

## 11 Formalism

all operators  $A, B$  which commute share a common set of eigenfunctions. we proved this in lecture 8

let  $Af_n = a_n f_n$ . and  $Bf_n = b_n f_n$  then  $[A, B]f_n = A(Bf_n) - B(Af_n) = A(b_n f_n) - B(a_n f_n) = a_n b_n f_n - b_n a_n f_n = 0$  as numbers DO commute. So operators which share common eigenfunctions commute.

This tells us a bit more about the uncertainty principle - if operators commute then they share a common set of eigenfunctions, so measuring one does not disturb the wavefunction for the measurement of the next. If they don't commute then in measuring we change the wavefunction so we can't then ask what the next observable is on the original wavefunction.

### 11.1 probability distributions

We interpret  $|\psi|^2$  as probability, so we form a probability distribution.

In 1D, the probability of finding the particle within  $dx$  of  $x$  is  $|\psi(x)|^2 dx = D(x)dx$  where  $D(x)$  is the probability distribution in  $x$ . Then probability we find it within  $a < x < b$  is  $\int_a^b D(x)dx$ . This is unity if we integrate  $-\infty \rightarrow \infty$

in 3D, spherical polars the probability of finding the particle within volume  $dV$  of position  $(r\theta\phi)$  is  $|\psi(r, \theta, \phi)|^2 dV = |\psi(r, \theta, \phi)|^2 r^2 \sin\theta dr d\theta d\phi$

and then we INTEGRATE to get the distribution function in whatever variable of interest. so radial probability - within  $dr$  of  $r$  is  $\int_\theta \int_\phi |\psi(r, \theta, \phi)|^2 dV = \int_\theta \int_\phi |\psi(r, \theta, \phi)|^2 r^2 \sin\theta dr d\theta d\phi = D(r)dr$

If we have a wavefunction which is split into radial wavefunction and spherical harmonics (so  $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$ ) then we can go a step further eg for radial probability - within  $dr$  of  $r$  is  $\int_\theta \int_\phi |\psi(r, \theta, \phi)|^2 dV = \int_\theta \int_\phi |R(r)|^2 |Y(\theta, \phi)|^2 r^2 \sin\theta dr d\theta d\phi = |R(r)|^2 r^2 dr = D(r)dr$

or for polar angle - probability to find electron within  $d\theta$  of  $\theta$  is

$$\int_r \int_\phi |\psi(r, \theta, \phi)|^2 dV = \int_r \int_\phi |R(r)|^2 |Y(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi = \int_\phi |Y(\theta, \phi)|^2 \sin \theta d\theta d\phi$$

$$= 2\pi |Y(\theta, \phi)|^2 \sin \theta d\theta = D(\theta) d\theta$$

## 11.2 Hermitian operators

we had  $\int \psi^* Q \psi dx = \int (Q \psi)^* \psi dx$  as our test for a hermitian operator, as this gives  $\langle Q \rangle = \langle Q \rangle^*$  i.e. a real value. But it turns out that this is equivalent to what looks like a slightly stronger condition which is  $\int g^* Q f dx = \int (Q g)^* f dx$

## 11.3 Dirac Notation

All functions of  $x$  form a vector space. our requirement that the wavefunctions be square integrable means these span a more restricted vector space called Hilbert space (by physicists) equivalent to the mathematicians  $L_2$ . mathematically, wavefunctions are abstract vectors and operators act on them via linear transformations to produce new vectors. So its all actually linear algebra.

Where we have 2 functions  $f, g$  each of which are square integrable then  $\int f^* g dx$  (called an inner product) is guaranteed to exist.

We can write this inner product in shorthand notation so  $\int f^* g dx = \langle f | g \rangle$  called Dirac notation. i.e. that everything to the left is complex conjugate, and the whole thing is an integral. so  $\langle f | g \rangle = \langle g | f \rangle^* = \int f^* g dx$ . Its kind of all a bracket so the  $\langle f$  bit is called a bra and the  $|g \rangle$  bit is a ket....

we showed our energy eigenfunctions are orthonormal i.e.

$$\int \psi_m^* \psi_n dx = \langle \psi_m | \psi_n \rangle = \delta_{mn}$$

and any operator  $Q$  acting on a function returns another function which is itself square integrable. so in dirac notation, our expectation values  $\langle Q \rangle = \int \psi^* Q \psi dx = \langle \psi | Q \psi \rangle$  (sometimes written as  $\langle \psi | Q | \psi \rangle$  but I like the

former as it makes it obvious that the operator acts on the wavefunction to its right)

and just to show how nice the new notation is, lets look at  $\langle \psi | xp\psi \rangle = \langle \psi | xf \rangle$  where  $f = p\psi$  then  $\langle x\psi | p\psi \rangle = \langle px\psi | \psi \rangle$  so we did in a few lines that  $(px)^* = (xp)$  which took us a long and tedious derivation in lecture 8.

## 12 Time independent perturbation theory

So we now have a property of the electrons which is spin. it can be spin up or spin down, but it has an associated (small) magnetic moment so it will have an associated (small) change in the energy. Working through the effect of this analytically is HARD, especially as there are other small effects which we have not included yet as well! but since the effects are small we can instead APPROXIMATE the answers using perturbation theory! and this is EASY(er). so lets go the easy way first and next year maybe you'll get to do it analytically!

Suppose we have a solution of the time independent Schroedinger equation for some potential. We have the eigenfunctions  $\psi_n^0$  corresponding to each energy level  $n$ , so that  $H^0\psi_n^0 = E_n^0\psi_n^0$ . Then these eigenfunctions are orthonormal so  $\int \psi_n^{0*}\psi_m^0 dx = \delta_{nm}$ .

now perturb the potential slightly, by putting a bump in the well. We want to find the new eigenfunctions and eigenvalues  $H\psi_n = E_n\psi_n$ . In general we can't solve this exactly for a more complicated potential so instead we use perturbation theory to obtain an approximate solution to the perturbed problem by building on the exact solutions of the unperturbed

So we write the new hamiltonian as the sum of two terms  $H = H^0 + \lambda H'$  where  $H'$  is the perturbation and the superscript 0 always deotes the unperturbed case. We are really just using  $\lambda$  to keep track of first order, second order etc terms. So then we can write  $\psi_n$  and  $E_n$  as a power series in  $\lambda$

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

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

where  $E_n^1$  is the first order correction to the nth energy and  $\psi_n^1$  is the first order correction to the nth eigenfunction. superscript 2 denotes the second order corrections etc. then

$$H\psi_n = E_n\psi_n$$

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

collect powers of  $\lambda$

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

$$E_n^0\psi_n^0 + \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0) + \lambda^2(E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0) + \dots$$

to zeroth order this is just  $H^0\psi_n^0 = E_n^0\psi_n^0$ .

## 12.1 first order theory

But to first order this tells us something new!

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

multiply by  $(\psi_n^0)^*$  and integrate

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

the nice thing here is that we haven't had to specify our volume element over the integral - its more general!

$$= E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1$$

$H^0$  is hermitian so

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

so this cancels and we are left with

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

Lets translate this back to normal notation. which is what we will ALWAYS have to do to calculate anything! we have our first order terms

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

multiply by  $(\psi_n^0)^*$  and integrate

$$\begin{aligned} \int (\psi_n^0)^* H^0 \psi_n^1 dx + \int (\psi_n^0)^* H' \psi_n^0 dx &= \int (\psi_n^0)^* E_n^0 \psi_n^1 dx + \int (\psi_n^0)^* E_n^1 \psi_n^0 dx \\ &= E_n^0 \int (\psi_n^0)^* \psi_n^1 dx + E_n^1 \end{aligned}$$

$H^0$  is hermitian so

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

so this cancels and we are left with

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

so the first order correction to the energy is the expectation value of the perturbation using the unperturbed eigenfunctions!

### 12.1.1 example: 1D square well with delta function

You are used to the kronekar delta where  $\delta_{mn} = 1$  if  $n = m$  or 0 otherwise. now I'm going to introduce you to the dirac delta which is the continuous version of the integer match. so

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

it collapses any integral to the value of the function at the point marked by the delta function. The delta function itself integrates to unity -  $\int \delta(x-x_0)dx = 1$

so if we have  $H' = \alpha\delta(x - a/2)$  then

$$\begin{aligned} E_n^1 &= \int \psi_n^{0*} H' \psi_n^0 dx \\ &= \frac{2}{a} \int_0^a \sin(n\pi x/a) \alpha \delta(x - a/2) \sin(n\pi x/a) dx \\ &= \frac{2\alpha}{a} \sin^2 n\pi/2 \end{aligned}$$

this is 0 if  $n$  is even, so there is no correction to even  $E_n^1$ . but  $2\alpha/a$  for odd  $n$ . For even  $n$  the wavefunction is zero at  $a/2$  so the perturbation has no effect. while for odd  $n$  it peaks here so the energies are shifted.