentum has a **magnetic Dipole Moment**
- Quantum Mechanics also leads to this conclusion (although to be precise we need Quantum Field theory to give a truly consistent understanding of e^- magnetic dipole moment).

$$\boldsymbol{\mu} = -g_s \frac{e}{2m_e} \mathbf{S}$$

where g_s is a correction due to quantum effects, the factor $\frac{e}{2m_e}$ is the classical proportionality between $\boldsymbol{\mu}$ and \mathbf{S} , the negative sign is there because the electron's charge is -1.

- Now we introduce a magnetic field in the z-direction B_z .
- There are two possible values for the interaction energy $-\mathbf{B} \cdot \boldsymbol{\mu}$ due to the quantisation of S_z .

$$\begin{aligned} \text{If } s_z = \hbar/2 & \quad -\mathbf{B} \cdot \boldsymbol{\mu} = +\frac{g_s e}{2m_e} \frac{\hbar}{2} B_z \\ \text{If } s_z = -\hbar/2 & \quad -\mathbf{B} \cdot \boldsymbol{\mu} = -\frac{g_s e}{2m_e} \frac{\hbar}{2} B_z \end{aligned}$$

which means that we have two discrete possible values of magnetic dipole moment.

- The combination of factors

$$\frac{e\hbar}{2m_e} \equiv \mu_B \quad \text{“Bohr Magnetron”}$$

- Of course typically potential energy of a system will be a combination of a spin-independent $V(r)$, and a spin-dependent term (arising, say, from a $\mathbf{B} \cdot \boldsymbol{\mu}$ interaction)
- Thus typically the form of the energy (Hamiltonian) for a spin 1/2 system (e.g. electron in an atom) will be

$$H = H_0 I + \frac{g_s e}{2m_e} \mathbf{B} \cdot \mathbf{S}$$

where H_0 could be Coulomb potential + kinetic energy, I is the identity matrix and so the H_0 term is spin-independent and $\mathbf{B} \cdot \mathbf{S} = B_x S_x + B_y S_y + B_z S_z$.

- Thus we can consider a modified form of the TDSE.

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

H is now a 2×2 matrix as well as a differential operator and Ψ is a two component vector, with each component being a function of (t, r, θ, ϕ) i.e.

$$\Psi = \begin{pmatrix} \psi_1(t, r, \theta, \phi) \\ \psi_2(t, r, \theta, \phi) \end{pmatrix}$$

- If \mathbf{B} -field is a constant then this equation (modified TDSE) is simple to analyse, write

$$\Psi = \Phi(t, r, \theta, \phi)\mathbf{u}$$

where \mathbf{u} is a two component vector.

- This gives

$$(H_0\Phi)\mathbf{u} + \Phi \frac{g_s e}{2m_e} (\mathbf{B} \cdot \mathbf{S})\mathbf{u} = i\hbar \frac{\partial \Phi}{\partial t} \mathbf{u} \quad (8.1)$$

this can only be satisfied if

$$(\mathbf{B} \cdot \mathbf{S})\mathbf{u} = \lambda \mathbf{u}$$

- If the rest of the problem is spherically symmetric, then we can always choose direction of x, y, z axes such that z - axis is in the \mathbf{B} direction.
- With this choice

$$\mathbf{B} = (0, 0, B_z)$$

then

$$BS_z\mathbf{u} = \lambda \mathbf{u}.$$

Since $S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ we learn that

$$\lambda = \pm \frac{\hbar B}{2}, \quad \text{for } \mathbf{u} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Putting this back into Eq. 8.1, we get two equations

$$\begin{aligned} \left(H_0 + \frac{g_s e}{2m_e} \frac{\hbar B}{2} \right) \phi_1(t, r, \theta, \phi) &= i\hbar \frac{\partial \phi_1}{\partial t} \\ \left(H_0 - \frac{g_s e}{2m_e} \frac{\hbar B}{2} \right) \phi_2(t, r, \theta, \phi) &= i\hbar \frac{\partial \phi_2}{\partial t} \end{aligned}$$

where ϕ_1 and ϕ_2 are top and bottom components of $\Phi = \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$.

- Now separate variables as usual for both equations

$$\begin{aligned}\phi_1(t, r, \theta, \phi) &= e^{-iE_1t/\hbar}\tilde{\phi}_1(r, \theta, \phi) \\ \phi_2(t, r, \theta, \phi) &= e^{-iE_2t/\hbar}\tilde{\phi}_2(r, \theta, \phi)\end{aligned}$$

Giving TISE for $\tilde{\phi}_1$ and $\tilde{\phi}_2$.

- Interpretation is simply that the **electrons can either have spin aligned with \mathbf{B} or anti-aligned and energies are shifted by $\pm g_s\mu_B B/2$.**
- Now consider dipole in **non-uniform \mathbf{B} -field.**
- Figure 8.5 shows a dipole in a non-uniform \mathbf{E} . The net force acting on the dipole

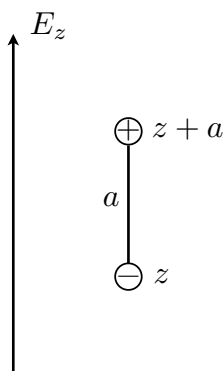


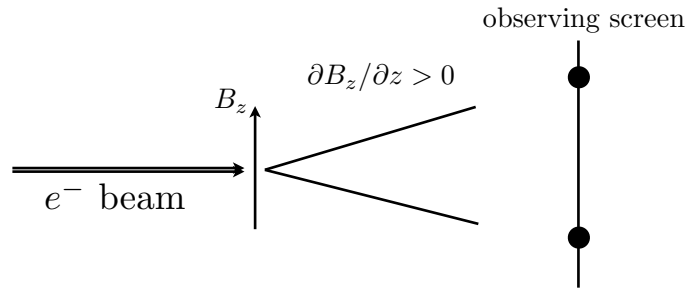
Figure 8.1: EDM in a non-uniform \mathbf{E} field.

$$F = qE(z + a) - qE(z) \simeq q(E(z) + a\frac{\partial E}{\partial Z} - E(z)) \simeq qa\frac{\partial E}{\partial Z} = p\frac{\partial E}{\partial Z}$$

Similarly if we have a magnetic dipole in a non-uniform field

$$F = \mu\frac{\partial B}{\partial z}.$$

- Now suppose we have a beam of electron going through a region of non-uniform B_z field



- The e^- s will experience a force wither up or down depending on which way their $\boldsymbol{\mu}$ (i.e. S_z) is pointing
- This is the essence of the Stern-Gerlach experiment - see page 33 of Bransden and Joachain.
- Important points to note
 - (1) Classically one would expect to see a continuous distribution of e^- deflections on observing screen (as classically S_z , and thus μ_z , can take on any value - not quantized)
 - (2) The experiment instead shows **two spots** (for spin 1/2 system) on screen $\rightarrow S_z$ is **quantised with 2 values**
 - (3) In detail when one calculates position of spots one finds they are twice as far apart as expected based upon

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

This is one of the (many) reasons why we are forced to introduce

$$g_s \simeq 2 = \text{“Gyromagnetic Ratio”}$$

So

$$\boldsymbol{\mu} = -\frac{g_s e}{2m_e} \mathbf{S}$$

8.6 Addition of Angular Momentum

- In many situations of physical interest we deal with systems of more than one particle. We therefore need to know how to deal with the system as a whole in terms of the distinct sub-systems (i.e. the individual particles).
- Look at the simplest case, the addition of two commuting angular momentum. Thus we have

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$$

where \mathbf{J}_1 and \mathbf{J}_2 are any two angular momentum corresponding to the independent sub-systems (i.e. the two particles) 1 and 2. Similarly $J_z = J_{1z} + J_{2z}$.

- Let $|j_1, m_1\rangle$ be a normalised simultaneous eigenvector of \mathbf{J}_1^2 and J_{1z} so that

$$\mathbf{J}_1^2 |j_1, m_1\rangle = j_1(j_1 + 1)\hbar^2 |j_1, m_1\rangle$$

and

$$J_{1z} |j_1, m_1\rangle = m_1\hbar |j_1, m_1\rangle.$$

- Similarly let $|j_2, m_2\rangle$ be a normalised simultaneous eigenvector of \mathbf{J}_2^2 and J_{2z} so that

$$\mathbf{J}_2^2 |j_2, m_2\rangle = j_2(j_2 + 1)\hbar^2 |j_2, m_2\rangle$$

and

$$J_{2z} |j_2, m_2\rangle = m_2\hbar |j_2, m_2\rangle.$$

- We can construct a normalised simultaneous eigenvector of $\mathbf{J}_1^2, \mathbf{J}_2^2, J_{1z}, J_{2z}$ belonging respectively to the eigenvalues $j_1(j_1 + 1)\hbar^2, j_2(j_2 + 1)\hbar^2, m_1\hbar$ and $m_2\hbar$ is given by the “direct product”

$$|j_1, j_2, m_1, m_2\rangle = |j_1, m_1\rangle |j_2, m_2\rangle.$$

- For a fixed value of j_1 , m_1 can take one of $2j_1 + 1$ values $(-j_1, -j_1 + 1, \dots, j_1)$ and for a fixed value of j_2 , m_2 can take $2j_2 + 1$ values $(-j_2, -j_2 + 1, \dots, j_2)$.
- Hence for given values of j_1, j_2 there are $(2j_1 + 1)(2j_2 + 1)$ “direct products” which form a complete set of orthonormal states.
- Apply J_z to the direct product, (remembering that $J_z = J_{1z} + J_{2z}$)

$$\begin{aligned} J_z |j_1, j_2, m_1, m_2\rangle &= (J_{1z} + J_{2z}) |j_1, m_1\rangle |j_2, m_2\rangle = (J_{1z} |j_1, m_1\rangle) |j_2, m_2\rangle + |j_1, m_1\rangle (J_{2z} |j_2, m_2\rangle) \\ &= (m_1 + m_2)\hbar |j_1, m_1\rangle |j_2, m_2\rangle = (m_1 + m_2)\hbar J_z |j_1, j_2, m_1, m_2\rangle \end{aligned}$$

which means that $|j_1, j_2, m_1, m_2\rangle$ is an eigenfunction of the total J_z with eigenvalue $(m_1 + m_2)\hbar$.

- This is confirmed by the fact that $\mathbf{J}_1^2, \mathbf{J}_2^2, J_{1z}, J_{2z}$ operators commute with $J_z = J_{1z} + J_{2z}$.
- Now consider the operator \mathbf{J}^2 (where $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$).

$$\mathbf{J}^2 = (\mathbf{J}_1 + \mathbf{J}_2)^2 = \mathbf{J}_1^2 + \mathbf{J}_2^2 + 2\mathbf{J}_1 \cdot \mathbf{J}_2$$

- Because all components of \mathbf{J}_1 commute with all of those of \mathbf{J}_2 and since $[\mathbf{J}_1^2, \mathbf{J}_1] = 0 = [\mathbf{J}_2^2, \mathbf{J}_2]$ it follows that $[\mathbf{J}^2, \mathbf{J}_1^2] = 0 = [\mathbf{J}^2, \mathbf{J}_2^2]$.

- However, as

$$\mathbf{J}_1 \cdot \mathbf{J}_2 = J_{1x}J_{2x} + J_{1y}J_{2y} + J_{1z}J_{2z}$$

and since J_{1z} does not commute with J_{1x} or J_{1y} , we find $[\mathbf{J}^2, J_{1z}] \neq 0$ similarly we find $[\mathbf{J}^2, J_{2z}] \neq 0$.

- Consequently, simultaneous eigenfunctions of \mathbf{J}^2 and J_z are eigenfunctions of \mathbf{J}_1^2 and \mathbf{J}_2^2 but not in general of J_{1z} and J_{2z}
- The bottom line is that the system can be formed in terms of two distinct descriptions.
 - In terms of eigenfunctions of $\mathbf{J}_1^2, \mathbf{J}_2^2, J_{1z}$ and J_{2z} or
 - in terms of eigenfunctions of $\mathbf{J}_1^2, \mathbf{J}_2^2, \mathbf{J}^2$ and J_z .
- We can describe the latter with eigenkets labelled $|j_2, j_1, j, m\rangle$ Thus we have for example

$$\mathbf{J}^2 |j_2, j_1, j, m\rangle = j(j+1)\hbar^2 |j_2, j_1, j, m\rangle$$

and

$$J_z |j_2, j_1, j, m\rangle = m\hbar |j_2, j_1, j, m\rangle$$

- Like the eigenkets $|j_1, j_2, m_1, m_2\rangle$ the eigenkets $|j_2, j_1, j, m\rangle$ form a complete orthonormal set.
- We can relate these two sets of states via a unitary transformation by inserting a complete set of states

$$|j_1, j_2, j, m\rangle = \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m\rangle$$

where $\langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m\rangle$ is the Clebsch-Gordon coefficient (sometimes written just as $\langle j_1, j_2, m_1, m_2 | j, m\rangle$).

- In order to find out what values of j we can have for given j_1 and j_2 we notice that since $|j_1, j_2, m_1, m_2\rangle$ is an eigenfunction of J_z with eigenvalue $(m_1 + m_2)\hbar$ we must have that

$$m = m_1 + m_2$$

so the double sum reduces to a single sum.

In other words the Clebsch-Gordon coefficients must vanish unless $m = m_1 + m_2$:

$$\langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m \rangle \quad \text{if} \quad m \neq m_1 + m_2$$

- We also know that the maximum values of m_1 and m_2 are j_1 and j_2 respectively, **so the maximum size of m is $j_1 + j_2$**
- In turn this means the maximum size of j is $j_1 + j_2$.
- **Consider some special cases:**
- 1) For $j = j_1 + j_2$ and $m = j_1 + j_2$ there is only one term on the RHS of $|j_1, j_2, j, m\rangle = \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m\rangle$ corresponding to $m_1 = j_1$ and $m_2 = j_2$. Thus

$$|j_1, j_2, (j_1 + j_2), (j_1 + j_2)\rangle = \langle j_1, j_2, j_1, j_2 | j_1, j_2, (j_1 + j_2), (j_1 + j_2)\rangle |j_1, j_2, j_1, j_2\rangle$$

and since the eigenkets are normalised

$$\langle j_1, j_2, j_1, j_2 | j_1, j_2, (j_1 + j_2), (j_1 + j_2)\rangle = 1$$

- 2) Now consider the state got which $m = j_1 + j_2 - 1$.
- In this case there are two possibilities - $m_1 = j_1, m_2 = j_2 - 1$ or $m_1 = j_1 - 1, m_2 = j_2$
- Thus, a state $|j_1, j_2, j, (j_1 + j_2 - 1)\rangle$ must be a linear combination of the two linearly independent eigenkets $|j_1, j_2, j_1, (j_2 - 1)\rangle$ and $|j_1, j_2, (j_1 - 1), j_2\rangle$
- There are two such combinations, one of them with $j = j_1 + j_2$ and the other (which is orthogonal to the first) with maximum value of $m = j_1 + j_2 - 1$ and therefore must have $j = j_1 + j_2 - 1$.
- 3) Move now to a state with $m = j_1 + j_2 - 2$, we see that there are 3 linearly independent states of this kind with $j = j_1 + j_2, j = j_1 + j_2 - 1, j = j_1 + j_2 - 2$.
- If we keep repeating this we find that the minimum value of j is $|j_1 - j_2|$, as all combinations have been exhausted

- For each value of j there are $2j + 1$ values of m so that the total number of eigenfunctions $|j_1, j_2, j, m\rangle$ is given by

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j + 1) = (2j_1 + 1)(2j_2 + 1)$$

- Let's look at an example of adding $j_1 = 1$ and $j_2 = 3/2$

Table 1: Allowed values of (m_1, m_2) and (j, m) for $j_1 = 1$ and $j_2 = 3/2$.

m_1	m_2	m	j
1	3/2	5/2	5/2
0	3/2	3/2	5/2, 3/2
1	1/2		
-1	3/2		
0	1/2	1/2	5/2, 3/2, 1/2
1	-1/2		
-1	1/2		
0	-1/2	-1/2	5/2, 3/2, 1/2
1	-3/2		
-1	-1/2		
0	-3/2	-3/2	5/2, 3/2
-1	-3/2	-5/2	5/2
Total: $(2j_1 + 1)(2j_2 + 1) = 12$		Total: $\sum_{j= j_1-j_2 }^{j_1+j_2} (2j + 1) = 12$	

- What we have learned is that for given values of j_1 and j_2 the allowed values of j are

$$j = |j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2$$

so that the three angular momentum quantum j_1, j_2 and j must satisfy the *triangle condition*

$$|j_1 - j_2| \leq j \leq j_1 + j_2$$

moreover for each value of j there are $2j + 1$ eigenfunctions such that $m = -j, -j + 1, \dots, 1$.

- The Clebsch Gordon coefficients can be determined by applying raising and lowering operators to $|j_1, j_2, j, m\rangle = \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2 | j_1, j_2, j, m\rangle$. See P319 of Bransden and Joachain.

9 Approximate Methods I

Rarely are there exact solutions to physics problems, where the energies and wave functions are known. This half of the course presents a number of approximate methods to deal with some of these problems.

9.1 Time-independent perturbation theory

- Often, Hamiltonian we want to solve is close to one we know how to solve:

$$H_\lambda = H_0 + \lambda V \quad (1)$$

eg. λV describes some external field (electric, magnetic) that we can dial up, with λ the amplitude.

- Suppose at $\lambda = 0$, the system is in an exact eigenstate of H_0 : $H_0|\phi_a\rangle = E_a|\phi_a\rangle$.
- Idea: we want to find for the perturbed system H_λ , the eigenstate $|\psi\rangle$

$$H_\lambda|\psi\rangle = (H_0 + \lambda V)|\psi\rangle = E_\lambda|\psi\rangle \quad (2).$$

Key: the perturbed eigenstate $|\psi\rangle$ is going to look a lot like the unperturbed one $|\phi_a\rangle$, when λ is small. So try a power series in λ :

$$E_\psi = E_a + \lambda E_b + \lambda^2 E_c ; \quad |\psi\rangle = |\phi_a\rangle + \lambda|b\rangle + \lambda^2|c\rangle \quad (3)$$

where E_b, E_c and the states $|b\rangle, |c\rangle$ are to be determined. We have only written terms up to order λ^2 . Substitute Eqs. (3) into (2), and equate terms with the same powers of λ on left hand side and right hand side:

$$\begin{aligned} \lambda^0 \text{eqn :} & \quad H_0|\phi_a\rangle &= E_a^0|\phi_a\rangle & \quad (\text{nothing new}) \\ \lambda^1 \text{eqn :} & \quad H_0|b\rangle + V|\phi_a\rangle &= E_a|b\rangle + E_b|\phi_a\rangle \\ \lambda^2 \text{eqn :} & \quad H_0|c\rangle + V|b\rangle &= E_a|c\rangle + E_b|b\rangle + E_c|\phi_a\rangle \end{aligned}$$

- λ^1 equation: multiply on left by the known $\langle\phi_a|$, and use that $H_0|\phi_a\rangle = E_a|\phi_a\rangle \Leftrightarrow \langle\phi_a|H_0 = E_a\langle\phi_a|$:

$$E_b = \langle\phi_a|V|\phi_a\rangle \quad (4) \quad \text{first order energy change}$$

- λ^2 equation: again multiply on left by $\langle \phi_a |$, and using the normalisation $\langle \phi_a | \phi_a \rangle = 1$,

$$E_c = \langle \phi_a | V | b \rangle - E_b \langle \phi_a | b \rangle \quad (4)$$

Now need to know what $|b\rangle$ is, in terms of states we know. Now for the unperturbed problem, we have the complete set of eigenstates $|k\rangle$ where $H_0|k\rangle = E_k|k\rangle$. (The state $|\phi_a\rangle$ belongs to this set.) This complete set is:

$$\begin{aligned} \text{orthogonal :} & \quad \langle j | k \rangle = 0 & \quad \text{for } j \neq k, \\ \text{normalized :} & \quad \langle j | j \rangle = 1 \end{aligned}$$

So expand $|b\rangle$ in terms of these known eigenstates with numerical coefficients b_k :

$$|b\rangle = \sum_k b_k |k\rangle \quad (5)$$

Substitute Eq. (5) into λ^1 eqn, and multiply from left by $\langle j |$ which we choose such that $\langle j | \neq \langle \phi_a |$:

$$b_j = \frac{\langle j | V | \phi_a \rangle}{E_a - E_j} \implies |b\rangle = \sum_j \frac{\langle j | V | \phi_a \rangle}{E_a - E_j} |j\rangle \quad (6)$$

Finally, substituting Eq. (6) into Eq. (4), using that $|j\rangle$ is an ortho-normal set of H_0 , we get,

$$E_c = \sum_{j \neq \phi_a} \frac{\langle \phi_a | V | j \rangle \langle j | V | \phi_a \rangle}{E_a - E_j} = \sum_{j \neq \phi_a} \frac{|\langle j | V | \phi_a \rangle|^2}{E_a - E_j} \quad (7) \quad \text{second order energy change}$$

- Collecting all, to order λ^2 , perturbation to the state $|\phi_a\rangle$ and its energy E_a :

$$E_\psi = E_a + \lambda E_b + \lambda^2 E_c = E_a + \langle \phi_a | \lambda V | \phi_a \rangle + \sum_{j \neq \phi_a} \frac{|\langle j | \lambda V | \phi_a \rangle|^2}{E_a - E_j} \quad (8)$$

$$|\psi\rangle = |\phi_a\rangle + \lambda |b\rangle + \dots = |\phi_a\rangle + \sum_j \frac{\langle j | \lambda V | \phi_a \rangle}{E_a - E_j} |j\rangle + \dots \quad (9)$$

9.2 Ex. 1: perturbed particle in a box

Here we do a simple example to illustrate the formalism.

- Particle in a box, length a , perturbed by a small potential

$$H = H_0 + \lambda V(x), \quad H_0 = \frac{p_x^2}{2m} + V_{box}(x)$$

$$V_{box}(x) = \begin{cases} 0 & : 0 < x < d, \\ \infty & : \text{otherwise.} \end{cases}$$

$$\lambda V(x) = \begin{cases} \epsilon & : 0 < x < b < d, \\ 0 & : \text{otherwise.} \end{cases}$$

- For H_0 , the complete set ($n = 1, 2, 3, \dots$) of energy eigenstates are:

$$\phi_n(x) = \langle x|n\rangle = \sqrt{\frac{2}{d}} \sin\left(\frac{n\pi x}{d}\right), \quad E_n = \frac{1}{2m} \left(\frac{\hbar n\pi}{d}\right)^2$$

- first order energy change for a given state $|\phi_a\rangle = |n\rangle$:

$$E_b = \langle n|\lambda V|n\rangle = \epsilon \int_0^b dx \phi_n^*(x)\phi_n(x) = \epsilon \left(\frac{b}{d} - \frac{1}{2n\pi} \sin\frac{2n\pi b}{d}\right)$$

- first order change to the state $|n\rangle$: using a notation similar to that of the previous section, we need to find the coefficient b_k in the series $|b\rangle = \sum_k |k\rangle$, where now, the label $k = 1, 2, 3, \dots$ refers to the complete set of eigenstates for H_0 above. This is worked out in Problem sheet 4.

9.3 Ex. 2: Quadratic Stark effect

- H atom: turn on electric field $\mathbf{E} = -\nabla\Phi$
- energy change due to potential Φ is just adding up the effect of the potential at the electron at position \mathbf{r}_e and at the nucleus at \mathbf{r}_p :

$$e(\Phi(\mathbf{r}_p) - \Phi(\mathbf{r}_e)) \approx -e \mathbf{r} \cdot \nabla\Phi(\mathbf{r}) = e \mathbf{r} \cdot \mathbf{E},$$

where $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_p$.

- Choose \mathbf{E} parallel to z -direction: $\mathbf{E} = \mathcal{E}\hat{z}$ (\hat{z} is the unit vector in the z -direction), and let the perturbation be:

$$\lambda V = e \mathbf{r} \cdot \mathbf{E} = e \mathcal{E} z$$

- The unperturbed Hamiltonian is just that of the hydrogen atom, see last lecture. Then, the complete set of eigenstates for the unperturbed H_0 is just the set of $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$, or in a brief ket notation: $|n l m\rangle$.

- first order energy change to the ground state $|1\ 0\ 0\rangle$:

$$\lambda E_b = e\mathcal{E}\langle 1\ 0\ 0|z|1\ 0\ 0\rangle = 0$$

again by parity argument: here in 3 dimensions, $\mathbf{r} \rightarrow -\mathbf{r}$, then $z \rightarrow -z$ also, but since the ground state is spherically symmetric, $|1\ 0\ 0\rangle \rightarrow |1\ 0\ 0\rangle$.

General principle:

If a perturbation takes the state $|a\rangle$ to some state that is completely orthogonal to state $|a\rangle$, then there is no first order energy correction to this state $|a\rangle$. In equation: if $V|a\rangle = \sum_{k \neq a} c_k |k\rangle$, then $E_b = \sum_{k \neq a} c_k \langle a|k\rangle = 0$.

- second order energy change to the ground state $|1\ 0\ 0\rangle$:

$$\lambda^2 E_c = (e\mathcal{E})^2 \sum_{n,l,m}^{(nlm) \neq (100)} \frac{|\langle n\ l\ m|z|1\ 0\ 0\rangle|^2}{E_{100} - E_{nlm}}$$

- Now, $[L_z, z] = 0$, implying that both $|n\ l\ m\rangle$ and $z|n\ l\ m\rangle$ are eigenstates of L_z . Then $\langle n\ l\ m|z|1\ 0\ 0\rangle \neq 0$ iff $m = 0$, to have the same L_z for the bra and ket.
- Parity argument: again, under $z \rightarrow -z$, $|1\ 0\ 0\rangle \rightarrow |1\ 0\ 0\rangle$, which means we require that under parity change, $|n\ l\ m\rangle \rightarrow -|n\ l\ m\rangle$. This restricts l to be odd integers. In fact, actually doing the integrals, only $l = 1$ is allowed.
- We finally get:

$$\lambda^2 E_c = (e\mathcal{E})^2 \sum_{n \geq 2} \frac{|\langle n\ 1\ 0|z|1\ 0\ 0\rangle|^2}{E_{100} - E_{n10}}$$

10 Approximate Methods II

10.1 Degenerate perturbation theory (time independent)

In derivation of second order perturbation theory, if somehow, there is a state $|k\rangle \neq |\phi_a\rangle$, but yet, they have the same energy, $E_k = E_a$, then the denominator in Eq. (7) blows up, ie, the second order energy correction is infinite! Key point: if there exists distinct states with the same energy, then the perturbation may connect these states, and the perturbation may no longer be small.

Instead of developing the general theory of degenerate perturbation, we shall just look at an example in the Hydrogen atom in an electric field $\mathbf{E} = \mathcal{E}\hat{z}$ (as in previous section).

10.2 Linear Stark effect

- Look now at the unperturbed eigenstate $|2\ 0\ 0\rangle$ with unperturbed energy E_{200} , affected by the same perturbation as before: $\lambda V = e\mathcal{E}z$.
- Key: in Hydrogen atom, energy does not depend on angular momentum l , but just on n from the radial part. Hence, the state $|2\ 0\ 0\rangle$ has unperturbed energy $E_{210} = E_{200}$. Furthermore, $A \equiv \langle 2\ 1\ 0 | z | 2\ 0\ 0 \rangle \neq 0$: perturbation mixes up states of same energy.
- Since it takes no energy to connect between these states, simplify by just keeping only these states in computing the perturbed energy. In matrix notation:

$$H = H_0 + e\mathcal{E}z = \begin{pmatrix} E_{200} & 0 \\ 0 & E_{200} \end{pmatrix} + e\mathcal{E} \begin{pmatrix} 0 & A^* \\ A & 0 \end{pmatrix} = \begin{pmatrix} E_{200} & e\mathcal{E}A^* \\ e\mathcal{E}A & E_{200} \end{pmatrix} \quad (10.1)$$

- Finding the perturbed energies means solving the time independent Schrodinger Equation in matrix form: $\sum_b H_{ab} v_b = E v_a$ for a 2 component eigenvector \mathbf{v} with components v_a . From linear algebra, this involves solving:

$$0 = \det(H - E\mathbf{1}) = \det \begin{pmatrix} E_{200} - E & e\mathcal{E}A^* \\ e\mathcal{E}A & E_{200} - E \end{pmatrix} \quad (10.2)$$

- Solution: let \pm label the two possible solutions. Then the energies and their corresponding eigenvectors are:

$$E_{\pm} = E_{200} \pm e\mathcal{E}\sqrt{A^*A} \quad (10.3)$$

$$v_{\pm} = \frac{1}{\sqrt{2}} (|2\ 0\ 0\rangle \pm |2\ 1\ 0\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \quad (10.4)$$

- **Physics:** from electromagnetism, total dipole moment: $\mathbf{p} = \mathbf{p}_0 + \alpha\mathbf{E}$, where \mathbf{p}_0 is the permanent dipole moment, the second term comes from induced dipole moment from the applied electric field \mathbf{E} , with polarizability of the atom α . Energy change is then $\delta E = -\mathbf{p} \cdot \mathbf{E}$.

- Quadratic Stark effect: no linear in \mathbf{E} part, because for the ground state $|1\ 0\ 0\rangle$, $\mathbf{p}_0 = 0$. Hence $\delta E = -\alpha|E|^2$.
- Linear Stark effect: there is a linear in \mathbf{E} part, which means the states $|v_{\pm}\rangle$ must have a permanent dipole moment such that $\delta E = -\mathbf{p}_0 \cdot \mathbf{E}$. (The state $|2\ 0\ 0\rangle$ itself does not have a permanent dipole.) Quiz: show that $\mathbf{p}_0 \propto \langle v_+ | e z | v_+ \rangle = e(A + A^*)/2 \neq 0$. Try doing the actual integrals to get the value of A itself.

11 Approximate Methods III

11.1 Effect of external magnetic field on the Hydrogen-like atom

When the hydrogen like atom is placed in a magnetic field, there are three perturbations to consider: i) effect on orbital angular momentum, ii) effect on intrinsic angular momentum (spin), and iii) relativistic effect— spin-orbit coupling. Reference: see eg. Bransden and Joachin Ch.12.3.

11.1.1 Orbital angular momentum

For a particle of charge Q , moving in external magnetic field \mathbf{B} : replace momentum by $\mathbf{p} \rightarrow \mathbf{p} - Q\mathbf{A}$, where the vector potential $\mathbf{B} = \nabla \times \mathbf{A}$. Hence the kinetic energy of the atom becomes:

$$H_{KE} = \frac{1}{2m} (\mathbf{p} + e\mathbf{A})^2$$

- First simplification: drop \mathbf{A}^2 part because its energy will be small compared to the $\mathbf{p} \cdot e\mathbf{A}$ term, for experimentally relevant B strength (even at 10^3 Tesla).
- In experiment, $\mathbf{B}(x)$ is essentially a *constant* (no x -dependence) over the size of the atom. Thus, take $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$, and rearranging the terms to the form $\mathbf{B} \cdot \mathbf{r} \times \mathbf{p} = \mathbf{B} \cdot \mathbf{L}$, we get:

$$\delta H_L(\mathbf{B}) = \frac{e}{2m} (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) = \frac{e\hbar}{2m} \mathbf{B} \cdot \mathbf{L} \quad (\text{i})$$

This is the energy change due to the orbital angular momentum of the charged electron. Classically, the circulating electron has an orbital angular momentum $\frac{e\hbar}{2m}$.

11.1.2 Spin angular momentum

Electron also has an intrinsic angular momentum (spin) \mathbf{S} which contributes further:

$$\delta H_S(\mathbf{B}) = \frac{e\hbar}{m} \mathbf{B} \cdot \mathbf{S} \quad (\text{ii})$$

Note carefully, compared to (i), there is no factor of 1/2 here. Ultimately, this is confirmed by experiments.

11.1.3 Relativistic effect: spin-orbit coupling

Going beyond the Schrodinger equation to include relativistic effects (Dirac equation), there is an extra term that couples the orbital and spin angular momentum:

$$\delta H_{LS} = \xi(r) \mathbf{L} \cdot \mathbf{S} = \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{S} \quad (\text{iii})$$

where as before, Z is the nuclear charge (but we still have only 1 electron).

Combining all (i + ii + iii), and taking the magnetic field to be along z direction,

$$H = H_0 + \frac{\mu_B}{\hbar} (L_z + 2S_z) B + \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{S} \quad (1)$$

where we take the unperturbed Hamiltonian to be that for the Hydrogen-like atom (previous lectures):

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} \quad (2)$$

Now, we study different regimes of B strength.

11.1.4 Strong field Zeeman effect

- When B is large enough to ignore spin orbit coupling $\mathbf{L} \cdot \mathbf{S}$ term (iii).

$$H \approx H_0 + \frac{\mu_B}{\hbar} (L_z + 2S_z) B$$

– quantum numbers of the one electron atom:

$$H_0 |n l m_l\rangle = E_n |n l m_l\rangle \quad ,$$

$$n = 1, 2, 3, \dots \quad l = 0, 1, 2, \dots, n-1 \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

– new: spin angular momentum quantum numbers: for a spin $S = 1/2$ electron,

$$\mathbf{S}^2 \rightarrow s(s+1) \hbar^2 = \frac{3}{4} \hbar^2, \quad S_z \rightarrow m_s \hbar = \pm \frac{1}{2} \hbar$$

Without magnetic field, the energy of the hydrogen-like atom does not depend on these spin quantum numbers. So we can write the eigenstates of H_0 with all these good quantum numbers: $H_0 |n l m_l s m_s\rangle = E_n |n l m_l s m_s\rangle$

- Now the perturbation $\delta H(B) = \frac{\mu_B}{\hbar} (L_z + 2S_z) B$ commutes with H_0 , so we can simultaneously diagonalise H_0 and $\delta H(B)$, using the eigenstates of H_0 . Thus, the perturbed energies are:

$$E_{n m_l m_s} = E_n + \mu_B (m_l + 2m_s) B \quad (3)$$

B field splits the degeneracies of spin \uparrow vs. spin \downarrow and for the different L_z .

- Add back spin-orbit term (iii) to the strong field Zeeman case: treat δH_{LS} as a perturbation. First order perturbation theory then gives:

$$E_{n l m_l m_s} = E_{n m_l m_s} + \langle n l m_l s m_s | \xi(r) \mathbf{L} \cdot \mathbf{S} | n l m_l s m_s \rangle$$

Remembering that eigenstates of H_0 factor into radial ($R_{nl}(r)$) and angular (Y_{lm_l}) and spin parts,

- angular and spin part:

$$\langle l m_l s m_s | \mathbf{L} \cdot \mathbf{S} | l m_l s m_s \rangle = \langle l m_l s m_s | L_z \cdot S_z | l m_l s m_s \rangle = m_l m_s \hbar^2$$

because $\langle l m_l s m_s | L_x | l m_l s m_s \rangle = \langle l m_l s m_s | L_y | l m_l s m_s \rangle = 0$

- radial part: (for $l > 0$, otherwise, this term is zero)

$$\lambda_{nl} = \hbar^2 \langle n l | \xi(r) | n l \rangle = \hbar^2 \int_0^\infty dr r^2 R_{nl}(r) \xi(r) R_{nl}(r) = - \left(\frac{e^2}{4\pi\epsilon_0\hbar c} \right)^2 \frac{z^2}{n} \frac{E_n}{l(l+1/2)(l+1)}$$

- Collecting all, (this is known as the Paschen-Back effect):

$$E_{n l m_l m_s} = E_{n m_l m_s} + m_l m_s \lambda_{nl} = E_{n m_l m_s} - \left(\frac{e^2}{4\pi\epsilon_0\hbar c} \right)^2 \frac{Z^2}{n} \frac{m_l m_s E_n}{l(l+1/2)(l+1)} \quad (4)$$

In addition to the m_l, m_s splitting of energies in the strong field Zeeman effect, there is now also the n, l splitting in the Paschen-Beck effect.

11.1.5 Weak field Zeeman effect

- Now, treat B -dependent terms (i) and (ii) as perturbations, and group the spin-orbit ($\mathbf{L} \cdot \mathbf{S}$) term (iii) with the unperturbed H_0 .
- Key: From previous lectures on addition of the spin and orbital angular momentum, define $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Now these operators $\mathbf{J}^2, J_z, \mathbf{L}^2, \mathbf{S}^2$ all commute with $\mathbf{L} \cdot \mathbf{S}$, hence the good quantum numbers that label the eigenstates of $H_0 + \xi(r) \mathbf{L} \cdot \mathbf{S}$ are now the eigenvalues of these operators: j, m_j, l, s . For a single electron, s can only be $1/2$ and we drop this label.

- So instead of the previous states $|n l m_l m_s\rangle$, we label the states by $|n l j m_j\rangle$. Thus,

$$\begin{aligned} \mathbf{J}^2 |n l j m_j\rangle &= j(j+1)\hbar^2 |n l j m_j\rangle & j = l \pm s = l \pm 1/2 \\ \mathbf{J} |n l j m_j\rangle &= m_j \hbar |n l j m_j\rangle & m_j = -j, -j+1, \dots, j \end{aligned}$$

This is another example of expanding one set of states in another basis. In particular, inserting a completeness relation $\sum_{m_l m_s} |n l m_l m_s\rangle \langle n l m_l m_s| = 1$,

$$|n l j m_j\rangle = \left(\sum_{m_l m_s} |n l m_l m_s\rangle \langle n l m_l m_s| \right) |n l j m_j\rangle = \sum_{m_l m_s} c_{m_l m_s; j m_j}^{n l} |n l m_l m_s\rangle$$

where $c_{m_l m_s; j m_j}^{n l} = \langle n l m_l m_s | n l j m_j \rangle$ are the so-called Clebsch-Gordon coefficients.

- In this new basis, we can compute the energy change for H_0 due to the spin-orbit term. Again, we can separate the $\mathbf{L} \cdot \mathbf{S}$ from the $\xi(r)$ part.
 - For the angular part, useful trick: rewrite $\mathbf{L} \cdot \mathbf{S} = (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)/2$. Then this operator acting on the state $|n l j m_j\rangle$ just gives the eigenvalue $\hbar^2[j(j+1) - l(l+1) - s(s+1)]/2$ with $s = 1/2$.
 - For the radial part, for $l > 0$, (just as in the previous section):

$$\langle n l | \xi(r) | n l \rangle = \frac{1}{2m^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{Z^3}{a_0^3 n^3 l(l+1/2)(l+1)}$$

Combining:

$$\begin{aligned} \delta E_{njl} &= \langle n l j m_j | \xi(r) \mathbf{L} \cdot \mathbf{S} | n l j m_j \rangle \\ &= \frac{1}{2} \hbar^2 \left[j(j+1) - l(l+1) - \frac{3}{4} \right] \frac{1}{2m^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{Z^3}{a_0^3 n^3 l(l+1/2)(l+1)} \end{aligned}$$

- It can be shown that the perturbation due to the weak magnetic field is then:

$$\begin{aligned} \delta E_{m_j} &= \langle n l j m_j | \frac{\mu_B}{\hbar} (L_z + 2S_z) B | n l j m_j \rangle = g_L \mu_B m_j B \\ g_L &= 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad (\text{Lande } g\text{-factor}) \end{aligned}$$

- Finally, collecting all, the perturbed energy in the weak B-field regime is:

$$E_{n j m_j l} = E_n + \delta E_{njl} + \delta E_{m_j}$$

12 Approximate Methods IV

12.1 Variational Method

This approximation method does not require a small perturbation to a known problem, unlike for perturbation theory. So this can be useful, but the method does rely on having good guesses for the trial wavefunction, and gives a bound for the ground state energy only.

12.1.1 Variational principle

We want to solve the problem:

$$H|\psi_i\rangle = E_i|\psi_i\rangle$$

This defines the energy eigenstates and eigenvalues (energies) for the Hamiltonian H . As H is Hermitian, we can always find (or construct) a complete orthonormal basis such that $\langle\psi_i|\psi_j\rangle = \delta_{ij}$.

- Now we do not know what these states or energies are. We can guess a state Φ_{var} which can be written generally as:

$$|\Phi_{var}\rangle = \sum_i c_i |\psi_i\rangle$$

- Then the expectation of the energy is:

$$E_{var}(\Phi_{var}) = \frac{\langle\Phi_{var}|H|\Phi_{var}\rangle}{\langle\Phi_{var}|\Phi_{var}\rangle} = \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} \quad (12.1)$$

- Now subtract the ground state energy E_0 on both sides of Eq. 12.1:

$$E_{var}(\Phi_{var}) - E_0 = \frac{\sum_i |c_i|^2 (E_i - E_0)}{\sum_i |c_i|^2} \quad (12.2)$$

By definition, $E_i \geq E_0$, (equality if and only if state $i = 0$ is the ground state). Thus every term on the right hand side of Eq. 12.2 is positive, which implies that the left side is also positive. This leads to:

Variational Principle: Any approximate trial wavefunction gives an energy that is always above (or at best equal to) the true ground state energy E_0 .

$$E_{var}(\Phi_{var}) = \frac{\langle \Phi_{var} | H | \Phi_{var} \rangle}{\langle \Phi_{var} | \Phi_{var} \rangle} \geq E_0$$

Strategy: Suppose the trial wavefunction depends on a parameter a . Then $E_{var}(\Phi(a))$ can be minimized with respect to a to get the best approximation to the ground state energy.

$$\text{Best approximation when: } \frac{dE_{var}(\Phi_{var}(a))}{da} = 0$$

- Special case: suppose our trial wavefunction is in fact the ground state $|\psi_0\rangle$ with energy E_0 , plus a little bit of some excited state $|\psi_e\rangle$ at energy E_e ($> E_0$):

$$|\Phi_{var}\rangle = \frac{1}{\sqrt{1 + |c_e|^2}} (|\psi_0\rangle + c_e |\psi_e\rangle)$$

(This state is already normalised.) We assume $|c_e| \ll 1$.

- Then,

$$E_{var}(\Phi_{var}) = \frac{\langle \Phi_{var} | H | \Phi_{var} \rangle}{\langle \Phi_{var} | \Phi_{var} \rangle} = \frac{E_0 + |c_e|^2 E_e}{1 + |c_e|^2} \approx E_0 + |c_e|^2 (E_e - E_0) > E_0$$

Important property: error in wavefunction $\sim |c_e|$, yet error in ground state energy is only $\sim |c_e|^2$.

12.1.2 Ex.1: 1D simple harmonic oscillator

$$H = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad H|n\rangle = E_n|n\rangle$$

Of course in this example, we know the exact energies $E_n = (n + 1/2) \hbar\omega$, and exact eigenstates $|n\rangle$, eg. the ground state $\phi_n(x) \propto \exp[-(x/\alpha)^2/2]$. But suppose we do not. Now the ground state is even in x , so lets try a normalised wavefunction that is also even in x :

$$\Phi_{var}(x, a) = \sqrt{\frac{2a^3}{\pi}} \frac{1}{x^2 + a^2} .$$

Then,

$$E_{var}(\Phi_{var}(a)) = \langle \Phi_{var}(a) | H | \Phi_{var}(a) \rangle = \frac{\hbar^2}{4ma^2} + \frac{1}{2}m\omega^2 a^2$$

By the variational principle, to find the best approximate energy, minimize E_{var} with respect to the parameter a :

$$\frac{dE_{var}(\Phi_{var}(a))}{da} = 0 \quad \implies \quad a_{min}^2 = \frac{\hbar}{\sqrt{2}m\omega} \quad \implies \quad E_{var}(\Phi_{var}(a_{min})) = \frac{1}{\sqrt{2}} \hbar\omega .$$

This is indeed bigger than the true ground state energy of $\hbar\omega/2$.

12.1.3 Ex.2: Ground state energy of Helium

Simplest model of He (which has 2 electrons and a nuclear charge $Z = +2e$):

$$H_{He} = -\frac{\hbar^2}{2m} (\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{2e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{(4\pi\epsilon_0) |\mathbf{r}_1 - \mathbf{r}_2|}$$

The last term describes the Coulomb interaction between the two electrons. The first two terms are just like two copies of Hydrogen-like atom, with kinetic energy and Coulomb energies between the nucleus (charge $+2e$) and one electron at r_1 and another at r_2 .

- If we drop the interaction between the two electrons, the ground state wavefunction would be:

$$\phi_{var}^0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0} \implies E_{var}(\phi_0) = 2E_0^{H(Z=2)}$$

where $E_0^{H(Z=2)}$ is just the ground state energy for one electron in a hydrogen-like atom of nuclear charge $Z = 2$. That the variational He energy is just twice the hydrogen-like atom energy is because when there is no interaction between the two electrons, the He Hamiltonian just factors out to precisely two copies of Hamiltonian of the hydrogen-like atom.

- We can do better: Key physics: each electron sees the nuclear charge partially screened by the other electron. So we can try an effective nuclear charge $Z < 2$, *i.e.*,

$$\Phi_{var}^0(\mathbf{r}_1, \mathbf{r}_2, Z) = \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 e^{-(r_1+r_2) Z/a_0}$$

- Calculation gives that (E_1 is the Rydberg energy):

$$\langle \Phi_{var}^0(Z) | H_{He} | \Phi_{var}^0(Z) \rangle = \left(-2Z^2 + \frac{27}{4}Z \right) E_1$$

Minimizing this with respect to Z gives:

$$Z_{min} = \frac{27}{16} \approx 1.688 < 2$$

Indeed there is some screening.

13 Approximate Methods V

In experiment, we sometimes apply a perturbation like an external force like electric field etc, starting at some particular time. Also, it is common to apply a perturbation that is inherently time-dependent, like a sinusoidally varying electric field. Thus, we need to be able to solve perturbation theory which has time dependence: this in fact reveals very rich quantum dynamics.

13.1 Time-dependent Perturbation Theory

We start with the unperturbed Hamiltonian with its associated unperturbed energies and unperturbed eigenstates: $H_0|n\rangle = E_n|n\rangle$.

- Now at time $t = 0$, we switch on a perturbation $\lambda V(t)$:

$$H(t < 0) = H_0, \quad H(t \geq 0) = H_0 + \lambda V(t)$$

Then we have the time-dependent Schrodinger equation (TDSE):

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = [H_0 + \lambda V(t)] |\psi(t)\rangle \quad (13.1)$$

which describes the time evolution of the state $|\psi(t)\rangle$.

- Let us assume that the system is prepared initially at $t \leq 0$ to be in the unperturbed eigenstate $|i\rangle$ where $H_0|i\rangle = E_i|i\rangle$:

$$|\psi(t = 0)\rangle = |i\rangle$$

- We want to find the probability that due to the perturbation, there is a transition from $|i\rangle$ to some other state $|f\rangle$, where $|f\rangle$ is also an unperturbed eigenstate of H_0 :

$$P_{fi}(t) = |\langle f|\psi(t)\rangle|^2$$

(The subscript i is to remind ourselves that the initial state is $|i\rangle$.)

- Since both initial and final states are from the set of unperturbed eigenstates, which form a complete, orthonormal set, we expand the unknown state $|\psi(t)\rangle$ in these:

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle$$

Substitute this into TDSE, and multiply by a bra $\langle k|$ to the left:

$$i\hbar \frac{d}{dt} c_k(t) = c_k(t) E_k + \sum_n \lambda V_{kn}(t) c_n(t) \quad (13.2)$$

where we have defined the matrix element $V_{kn}(t) = \langle k|V(t)|n\rangle$. We have as usual, used the orthonormality property $\langle k|n\rangle = \delta_{kn}$.

- For $\lambda = 0$ (no perturbation), clearly, the solution to Eq.13.2 is just $c_k(t) = b_k \exp(-iE_k t/\hbar)$, with b_k a constant that can be determined from the initial condition.

- Key: we guess that when $\lambda \neq 0$ (but still small), $c_k(t)$ still looks quite like b_k , at least shortly after the perturbation is switched on, so we guess:

$$c_k(t) = b_k(t) \exp(-iE_k t/\hbar) \quad (13.3)$$

The idea is essentially that $\exp(-iE_k t/\hbar)$ deals with the time evolution of the H_0 bit, and the new coefficient $b_k(t)$ deals with any leftover time dependence coming from the perturbation.

Substituting Eq.13.3 into Eq.13.2, cancelling common terms and multiplying by $e^{iE_k t/\hbar}$ on both sides gives:

$$i\hbar \frac{d}{dt} b_k(t) = \lambda \sum_n \exp(i\omega_{kn}t) V_{kn}(t) b_n(t) \quad (13.4)$$

where $\omega_{kn} = (E_k - E_n)/\hbar$ is the energy difference between states $|k\rangle$ and $|n\rangle$. So far, this is still an exact equation derived from the TDSE.

- Now, just as for time-independent perturbation theory, we expand the unknown coefficient $b_k(t)$ in a series in the small parameter λ :

$$b_k(t) = b_k^{(0)}(t) + \lambda b_k^{(1)}(t) + \lambda^2 b_k^{(2)}(t) + \dots \quad (13.5)$$

where the superscripts (0) , (1) etc identify the order of the coefficients.

Again, just as for time-independent perturbation theory, substitute Eq.13.5 into Eq.13.4 and equate term by term the bits multiplying a particular order in λ :

$$\begin{aligned} \lambda^0 \text{eqn} : \quad & i\hbar \frac{d}{dt} b_k^{(0)}(t) = 0 \\ \lambda^1 \text{eqn} : \quad & i\hbar \frac{d}{dt} b_k^{(1)}(t) = \sum_n \exp(i\omega_{kn}t) V_{kn}(t) b_n^{(0)}(t) \end{aligned}$$

(One can see that generally, the left hand side $i\hbar \frac{d}{dt} b_k^{(q)}(t)$ is proportional to on the right hand side one order lower $b_n^{(q-1)}(t)$, but we do not need this here.)

- For the λ^0 equation, we can immediately solve it, and use the initial condition that $|\psi(t=0)\rangle = |i\rangle$, which means the only non-zero coefficient is for $k = i$:

$$\lambda^0 \text{ eqn} \implies b_k^{(0)}(t) = b_k^{(0)}(t=0) = \delta_{ki} \quad (13.6)$$

We can also integrate the λ^0 equation directly, and use the initial condition of Eq.13.6 to get rid of the sums (since only one term $n = i$ is non zero and contributes to the sum):

$$\lambda^1 \text{ eqn} \implies b_k^{(1)}(t) = \frac{1}{i\hbar} \sum_n \int_0^t d\tilde{t} \exp(i\omega_{kn}\tilde{t}) V_{kn}(\tilde{t}) b_n^{(0)}(\tilde{t}) = \frac{1}{i\hbar} \int_0^t d\tilde{t} \exp(i\omega_{ki}\tilde{t}) V_{ki}(\tilde{t}) \quad (13.7)$$

This is the key result we need for calculating transition probabilities:

- The transition probability from $|i\rangle$ to some other state $|f\rangle$ at t is:

$$P_{fi}(t) = |\langle f|\psi(t)\rangle|^2 = \left| \sum_n b_n(t) \langle f|n\rangle \right|^2 = |b_f(t)|^2 \approx \left| b_f^{(0)}(0) + \lambda b_f^{(1)}(t) \right|^2$$

For the state $|f\rangle \neq |i\rangle$, we then get:

$$P_{fi}(t) \approx \left| \lambda b_f^{(1)}(t) \right|^2 = \left(\frac{\lambda}{\hbar} \right)^2 \left| \int_0^t d\tilde{t} \exp(i \omega_{fi} \tilde{t}) V_{fi}(\tilde{t}) \right|^2 \quad (8)$$

13.2 Application to a special case: sinusoidal or constant in time perturbation

Let $V(t) = \hat{V}_0 \cos(\Omega t)$, with Ω the frequency of the perturbation. Then

$$V_{fi}(t) = V_{fi} \cos(\Omega t), \quad V_{fi} = \langle f|\hat{V}_0|i\rangle$$

Doing the time integral in Eq.8 gives:

$$P_{fi}(t, \Omega) \approx \left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 \left| \frac{\exp[it(\omega_{fi} + \Omega)] - 1}{\omega_{fi} + \Omega} + \frac{\exp[it(\omega_{fi} - \Omega)] - 1}{\omega_{fi} - \Omega} \right|^2 \quad (9)$$

A special case of Eq.(9) is when the frequency of the perturbation $\Omega = 0$, which is a constant perturbation (except that it is switched on at $t > 0$):

$$P_{fi}(t, \Omega = 0) \approx \left(\frac{\lambda |V_{fi}|}{\hbar} \right)^2 \left| \frac{\exp[it \omega_{fi}] - 1}{\omega_{fi}} \right|^2 = \left(\frac{\lambda |V_{fi}|}{\hbar} \right)^2 \left[\frac{\sin(t \omega_{fi}/2)}{\omega_{fi}/2} \right]^2 \quad (9a)$$

- **Selection rules:** For either $\Omega = 0$ or $\Omega \neq 0$ cases, if the perturbation matrix element $V_{fi} = \langle f|\hat{V}_0|i\rangle = 0$, there can be no transition at all from $|i\rangle$ to this state $|f\rangle$ at any t . This is the basis for selection rules in atomic and molecular physics.
- **Resonant transition:** From Eq. 9, if $\Omega \approx \pm\omega_{fi}$, the probability very quickly grows to one (and then the perturbation theory breaks down). This means the system very quickly makes the transition into this specific state $|f\rangle$ when the resonance condition $\Omega = \pm\omega_{fi}$ is satisfied. Lets take $\Omega > 0$. Then, if $E_f > E_i$, the system **absorbs** a quanta of energy of $\hbar\Omega$ from the perturbation to go from $|i\rangle$ to state $|f\rangle$. Conversely, if $E_f < E_i$, the system has an **induced emission** when going from $|i\rangle$ to state $|f\rangle$.

Eg. absorption case: dropping the $\omega_{fi} + \Omega$ term being much smaller than the resonant term $\omega_{fi} - \Omega$, we get:

$$P_{fi}(t, \Omega > 0) \approx \left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 \left| \frac{\exp [it (\omega_{fi} - \Omega)] - 1}{(\omega_{fi} - \Omega)} \right|^2 = \left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 \left[\frac{\sin (t (\omega_{fi} - \Omega)/2)}{(\omega_{fi} - \Omega)/2} \right]^2$$

This has a maximum at $\omega_{fi} = \Omega$, with height $\left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 t^2$ and hence grow quickly with time. The peak at that position has width $4\pi/t$ which gets sharper in time.

14 Revision on Hydrogen-like atom

These notes are essentially a revision of Y2 quantum mechanics: it also serves as a list of learning outcomes.

14.1 Hydrogen-like atoms

single e^- in a central (Coulomb) potential of a charge Ze nucleus

- Central potential: only depends on radial distance r between e^- and nucleus; Coulomb means $1/r$ dependence:

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

Hamiltonian is then:

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} \quad (1)$$

and this is to be used in the time-independent Schrodinger equation $H\psi(\mathbf{r}) = E\psi(\mathbf{r})$.

- Solution using separation of variables

$$\psi(\mathbf{r}) \rightarrow \psi(\mathbf{r})_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi) \quad (2)$$

Remember: in spherical polar, ($x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$, $z = r \cos \theta$):

$$\nabla^2 \rightarrow \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\mathbf{L}^2}{\hbar^2 r^2} \quad \mathbf{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

where \mathbf{L} is the angular momentum operator. Substituting (2) into (1) leads to a separation into two equations: radial and angular.

14.2 Angular (θ, ϕ) equation

Thanks to central potential: $[\mathbf{L}^2, V(r)] = 0$. But also, $[\mathbf{L}^2, -\frac{\hbar^2}{2m}\nabla^2] = 0$. Thus $[\mathbf{L}^2, H] = 0$ and in fact $[\mathbf{L}, H] = 0$. This means:

- Wave function of H atom is also eigen-fuction of \mathbf{L} operator. Indeed,

$$\mathbf{L}^2 Y_{lm}(\theta, \phi) = l(l+1) \hbar^2 Y_{lm}(\theta, \phi) \quad Y_{lm}(\theta, \phi) = P_l^m(\theta, \phi) e^{im\phi} \quad (3)$$

where the orbital angular momentum quantum number l and azimuthal quantum number m satisfies:

$$l = \text{integers} \geq 0, \quad -l \leq m \leq l$$

and the associated Laguerre polynomials:

l	m	$P_l^m(\theta, \phi)$
0	0	1
1	0	$\cos \theta$
1	± 1	$\sin \theta$
2	0	$3 \cos^2 \theta - 1$
2	± 1	$\sin \theta \cos \theta$
2	± 2	$\sin^2 \theta$

- $Y_{lm}(\theta, \phi)$ are spherical harmonics, they satisfy orthonormality:

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta Y_{l'm'}^*(\theta, \phi) Y_{lm}(\theta, \phi) = \delta_{l'l} \delta_{m'm'}$$

Or in bra-ket notation:

$$\langle l', m' | l, m \rangle = \delta_{l'l} \delta_{m'm'}$$

where $\delta_{l'l} = 1$ if and only if $l = l'$, otherwise when $l \neq l'$, $\delta_{l'l} = 0$.

14.3 Radial (r) equation

- Substituting (3), (2) into (1) gives the radial equation:

$$\left[-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\mathbf{L}^2}{\hbar^2 r^2} \right) + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{(4\pi\epsilon_0)r} \right] R_{nl}(r) = E_n R_{nl}(r) \quad (4)$$

Remember that by definition of polar coordinates, $r > 0$.

- Eq. (4): no m -dependence \implies energies E_n has no m -dependence, i.e. $(2l + 1)$ fold degeneracy (same energy for $-l \leq m \leq l$). This comes from the central potential which is spherically symmetric $\implies H$ that is rotationally invariant, and so energy cannot depend on m . (Remember, $[\mathbf{L}, H] = 0$, and m is the projection of the angular momentum on the \hat{z} -axis: $L_z = -i\hbar \frac{\partial}{\partial \phi}$, $L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi)$.)
- Behaviour of $R_{nl}(r)$: define $u_{nl}(r) = rR_{nl}(r)$. Then Eq. (4) becomes:

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2 u_{nl}(r)}{dr^2} + V_{eff}(r)u_{nl}(r) = E_n u_{nl}(r) \quad , \quad V_{eff}(r) = -\frac{Ze^2}{(4\pi\epsilon_0)r} + \frac{l(l+1)\hbar^2}{2mr^2} \quad (5)}$$

This is a 1-dimensional Schrodinger equation, with the first term in V_{eff} for the Coulomb potential, the second part is for the centrifugal potential.

- General solution of Eq. (5) involves the Laguerre polynomials with a new quantum number n , in addition to the angular momentum l , with the restriction:

$$\boxed{n = 1, 2, 3, \dots, \quad l = 0, 1, 2, \dots, n - 1}$$

n	l	$R_{nl}(r)$
1	0	$2 \left(\frac{z}{a}\right)^{3/2} \exp - \left(\frac{Zr}{a}\right)$
2	0	$2 \left(\frac{z}{a}\right)^{3/2} \left(1 - \frac{zr}{2a}\right) \exp - \left(\frac{Zr}{2a}\right)$
2	1	$\frac{1}{\sqrt{3}} \left(\frac{z}{2a}\right)^{3/2} \left(\frac{zr}{a}\right) \exp - \left(\frac{Zr}{2a}\right)$

$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \equiv a_0$ is the Bohr radius.

The corresponding energies are of the Bohr form:

$$\boxed{E_n = -\frac{m}{2\hbar^2} \left(\frac{Ze^2}{(4\pi\epsilon_0)r}\right)^2 \frac{1}{n^2} \quad n = 1, 2, 3, \dots}$$

Note: E_n has no angular momentum l dependence: this is special to Coulomb interaction.

- These are bound state energies: $E_n < 0$: ie it costs energy to take an electron far away from the nucleus. Indeed, the $\exp - \left(\frac{Zr}{a}\right)$ bit ensures the electron to be close to the nucleus. The Schrodinger equation (5) also has $E > 0$ solutions: these are scattering states where a far away energetic electron can just "bounce off" the nucleus and run off to very far away again. We do not study these here.

- Spectroscopic notation: the different l wavefunctions (also called orbitals in atomic physics) are

given names:

$l =$	0	1	2	3	...
label	s	p	d	f	...