Brief review of Quantum Mechanics (QM)

Note: This is a collection of several formulae and facts that we will use throughout the course. It is by no means a complete discussion of QM, nor will I attempt to justify any of it.

Let me start by discussing **systems with a single quantum particle** (we will call this the electron, although it could be any quantum particle of finite mass).

Important facts:

- the state of such a system is described by a wavefunction $\psi(\vec{r},t)$, which is generally a complex function. Its physical meaning is that:

$$|\psi(\vec{r},t)|^2 dV$$

is the probability to find, at time t, the electron within a small volume dV centred at point $\vec{r}$. From this we can infer that the wavefunction must be continuous (probabilities cannot change abruptly) and also normalized:

$$\int dV |\psi(\vec{r},t)|^2 = 1$$

The integral is over the entire space, and it simply says that the particle is certainly somewhere, so the total probability to find it in the universe must be 1.

- the evolution of the wavefunction is governed by the Schrödinger equation (we will deal exclusively with non-relativistic particles; for relativistic ones, one should use the Dirac equation):

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \hat{H}\psi(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r},t)$$

Here, $\hbar = h/(2\pi)$ is related to Planck's constant h, $\hat{H}$ is an operator known as the Hamiltonian. Operator simply means that it acts on the wavefunction and does something to it – what precisely is shown by the final part. We see that there are two terms, the first is related to the kinetic energy and consists of taking derivatives from the wavefunction. More specifically:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

in cartesian coordinates where $\vec{r} = x\vec{e}_x + y\vec{e}_y + z\vec{e}_z$. If we'd rather use, for instance, spherical coordinates where $\vec{r} = r\vec{e}_r$ is specified by r, θ, ϕ (see figure), then:

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

The second term in the Hamiltonian describes the potential energy $V(\vec{r})$ in which the particle moves – we will always take this to be time-independent in this course. Much of what I say next is only valid for such time-independent potentials, so be careful if you wish to extend this to time-dependent potentials.

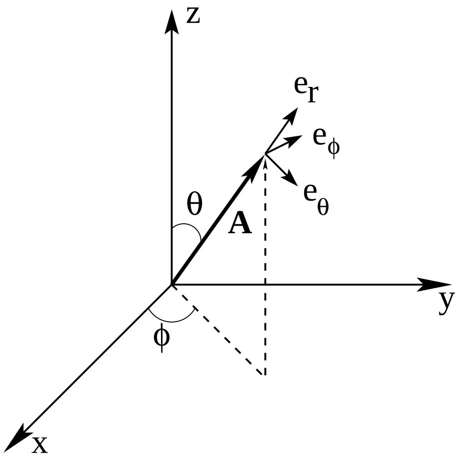

Fig 1. Spherical coordinate system.

• for reasons which will become apparent soon, in this course we will mainly wish to know the **eigenstates and eigenfunctions** of this Schrödinger equation. They have the general form:

$$\psi_E(\vec{r}, t) = e^{-\frac{i}{\hbar}Et}\phi_E(\vec{r}),$$

where E is an energy (known as an eigenenergy) for which the time-independent Schrödinger equation:

$$\hat{H}\phi_E(\vec{r}) = E\phi_E(\vec{r})$$

has a physically acceptable solution for $\phi_E(\vec{r})$ (continuous, normalizable, etc). Note that $|\psi_E(\vec{r}, t)|^2 = |\phi_E(\vec{r})|^2$, so if the particle happens to be in such a state, the probability to find it at various places does not change in time (this is one of the reasons why these states are very important).

Since there will generally be many possible solutions, we need to index the wavefunctions somehow. Above I indexed them by their energy, but typically we will use some "quantum numbers" to tell us which specific solution we are talking about.

The collection of all allowed values of E is called the **spectrum**. If a given E has a single corresponding eigenfunction $\phi_E(\vec{r})$, we call that state non-degenerate. If there are several linearly independent such eigenfunctions, we call that level degenerate. I will use "state", "level", "eigenstate" interchangeably, and all mean essentially the same thing. The state with the lowest energy is called the **ground-state**; all other states are **excited states**.

Before going on, let me give you two simple examples:

(a) 1D particle in an infinite well

1D means that we consider only motion along one axis, usually x-axis. This is a convenient simplification, since once we know this solution, we can easily generalize to 2D and 3D motion in similar potentials.

The infinite quantum well is defined by:

$$V(x) = \begin{cases} 0, & 0 < x < L \\ \infty, & \text{otherwise} \end{cases}$$

and is a simple way of describing the particle in a box. Of course, an infinite potential outside the box is physically impossible, but this turns out to be a good approximation if that potential is much much larger than the typical energy of the particle in the box.

Let's solve this. First, we note that the particle cannot be outside the box (no way to give it infinite energy), so the wavefunction must vanish there (no probability to find the particle in those regions). Since the wavefunction is continuous, it follows that we must have $\phi(x = 0) = \phi(x = L) = 0$.

Inside the box, the Schrödinger equation reads:

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} = E\phi(x)$$

so we're trying to find for what values of E we have acceptable solutions. You should convince yourself that there is no acceptable solution if $E < 0$ (ask me if this gives you trouble!). So then let's look at $E = \frac{\hbar^2 k^2}{2m} > 0$, with $k > 0$. The ODE is now trivial:

$$\frac{d^2\phi(x)}{dx^2} = -k^2\phi(x) \rightarrow \phi(x) = a\cos(kx) + b\sin(kx)$$

where we must also have $\phi(x=0)=\phi(x=L)=0$. The first condition gives us $a=0$. We then must have $b\neq 0$, otherwise $\phi=0$, which is not normalizable. For the second boundary condition to work when b is finite, we must have $\sin(kL)=0 \rightarrow kL=n\pi$, where $n=1,2,...$ is an integer. Note that I threw $n=0$ out. Is that right?

So the allowed solutions are indexed by n (this is our quantum number for this problem), and read:

$$k_n=\frac{n\pi}{L}\rightarrow E_n=\frac{\hbar^2k_n^2}{2m}=n^2\frac{\hbar^2\pi^2}{2mL^2}, \phi_n(x)=\sqrt{\frac{2}{L}}\sin(k_nx)$$

The constant in $\phi_n(x)$ is such that the eigenfunction is normalized. If you need some practice with integrals, check that. If you need some practice with QM, solve this problem for a 2D and then a 3D infinite quantum well. In the latter cases, figure out what are the degeneracies of the various levels.

(b) 1D simple harmonic oscillator

In this case, $V(x)=\frac{m\omega^2x^2}{2}$ is the potential of a harmonic oscillator, which, in the classical case, would oscillate with period $T=2\pi/\omega$. Here the particle can be anywhere $-\infty<x<\infty$, so we don't have explicit boundary conditions like in the previous problem. The solution still must be normalizable, which means that $\phi(x)$ cannot blow up as $|x|\rightarrow\infty$ – quite the opposite, it should decrease fast enough so that the integral of $|\phi(x)|^2$ is finite. This condition will now select the allowed eigenfunctions and eigenenergies.

The only difficulty here is to figure out what are the solutions of the ODE:

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2}+\frac{m\omega^2x^2}{2}\phi(x)=E\phi(x)$$

The details are pure math and you can follow them in any standard QM textbook (this is why you have to study ODEs and PDEs, though, to be able to go through this step). The end result is that we again have a single quantum number, which is also an integer but now including 0: $n=0,1,2,....$, the allowed energies are:

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

and the eigenfunctions are:

$$\phi_n(x)=\frac{1}{\sqrt{2^nn!}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}e^{-\frac{m\omega x^2}{2\hbar}}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$$

where $H_n(x)=(-1)^ne^{x^2}\frac{d^n}{dx^n}\left(e^{-x^2}\right)$ are the Hermite polynomials. This might look a bit scary, but if you plug some values in, you'll find that $H_0(x)=1, H_1(x)=x, H_2(x)=x^2-1,...$ so they are simple polynomials. The exponential that appears in the wavefunctions insures that they decrease fast as $|x|\rightarrow\infty$, as we know they have to. The rest is the normalization coefficient.

In case you're experiencing some ODE-solving-induced fears just now, let me assure you that in this course, we won't need to solve any ODE more complicated than in problem (a), which is the simplest possible. For more complicated examples, like (b), I will either just give you the results and you'll have to wait to study the details in QM, if you haven't already; or we'll work through it together if they are simple enough. I don't expect this to be any problem, in the end.

In more complicated case, we may have more quantum numbers and more complicated spectra, but the basic idea is the same.

I don't think we will use this at all, but just for completeness let me mention that the set of eigenstates is complete, meaning that any (reasonably well-behaved) function can be written as a linear combination of these eigenfunctions, i.e. there exist a unique set of numbers c_α such that

$$f(\vec{r}) = \sum_\alpha c_\alpha \phi_\alpha(\vec{r}),$$

where here α would list all possible quantum numbers. By reasonably well-behaved I mean that f should be continuous or at most have a few jump discontinuities, i.e. not do anything too crazy.

The reason why this property is very useful is because we can apply it to the initial wavefunction, which is well-behaved:

$$\psi(\vec{r}, t=0) = \sum_\alpha c_\alpha \phi_\alpha(\vec{r}) \rightarrow \psi(\vec{r}, t) = \sum_\alpha c_\alpha e^{-\frac{i}{\hbar}E_\alpha t} \phi_\alpha(\vec{r}),$$

The second equality is a consequence of the linearity of Schrödinger's equation, and shows that once we've figured out the eigenfunctions and the spectrum, and what the constants c_α are for the original state, then we know the state at all times.

To find c_α, we use the fact that the eigenfunctions are orthonormal:

$$\int dV \phi_\alpha^*(\vec{r}) \phi_\beta(\vec{r}) = \delta_{\alpha,\beta}$$

where $\delta_{\alpha,\beta} = 1$ if all the quantum numbers for the two eigenfunctions are equal to each other, and zero otherwise. You should convince yourself that this gives:

$$c_\alpha = \int dV \phi_\alpha^*(\vec{r}) \psi(\vec{r}, t=0)$$

as the correct coefficients in the decomposition of the initial wavefunction.

So far I only discussed the spatial location of the particle. It turns out that quantum particles also have **spin** – this is a purely quantum mechanical property, without classical analog, but for our purposes you can think of it as a tiny magnetic moment associated with the particle. Its value is quantized, for example the electron has spin $S = 1/2$. In general, S can be any integer or half-integer number, and for a given S, the projection of the spin along an axis can only take the values $S_z = -S, -S+1, ..., S-1, S$, i.e. $2S+1$ values are possible. If there is no magnetic field (which is what we will assume for most of the course) all these orientations of the spin have the same energy. (Well, one can add terms in the Hamiltonian to describe something known as spin-orbit coupling, in which case states with different spin projections will have different energies, so my last statement is not always true. However, this spin-orbit coupling is a relativistic correction, and we won't bother with such fancy things in this course).

Going back to the electron, one usually calls the state with $s_z = +1/2$ as **spin up**, and the one with $s_z = -1/2$ as **spin down**. The existence of both possibilities leads to extra degeneracies of the spectrum. For instance, a complete specification of the state of an electron in the infinite well is characterized by both n and s_z: I could have a spin-up electron in state $n = 3$, or a spin-down electron in that state, and these are distinct because of the spin, even though they have precisely the same spatial wavefunction. In terms of notation, I would write the complete wavefunction as:

$$\Psi_\sigma(\vec{r}, t) = \psi(\vec{r}, t)\chi_\sigma$$

where the last bit is different if $\sigma =\uparrow$ or $\sigma =\downarrow$, i.e. it is a way to show which spin we have for this electron. One could go into many more details, but I think this will suffice for what we need.

Now, a few facts about **systems with more identical quantum particles**. If there are N particles, the general state of the system will be described by something like:

$$\psi(\vec{r_1}, ..., \vec{r_N}, t)\chi_{\sigma_1,...,\sigma_N}$$

where the first part has information about the probability of finding the various particles around their corresponding locations, and the second part tells us what are their spins doing. In the absence of magnetic fields, the spins cannot change and the evolution of the spatial part is given by a generalized Schrödinger equation.

If there are no interactions between particles, then the Hamiltonian for the full system is $\hat{H} = \sum_{i=1}^{N} \hat{H}_i$, where $\hat{H}_i$ would be the Hamiltonian if only particle i existed, and depends only on $\vec{r_i}$. If there are interactions, then we need to add interaction energies that depend on the positions of two or more particles, so we can no longer "split" the Hamiltonian in a simple sum.

We will generally assume our electrons to be non-interacting (this should sound very crazy to you, because we know that there are strong Coulomb repulsions between charged particles like the electrons, so how come we can ignore them? I'll try to give you some physical answers as we go along, but ask me more when we get there, if you're not satisfied). In any event, if we can take $\hat{H} = \sum_{i=1}^{N} \hat{H}_i$, then you can convince yourself that the eigenfunctions for the whole system are simply products of the eigenfunctions for each particle, and the eigenenergies are the sums of the individual particle energies (as expected if there are no interactions).

For example, suppose we have two electrons in the infinite well, one in level n and the other one in level m. This is an eigenstate of the whole (two-particle) problem, with energy $E_{n,m} = E_n + E_m$. You might guess that the eigenfunction is simply $\phi_{n,m}(x_1, x_2) = \phi_n(x_1)\phi_m(x_2)$, since I said that electron 1 is in level n and electron 2 is in level m. Mathematically, this guess satisfies the Schrödinger equation and is normalizable etc. Physically, though, it has a major problem, namely that electrons are indistinguishable so I cannot possibly say which one is in which level. In other words, I might have, just as well, $\phi_m(x_1)\phi_n(x_2)$ as a solution, but this is not distinguishable from the first.

The way around this is that for electrons (and any other particles with half-integer spin, which are called fermions), the correct wavefunction is the fully antisymmetrized combination of all permutations we can make between which particle is in which state. For two electrons, this means that the eigenfunction is, actually:

$$\phi_{n,m}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\phi_n(x_1)\phi_m(x_2) - \phi_m(x_1)\phi_n(x_2)\right]$$

so that $\phi_{n,m}(x_1, x_2) = -\phi_{n,m}(x_2, x_1)$. This last equality shows that if I interchange the particles, the wavefunction must change the sign. Note that the probability stays the same (because of the square), as it should. For more particles (if they are fermions), I have to make sure that any time I exchange any two of them, the wavefunction changes its sign.

For your information: if the particles have integer spin, they are called bosons and then we need to take the symmetric combination, so that $\phi_{n,m}(x_1, x_2) = +\phi_{n,m}(x_2, x_1)$ (but we won't deal with many bosons in this course).

Back to our electrons: what I just said seems to imply that I cannot have both electrons in the same level, since if $n = m$, obviously $\phi_{n,n}(x_1, x_2) = 0$. This is not quite right, and that is because we forgot that we also have to specify the spin in order to fully specify the state.

So, let's rewind. Suppose both electrons have spin up, and one is in level n and one in m. Then, the wavefunction could either be $\phi_n(x_1)\phi_m(x_2)\chi_{1\uparrow}\chi_{2\uparrow}$ (the last bits just show that both electrons have spin up), or we could have $\phi_m(x_1)\phi_n(x_2)\chi_{1\uparrow}\chi_{2\uparrow}$. The only way to make a fully antisymmetric wave-function, now, is:

$$\psi_{n,m,\uparrow,\uparrow}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\phi_n(x_1)\phi_m(x_2) - \phi_m(x_1)\phi_n(x_2)\right]\chi_{1\uparrow}\chi_{2\uparrow}$$

In other words, since both electrons have spin up, changing one with the other won't affect the spin part but it will exchange $x_2 \leftrightarrow x_1$, so the wavefunction can only be antisymmetric due to its spatial part. Now we see that indeed, we cannot have $n = m$ because then the wavefunction vanishes (so it is not normalizable). In other words, we cannot put two spin-up electrons in the same level, but there's no problem putting them on different levels $n \neq m$ (in case you're wondering, the $1/\sqrt{2}$ factor is to normalize the total wavefunction. Check it!). Very similar arguments apply to two spin-down electrons, and we arrive at the same conclusion: they can't both occupy the same level.

What if one electron has spin-up, and one has spin-down? Well, now I could have 4 possible choices: $\phi_n(x_1)\phi_m(x_2)\chi_{1\uparrow}\chi_{2\downarrow}$, $\phi_n(x_1)\phi_m(x_2)\chi_{1\downarrow}\chi_{2\uparrow}$, $\phi_m(x_1)\phi_n(x_2)\chi_{1\uparrow}\chi_{2\downarrow}$, $\phi_m(x_1)\phi_n(x_2)\chi_{1\downarrow}\chi_{2\uparrow}$, i.e. either electron 1 is in state n with spin up and then 2 is in m with spin-down, or all other permutations.

It turns out that we can make two fully anti-symmetrized functions out of these "pieces". The first is known as the "singlet", and is given by:

$$\psi_{n,m,singlet}(x_1,x_2) \propto \left[\phi_n(x_1)\phi_m(x_2) + \phi_m(x_1)\phi_n(x_2)\right]\left[\chi_{1\uparrow}\chi_{2\downarrow} - \chi_{1\downarrow}\chi_{2\uparrow}\right]$$

Here, the spatial part is unchanged if I interchange $1 \leftrightarrow 2$, but the spin part gets a minus sign, so indeed the whole wavefunction is antisymmetric if I exchange the particles (exchanging means both locations and spins).

Note that in this singlet state, I am allowed to put both particles in the same level $n = m$! So, we are allowed to put two electrons in the same level, if one has spin up and one has spin down, and the spins are in a so-called singlet (that antisymmetric combination).

I can also get an antisymmetric total wavefunction by making the spin part symmetric and the spatial part antisymmetric. This belongs to the "triplet":

$$\psi_{n,m,triplet}(x_1,x_2) \propto \left[\phi_n(x_1)\phi_m(x_2) - \phi_m(x_1)\phi_n(x_2)\right]\left[\chi_{1\uparrow}\chi_{2\downarrow} + \chi_{1\downarrow}\chi_{2\uparrow}\right].$$

In this case $n = m$ is not allowed!

If we have time to discuss magnetic properties towards the end of the course, we'll discuss a bit more about singlets and triplets, and spins in general. For most of the course, what I need you to remember is that we can place at most 2 electrons in a non-degenerate level, one with spin-up and one with spin-down. This is an illustration of the Pauli principle, which says that a quantum level (where spin projection must also be specified) can be occupied by at most one fermion.

This short discussion should give you a hint why we prefer to work with non-interacting particles. In this case, if we know the spectrum for a particle, we know what happens for any number of particles: we just have to occupy levels making sure to not violate Pauli's principle, and properly antisymmetrize the products of individual states to get the wavefunction. The energy is just the sum of the individual electron energies.

For interacting particles, we need to start from scratch and recalculate the spectrum by solving the full Schrödinger equation any time we add a new particle, because the new particle will change the states of all previously existing particles through interactions. So, the wavefunctions don't factorize into simple products (plus the antisymmetrization) and the total energy is not simply a sum of all the individual energies. Things are much much more difficult in that case, and in fact how to properly deal with systems where interactions are "big" (i.e., roughly speaking, we can't treat them by perturbation theory) is still the biggest challenge in condensed matter physics – actually, probably in all of physics.