Physics 505
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1 Free particles

1.1 The rules

The answer that QM gives to the question "where is a particle?" is a probability distribution $f(x,t)$ such that

$$\text{Prob}\{a < x < b\} = \int_a^b f(x,t)dx, \qquad \int_{-\infty}^{\infty} f(x,t)dx = 1$$

If we are in 3D we have $f(x,y,z,t)$.

The rule is as follows: at any given time t, the particle is described by a complex wave-function $\psi(x,t)$ such that

$$f(x,t) = |\psi(x,t)|^2.$$

Thus ψ encodes in it the probability distribution for the particle as well as a phase which has no obvious physical meaning but is very important for interference phenomena!

We can also ask the question "what is the momentum of the particle?" The answer is another probability distribution $\hat{f}(p,t)$ such that

$$\text{Prob}\{a < p < b\} = \int_a^b \hat{f}(p,t)dx, \qquad \int_{-\infty}^{\infty} f(p,t)dp = 1$$

The rules also say that at any given time t there is another complex valued function $\hat{\psi}(p,t)$ such that

$$f(p,t) = |\hat{\psi}(p,t)|^2.$$

The rules say that if we already know $\psi(x,t)$ we can determine $\hat{\psi}(p,t)$ via a Fourier transform:

$$\hat{\psi}(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{-\frac{ipx}{\hbar}} \psi(x,t).$$

Finally, the rules say that if you know that the particle has mass m and is moving in a potential energy of $V(x,t)$ then the time evolution of $\psi(x,t)$ is determined from Schrödinger's equation:

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

Where is all this coming from?

1.2 Plane waves

Let us forget about QM, for the moment, and discuss ordinary waves. Let us consider a plane wave with frequency f and wavelength λ. It is convenient to work with the angular velocity and wave-number:

$$\omega = 2\pi\nu, \qquad k = \frac{2\pi}{\lambda}.$$

A wave means that there is some quantity $\psi(x,t)$ which varies sinusoidally:

$$\psi(x,t) = \psi_0 \cos(kx - \omega t + \phi_0).$$

$\psi(x,t)$ means different things for different waves. It could be, for example, the pressure as a function of position and time (for sound waves) or the electric field for EM waves.

There is a sense in which this wave is moving. To see how fast, let's see how to keep the phase $kx - \omega t$ constant. We need:

$$x = \frac{\omega}{k} t + \text{const.}$$

We define the **phase-velocity** to be:

$$v_{ph} \equiv \frac{\omega}{k} = \lambda\nu.$$

Light-waves in vacuum satisfy $\omega = kc$ and therefore $v_{ph} = c$. Usually, waves can have various k's but ω is determined as a function of k for the particular problem:

$$\omega(k) = \text{dispersion relation.}$$

Sound waves have a dispersion relation that depends on the particular material. Similarly EM waves have $\omega(k) = kc$ in vacuum but a different formula inside different materials.

1.3 Wave packets

What about waves that come in a pulse? The idea of Fourier-analysis (or spectral analysis) is that they can be decomposed into component plane waves:

$$\psi(x,t) = \int_{-\infty}^{\infty} dk\, A(k)\cos(kx - \omega(k)t + \phi_0(k)).$$

How can that be localized? Let us take $\phi_0(k) = 0$ and $\omega(k) = kc$ and:

$$A(k) = \begin{cases} A_0 & \text{for } k_0 - \epsilon < k < k_0 + \epsilon \\ 0 & \text{otherwise} \end{cases}$$

We do the integral and find:

$$\psi(x,t) = A_0 \int_{k_0-\epsilon}^{k_0+\epsilon} \cos k(x-ct) = \frac{2A_0 \sin \epsilon(x-ct)}{x-ct} \sin k_0(x-ct).$$

but how did it happen that the wave became localized? Let us take very large $x - ct$. It has contributions of $\cos k(x-ct)$ with k running from $k_0 - \epsilon$ to $k_0 + \epsilon$. If $\epsilon(x-ct) \gg 2\pi$ then the phases $k(x-ct)$ fluctuate fast and cancel each other. the only region in which there are no cancelations is near $x - ct \approx 0$.

1.4 Phase velocity and Group velocity

Let us push this idea further. It is easier to work with complex numbers. Take:

$$\psi(x,t) = \int_{-\infty}^{\infty} dk\, A(k) e^{i(kx-\omega(k)t)}$$

Let us assume that $A(k)$ is a bump function and let us expand:

$$\omega(k) = \omega(k_0) + (k-k_0)\omega_0' + \frac{1}{2}(k-k_0)^2\omega_0'' + \cdots$$

Now let us integrate and keep only the leading terms (because $(k-k_0)^2$ is assumed small when $A(k)$ is large).

$$\psi(x,t) = \int_{-\infty}^{\infty} A(k) e^{i[kx-\omega_0 t-(k-k_0)\omega_0' t+\cdots]} = e^{i(k_0\omega_0'-\omega_0)t} \int_{-\infty}^{\infty} dk\, A(k) e^{ik[x-\omega_0' t]}$$

We can write:

$$\psi(x,t) = e^{i(k_0\omega_0' - \omega_0)t}\psi(x - \omega_0' t, 0) + \cdots$$

So the wave packet actually moves with velocity

$$v_g = \omega_0' = \frac{d\omega}{dk}.$$

This is called the **group-velocity**. We can understand this by trying to figure out at a given time t, what x do we need to plug so that all the phases $kx - \omega(k)t$ would be roughly the same and won't interfere. We find the equation:

$$\frac{d}{dk}(kx - \omega(k)t)|_{k=k_0} = 0 \Longrightarrow x - \omega'(k_0)t = \text{constant}.$$

We discovered that the wave-packet doesn't move with velocity $v_{ph} = \omega/k$ but rather with velocity $v_g = d\omega/dk$. If $\omega(k) = kv$ is a linear relation, it doesn't matter. But if $\omega(k)$ is non-linear $v_g \neq v_{ph}$!

1.5 Particles as waves

We have said that a particle is a wave. If the energy is E and the momentum is p, then the frequency and wavelength are:

$$\nu = \frac{E}{h}, \qquad \lambda = \frac{h}{p}.$$

Therefore,

$$E = \hbar\omega, \qquad p = \hbar k.$$

The dispersion relation for particles is therefore:

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

The phase velocity is:

$$v_{ph} = \frac{\omega(k)}{k} = \frac{\hbar}{2m}k = \frac{p}{2m}$$

and the group velocity is:

$$v_g = \frac{d\omega(k)}{k} = \frac{p}{m}.$$

What does that mean? It means that a wave packet of a particle with momentum p moves with velocity p/m which is what we expect!

For particles we assume some unknown kind of function $\psi(x,t)$ that can be negative or, in fact, complex.

Its decomposition into plane waves is:

$$\psi(x,t) = \int_{-\infty}^{\infty} A(k) e^{ikx - i\frac{\hbar k^2}{2m}t} dk$$

Since ψ is complex we cannot interpret it as the probability distribution itself. A probability distribution has to be a nonnegative quantity. It turns out that $|\psi(x,t)|^2$ is the correct probability distribution.

1.6 Average position and the uncertainty

Now we can write down formulas for the average position and the uncertainty in the position.

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x |\psi(x,t)|^2 dx, \\ (\Delta x)^2 &= \langle (x - \langle x \rangle)^2 \rangle = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 |\psi(x,t)|^2 dx \end{aligned}$$

1.7 Momentum distribution function

How do we determine the momentum distribution function? Since $A(k)$ is the "weight" of wave-number k it is natural to expect that if $A(k)$ is large the contribution of this particular wave-number is large. Since $p = \hbar k$, it seems that $A(\frac{p}{\hbar})$ is related to the distribution function of momentum. But $A(k)$ can be negative or complex. The correct thing to do, turns out to be:

$$\hat{f}(p) = \frac{2\pi}{\hbar} |A(\frac{p}{\hbar})|^2$$

Let us perform a check on this. We know that:

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

Let's check that:

$$\int_{-\infty}^{\infty} \hat{f}(p) dp = 1.$$

We have the following Fourier transform relations:

$$\begin{aligned} \psi(x,t) &= \int_{-\infty}^{\infty} dk\, A(k) e^{i(kx-\omega(k)t)}, \\ A(k) &= \frac{1}{2\pi} e^{i\omega(k)t} \int_{-\infty}^{\infty} dx\, \psi(x,t) e^{-ikx}. \end{aligned} \tag{1}$$

So,

$$\begin{aligned} \int_{-\infty}^{\infty} \hat{f}(p)dp &= \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} |A(\frac{p}{\hbar})|^2 dp = 2\pi \int_{-\infty}^{\infty} |A(k)|^2 dk \\ &= \int dk\, dx\, A(k) e^{-i\omega(k)t} \psi^*(x,t) e^{ikx} = \int dx\, \psi(x,t)\psi^*(x,t) = 1. \end{aligned}$$

We define:

$$\hat{\psi}(p,t) = \sqrt{\frac{2\pi}{\hbar}} e^{-i\omega(\frac{p}{\hbar})t} A(\frac{p}{\hbar}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dx\, \psi(x,t) e^{-i\frac{p}{\hbar}x}.$$

1.8 Schrödinger's equation for a free particle

Let us try to come up with an equation that the free-particle satisfies. We have:

$$\begin{aligned} \psi_p(x,t) &= e^{i\left[\frac{p}{\hbar}x - \frac{E}{\hbar}t\right]}, \\ \frac{\partial\psi}{\partial t} &= -\frac{iE}{\hbar}\psi, \\ \frac{\partial^2\psi}{\partial x^2} &= -\frac{p^2}{\hbar^2}\psi, \end{aligned}$$

But

$$E = \frac{p^2}{2m}.$$

So,

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

1.9 Momentum average

How do we calculate $\langle p \rangle$?

$$\begin{aligned} \langle p \rangle &= \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} p\, dp\, |A(\frac{p}{\hbar})|^2 = 2\pi\hbar \int_{-\infty}^{\infty} k |A(k)|^2 dk \\ &= \hbar \int dk\, dx\, kA(k) e^{-i\omega(k)t} \psi^*(x,t) e^{ikx} = -i\hbar \int dk\, dx\, A(k) e^{-i\omega(k)t} \psi^*(x,t) \frac{\partial e^{ikx}}{\partial x} \\ &= i\hbar \int dx\, \psi(x,t) \frac{\partial\psi^*(x,t)}{\partial x} = -i\hbar \int dx\, \psi(x,t)^* \frac{\partial\psi(x,t)}{\partial x}. \end{aligned}$$

(using integration by parts in the last 2 steps.)

We can now prove that:

$$\frac{d}{dt}\langle x\rangle = \frac{1}{m}\langle p\rangle$$

To do that we write down:

$$\begin{aligned}\frac{d}{dt}\langle x\rangle &= \int x\psi^*\frac{\partial\psi}{\partial t} + \int x\psi\frac{\partial\psi^*}{\partial t} = \frac{i\hbar}{2m}\int x\psi^*\frac{\partial^2\psi}{\partial x^2} - \frac{i\hbar}{2m}\int x\psi\frac{\partial^2\psi^*}{\partial x^2} \\ &= \frac{i\hbar}{2m}\int x\psi^*\frac{\partial^2\psi}{\partial x^2} - \frac{i\hbar}{2m}\int x\frac{\partial^2\psi}{\partial x^2}\psi^* - \frac{i\hbar}{m}\int\frac{\partial\psi}{\partial x}\psi^* \\ &= = -\frac{i\hbar}{m}\int\frac{\partial\psi}{\partial x}\psi^* = \frac{1}{m}\langle p\rangle.\end{aligned}$$

(using integration by parts.)

1.10 Spreading

In the homework you will be asked to prove that

$$\frac{d^2}{dt^2}\left\{\Delta x^2\right\} = \frac{2}{m^2}\Delta p^2$$

This implies that

$$\Delta x^2 = \frac{1}{m^2}\Delta p^2 t^2 + C_1 t + C_0$$

After a long time, the spread Δx of a free particle wave packet increases linearly with time.

2 Schrödinger's equation and simple solutions

2.1 Schrödinger's equation

We have seen that Schrödinger's equation is a consequence of the relation:

$$E = \frac{p^2}{2m},$$

translated into a relation between angular velocity $\omega(k)$ and the wave-number k. What if the particle is moving in a potential $V(x)$, such that the force on it is $F = -V'(x)$? Schrödinger's guess was that we have to write:

$$E = \frac{p^2}{2m} + V$$

but this doesn't make sense anymore, since p and E would have to change as a function of x, and in QM we cannot talk about $p(x)$ which would mean that we know both p and x. Instead we change the differential equation that the wave-function satisfies.

$$\begin{aligned} E\psi(x,t) &\sim i\hbar\frac{\partial\psi}{\partial t}, \\ \frac{p^2}{2m}\psi(x,t) &\sim -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}, \\ V(x,t)\psi(x,t) &= V(x,t)\psi, \end{aligned}$$

Even though the separate terms do not make sense, Schrödinger suggested that summing them up still gives the correct equation:

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

2.2 Probability current

Schrödinger's equation allows us to determine $\psi(x,t)$ at a later time, given $\psi(x,0)$ at $t=0$. The first thing we have to check is that indeed the total probability remains 1. That is, if

$$\int_{-\infty}^{\infty} |\psi(x,0)|^2 dx = 1,$$

then also,

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

The idea is to calculate

$$\frac{d}{dt}|\psi(x,t)|^2.$$

Let us denote $\rho(x,t) = |\psi(x,t)|^2$. We define the **current density**:

$$j(x,t) = \frac{i\hbar}{2m}(\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}).$$

In exercise (1) you'll have to show that:

$$\frac{\partial\rho}{\partial t} = -\frac{\partial j}{\partial x}.$$

As a result, if ψ falls off fast enough at $\pm\infty$:

$$\frac{d}{dt}\int \rho(x,t)dx = -\int \frac{\partial j(x,t)}{\partial x}dx = -j(x,t)|_{-\infty}^{\infty} = 0.$$

2.3 Separation of variables

We will now consider time-independent potentials, $V(x)$. To solve Schrödinger's equation we use **separation of variables**. We look for solutions of the form

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

It is easy to see that $\phi(t)$ must be an exponential. We write it as:

$$\phi(t) = e^{-i\frac{E}{\hbar}t}$$

The equation becomes

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

In principle, for every E we should be able to find $\psi(x)$. In some cases however, there are values of E which are not allowed. **Why?** Because the boundary conditions on ψ are not satisfied.

2.4 Infinite potential well

We take the potential:

$$V(x) = \begin{cases} \infty & \text{for } x < -a \\ 0 & \text{for } -a < x < a \\ \infty & \text{for } a < x \end{cases}$$

What does ∞ mean? It means that $\psi(x) = 0$ outside $-a < x < a$. The solutions are:

$$\psi_n(x) = \frac{1}{\sqrt{a}}\sin\frac{n\pi}{a}x, \qquad n = 1, 2, \ldots$$

The energies are:

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

2.5 Potential well

We take the potential:

$$V(x) = \begin{cases} 0 & \text{for } x < -a \\ -U_0 & \text{for } -a < x < a \\ 0 & \text{for } a < x \end{cases}$$

The wave-function is made of 3 separate functions:

$$\psi(x) = \begin{cases} \psi_A & \text{for } x < -a \\ \psi_B & \text{for } -a < x < a \\ \psi_C & \text{for } a < x \end{cases} \tag{2}$$

The gluing conditions are:

$$\psi_A(-a) = \psi_B(-a), \qquad \psi'_A(-a) = \psi'_B(-a),$$

Why? Because otherwise the ψ'' term in Schrödinger's equation would be infinite! (It is good to keep in mind that this potential is a model for a smooth potential that is very steep.) Let us assume that $E < 0$. (We will discuss the other case at a later class.) We find the solutions:

$$\begin{aligned} \psi_A(x) &= Ae^{\kappa x}, \qquad \kappa = \frac{1}{\hbar}\sqrt{2m|E|}, \\ \psi_B(x) &= B_0 \cos kx + B_1 \sin kx, \qquad k = \frac{1}{\hbar}\sqrt{2m(U_0 - |E|)}, \\ \psi_C(x) &= Ce^{-\kappa x}, \qquad \kappa = \frac{1}{\hbar}\sqrt{2m|E|}, \end{aligned}$$

Let us write:

$$\kappa = \sqrt{k_0^2 - k^2}, \qquad k_0 \equiv \frac{1}{\hbar}\sqrt{2mU_0}$$

The boundary conditions are:

$$\begin{aligned} \psi_A(-a) &= \psi_B(-a), \\ \psi'_A(-a) &= \psi'_B(-a), \\ \psi_C(a) &= \psi_B(a), \\ \psi'_C(a) &= \psi'_B(a), \end{aligned}$$

Substituting the expressions for ψ_A, ψ_C and ψ_B we find:

$$\begin{aligned} Ae^{-\kappa a} &= B_0 \cos ka - B_1 \sin ka, \\ \kappa Ae^{-\kappa a} &= kB_0 \sin ka + kB_1 \cos ka, \\ Ce^{-\kappa a} &= B_0 \cos ka + B_1 \sin ka, \\ -\kappa Ce^{-\kappa a} &= -kB_0 \sin ka + kB_1 \cos ka, \end{aligned}$$

From the first two equations we find

$$B_0(\kappa \cos ka - k \sin ka) = B_1(\kappa \sin ka + k \cos ka)$$

From the last two equations we find:

$$B_0(\kappa \cos ka - k \sin ka) = -B_1(\kappa \sin ka + k \cos ka)$$

It follows that:

$$B_0(\kappa \cos ka - k \sin ka) = B_1(\kappa \sin ka + k \cos ka) = 0.$$

We can see that if both $B_0 = 0$ and $B_1 = 0$ then the wave function would have to be zero identically. This is not what we want. There are two remaining cases to consider:

1. $B_1 = 0$ and $B_0 \neq 0$.
2. $B_0 = 0$ and $B_1 \neq 0$.

Let us analyze them separately.

2.5.1 The case $B_1 = 0$ and $B_0 \neq 0$

We find the equation:

$$\kappa \cos ka - k \sin ka = 0 \Longrightarrow k^2 \sin^2 ka = \kappa^2 \cos^2 ka = (k_0^2 - k^2) \cos^2 ka$$

We therefore find:

$$k^2 = k_0^2 \cos^2 ka \Longrightarrow k = \pm k_0 \cos ka.$$

Recall that k_0 is given and we have to solve for k, from which we can obtain the energy levels:

$$E = U_0 + \frac{\hbar k^2}{2m}$$

We can solve $k = \pm k_0 \cos ka$ graphically. (**Draw the graphs of** $y = \cos ax$ **and** $y = x$**.**) Note that there is always one solution in the range:

$$0 < k < \frac{\pi}{2a}.$$

Now suppose we have a solution to $k = \pm k_0 \cos ka$. It also satisfies $k^2 = k_0^2 \cos^2 ka$ and $k^2 \sin^2 ka = \kappa^2 \cos^2 ka$. But we cannot be sure that it satisfies $\kappa \cos ka - k \sin ka = 0$ because it might satisfy $\kappa \cos ka = -k \sin ka$ instead of $\kappa \cos ka = k \sin ka$. Thus, we have to add the extra condition that $k \tan ka >$

0. Then we are assured that both $\cos ka$ and $k \sin ka$ have the same sign. This means that for $k > 0$ we exclude all solutions in the regions where $\tan ka < 0$. That is, we exclude the regions:

$$\frac{\pi}{2a} < k < \frac{\pi}{a}, \frac{3\pi}{2a} < k < \frac{2\pi}{a}, \frac{5\pi}{2a} < k < \frac{3\pi}{a}, \ldots$$

2.5.2 The case $B_0 = 0$ and $B_1 \neq 0$

We find the equation:

$$\kappa \sin ka + k \cos ka = 0 \Longrightarrow k^2 \cos^2 ka = \kappa^2 \sin^2 ka = (k_0^2 - k^2) \sin^2 ka$$

We therefore find:

$$k^2 = k_0^2 \sin^2 ka \Longrightarrow k = \pm k_0 \sin ka.$$

We can again solve $k = \pm k_0 \sin ka$ graphically. (**Draw the graphs of** $y = \sin ax$ **and** $y = x$**.**)

Now suppose we have a solution to $k = \pm k_0 \sin ka$. It also satisfies $k^2 = k_0^2 \sin^2 ka$ and $k^2 \cos^2 ka = \kappa^2 \sin^2 ka$. But we cannot be sure that it satisfies $\kappa \sin ka + k \cos ka = 0$ because it might satisfy $\kappa \sin ka = k \cos ka$ instead of $\kappa \sin ka = -k \cos ka$. Thus, we have to add the extra condition that $k \cot ka < 0$. Then we are assured that both $\sin ka$ and $k \cos ka$ have the opposite sign. This means that for $k > 0$ we exclude all solutions in the regions where $\tan ka > 0$. That is, we exclude the regions:

$$0 < k < \frac{\pi}{2a}, \frac{\pi}{a} < k < \frac{3\pi}{2a}, \frac{2\pi}{a} < k < \frac{5\pi}{2a}, \ldots$$

2.6 General properties of the solution

Let us assume that $U(x) \to 0$ at $x \to \pm\infty$.

- The solutions are real.
- There is a solution which is physically OK for any $E > 0$.
- For $E < 0$ only discrete values are allowed. There can be a finite or infinite number of them. In 1D there is always at least one. In higher dimensions there could be none.

If $E > 0$ then for large values of $|x|$ the solutions take the form

$$\psi \approx a\cos(kx + \delta), \qquad k = \frac{1}{\hbar}\sqrt{2mE}$$

If $E < 0$ then,

$$\psi \approx Ae^{\kappa x} + Be^{-\kappa x}, \qquad \kappa = \frac{1}{\hbar}\sqrt{2m|E|}$$

However, only the solutions with $A = 0$ for $x \to \infty$ and $B = 0$ for $x \to -\infty$ are physical. Because $\int |\psi|^2 dx$ is infinite. **Why wasn't this a problem when $E > 0$?** Because we could still make localized wave-packets. Thus, for $E < 0$ we get two more equations from the regions $x \to \pm\infty$ and these are enough to give us an equation for E.

The question of whether there is an infinite number or a finite number of bound states is related to the question of whether U falls off faster than $1/|x|^2$ or not. One can use the uncertainty principle to argue that the particle could be arbitrarily far from the origin.

2.7 A comment on bound states

In 1D every potential V that satisfies $V < 0$ everywhere and $V \to 0$ at $x \to \pm\infty$ has at least one bound state. This is because of the following reason (that will be explained later on in the course). If $V_1(x) > V_0(x)$ for all x and there is a bound state for V_1 then there is also a bound state for V_0 with lower energy. Now, for V_1 we can choose a well potential and for V_0 we can choose our potential V. In 3D, on the other hand, potential wells which are shallow enough don't bind!

2.8 δ-functions

We now turn to a more mathematical subject that will be useful later on. Let us ask the following question. Suppose we know that the particle is at $x = 0$. What is its probability density? Let us look at the limit of the following functions:

$$f_a(x) = \begin{cases} 0 & \text{for } x < -a \\ \frac{1}{2a} & \text{for } -a < x < a \\ 0 & \text{for } a < x \end{cases} \tag{3}$$

as $a \to \infty$. We formally define:

$$\delta(x) = \lim_{a\to\infty} f_a(x).$$

The limit does not, strictly speaking, exist. However, mathematically, what we are doing is called a **weak limit**. It means that for any continuous function, $g(x)$, we have a well-defined limit to the integrals:

$$f(0) = \lim_{a\to\infty} \int_{-\infty}^{\infty} f_a(x)g(x)dx.$$

We thus formally define $\delta(x)$ to be the limit. However, we are only going to use it inside integrals. If we have a formula where $\delta(x)$ appears without an integral, we have to keep in mind that to understand it we have to think what will happen if we integrate the formula.

The δ-function satisfies:

$$\begin{aligned}
\delta(x) &= 0, \qquad x \neq 0, \\
f(x) &= \int_{-\infty}^{\infty} \delta(x-y)f(y)dy, \\
f(x) &= \int_{-\epsilon}^{\epsilon} \delta(x-y)f(y)dy, \qquad \epsilon > 0, \\
\delta(x) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}dk, \\
\delta(x) &= \lim_{a\to 0} \sqrt{\frac{\pi}{a}} e^{-\frac{x^2}{a}}.
\end{aligned}$$

As an example, let us take the question from the prelim of 1997. The question has $V(x) = \lambda\delta(x)$. What does that mean?

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

This means that for $x < 0$ and $x > 0$, ψ satisfies the free equation:

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

So what does the δ-function do? It affects the boundary conditions. Let us integrate from $-\epsilon$ to $+\epsilon$ for ϵ very small. We find

$$0 = -\frac{\hbar^2}{2m}(\psi'(\epsilon) - \psi'(-\epsilon)) + \lambda\psi(0)$$

So the derivative of ψ is discontinuous at 0.

Physics 505
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Hilbert spaces and Operators

3 Questions we can or cannot answer so far

Given the wave function $\psi(x)$, and what we have studied so far, we can answer questions like:

- What is the probability distribution for position x?
- What is the probability distribution for momentum p?
- What will be the probability distributions at later times?

We haven't discussed this last week, but **probability** means that we do some experiment to determine the quantity. For example, what experiment could determine the position of a particle? Put a photographic film, or just look at the μ-detector down the hallway!

But what about questions like:

- What is the probability that the particle has a given energy E?
- What is the probability distribution for other quantities like xp, say, or $x^2 + p^2$?
- Why can we not ask questions about x and p simultaneously?
- What is the criterion that two quantities A and B can be specified simultaneously?
- What about more complicated quantum mechanical systems where particles can be created or absorbed?

We will now describe the most general rules of QM.

So far we have the following rules:

- A particle is described by a function $\psi(x)$.
- The average position is $\int \psi^* x \psi dx$.
- The average momentum is $-i\hbar \int \psi^* \frac{\partial \psi}{\partial x} dx$.

- The time dependence is given by Schrödinger's equation:

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

4 Hilbert spaces and operators

For a general QM system you need three things:

1. A **Hilbert space** that corresponds to the space of states of the system.
2. A set of **Hermitian operators** that corresponds to the physical observable quantities.
3. A **Hamiltonian** operator that describes the time evolution.

Let us discuss these separately.

For our purposes, in the case we studied so far, the Hilbert space is just a term that describes all the possible wave-functions $\psi(x)$. In the case of a free particle, or when the potential goes to zero at infinity, the Hilbert space is the space of all functions with:

$$\int |\psi(x)|^2 < \infty.$$

Note that for $\psi(x)$ to be a wave-function of a particle it has to satisfy:

$$1 = \int |\psi(x)|^2,$$

but for the definition of the Hilbert space we drop this **normalization** condition.

In the case of an infinite potential well, the Hilbert space will be the collection of all functions that vanish outside $0 < x < a$.

Note: I am not being very rigorous mathematically, because I don't discuss very carefully singularities of the functions Mathematically, we might also wish to demand that $\int |\psi'|^2 < \infty$.

Also, we will find it convenient to add functions like e^{ikx} whose integral doesn't converge.

A general Hilbert space satisfies two requirements:

- It is a vector space. That means that if $\psi(x)$ and $\phi(x)$ are two allowed wave-functions then $\psi(x) + \phi(x)$ is also allowed. More abstractly, we denote (unnormalized) states by $|a\rangle$ and $|b\rangle$. If $|a\rangle$ and $|b\rangle$ are states, then $|a\rangle + |b\rangle$ is also a state. Also if λ is a complex number then $\lambda|a\rangle$ is also in the Hilbert space.

- There is a way to get the "absolute-value" of a state by a formula that generalizes $\int |\psi|^2 dx$. Moreover, given two functions $\psi(x)$ and $\phi(x)$ there is a way to get a complex number out of them: $\int \phi(x)^* \psi(x) dx$. When the two functions are the same we get the previous integral $\int |\psi|^2 dx$ which we require to be positive. For an abstract Hilbert space we have the **inner product** which takes two states $|a\rangle$ and $|b\rangle$ and makes a complex number $\langle b|a\rangle$. We also require that $\langle a|a\rangle$ is always a **real nonnegative** number and is zero only if $|a\rangle = 0$.

  This **inner product** satisfies:

$$\langle a|b\rangle = \langle b|a\rangle^*.$$

  It also satisfies that if $|d\rangle = |b\rangle + |c\rangle$ then

$$\langle a|d\rangle = \langle a|b\rangle + \langle a|c\rangle.$$

  Also, if $|c\rangle = \lambda|b\rangle$ then

$$\langle c|a\rangle = \lambda^* \langle b|a\rangle, \qquad \langle a|c\rangle = \lambda \langle a|b\rangle.$$

- We have **operators** that take a function $\psi(x)$ and make another function out of it, like $x\psi(x)$ or $-i\hbar\partial\psi/\partial x$ or

$$\psi(x) \to \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x)$$

  In the abstract case, an operator $\hat{O}$ is a rule that transforms states, like $|a\rangle$, to other states $O|a\rangle = |Oa\rangle$ such that

$$O(|a\rangle + |b\rangle) = |Oa\rangle + |Ob\rangle, \qquad O(\lambda|a\rangle) = \lambda|Oa\rangle.$$

  To any physical quantity like x or p, we associate an operator $\hat{O}$ like $x\cdot$ or $-i\hbar\partial/\partial x$. The rules then say that given a state $|a\rangle$ (a function

$\psi(x)$) which describes a state if $\langle a|a\rangle = 1$, then the average of $\hat{O}$ in the state $|a\rangle$ is given by:

$$\langle \hat{O} \rangle = \langle a|\hat{O}a\rangle.$$

These averages always have to be **real**. What does that mean about $\hat{O}$? Such an operator is called **Hermitian**. We will see later what this means in more detail.

- There is one special Hermitian operator which we call **the Hamiltonian** and denote by $\hat{H}$, such that the time evolution of any state is described by:

$$i\hbar \frac{\partial}{\partial t}|a,t\rangle = \hat{H}|a,t\rangle.$$

Here $|a,t\rangle$ is the state of the system at time t.

- If $\hat{H}$ is time independent we can find solutions in the form

$$|a,t\rangle = e^{-\frac{i}{\hbar}E_a t}|a\rangle$$

where $|a\rangle$ satisfies:

$$H|a\rangle = E_a|a\rangle$$

The states $|a\rangle$ have well-defined energy E_a.

5 Example: a 2-state system

One of the simplest systems is a system that has just two states. Let us call them $|1\rangle$ and $|2\rangle$. This seems like a simplified situation but it has many applications. For example: spin-$\frac{1}{2}$ particles, atoms in a laser, etc. A generic state of the system is given by two complex numbers a_1 and a_2 as follows:

$$|a\rangle = a_1|1\rangle + a_2|2\rangle.$$

We can also represent it by a vector:

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

Any (linear) operator is represented by a 2×2 matrix with complex entries such that:

$$O|a\rangle = \begin{pmatrix} O_{11} & O_{12} \\ O_{21} & O_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} O_{11}a_1 + O_{12}a_2 \\ O_{21}a_1 + O_{22}a_2 \end{pmatrix}$$

Let us see what are the requirements that $\langle a|Oa\rangle$ will be real for any $|a\rangle$. We have:

$$\langle a|b\rangle = a_1^* b_1 + a_2^* b_2.$$

We calculate:

$$\langle a|Oa\rangle = O_{11}|a_1|^2 + O_{22}|a_2|^2 + O_{12}a_1^* a_2 + O_{21}a_2^* a_1.$$

In order for this to be real we need O_{11} and O_{22} to be real (take $a_1 = 1$ and $a_2 = 0$) and $O_{12} = O_{21}^*$. In other words, O is a hermitian matrix. Now let us take:

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21}^* & H_{22} \end{pmatrix}$$

Suppose H is independent of time (i.e. H_{ij} are numbers). To be a state with a well-defined energy, we need:

$$H|a\rangle = E_a|a\rangle.$$

This means that $|a\rangle$ is an eigen-vector of the matrix H with eigenvalue E_a. Recall that a Hermitian matrix always has real eigenvalues, so the energies, E_a are always real. We find:

$$E_a = \frac{H_{11} + H_{12} \pm \sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2}}{2},$$

So in general there are 2 possible energy states.

6 Expansion in a complete set of states

Any wave function $\psi(x)$ can be Fourier transformed as follows:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \hat{\psi}(k) e^{ikx}, \qquad \hat{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, \psi(x) e^{-ikx}.$$

Thus, any wave function can be written as a sum of "simpler" wave functions e^{ikx} which have a specific wave-number k and therefore a specific momentum $p = \hbar k$. This is true whether the particle is free or not!

Now let us take the problem of a particle in an infinite potential well of size a. The wavefunctions are nonzero only in the region $0 < x < a$. They are:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x, \qquad E_n = \frac{\hbar^2 \pi^2}{2ma^2} n^2, \qquad n = 1, 2, \ldots$$

Any function $\psi(x)$ that vanishes outside the region $0 < x < a$ can be expanded in the discrete Fourier expansion:

$$\psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

c_n are complex numbers. We think of it as if the function $\psi(x)$ describes a particle which is in a combination of states ψ_n. If $\int |\psi(x)|^2 dx = 1$, what does it say about the c_n's?

$$\int \psi(x)^* \psi(x) dx = \sum_{n,m} c_n^* c_m \int \psi_n(x)^* \psi_m(x) dx$$

Now we can calculate:

$$\int \psi_n(x)^* \psi_m(x) dx = \delta_{nm} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{otherwise} \end{cases}$$

so

$$\int |\psi(x)|^2 dx = \sum_{n=1}^{\infty} |c_n|^2$$

What is the interpretation of c_n? It is natural to interpret $|c_n|^2$ as the probability that the particle will be in the state $\psi_n(x)$ or in other words, will have the definite energy E_n. But what does that mean? The particle is already in the state $\psi(x)$, how can it also be in the state $\psi_n(x)$? To explain this, we will have to think when we are going to ask such a question practically. This has to do with the questions that we ask in the experiment. We will get to this subject shortly. But first let us talk more in general.

7 complete orthonormal set (abstractly)

The situation happens quite often. We have a set of wave-functions:

$$\psi_1(x), \psi_2(x), \cdots$$

such that all the other relevant functions (in our previous case, those that vanish outside $0 < x < a$) can be expanded as:

$$\psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x).$$

To specify $\psi(x)$, all we need to specify is the complex coefficients $c_1, c_2, \ldots$. Let us also suppose that the ψ_n's satisfy the **orthonormality** condition:

$$\int \psi_n(x)^* \psi_m(x) dx = \delta_{nm}$$

In this case we can calculate c_n, given $\psi(x)$, as follows:

$$c_n = \int \psi_n(x)^* \psi(x) dx.$$

It also follows that:

$$1 = \int |\psi(x)|^2 dx = \sum_{n=1}^{\infty} |c_n|^2.$$

So, we see that in general, if we have a set of **orthonormal** functions, which is **complete**, i.e. every function $\psi(x)$ can be expanded in them, it makes sense, mathematically, to ask the following question:

Given a particle in the state with wave-function $\psi(x)$, suppose we make an experiment that forces the particle to turn into having one of the following wave-functions:

$$\psi_1, \psi_2, \cdots$$

(we will see how to do that later) What is the probability that we get the n^{th} wave-function? The answer is $|c_n|^2$, where c_n is given by:

$$c_n = \int \psi_n(x)^* \psi(x) dx.$$

Why am I saying that it makes sense to ask the question? Because of the following reasons:

- The probabilities sum up to one: $\sum |c_n|^2 = 1$.
- If we start with $\psi(x) = \psi_m(x)$ the answer should be that the probability is one if $n = m$ and zero otherwise. This is true.

But how do we get such a series of complete orthonormal functions $\psi_n(x)$ and how do we make a physical experiment that forces the issue of which function this is?

Let us make contact with the physical quantities of position x and momentum p. What are they in Quantum Mechanics?

8 Hermitian Operators

We have seen that x and p are replaced with operators $\hat{x}$ and $\hat{p}$:

$$\begin{aligned}\hat{x} : \psi(x) &\longrightarrow x\psi(x),\\ \hat{p} : \psi(x) &\longrightarrow -i\hbar\tfrac{\partial\psi(x)}{\partial x},\end{aligned}$$

in general a physical quantity O is replaced with an operator $\hat{O}$. The rules say that the average of O (position, momentum, energy, ...) in a state $|a\rangle$ (wave function $\psi(x)$) is calculated as:

$$\langle O\rangle = \langle a|\hat{O}|a\rangle.$$

A physical operator must give a **real** average. Why is the momentum average real? because of integration by parts:

$$(\langle p\rangle)^* \;=\; i\hbar\int\psi\frac{\partial\psi^*}{\partial x} = -i\hbar\int\psi^*\frac{\partial\psi}{\partial x} = \langle p\rangle.$$

Let us see what else we can deduce about $\hat{O}$. Define:

$$|c\rangle = |a\rangle + \lambda|b\rangle.$$

For any complex number λ we get another $|c\rangle$. We know that:

$$\langle c|\hat{O}|c\rangle = \langle a|\hat{O}|a\rangle + |\lambda|^2\langle b|\hat{O}|b\rangle + \lambda\langle a|\hat{O}|b\rangle + \lambda^*\langle b|\hat{O}|a\rangle$$

So

$$\lambda\langle a|\hat{O}|b\rangle + \lambda^*\langle b|\hat{O}|a\rangle$$

must always be real. If we have that $\lambda A + \lambda^* B$ is real for any λ we put $\lambda = 1$ and we get $A + B$ is real which means that the imaginary part of A is minus the imaginary part of B. If we put $\lambda = i$ we get $A - B$ is imaginary which means that the real parts are the same. so $A = B^*$. So:

$$\langle a|\hat{O}b\rangle = \langle b|\hat{O}|a\rangle^* = \langle\hat{O}a|b\rangle$$

An operator that is physical has to satisfy this. As far as mathematics goes, an operator that satisfies this relation is called **Hermitian**.

9 Hermitian adjoint of an operator

Another way of saying this is as follows. Given any operator (physical or not) we can define the **Hermitian adjoint**, denoted $\hat{O}^\dagger$, as follows. The statement is that there exists an operator $\hat{O}^\dagger$ such that for any $|b\rangle$ and $|a\rangle$ we have the relation:

$$\langle \hat{O}^\dagger b|a\rangle = \langle b|\hat{O}a\rangle.$$

10 Example

In the 2-dimensional Hilbert space we studied above let us take:

$$\hat{O}|a\rangle = \begin{pmatrix} O_{11} & O_{12} \\ O_{21} & O_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} O_{11}a_1 + O_{12}a_2 \\ O_{21}a_1 + O_{22}a_2 \end{pmatrix}$$

that we calculated above, and let us take

$$|b\rangle = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}.$$

Then:

$$\begin{aligned} \langle b|\hat{O}a\rangle &= O_{11}a_1b_1^* + O_{12}a_2b_1^* + O_{21}a_1b_2^* + O_{22}a_2b_2^* \\ &= a_1(O_{11}b_1^* + O_{21}b_2^*) + a_2(O_{12}b_1^* + O_{22}b_2^*) \\ &= a_1(O_{11}^*b_1 + O_{21}^*b_2)^* + a_2(O_{12}^*b_1 + O_{22}^*b_2)^* \end{aligned}$$

So if we define:

$$\hat{O}^\dagger|b\rangle = \begin{pmatrix} O_{11}^*b_1 + O_{21}^*b_2 \\ O_{12}^*b_1 + O_{22}^*b_2 \end{pmatrix}$$

We have:

$$\langle b|\hat{O}a\rangle = \langle \hat{O}^\dagger b|a\rangle$$

In general if O_{ij} is the matrix element of $\hat{O}$ then

$$(\hat{O}^\dagger)_{ij} = \hat{O}_{ji}^*$$

11 Formulas for Hermitian conjugation

Suppose we have two operators $\hat{A}$ and $\hat{B}$ and we know their conjugates $\hat{A}^\dagger$ and $\hat{B}^\dagger$. We have a few rules as follows:

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger, \qquad (\lambda\hat{A} + \mu\hat{B})^\dagger = \lambda^*\hat{A}^\dagger + \mu^*\hat{B}^\dagger$$

We also have

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

We have found that Hermitian operators satisfy:

$$\langle a|\hat{O}b\rangle = \langle \hat{O}a|b\rangle$$

We can also write this as:

$$\langle \hat{O}^\dagger a|b\rangle = \langle \hat{O}a|b\rangle$$

For any $|a\rangle$ and $|b\rangle$. This implies $\hat{O} = \hat{O}^\dagger$.

12 Example: the operator for xp

Let us see what operator corresponds to $x \cdot p$. The first guess is to take:

$$x \cdot p \longrightarrow \hat{x}\hat{p}.$$

But this is not Hermitian:

$$(\hat{x}\hat{p})^\dagger = \hat{p}\hat{x} \neq \hat{x}\hat{p}.$$

In particular

$$\begin{aligned} \hat{p}\hat{x}\psi(x) &= -i\hbar\frac{\partial}{\partial x}(x\psi(x)) = -i\hbar\psi(x) - i\hbar x\frac{\partial\psi}{\partial x}, \\ \hat{x}\hat{p}\psi(x) &= -i\hbar x\frac{\partial\psi}{\partial x}. \end{aligned}$$

(**What do we do?**) One way to solve the problem is to define:

$$x \cdot p \longrightarrow \frac{1}{2}(\hat{x}\hat{p} + \hat{p}\hat{x}).$$

But there might be other ways. One has to see in the particular problem why exactly we need to have the operator corresponding to xp and then decide what to do.

13 Commutation relations

Since $\hat{A} \cdot \hat{B}$ is not necessarily the same as $\hat{B} \cdot \hat{A}$ it makes sense to define the difference:

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

This is called the **commutator** of $\hat{A}$ and $\hat{B}$.

14 Uncertainty relations

Given a state $|a\rangle$ let us define:

$$x_0 = \langle a|\hat{x}|a\rangle, \qquad p_0 = \langle a|\hat{p}|a\rangle.$$

and the operator:

$$\hat{O} = (\hat{x} - x_0) + i\lambda(\hat{p} - p_0)$$

Let us take λ to be real. Then $\hat{O}^\dagger = (\hat{x} - x_0) - i\lambda(\hat{p} - p_0)$. Let us define: $|b\rangle = \hat{O}|a\rangle$. Let us assume that $|a\rangle$ is normalized: $\langle a|a\rangle = 1$, and let's calculate:

$$\begin{aligned}\langle b|b\rangle &= \langle a|\hat{O}^\dagger\hat{O}|a\rangle = \langle a|(\hat{x} - x_0)^2|a\rangle + \lambda^2\langle a|(\hat{p} - p_0)^2|a\rangle + i\lambda\langle a|[\hat{x} - x_0, \hat{p} - p_0]|a\rangle \\ &= \Delta x^2 + \lambda^2\Delta p^2 - \hbar\lambda\end{aligned}$$

This is nonnegative for any λ. In particular, take $\lambda = \Delta x/\Delta p$. We find,

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

We can generalize to any two Hermitian operators:

$$0 \leq \Delta A^2 + \lambda^2\Delta B^2 + i\lambda\langle[\hat{A}, \hat{B}]\rangle,$$

so the discriminant is positive which means that:

$$4\Delta A^2\Delta B^2 \geq |\langle[\hat{A}, \hat{B}]\rangle|^2.$$

Note that $i[\hat{A}, \hat{B}]$ is a Hermitian operator.

15 Experiment and observables

Hermitian operators have the property that they have **real** eigenvalues and, furthermore, the eigenvectors corresponding to different eigenvalues are orthonormal to each other. What's more, in many cases of interest, the eigenvectors form a **complete set**. (We know that this is true about matrices. It is not necessarily true for infinite dimensional Hilbert spaces but it is always true for eigenvalues of Hamiltonians with potentials that are bounded from below.)

Thus, the set of eigenvectors of the Hamiltonian $\hat{H}$ forms a complete set of states. In general, we can do a physical measurement that measures some physical quantity (x, p, x^2+p^2 etc.). This corresponds to a Hermitian operator $\hat{O}$. The Hermitian operator has a complete set of eigenvectors:

$$\hat{O}|n\rangle = \lambda_n|n\rangle, \qquad n = 1, 2, \ldots$$

(For example, for the Hamiltonian $\lambda_n = E_n$)

An appropriate measurement forces the particle to be in one of these eigenstates. Thus, if we start with any state $|a\rangle$ and ask what is the probability that as a result of the measurement $\hat{O}$ will have the value λ_n the answer is as follows. Expand:

$$|a\rangle = \sum_n c_n|n\rangle, \qquad c_n = \langle n|a\rangle.$$

The probability is then $|c_n|^2$.

16 Compatible operators

Two Hermitian operators are said to be **compatible** if they commute with each other. This means that $[\hat{A}, \hat{B}] = 0$.

For compatible operators there is no restriction on $\Delta A \Delta B$. What's more, if $|a\rangle$ is an eigenstate of $\hat{A}$:

$$\hat{A}|a\rangle = \lambda|a\rangle \Longrightarrow \hat{A}\hat{B}|a\rangle = \lambda\hat{B}|a\rangle$$

then $\hat{B}|a\rangle$ is also an eigenstate with the same eigenvalue (unless it is zero). For compatible operators, one can find a basis of **mutual** eigenstates $|a, b\rangle$ such that,

$$\hat{A}|a, b\rangle = a|a, b\rangle, \qquad \hat{B}|a, b\rangle = b|a, b\rangle.$$

Operators that are compatible with $\hat{H}$ are very useful.

17 Expansion in a complete set of states – the continuum case

Above we assumed that the set of eigenstates of the operator $\hat{O}$ is discrete, $\lambda_1, \lambda_2, \ldots$ Some operators $\hat{O}$ have a continuum of eigenvalues and not a dis-

crete set. Other operators may have a combination of a discrete series and then a continuum. (**like what?**) Like a Hamiltonian of a potential well.

Let us take the operator $\hat{p}$. What are its eigenvalues? These are states $|p\rangle$ with wavefunction $\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$. Note that they cannot be normalized!

Any other state $|a\rangle$ with corresponding wave function $\psi(x)$ can be expanded as:

$$|a\rangle = \int dp\, c(p)|p\rangle, \qquad c(p) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{-ipx/\hbar}\psi(x)dx = \langle p|a\rangle.$$

What does orthonormality mean here? If we put $|a\rangle = |p'\rangle$ we must have $c(p) = \delta(p - p')$. **Why?** because there is only one way to write $|a\rangle$ as a combination of $|p\rangle$'s and that is with $c(p) = \delta(p - p')$. So from the formula above we learn:

$$\langle p|p'\rangle = \delta(p - p').$$

Note that this formula is **formal**. If we actually try to do the integral that defines $\langle p|p'\rangle$ we will get nonsense. The formula is only a shorthand for the theorem that if $|a\rangle = \int c(p')|p'\rangle dp'$ then $c(p) = \langle p|a\rangle$.

The basis we have just described is the one for which $\hat{p}$ is diagonal. That means that it satisfies:

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

What about the basis where $\hat{x}$ is diagonal? What wave function $\psi(x)$ would satisfy $x\psi(x) = x_0\psi(x)$? This must be $\psi_{x_0}(x) = \delta(x - x_0)$. Now we can write any state as:

$$|a\rangle = \int dx' c(x')|x'\rangle.$$

What would the $c(x')$ coefficients be? They are just $\psi_a(x)$, the wave function of $|a\rangle$. We also have:

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

To sum up:

$$\langle x|a\rangle = \psi_a(x).$$

18 Unitary operators

Hermitian matrices are matrices that satisfy $A^\dagger = A$. They have the property that their eigenvalues are real numbers.

Unitary matrices are matrices U that satisfy $U^\dagger = U^{-1}$. **What proerties do their eigenvalues have?** They are of the form $e^{i\delta}$. An easy way to remember this is to think what happens in the basis where they are diagonal. From linear algebra we recall that if A is Hermitian then e^{iA} is unitary. The matrix e^{iA} is defined as the Taylor series:

$$e^{iA} = 1 + iA - \frac{1}{2!}A^2 - \frac{i}{3!}A^3 + \frac{1}{4!}A^4 + \cdots$$

What is a more practical way to calculate e^{iA}? Given A we can change to a basis where A is diagonal. Then,

$$A = \begin{pmatrix} a_1 & & \\ & a_2 & \\ & & \ddots \end{pmatrix} \longrightarrow e^{iA} = \begin{pmatrix} e^{ia_1} & & \\ & e^{ia_2} & \\ & & \ddots \end{pmatrix}.$$

Generalizing to operators, we define unitary operators as operators that satisfy $\hat{U}^\dagger \hat{U} = 1$. The operator 1 is the operator that leaves the state as it is.

Let us summarize:

- If $\hat{A}$ is Hermitian then $e^{i\hat{A}}$ is unitary.
- Unitary operators have eigenvalues of the form $e^{i\phi}$.
- If $\hat{U}$ is unitary then $\langle \hat{U}a|\hat{U}b\rangle = \langle a|b\rangle$.

(These are all statements that we know about unitary matrices from linear algebra.)

19 Examples of unitary operators

A unitary operator in Quantum mechanics can be recognized by checking that it obeys:

$$\langle a|b\rangle = \langle \hat{U}a|\hat{U}b\rangle,$$

for all $|a\rangle$ and $|b\rangle$. Let us take a few examples.

$$\begin{aligned} \hat{U} : \psi(x) &\longrightarrow -\psi(x), \\ \hat{U}' : \psi(x) &\longrightarrow \psi(-x), \\ \hat{U}_a : \psi(x) &\longrightarrow \psi(x+a), \\ \hat{U}_k : \psi(x) &\longrightarrow e^{ikx}\psi(x), \end{aligned}$$

What are the eigenvalues of these operators? Note the difference between $\hat{U}$ and $\hat{U}'$. $\hat{U}'$ has both 1 and -1 eigenvalues.

Note that $\hat{U}_k$ can be written as $e^{i\hat{A}}$ for $\hat{A} = k\hat{x}$. What about $\hat{U}_a$? We claim that $\hat{A} = \frac{a}{\hbar}\hat{p}$. To see this note that:

$$e^{i\hat{A}} = e^{a\frac{d}{dx}} = 1 + a\frac{d}{dx} + \frac{1}{2!}a^2\frac{d^2}{dx^2} + \cdots$$

Which is just Taylor's series. However, not every function can be expanded in a Taylor series so what is a better argument? To change basis to the momentum basis!

$$|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int e^{ipx}|x\rangle$$

(This is just saying what the wave-function of $|p\rangle$ is!) Then:

$$\hat{U}_a|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int e^{\frac{i}{\hbar}px}\hat{U}_a|x\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int e^{\frac{i}{\hbar}px}|x-a\rangle = e^{\frac{i}{\hbar}pa}|p\rangle.$$

(Note that $\hat{U}_a|x_0\rangle$ has the wavefunction $\delta(x+a-x_0)$ so $\hat{U}_a|x_0\rangle = |x_0 - a\rangle$.)

20 Unitary operators acting on other operators

Suppose $\hat{U}(a) = e^{\frac{i}{\hbar}a\hat{p}}$ is the unitary operator discussed above that does $\hat{U}(a)|x\rangle = |x-a\rangle$. Let us calculate $\hat{U}(a)\hat{x}\hat{U}(a)^{-1}$ and $\hat{U}(a)\hat{p}\hat{U}(a)^{-1}$. We can calculate the first one in the basis $|x_0\rangle$:

$$\hat{U}(a)\hat{x}\hat{U}(a)^{-1}|x_0\rangle = \hat{U}(a)\hat{x}|x_0+a\rangle = \hat{U}(a)(x_0+a)|x_0+a\rangle = (x_0+a)|x_0\rangle.$$

There is another way of doing this. Define $\hat{O}(a) = \hat{U}(a)\hat{x}\hat{U}(a)^{-1}$. Let us calculate $d\hat{O}/da$. First note that:

$$\hat{U}(a)^{-1} = e^{-\frac{i}{\hbar}a\hat{p}} = \hat{U}(-a).$$

$$\begin{aligned}\frac{d\hat{O}(a)}{da} &= \frac{d\hat{U}(a)}{da}\hat{x}\hat{U}(-a) + \hat{U}(a)\hat{x}\frac{d\hat{U}(-a)}{da} = \frac{i}{\hbar}e^{\frac{i}{\hbar}a\hat{p}}\hat{p}\hat{x}e^{-\frac{i}{\hbar}a\hat{p}} - \frac{i}{\hbar}e^{\frac{i}{\hbar}a\hat{p}}\hat{x}\hat{p}e^{-\frac{i}{\hbar}a\hat{p}} \\ &= \frac{i}{\hbar}e^{\frac{i}{\hbar}a\hat{p}}\left\{\hat{p}\hat{x} - \hat{x}\hat{p}\right\}e^{-\frac{i}{\hbar}a\hat{p}} = e^{\frac{i}{\hbar}a\hat{p}}e^{-\frac{i}{\hbar}a\hat{p}} = 1.\end{aligned}$$

So

$$\hat{O}(a) = a + \widehat{\text{const}}.$$

The constant operator can be determined from:

$$\hat{O}(0) = \hat{x} \Longrightarrow \widehat{\text{const}} = \hat{x} \Longrightarrow \hat{O}(a) = \hat{x} + a.$$

21 Translation in time

Now we return to Schrödinger's equation. In the Hilbert space notation we can write it as:

$$i\hbar\frac{d}{dt}|t\rangle = \hat{H}(t)|t\rangle$$

where $\hat{H}$ is the Hermitian (perhaps time-dependent) Hamiltonian operator. $|t\rangle$ represents the state of the particle at time t. In the case of functions $\psi(x)$ we use the Hamiltonian

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

We now define the **time-translation** operator $\hat{U}(t', t)$ (for $t' \geq t$) as follows. Given a state $|a\rangle$ we think of it as a state at time t and solve Schrödinger's equation with the initial condition that $|t\rangle = |a\rangle$. We then find $|t'\rangle$ and define

$$\hat{U}(t', t)|t\rangle = |t'\rangle.$$

$\hat{U}(t', t)$ is the operator that takes us from time t to a later time t'. Is $\hat{U}$ **Hermitian? Unitary?** or **None?** It is Unitary. We will prove it below. First let us see what it satisfies.

- $\hat{U}(t, t) = 1$, the identity operator.
- $\hat{U}(t'', t) = \hat{U}(t'', t')\hat{U}(t', t)$.

Next we calculate:

$$i\hbar\frac{\partial}{\partial t'}\hat{U}(t', t)|t\rangle = i\hbar\frac{\partial}{\partial t'}|t'\rangle = \hat{H}(t')|t'\rangle = \hat{H}(t')\hat{U}(t', t)|t\rangle.$$

This is true for any initial value of $|t\rangle$. So we find that as an **operator** we have:

$$i\hbar\frac{\partial}{\partial t'}\hat{U}(t', t) = \hat{H}(t')\hat{U}(t', t).$$

The way to think about it is as follows. in the simple Hilbert spaces we had, $\hat{U}$ would be a matrix such that each element of it is a function of t' and t. The left-hand-side (LHS) is an equation for every element of the matrix $\hat{U}$ and is a differential equation in t'. Let us also calculate $i\hbar\frac{\partial}{\partial t}\hat{U}(t', t)$. We do

this as follows:

$$\begin{aligned} 0 &= i\hbar\frac{\partial}{\partial t}|t'\rangle = i\hbar\frac{\partial}{\partial t}\left(\hat{U}(t',t)|t\rangle\right) = i\hbar\left(\frac{\partial}{\partial t}\hat{U}(t',t)\right)|t\rangle + i\hbar\hat{U}(t',t)\frac{\partial}{\partial t}|t\rangle \\ &= i\hbar\left(\frac{\partial}{\partial t}\hat{U}(t',t)\right)|t\rangle + \hat{U}(t',t)\hat{H}(t)|t\rangle, \\ i\hbar\frac{\partial}{\partial t}\hat{U}(t',t) &= -\hat{U}(t',t)\hat{H}(t). \end{aligned}$$

In the time-independent case things are much simpler. We have

$$\hat{U}(t',t) = e^{-\frac{i}{\hbar}(t'-t)\hat{H}}.$$

One way to see this is to go to a basis of eigenstate of $\hat{H}$.

To prove that $U(t',t)$ is unitary in general, we can differentiate $U(t',t)^\dagger U(t',t)$ and show that it stays 1. First note that:

$$\frac{\partial\hat{U}(t',t)^\dagger}{\partial t'} = \left\{-\frac{i}{\hbar}\hat{H}(t')\hat{U}(t',t)\right\}^\dagger = \frac{i}{\hbar}\hat{U}(t',t)^\dagger\hat{H}(t')$$

$$\begin{aligned} \frac{\partial}{\partial t'}\left\{\hat{U}(t',t)^\dagger\hat{U}(t',t)\right\} &= \frac{\partial\hat{U}(t',t)^\dagger}{\partial t'}\hat{U}(t',t) + \hat{U}(t',t)^\dagger\frac{\partial\hat{U}(t',t)}{\partial t'} \\ &= \frac{i}{\hbar}\hat{U}(t',t)^\dagger\hat{H}(t')\hat{U}(t',t) - \frac{i}{\hbar}\hat{U}(t',t)^\dagger\hat{H}(t')\hat{U}(t',t) = 0. \end{aligned}$$

The initial condition is at $t' = t$ where we have:

$$\hat{U}(t,t)^\dagger\hat{U}(t,t) = 1.$$

So $\hat{U}(t',t)^\dagger\hat{U}(t',t) = 1$ for all t'.

22 Heisenberg picture for operators

Suppose we wish to calculate the expectation value of an operator as a function of time. Suppose we know that at time $t = 0$ the state was $|a\rangle$. Then

$$\begin{aligned} \langle\hat{O}\rangle_t &= \langle t|\hat{O}|t\rangle = \langle\hat{U}(t,0)a|\hat{O}|\hat{U}(t,0)a\rangle \\ &= \langle a|\hat{U}(t,0)^\dagger\hat{O}\hat{U}(t,0)|a\rangle = \langle a|\hat{U}(t,0)^{-1}\hat{O}\hat{U}(t,0)|a\rangle. \qquad (4) \end{aligned}$$

One can define:

$$\hat{O}\{t\} = \hat{U}(t,0)^{-1}\hat{O}\hat{U}(t,0) = \hat{U}(t,0)^\dagger\hat{O}\hat{U}(t,0)$$

Let us see what this satisfies. First $\hat{O}\{0\} = \hat{O}$. Next we find:

$$\langle \hat{O} \rangle_t = \langle a | \hat{O}\{t\} | a \rangle.$$

The derivative is:

$$\begin{aligned} i\hbar \frac{d}{dt}\hat{O}\{t\} &= i\hbar \frac{d\hat{U}(t,0)^\dagger}{dt}\hat{O}\hat{U}(t,0) + i\hbar \hat{U}(t,0)^\dagger \hat{O}\frac{d\hat{U}(t,0)}{dt} \\ &= -\hat{U}(t,0)^\dagger \hat{H}(t)\hat{O}\hat{U}(t,0) + \hat{U}(t,0)^\dagger \hat{O}\hat{H}(t)\hat{U}(t,0) \\ &= -\hat{U}(t,0)^\dagger \hat{H}(t)\hat{U}(t,0)\hat{U}(t,0)^\dagger \hat{O}\hat{U}(t,0) + \hat{U}(t,0)^\dagger \hat{O}\hat{U}(t,0)\hat{U}(t,0)^\dagger \hat{H}(t)\hat{U}(t,0) \\ &= -\hat{H}\{t\}\hat{O}\{t\} + \hat{O}\{t\}\hat{H}\{t\} = [\hat{O}\{t\}, \hat{H}\{t\}]. \end{aligned}$$

Note the difference between $\hat{H}(t)$ and:

$$\hat{H}\{t\} = U(t,0)^\dagger \hat{H}(t) U(t,0).$$

23 Example

Take the Hamiltonian

$$\hat{H}(t) = \frac{1}{2m}\hat{p}^2 + V(\hat{x}, t).$$

We can write: $\hat{p} = \hat{p}\{0\}$ and $\hat{x} = \hat{p}\{0\}$. Then:

$$\begin{aligned} \hat{H}(t) &= \frac{1}{2m}\hat{p}\{0\}^2 + V(\hat{x}\{0\}, t), \\ \hat{H}\{t\} &= \frac{1}{2m}\hat{p}\{t\}^2 + V(\hat{x}\{t\}, t), \end{aligned}$$

We find the equations:

$$i\hbar \frac{d}{dt}\hat{x}\{t\} = [\hat{H}\{t\}, \hat{x}\{t\}] = \frac{1}{m}\hat{p}\{t\}.$$

We use the fact that:

$$\begin{aligned} [\hat{x}\{t\}, \hat{p}\{t\}] &= \hat{U}(t,0)^\dagger \hat{x}\hat{U}(t,0)\hat{U}(t,0)^\dagger \hat{p}\hat{U}(t,0) - \hat{U}(t,0)^\dagger \hat{p}\hat{U}(t,0)\hat{U}(t,0)^\dagger \hat{x}\hat{U}(t,0) \\ &= \hat{U}(t,0)^\dagger \left\{\hat{x}\hat{p} - \hat{x}\hat{p}\right\} \hat{U}(t,0) = i\hbar. \end{aligned}$$

Physics 505
Week 4, Oct 7, 1999
Ori Ganor

Angular Momentum

24 Free particle in 3D

Schrödinger's equation for a particle in 3D looks like this:

$$-i\hbar\frac{\partial\psi(x,y,z,t)}{\partial t} = \left[-\frac{\hbar^2}{2M}\nabla^2 + V(x,y,z,t)\right]\psi(x,y,z,t),$$

where

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

When V is independent of time we are looking for eigenvalues of

$$\hat{H} = \frac{1}{2M}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + V(\hat{x},\hat{y},\hat{z}).$$

25 spherical variables

It often happens that V depends only on $r = \sqrt{x^2+y^2+z^2}$. We can then change to spherical variables:

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

The Laplacian becomes

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

We look for solutions of Schrödinger's equation by separation of variables:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

We get the requirements:

$$\begin{aligned} ER &= -\frac{\hbar^2}{2M}\cdot\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\hbar^2}{2M}\cdot\frac{\lambda}{r^2}R + V(r)R, \\ \lambda Y &= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}. \end{aligned}$$

The aim of this week is to find the functions Y and the eigenvalues λ.

26 Angular momentum

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

It is helpful to summarize this as:

$$\hat{L}_i = \sum_{jk} \epsilon_{ijk}\hat{x}_j\hat{p}_k$$

where

$$\begin{aligned} \epsilon_{123} = \epsilon_{231} = \epsilon_{312} &= +1, \\ \epsilon_{321} = \epsilon_{132} = \epsilon_{213} &= -1, \end{aligned}$$

and $\epsilon_{ijk} = 0$ if two out of i, j, k are equal. Note that since $\hat{y}$ and $\hat{p}_z$ commute, it does not matter in which order we write $\hat{y}\hat{p}_z$ or $\hat{p}_z\hat{y}$. We wish to understand what possible eigenvalues these operators can take. For that, we calculate the commutation relations:

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

This means that we cannot specify angular momentum in two directions simultaneously unless all of them are zero. For example, if $\hat{L}_z|a\rangle = l_z|a\rangle$ and $\hat{L}_y|a\rangle = l_y|a\rangle$ then

$$\hat{L}_x|a\rangle = -\frac{i}{\hbar}[\hat{L}_y, \hat{L}_z]|a\rangle = 0$$

The other commutators then imply that the rest are zero as well.

Can we find another compatible operator? It turns our that

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

commutes with $\hat{L}_x$,$\hat{L}_y$ and $\hat{L}_z$. So we can look for mutual eigenstates of $\hat{L}_z$ and $\hat{L}^2$.

We can also calculate how $\hat{L}_x$,$\hat{L}_y$ and $\hat{L}_z$ act on a function $\psi(r, \theta, \phi)$. It is easier to write the expressions for $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$. It turns out that:

$$\hat{L}_z\psi = -i\hbar\frac{\partial\psi}{\partial\phi}, \qquad \hat{L}_+ = \hbar e^{i\phi}(\frac{\partial}{\partial\theta} + i\cot\theta\,\frac{\partial}{\partial\phi}), \qquad \hat{L}_- = \hbar e^{-i\phi}(-\frac{\partial}{\partial\theta} + i\cot\theta\,\frac{\partial}{\partial\phi}).$$

We have seen that $\hat{L}_z$ commutes neither with $\hat{L}_x$ nor with $\hat{L}_y$. So, in general we cannot specify mutual eigenfunctions. (This is true **except for what**

case? Except for functions $\psi(r)$ that are independent of both θ and ϕ.) Let us calculate:

$$\begin{aligned}
[\hat{L}_x^2, \hat{L}_z] &= \hat{L}_x[\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z]\hat{L}_x = -i\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x), \\
[\hat{L}_y^2, \hat{L}_z] &= \hat{L}_y[\hat{L}_y, \hat{L}_z] + [\hat{L}_y, \hat{L}_z]\hat{L}_y = i\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x), \\
[\hat{L}_z^2, \hat{L}_z] &= 0, \\
[\hat{L}^2, \hat{L}_z] &= 0.
\end{aligned}$$

Similarly,

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

We can also write down:

$$\begin{aligned}
\hat{L}^2 &= \hat{L}_+\hat{L}_- + \hat{L}_z^2 - \hbar\hat{L}_z, \\
\hat{L}^2 &= \hat{L}_-\hat{L}_+ + \hat{L}_z^2 + \hbar\hat{L}_z,
\end{aligned}$$

We can substitute the expressions for $\hat{L}_z$ and $\hat{L}_\pm$ found above, and write:

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

27 The differential equation

We wish to find eigenvalues of $\hat{L}^2$.

$$\hat{L}^2\Phi(\theta,\phi) = \lambda\hbar^2\Phi(\theta,\phi).$$

We do in by separation of variables.

$$\Phi(\theta,\phi) = Y(\theta)\varphi(\phi)$$

This requires

$$\frac{d^2\varphi}{d\phi^2} = \mu\varphi.$$

μ has to be a constant. This implies $\varphi = e^{im\phi}$ and $\mu = m^2$. Here m must be an integer. **Why?** because ϕ is periodic. This also means that:

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

The remaining equation for Y now looks like:

$$-\frac{m^2}{\sin^2\theta}Y + \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dY}{d\theta}\right) = \lambda Y$$

We can change variables to $\xi = \cos\theta$ and find:

$$-\frac{1}{\sin\theta}\frac{d}{d\theta} = \frac{d}{d\xi}$$

Thus:

$$-m^2Y + (1-\xi^2)\frac{d}{d\xi}\left((1-\xi^2)Y'(\xi)\right) = \lambda(1-\xi^2)Y$$

Here $-1 < \xi < 1$. We can write it as:

$$Y'' - \frac{2\xi}{1-\xi^2}Y' - \frac{\lambda}{1-\xi^2}Y - \frac{m^2}{(1-\xi^2)^2}Y = 0.$$

The coefficients are singular and in general the solutions can be singular. We require that there is no singularity, i.e. the solutions are finite at $x = \pm 1$. To see what this means let us change variables again to $x = 1 - y$:

$$Y'' + \frac{2-2y}{y(2-y)}Y' - \frac{\lambda}{y(2-y)}Y - \frac{m^2}{y^2(2-y)^2}Y = 0.$$

Near $y \approx 0$ the solution behaves as $Y \sim y^s$ with:

$$s(s-1) + s - \frac{1}{4}m^2 = 0 \Longrightarrow s = \pm m.$$

For $m \neq 0$ only the solution $Y \sim y^{|m|}$ is physical. For $m = 0$ there is one solution that behaves like a nonzero constant. The other behaves like $Y \sim \log y$. In fact if the first solution is Y_0 then the second is $Y_0 \log y + Y_1$ where Y_1 is analytic.

28 Legendre Polynomials

The solution of the equation is the **associated Legendre functions** that are defined as follows:

$$P_l^m(y) = (1-y^2)^{m/2}\left(\frac{d}{dy}\right)^m P_l(y), \qquad m = 0, 1, 2, \ldots,$$

where the **Legendre polynomials** are defined as:

$$P_l(y) = \frac{1}{2^l l!}\left(\frac{d}{dy}\right)^l (y^2-1)^l.$$

29 Spherical harmonics

The wave functions that are the eigenvalues are called **spherical harmonics**. They are:

$$Y_{lm}(\theta,\phi) = \begin{cases} (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\phi} P_l^m(\cos\theta) & \text{for } m \geq 0 \\ \sqrt{\frac{(2l+1)(l+m)!}{4\pi(l-m)!}} e^{im\phi} P_l^{-m}(\cos\theta) & \text{for } m \leq 0 \end{cases}$$

The solutions, given the boundary conditions of being finite, turn out to be:

$$Y_{lm}(\theta,\phi) = (-1)^l \sqrt{\frac{(2l+1)(l+m)!}{4\pi(l-m)!}} \frac{1}{2^l l! \sin^m\theta} \frac{d^{l-m}}{d(\cos\theta)^{l-m}} \sin^{2l}\theta\, e^{im\phi}.$$

How is the normalization determined?

$$1 = \int |Y_{lm}|^2 \sin\theta\, d\theta\, d\phi$$

The $(-1)^l$ is just a matter of convention. We will see how to get the solution soon. Here $\lambda = l(l+1)$.

30 Properties

What does the **orthonormality** condition turn into in spherical variables:

$$\int \sin\theta\, d\theta\, d\phi Y_{l'm'}(\theta,\phi)^* Y_{lm}(\theta,\phi) = \delta_{ll'}\delta_{mm'}.$$

For a complete set of functions:

$$\psi_1(x), \psi_2(x), \cdots$$

we also have:

$$\sum_n \psi_n(x)^* \psi_n(x') = \delta(x - x').$$

to prove it just take any wave function $\psi(x)$ and integrate both sides. We get:

$$\sum_n c_n \psi_n(x') = \psi(x'), \qquad c_n = \int \psi_n(x)^* \psi(x) dx.$$

The spherical harmonics are no exception. We have:

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}(\theta,\phi) Y_{lm}(\theta',\phi')^* = \frac{1}{\sin\theta} \delta(\theta - \theta')\delta(\phi - \phi').$$

What this means is that any function $\psi(\theta, \phi)$ can be written as:

$$\psi(\theta,\phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm} Y_{lm}(\theta,\phi), \qquad c_{lm} = \int Y_{lm}(\theta,\phi)^* \psi(\theta,\phi) \sin\theta \, d\theta \, d\phi$$

As an example we can state the following useful identity:

$$P_l(\mathbf{n}\cdot\mathbf{n}') = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{lm}(\theta,\phi) Y_{lm}(\theta',\phi')^*.$$

Here $\mathbf{n}$ is a unit vector in direction (θ, ϕ) and $\mathbf{n}'$ is a unit vector in direction (θ', ϕ').

We first point out that $P_l(\mathbf{n}\cdot\mathbf{n}')$, like any function of θ and ϕ, can be written as a sum:

$$\sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} c_{l'm'}(\theta',\phi') Y_{l'm'}(\theta,\phi)$$

The functions $c_{l'm'}(\theta', \phi')$ can also be expanded as:

$$c_{l'm'} = \sum_{l''m''} a_{l'm'l''m''} Y_{l''m''}(\theta',\phi')^*$$

So we just have to determine the coefficients $a_{l'm'l''m''}$.

31 Solution via commutation relations

Let us try to solve the problem of eigenvalues of $\hat{L}^2$ without ever writing a differential equation! We note the following:

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

Suppose ψ is a wavefunction with eigenvalues:

$$\hat{L}^2 \psi = \hbar^2 \lambda \psi, \qquad \hat{L}_z \psi = \hbar m \psi.$$

Then, what do we know about $\hat{L}_+\psi$? We know that it has the same eigenvalue of $\hat{L}^2$ and its $\hat{L}_z$ eigenvalue is bigger by $\hbar$. Hence, we call $\hat{L}_+$ a **raising operator**. Now suppose we start with a certain value $|m\rangle$ and given eigenvalue λ. Then

$$\hat{L}_+^n |m\rangle = \underbrace{\hat{L}_+ \cdots \hat{L}_+}_{n} |m\rangle$$

has $\hat{L}_z$ eigenvalue of $(m+n)$. Similarly $\hat{L}_-^n|m\rangle$ has $\hat{L}_z$ eigenvalue of $(m-n)$. We cannot take n too big. **Why?** Because $\hat{L}_z^2$ cannot exceed $\hat{L}^2$. Why is that true in QM as well? Set

$$|a\rangle = \hat{L}_+|m\rangle.$$

We have

$$0 \leq \langle a|a\rangle = \langle m|\hat{L}_+^\dagger \hat{L}_+|m\rangle = \langle m|\hat{L}_-\hat{L}_+|m\rangle = \langle m|(\hat{L}^2 - \hat{L}_z^2 - \hat{L}_z)|m\rangle = \hbar^2(\lambda - m(m+1))\langle m|m\rangle.$$

So:

$$\lambda \geq m(m+1).$$

So, if we apply $\hat{L}_+$ many times at some point we get 0. Let us denote this highest value by l. Then:

$$\hat{L}_+|l\rangle = 0.$$

Assuming $|l\rangle \neq 0$. Thus we find from the inequality above that: $\lambda = l(l+1)$. We can now act with $\hat{L}_-$ to get wavefunctions with ever lower m. Let us denote by $|m\rangle$ the **normalized** wave function. Let us set $|b\rangle = \hat{L}_-|m\rangle$ and calculate

$$\langle b|b\rangle = \langle m|\hat{L}_+\hat{L}_-|m\rangle = \hbar^2(l(l+1) - m(m-1)) = \hbar^2(l+1-m)(l+m)$$

So:

$$|m-1\rangle = \frac{1}{\hbar\sqrt{(l+m)(l+1-m)}}\hat{L}_-|m\rangle.$$

How low can we get with m**?** We can go on until we get $|b\rangle = \hat{L}_-|m\rangle = 0$. This implies:

$$\langle b|b\rangle = \hbar^2(l+1-m)(l+m) = 0 \Longrightarrow m = -l.$$

We find:

$$|lm\rangle \sim \hat{L}_+^{l+m}|l, -l\rangle$$

Now let us work out the normalization. For,

$$|a\rangle = \hat{L}_+|lm\rangle,$$

we found

$$\langle a|a\rangle = \hbar^2(l(l+1) - m(m+1)) = \hbar^2(l-m)(l+m+1)$$

So:

$$\begin{aligned} |lm\rangle &= \frac{1}{\hbar^{l+m}\sqrt{(l+m)(l+m-1)\cdots 1\cdot(l-m+1)(l-m+2)\cdots(2l)}}\hat{L}_+^{l+m}|l,-l\rangle \\ &= \hbar^{-(l+m)}\sqrt{\frac{(l-m)!}{(l+m)!(2l)!}}\hat{L}_+^{l+m}|l,-l\rangle. \end{aligned} \tag{5}$$

32 To sum up

1. The eigenvalues of $\hat{L}^2$ are $\hbar^2 l(l+1)$ with $l = 0, 1, 2, \ldots$ an integer.
2. For a given l, we get states $|l,m\rangle$ with $\hat{L}_z$ eigenvalue of $\hbar m$ and $m = -l, -(l-1), \ldots, 0, \ldots, (l-1), l$. There are $(2l+1)$ states.
3. There is the following relation: $|m-1\rangle = \frac{1}{\hbar\sqrt{(l+m)(l+1-m)}}\hat{L}_-|m\rangle$. Similarly: $|m+1\rangle = \frac{1}{\hbar\sqrt{(l-m)(l+m+1)}}\hat{L}_+|m\rangle$.
4. We can repeat this to write: $|lm\rangle = \hbar^{-(l+m)}\sqrt{\frac{(l-m)!}{(l+m)!(2l)!}}\hat{L}_+^{l+m}|l,-l\rangle$. Similarly: $|lm\rangle = \hbar^{-(l-m)}\sqrt{\frac{(l+m)!}{(l-m)!(2l)!}}\hat{L}_-^{l-m}|l,l\rangle$.

The wave-functions of a particle in a potential $V(r)$ are of the form:

$$\psi(r,\theta,\phi) = R_l(r)Y_{lm}(\theta,\phi).$$

1. To determine $R_l(r)$ we need to know the potential $V(r)$. It then satisfies:
$$ER = -\frac{\hbar^2}{2M}\cdot\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\hbar^2}{2M}\cdot\frac{\lambda}{r^2}R + V(r)R.$$
2. To determine Y_{lm} we **do not** need to know $V(r)$.
3. There are $(2l+1)$ different values of m for any given value of l. These values are $m = -l, \ldots, l$.
4. For different l's one can, in general, have different wave-functions R_l and different energies E_l.
5. For a given l there are several solutions $R_{ln}(r)$ and energies E_{ln}.

6. For each such solution, there are $(2l+1)$ corresponding states all with the same energy and radial part $R_{ln}(r)$. They differ just in the value of m in Y_{lm}.

33 The wave functions

We can find the wave function $|l,l\rangle$ by writing:

$$\hat{L}_+|l,l\rangle = 0 \Longrightarrow e^{i\phi}(\frac{\partial}{\partial\theta} + i\cot\theta\,\frac{\partial}{\partial\phi})\psi_{ll}(\theta,\phi) = 0$$

since $\psi_{ll} = Y(\theta)e^{il\phi}$ we find:

$$Y' - l\cot\theta\, Y = 0 \Longrightarrow Y = c\sin^l\theta.$$

34 Half integral spin

If we are talking about a wave-function $\psi(x,y,z)$ of a particle we have seen that m must be an integer because the wave function must be periodic in ϕ. However, if we just have operators $\hat{J}_x, \hat{J}_y$ and $\hat{J}_z$ with the same commutation relations as $\hat{L}_x, \hat{L}_y$ and $\hat{L}_z$ we can have more possibilities. Let us assume that we have a finite dimensional Hilbert space for which such a triple of operators with the given commutation relations exist. This will be relevent to spin-$\frac{1}{2}$ particles. As before $\hat{J}_z$ and $\hat{J}^2$ commute and we are looking for states which are mutual eigenstates. As before if we start with a state and apply $\hat{J}_+$ many times we eventually get a state $|j,j\rangle$ such that $\hat{J}_+|j,j\rangle = 0$. For this state, we have seen that

$$\hat{J}^2|j,j\rangle = \hbar^2 j(j+1)|j,j\rangle, \qquad \hat{J}_z|j,j\rangle = \hbar j|j,j\rangle.$$

j does not necessarily have to be an integer. Now we apply $\hat{J}_-$ and obtain the states:

$$|j,j-1\rangle, |j,j-2\rangle, \cdots, |j,m\rangle, \cdots$$

This would have to stop once we reach a state that satisfies

$$\hat{J}_-|j,m\rangle = 0 \Longrightarrow m = -j.$$

On the other hand $|j,m\rangle$ is obtained from $|j,j\rangle$ by an applying $\hat{J}_-$ an integer number of times so:

$$j-(-j)=2j=\text{integer}.$$

The smallest value of j is $j=0$. The next possible value is $j=\frac{1}{2}$. This system has two states:

$$|j=\frac{1}{2},m=+\frac{1}{2}\rangle,\qquad |j=\frac{1}{2},m=-\frac{1}{2}\rangle.$$

These are often denoted as:

$$|\uparrow\rangle,|\downarrow\rangle.$$

$\hat{J}_x,\hat{J}_y$ and $\hat{J}_z$ are denoted in this case by $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$. Given what we said above, once can find how $\hat{S}_i$ act in this basis. They act as follows:

$$\hat{S}_x=\frac{\hbar}{2}\sigma_x,\qquad \hat{S}_y=\frac{\hbar}{2}\sigma_y,\qquad \hat{S}_z=\frac{\hbar}{2}\sigma_z.$$

The **Pauli matrices** are given by:

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

Note that they are Hermitian matrices with eigenvalues ±1.

35 Generators of rotation

An infinitesimal rotation of a system around an axis $\vec{n}$ and by angle ϵ (counter clockwise) is given by:

$$\psi^{(new)}(\vec{r})=\psi^{(old)}(\vec{r}-\epsilon\vec{n}\times\vec{r})=\psi^{(old)}(\vec{r})-(\epsilon\vec{n}\times\vec{r})\cdot\nabla\psi^{(old)}=(1-\epsilon\vec{n}\cdot\vec{r}\times\nabla)\psi^{(old)}$$

So an infinitesimal rotation adds:

$$-\frac{i}{\hbar}\epsilon\vec{n}\cdot\hat{L}\psi.$$

A large rotation can be written in terms of Euler angles α,β and γ. It is useful to define the following functions

$$\mathcal{D}^{(j)}_{m'm}(\alpha\beta\gamma)=\langle j,m'|e^{-\frac{i}{\hbar}\alpha\hat{J}_z}e^{-\frac{i}{\hbar}\beta\hat{J}_y}e^{-\frac{i}{\hbar}\gamma\hat{J}_z}|j,m\rangle=e^{-i(m'\alpha+m\gamma)}\langle j,m'|e^{-\frac{i}{\hbar}\beta\hat{J}_y}|j,m\rangle.$$

36 Matrix elements of position and momentum

The purpose of this section is to get some general features of **matrix elements** of vectors. We have seen that the wave-functions are in general of the form

$$\psi(r,\theta,\phi) = R_{ln}(r)Y_{lm}(\theta,\phi).$$

Here n denotes a general "tag" to indicate that there are several (perhaps a continuum) of solutions to:

$$E_{ln}R_{ln} = -\frac{\hbar^2}{2M}\cdot\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\hbar^2}{2M}\cdot\frac{\lambda}{r^2}R_{ln} + V(r)R_{ln},$$

for a given l.

Let us denote this state by $|nlm\rangle$. Let us take another state $|n'l'm'\rangle$.

We wish to consider the following expressions:

$$\langle n'l'm'|\hat{x}|nlm\rangle, \qquad \langle n'l'm'|\hat{y}|nlm\rangle, \qquad \langle n'l'm'|\hat{z}|nlm\rangle.$$

As we will see later on in this course, such "matrix-elements" are extremely important because they appear in questions like: **what is the probability that the particle in state $|nlm\rangle$ will absorb or emit a photon and thereby enter the state $|n'l'm'\rangle$?**

It turns out that there are some general features of such matrix elements that can be stated without knowing $V(r)$. We have the following expressions:

$$\begin{aligned}
\langle n'l'm'|\hat{x}|nlm\rangle &= \int \psi^*_{n'l'm'} r\sin\theta\cos\phi\,\psi_{nlm} r^2 dr\sin\theta d\theta d\phi \\
&= \int r^3 R^*_{n'l'}R_{nl}dr\int Y^*_{l'm'}Y_{lm}\sin\theta\cos\phi\,\sin\theta d\theta d\phi, \\
\langle n'l'm'|\hat{y}|nlm\rangle &= \int \psi^*_{n'l'm'} r\sin\theta\sin\phi\,\psi_{nlm} r^2 dr\sin\theta d\theta d\phi = \cdots, \\
\langle n'l'm'|\hat{z}|nlm\rangle &= \int \psi^*_{n'l'm'} r\cos\theta\,\psi_{nlm} r^2 dr\sin\theta d\theta d\phi = \cdots,
\end{aligned}$$

They all have a piece $\int r^3 R^*_{n'l'}R_{nl}dr$ that is impossible to calculate without knowing $V(r)$ but is independent of m and m'. They also have and another piece that can be calculated without knowing $V(r)$:

$$\int Y^*_{l'm'}Y_{lm}\sin\theta\cos\phi\sin\theta d\theta d\phi,\ \int Y^*_{l'm'}Y_{lm}\sin\theta\sin\phi\sin\theta d\theta d\phi,\ \int Y^*_{l'm'}Y_{lm}\cos\theta\sin\theta d\theta d\phi.$$

Let us define:

$$\hat{x}_\pm = \hat{x} \pm i\hat{y}.$$

Let us calculate the commutation relations:

$[\hat{L}_+, \hat{x}_+] = 0$ $\quad [\hat{L}_z, \hat{x}_+] = \hbar\hat{x}_+$ $\quad [\hat{L}_-, \hat{x}_+] = -2\hbar z$
$[\hat{L}_+, \hat{x}_-] = 2\hbar z$ $\quad [\hat{L}_z, \hat{x}_-] = -\hbar\hat{x}_-$ $\quad [\hat{L}_-, \hat{x}_-] = 0$
$[\hat{L}_+, \hat{z}] = -\hbar\hat{x}_+$ $\quad [\hat{L}_z, \hat{z}] = 0$ $\quad [\hat{L}_-, \hat{z}] = \hbar\hat{x}_-$

What does that mean? Let us start with $\langle n'l'm'|\hat{x}_+|nlm\rangle$. Note that:

$$\hat{L}_z\hat{x}_+|nlm\rangle = \hat{x}_+\hat{L}_z|nlm\rangle + [\hat{L}_z, \hat{x}_+]|nlm\rangle = \hbar(m+1)|nlm\rangle.$$

So $\langle n'l'm'|\hat{x}_+|nlm\rangle = 0$ unless $m+1 = m'$. (Eigenstates with different eigenvalues of $\hat{L}_z$ are orthogonal.) Similarly, $\langle n'l'm'|\hat{x}_-|nlm\rangle = 0$ unless $m-1 = m'$ and $\langle n'l'm'|\hat{z}|nlm\rangle = 0$ unless $m = m'$.

We continue to calculate:

$$\begin{aligned}\langle n'l'm'|\hat{x}_+|nlm\rangle &= \hbar^{-(l+m)}\sqrt{\frac{(l-m)!}{(l+m)!(2l)!}}\langle n'l'm'|\hat{x}_+\hat{L}_+^{l+m}|l,-l\rangle \\ &= \hbar^{-(l+m)}\sqrt{\frac{(l-m)!}{(l+m)!(2l)!}}\langle n'l'm'|\hat{L}_+^{l+m}\hat{x}_+|l,-l\rangle.\end{aligned}$$

Now notice that:

$$\begin{aligned}\hat{L}_-^{l+m}|n'l'm'\rangle &= \hbar\sqrt{(l'+m')(l'+1-m')}\hat{L}_-^{l+m-1}|n'l'm'\rangle = \cdots \\ &= \hbar^{l+m}\sqrt{\frac{(l'+m')!(l'+1-m')!}{(l'+m'-l-m)!(l'+1-m'-l-m)!}}|n'l'(m'-l-m)\rangle.\end{aligned}$$

So unless

$$m'-l-m = 1-l \geq -l' \Longrightarrow l' \geq l-1,$$

The matrix element in question is zero. Similarly we can start by writing $|n'l'm'\rangle$ using $\hat{L}_-^{l'-m'}|n'l'l'\rangle$ we find:

$$l \geq m+l'-m' = l'-1 \Longrightarrow l' \leq l+1.$$

We can also obtain relations $l \geq l'-1$ and $l \leq l'+1$. To do this, we start with:

$$|n'l'm'\rangle = \hbar^{-(l'+m')}\sqrt{\frac{(l'-m')!}{(l'+m')!(2l')!}}\hat{L}_+^{l'+m'}|l',-l'\rangle$$

Now we have to use:

$$\hat{L}_-^{l'+m'}\hat{x}_+ = \hat{x}_+\hat{L}_-^{l'+m'} - 2(l'+m')\hbar\hat{z}\hat{L}_-^{l'+m'-1} - \hbar^2(l'+m')(l'+m'-1)\hat{x}_-\hat{L}_-^{l'+m'-2}.$$

To see this we write:

$$\begin{aligned}
\hat{L}_-^{l'+m'}\hat{x}_+ &= \hat{L}_-^{l'+m'-1}[\hat{L}_-,\hat{x}_+] + \hat{L}_-^{l'+m'-1}\hat{x}_+\hat{L}_- \\
&= \hat{L}_-^{l'+m'-1}[\hat{L}_-,\hat{x}_+] + \hat{L}_-^{l'+m'-2}[\hat{L}_-,\hat{x}_+]\hat{L}_- + \hat{L}_-^{l'+m'-2}\hat{x}_+\hat{L}_-^2 \\
&= \cdots = \hat{L}_-^{l'+m'-1}[\hat{L}_-,\hat{x}_+] + \hat{L}_-^{l'+m'-2}[\hat{L}_-,\hat{x}_+]\hat{L}_- + \cdots + [\hat{L}_-,\hat{x}_+]\hat{L}_-^{l'+m'-1} \\
&= -2\hbar\hat{L}_-^{l'+m'-1}\hat{z} - 2\hbar\hat{L}_-^{l'+m'-2}\hat{z}\hat{L}_- - \cdots - 2\hbar\hat{z}\hat{L}_-^{l'+m'-1}.
\end{aligned}$$

Now we repeat the same procedure with

$$\begin{aligned}
\hat{L}_-^k\hat{z} &= \hat{L}_-^{k-1}[\hat{L}_-,\hat{z}] + \hat{L}_-^{k-1}\hat{z}\hat{L}_- = \hat{L}_-^{k-1}[\hat{L}_-,\hat{z}] + \hat{L}_-^{k-2}[\hat{L}_-,\hat{z}]\hat{L}_- + \hat{L}_-^{k-2}\hat{z}\hat{L}_-^2 \\
&= \cdots = \hat{L}_-^{k-1}[\hat{L}_-,\hat{z}] + \hat{L}_-^{k-2}[\hat{L}_-,\hat{z}]\hat{L}_- + \cdots + [\hat{L}_-,\hat{z}]\hat{L}_-^{k-1} \\
&= +\hbar\hat{L}_-^{k-1}\hat{x}_- + \hbar\hat{L}_-^{k-2}\hat{x}_-\hat{L}_- + \cdots + \hbar\hat{x}_-\hat{L}_-^{k-1} \\
&= k\hbar\hat{L}_-^{k-1}\hat{x}_-.
\end{aligned}$$

Now all $\hat{L}_-$'s appear on the right. The matrix element is zero unless:

$$m - (l' + m' - 2) \geq -l \Longrightarrow l \geq l' - 1.$$

To sum up:

1. The matrix element $\langle n'l'm'|\hat{x}_+|nlm\rangle$ is zero unless $m' = m + 1$ and $|l - l'| \leq 1$. Note that it is also zero for $l = l' = 0$ (**Why?**) because $m' = m + 1$ could never be satisfied.

2. Given any one element $\langle n'l'(m+1)|\hat{x}_+|nlm\rangle$, one can determine all the other $\langle n'l'(m'+1)|\hat{x}_+|nlm'\rangle$ element as multiples by known coefficients. One can also determine all other $\langle n'l'(m-1)|\hat{x}_-|nlm\rangle$ and $\langle n'l'm|\hat{z}|nlm\rangle$ for the same l and l' values. Note that we cannot relate the coefficients to other l and l' values.

37 Other vectors

In fact, the general statements that we made are true for any vector quantity. What is a vector? Notice the commutation relations:

$$[\hat{L}_i, \hat{x}_j] = i\hbar\sum_k \epsilon_{ijk}\hat{x}_k$$

Any set of three operators $\hat{v}_1$, $\hat{v}_2$ and $\hat{v}_3$ that satisfy the 9 commutation relations:

$$[\hat{L}_i, \hat{v}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{v}_k$$

are called the **components of a vector**. Other examples are the momentum, $\hat{p}_x, \hat{p}_y$ and $\hat{p}_z$ and the angular momentum itself.

Physics 505
Week 7, Nov 9, 1999
Ori Ganor

Electric and Magnetic fields

38 Maxwell's equations

We will work in cgs units. Maxwell's equations read:

$$\vec{\nabla} \cdot \vec{E} = \rho, \ \vec{\nabla} \cdot \vec{B} = 0, \ \vec{\nabla} \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}, \ \vec{\nabla} \times \vec{B} = \frac{1}{c}\vec{J} + \frac{1}{c}\frac{\partial \vec{E}}{\partial t}.$$

The force on a particle is:

$$m\frac{d\vec{v}}{dt} = q\vec{E} + \frac{q}{c}\vec{v} \times \vec{B}.$$

For electric fields (with $\vec{B} = 0$) one can define a potential V such that:

$$\vec{E} = -\vec{\nabla} V.$$

For magnetic fields one can define a vector potential $\vec{A}$ such that:

$$\vec{B} = \vec{\nabla} \times \vec{A}.$$

There is a *gauge freedom* in the definition of $\vec{A}$. If we take any function Λ and define:

$$\vec{A}_1 = \vec{A} + \vec{\nabla}\Lambda$$

we get the same $\vec{\nabla} \times \vec{A}_1 = \vec{\nabla} \times \vec{A}$.

For nonstatic configurations one can still find a vector potential but this time:

$$\vec{B} = \vec{\nabla} \times \vec{A}, \qquad \vec{E} = -\vec{\nabla} V - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}.$$

We also define the flux through a surface as:

$$\Phi = \oint \vec{B} \cdot dA = \oint \vec{A} \cdot d\vec{s}.$$

39 Electric fields

Including electric fields in Schrödinger's equation is done in two steps. First we find an appropriate potential V such that $E = -\vec{\nabla}V$ and then we set the potential energy to qV where q is the charge of the particle. Thus the Hamiltonian for schrödinger's equation for a particle is an electric field is:

$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + qV = \frac{\vec{\hat{p}}^2}{2m} + qV.$$

The classical equations of motion are replaced by the closest thing we can get in QM – averages of operators.

Thus:

$$\frac{d}{dt}\langle\vec{\hat{r}}\rangle = \frac{i}{\hbar}\langle[\hat{H}, \vec{\hat{r}}]\rangle = \frac{1}{m}\langle\vec{\hat{p}}\rangle,$$

and

$$\frac{d}{dt}\langle\vec{\hat{p}}\rangle = \frac{i}{\hbar}\langle[\hat{H}, \vec{\hat{p}}]\rangle = -\langle q\vec{\nabla}V\rangle.$$

40 Magnetic fields

Suppose we have a particle in a static magnetic field $\vec{B}$ (independent of time). How do we describe it with Schrödinger's equation? The immediate problem is that in general there is no potential energy associated with a magnetic field! To find the solution let us start with:

$$\hat{H}_0 = \frac{\vec{\hat{p}}^2}{2m}$$

and see what extra terms we have to add in order to describe the magnetic field. What will guide us? The classical equations of motion should be satisfied on average. As a first try we write:

$$\frac{d}{dt}\langle\vec{\hat{v}}\rangle \longrightarrow \frac{q}{mc}\langle\vec{\hat{v}} \times \vec{B}\rangle.$$

Here we treat $\vec{B}$ as an operator. Note that in general:

$$\vec{\hat{p}} \times \vec{B} - \vec{B} \times \vec{\hat{p}} = -i\hbar \vec{\nabla} \times \vec{B} \neq 0,$$

so we should be careful whether we write $\vec{\hat{p}} \times \vec{B}$ or $\vec{B} \times \vec{\hat{p}}$. However, if we set $\vec{J} = 0$ and $\frac{\partial \vec{E}}{\partial t} = 0$, Maxwell's equations tell us that $\vec{\nabla} \times \vec{B} = 0$ and $\vec{\hat{p}} \times \vec{B} = \vec{B} \times \vec{\hat{p}}$. It is convenient to denote:

$$\hat{p}_k = -i\hbar \frac{\partial}{\partial x_k}, \qquad k = 1, 2, 3$$

We need $[\hat{H}, \hat{v}_i]$ to be linear in $\hat{v}$. Let us first try:

$$\hat{H}_1 = \frac{1}{2m} \sum_{k=1}^{3} \hat{p}_k^2 - \frac{q}{2mc} \sum (\hat{p}_k \hat{A}_k + \hat{A}_k \hat{p}_k)$$

Here $\hat{A}_k$ are three operators that are functions of $\hat{x}_1, \hat{x}_2, \hat{x}_3$ (but not the $\hat{p}$'s). We have written $\hat{p}\hat{A} + \hat{A}\hat{p}$ to make the Hamiltonian Hermitian. Now we calculate:

$$\begin{aligned} [\hat{H}_1, \hat{p}_j] &= -\frac{q}{2mc} \sum_k \hat{p}_k [\hat{A}_k, \hat{p}_j] - \frac{q}{2mc} \sum_k [\hat{A}_k, \hat{p}_j] \hat{p}_k \\ &= -\frac{i\hbar q}{2mc} \sum_k \left(\hat{p}_k \frac{\partial \hat{A}_k}{\partial x_j} + \hat{p}_k \frac{\partial \hat{A}_k}{\partial x_j} \right). \end{aligned}$$

In this equation $\frac{\partial \hat{A}_k}{\partial x_j}$ means that we first differentiate A_k with respect to x_j *as a function* (not as an operator) and then replace each x_l in the result with the corresponding operator $\hat{x}_l$. Now we can calculate:

$$\frac{d}{dt} \langle \hat{p}_j \rangle = \frac{i}{\hbar} \langle [\hat{H}_1, \hat{p}_j] \rangle = \frac{q}{2mc} \sum_{k=1}^{3} \left(\hat{p}_k \frac{\partial \hat{A}_k}{\partial x_j} + \hat{p}_k \frac{\partial \hat{A}_k}{\partial x_j} \right).$$

Let us calculate the components of $\vec{v} \times \vec{B}$:

$$(\vec{v} \times \vec{B})_j = \sum_k \left(v_k \frac{\partial A_k}{\partial x_j} - v_k \frac{\partial A_j}{\partial x_k} \right).$$

So, classically,

$$\frac{dp_j}{dt} = \frac{q}{mc} \sum_k \left(p_k \frac{\partial A_j}{\partial x_k} - p_k \frac{\partial A_k}{\partial x_j} \right).$$

It seems that $\hat{H}_1$ gives us only part of what we want! **But something else has changed!** Let us calculate what is v in the presence of a magnetic field. We can calculate the quantum-mechanicial analog of the velocity from:

$$\frac{d}{dt}\langle\hat{x}_j\rangle = \frac{i}{\hbar}\langle[\hat{H}_1, \hat{x}_j]\rangle$$

$$\begin{aligned}[\hat{H}_1, \hat{x}_j] &= \frac{1}{2m}[\sum \hat{p}_k^2, \hat{x}_j] - \frac{q}{2mc}\sum_k [\hat{p}_k, \hat{x}_j]\hat{A}_k - \frac{q}{2mc}\sum_k \hat{A}_k[\hat{p}_k, \hat{x}_j] \\ &= -\frac{i\hbar}{m}\hat{p}_j + \frac{i\hbar q}{mc}\hat{A}_j\end{aligned}$$

So

$$\frac{d}{dt}\langle\hat{x}_j\rangle = \frac{1}{m}\langle\hat{p}_j - \frac{q}{c}\hat{A}_j\rangle$$

and we should make the replacement:

$$mv_j \to \hat{p}_j - \frac{q}{c}\hat{A}_j = -i\hbar\frac{\partial}{\partial x_j} - \frac{q}{c}\hat{A}_j.$$

Note that the momentum is mv_j, however, our conventions will be such that we keep the definition:

$$\hat{p}_j \equiv -i\hbar\frac{\partial}{\partial x_j}$$

Thus $\hat{p}_j$ is no longer the kinematical momentum. It is sometimes called *canonical momentum.* Now we can calculate:

$$\begin{aligned}m\frac{d}{dt}\langle\hat{v}_j\rangle &= \frac{i}{\hbar}\langle[\hat{H}_1, \hat{p}_j - \frac{q}{c}\hat{A}_j]\rangle \\ \frac{i}{\hbar}[\hat{H}_1, \hat{p}_j] &= \frac{q}{2mc}\sum_k(\hat{p}_k\frac{\partial\hat{A}_k}{\partial x_j} + \hat{p}_k\frac{\partial\hat{A}_k}{\partial x_j}), \\ -\frac{iq}{\hbar c}[\hat{H}_1, \hat{A}_j] &= -\frac{iq}{2m\hbar c}[\sum_k \hat{p}_k^2, \hat{A}_j] \\ &\quad + \frac{iq^2}{2m\hbar c^2}[\sum_k \hat{p}_k\hat{A}_k, \hat{A}_j] + \frac{iq^2}{2m\hbar c^2}[\sum_k \hat{A}_k\hat{p}_k, \hat{A}_j] \\ &= -\frac{q}{2mc}\sum_k(\hat{p}_k\frac{\partial\hat{A}_j}{\partial x_k} + \frac{\partial\hat{A}_j}{\partial x_k}\hat{p}_k) + \frac{q^2}{mc^2}\sum_k \hat{A}_k\frac{\partial\hat{A}_j}{\partial x_k}\end{aligned}$$

Altogether we find:

$$m\frac{d}{dt}\langle\hat{v}_j\rangle = \frac{q}{2mc}\sum\langle\hat{p}_k\left(\frac{\partial\hat{A}_k}{\partial x_j} - \frac{\partial\hat{A}_j}{\partial x_k}\right)\rangle$$

$$
\begin{aligned}
&+\frac{q}{2mc}\sum\langle\left(\frac{\partial\hat{A}_k}{\partial x_j}-\frac{\partial\hat{A}_j}{\partial x_k}\right)\hat{p}_k\rangle+\frac{q^2}{mc^2}\langle\sum_k\hat{A}_k\frac{\partial\hat{A}_j}{\partial x_k}\rangle\\
=\;&\frac{q}{2mc}\langle\vec{\hat{p}}\times\vec{B}-\vec{B}\times\vec{\hat{p}}\rangle+\frac{q^2}{mc^2}\langle\sum_k\hat{A}_k\frac{\partial\hat{A}_j}{\partial x_k}\rangle\\
=\;&\frac{q}{2mc}\langle\vec{\hat{v}}\times\vec{B}-\vec{B}\times\vec{\hat{v}}\rangle+\frac{q^2}{mc^2}\langle\sum_k\hat{A}_k\frac{\partial\hat{A}_k}{\partial x_j}\rangle
\end{aligned}
$$

The linear term in $\vec{A}$ (i.e. the one containing $\vec{B}$) is OK. However, we get an extra term to cancel. We can do this by adding an extra piece to the Hamiltonian so that:

$$\hat{H}=\frac{1}{2m}\sum_k\hat{p}_k^2-\frac{q}{2mc}\sum_k(\hat{p}_k\hat{A}_k+\hat{A}_k\hat{p}_k)+\frac{q^2}{2mc^2}\sum_k\hat{A}_k\hat{A}_k.$$

41 Summary

1. To describe a particle in a static magnetic field, we need to find a vector potential $\vec{A}$ such that $\vec{B}=\vec{\nabla}\times\vec{A}$.

2. The classical velocity should be replaced with the Hermitian operator:
$$v_k\longrightarrow\hat{v}_k\equiv-\frac{i\hbar}{m}\frac{\partial}{\partial x_k}-\frac{q}{mc}\hat{A}_k$$

3. The Hamiltonian is:
$$\hat{H}=\frac{1}{2}m\sum_k\hat{v}_k^2$$

4. In the presence of both electric and magnetic fields we must find the vector potential $\vec{A}(x_1,x_2,x_3,t)$ and $V(x_1,x_2,x_3,t)$ such that $\vec{B}=\vec{\nabla}\times\vec{A}$ and $\vec{E}=-\vec{\nabla}V-\frac{1}{c}\frac{\partial\vec{A}}{\partial t}$. We then set $\hat{v}_k$ as before and
$$\hat{H}=\frac{1}{2}m\sum_k\hat{v}_k^2+qV.$$

42 Commutation relations of velocity

We can calculate $[\hat{v}_j,\hat{v}_k]$.

$$
\begin{aligned}
[\hat{v}_j,\hat{v}_k]&=[-\frac{i\hbar}{m}\frac{\partial}{\partial x_j}-\frac{q}{mc}\hat{A}_j,-\frac{i\hbar}{m}\frac{\partial}{\partial x_k}-\frac{q}{mc}\hat{A}_k]\\
&=\frac{iq\hbar}{m^2c}\left(\frac{\partial\hat{A}_k}{\partial x_j}-\frac{\partial\hat{A}_j}{\partial x_k}\right)=\frac{iq\hbar}{m^2c}\sum_{l=1}^{3}\epsilon_{jkl}\hat{B}_l.
\end{aligned}
$$

Here $\hat{B}_l$ is the magnetic field operator. Using this commutation relation it is easier to check that the equations of motion are satisfied. However, we will have to use Ehrenfest's rule for operators that have *explicit* time dependence because $\hat{v}$ contains $A(x,y,z,t)$ that depends explicitly on time. The rule is:

$$\frac{d}{dt}\langle\hat{O}(t)\rangle_t = \frac{i}{\hbar}\langle[\hat{H},\hat{O}(t)]\rangle_t + \langle\frac{\partial\hat{O}(t)}{\partial t}\rangle_t$$

Here the subscript t means that we evaluate the expectation value at time t. The expectation value $\langle\hat{O}(t)\rangle$ depends on time both because $\hat{O}(t)$ depends explicitly on time but also because the wave-function $\psi(x,y,z,t)$ depends on time. We find:

$$\frac{d}{dt}\langle\hat{v}_k(t)\rangle_t = \frac{i}{\hbar}\langle[\hat{H},\hat{v}_k(t)]\rangle_t + \langle\frac{\partial\hat{v}_k(t)}{\partial t}\rangle_t$$

We now calculate:

$$\frac{i}{\hbar}[\hat{H},\hat{v}_k] = \frac{im}{2\hbar}[\sum_l \hat{v}_l\hat{v}_l,\hat{v}_k] + \frac{i}{\hbar}[qV,\hat{v}_k],$$

and

$$\begin{aligned}
\frac{im}{2\hbar}[\sum_l \hat{v}_l\hat{v}_l,\hat{v}_k] &= \frac{im}{2\hbar}\sum_l \hat{v}_l[\hat{v}_l,\hat{v}_k] + \frac{im}{2\hbar}\sum_l [\hat{v}_l,\hat{v}_k]\hat{v}_l \\
&= -\frac{q}{2mc}\sum_{j=1}^{3}\epsilon_{lkj}(\hat{v}_l\hat{B}_j + \hat{B}_j\hat{v}_l) = \frac{q}{2mc}(\vec{v}\times\vec{B} - \vec{B}\times\vec{v})_k, \\
\frac{i}{\hbar}[qV,\hat{v}_k] &= -\frac{q}{m}\frac{\partial V}{\partial x_k}. \\
\frac{\partial\hat{v}_k(t)}{\partial t} &= -\frac{q}{mc}\frac{\partial\hat{A}_k}{\partial t}.
\end{aligned}$$

Altogether we find:

$$\frac{d}{dt}\langle\vec{\hat{v}}\rangle = \frac{q}{2mc}\langle\vec{\hat{v}}\times\vec{B} - \vec{B}\times\vec{\hat{v}}\rangle - \frac{q}{m}\langle\vec{E}\rangle.$$

43 Constant magnetic field and Landau levels

Let us solve the energy levels in the case of a constant magnetic field. We can take it to be in the direction of $z \equiv x_3$. We can then take $\vec{A}$ to be:

$$A_1 \equiv A_x = 0,\ A_2 \equiv A_y = Bx,\ A_3 \equiv A_z = 0,$$

Schrödinger's equation becomes:

$$\left[-\frac{1}{2m}\left(\hat{p}_x^2+(\hat{p}_y-\frac{q}{c}Bx)^2+\hat{p}_z^2\right)\right]\psi=E\psi$$

Note that:

$$[\hat{H},\hat{p}_y]=[\hat{H},\hat{p}_z]=0.$$

This means that states can be characterized by specific values of p_y and p_z. So we look for functions of the form:

$$\Psi(x,y,z)=e^{\frac{i}{\hbar}(p_z z+p_y y)}\phi(x).$$

We see that the equation for $\phi(x)$ becomes the Schrödinger equation for a harmonic oscillator centered at

$$x_0=\frac{p_y c}{qB}.$$

The angular frequency is:

$$\omega=\frac{qB}{mc}.$$

The energy levels are:

$$\frac{p_z^2}{2m}+\frac{\hbar qB}{mc}(n+\frac{1}{2}).$$

The energy is independent of p_y. These are called *Landau levels*. There is an infinite number of levels for each n and p_z because p_y can be arbitrary.

We can compare this with the classical formulae. Classically, the trajectory is a helix. The frequency ω is the classical angular-frequency of the projection of the trajectory on the $x-y$ plane. It is not a surprise that we get a harmonic oscillator. The projection of a circular motion with constant velocity is a simple harmonic motion on each coordinate.

44 Gauge transformations

The results above seem puzzling at first! Since B is only in the z-direction we would have expected x and y to enter on an equal footing in the wave-function! In fact this puzzle is the tip of a bigger issue.

There are different forms of $\vec{A}$ that would give the same $\vec{B}$. Given $\vec{A}$ we can replace it with:

$$\vec{A}\to\vec{A}_1=\vec{A}+\vec{\nabla}\Lambda,$$

where Λ is an arbitrary function of space. However, Schrödinger's equation is obviously changed! Could it give the same wave-function? The answer is NO! However, If ψ is a solution of Schrödinger's equation for $\vec{A}$ then:

$$\psi_1 = e^{\frac{ig}{\hbar c}\Lambda}\psi$$

will be a solution for $\vec{A} + \vec{\nabla}\Lambda$. Moreover, expectation values of velocities will not change because:

$$(\hat{p}_k - \frac{q}{c}\hat{A}_k - \frac{q}{c}\frac{\partial \Lambda}{\partial x_k})\psi_1 = e^{\frac{ig}{\hbar c}\Lambda}(\hat{p}_k - \frac{q}{c}\hat{A}_k)\psi.$$

When we calculate $\langle \hat{v}_k \rangle$ the phase will cancel out.

45 Linear approximation and dipole moment

Let us consider a particle in a constant magnetic field but with an arbitrary electric potential V. Let us set:

$$A_k = \frac{1}{2}\sum_{lm} \epsilon_{klm} B_l x_m.$$

It is not hard to check that this will give $\vec{B} = \vec{\nabla} \times \vec{A}$ as it should. Now let us check, to linear order in B_l, what is the effect on the Hamiltonian. The extra term due to $\vec{A}$ is:

$$-\frac{q}{4Mc}\sum_{klm} \epsilon_{klm} B_l (\hat{x}_m \hat{p}_k + \hat{p}_k \hat{x}_m) = -\frac{q}{2Mc}\sum B_l \hat{L}_l = -\frac{q}{2Mc}\vec{B} \cdot \vec{\hat{L}}.$$

For example, if the potential is spherically symmetric we can take $\vec{B}$ in the z-direction (we just define our z-direction to be the direction of $\vec{B}$. We find that, to first order in B, the wave-functions are characterized by $|nlm\rangle$, as in the usual case of a spherically symmetric potential, but there is an extra addition to the energy:

$$E_{nlm} = E_{nl} - \frac{\hbar q}{2Mc} Bm$$

where E_{nl} is the energy without the magnetic field. $\frac{q}{2Mc}\hat{L}$ is called the *magnetic dipole moment.*

46 Interaction with spin

The magnetic field has a similar effect on particles with spin. In addition to what we found previously, we have to add an extra term

$$g_s \frac{q}{2Mc} \vec{B} \cdot \hat{S}.$$

However, we have to add the *Landé factor* g_s that indicates some internal structure. For electrons

$$g_s = 2$$

to a very high degree of approximation. The factor of 2 can only be explained from the relativistic theory (i.e. the Dirac equation)! There are extra minute corrections that follow from QED. For protons we have the factor 5.59. The value in excess of $\frac{q}{Mc}\hat{S}$ is called the *anomalous magnetic moment*. It is $1.79e/(m_p c)$ for protons. Neutrons are uncharged but they are composed of charged quarks which create a magnetic dipole moment of:

$$M_n = -3.83 \frac{e}{2M_n c} \hat{S}$$

for neutrons.

Returning to electrons, we found that, to linear order, an electron in a magnetic field is described by the extra term in $\hat{H}$:

$$-\frac{q}{2Mc} \vec{B} \cdot (\hat{L} + 2\hat{S}) + O(B)^2.$$

The full Hamiltonian for electrons in any (not necessarily constant) electric and magnetic field is:

$$\hat{H} = \frac{1}{2} M \sum_k \hat{v}_k^2 + qV + \frac{|e|}{Mc} \vec{B} \cdot \vec{\hat{S}}.$$

Here $\vec{\hat{S}}$ is the spin-operator (described by three 2×2 matrices).

47 The Aharonov Bohm effect

We now turn to an interesting and important QM effect that is *nonlocal*. Let us take a cylinder with axis in the z-direction and with radius R. Suppose we

arrange the potential to be ∞ inside the cylinder such that a charged particle will never be able to enter the region $x^2 + y^2 < R^2$. The particle is described by a wave-function $\psi(x, y, z)$ that is zero inside the cylinder. Suppose we turn on a magnetic field that is only inside the cylinder. We can think of putting a concentric solenoid inside the cylinder that creates a magnetic field in the z-direction such that the flux lines stay inside the region $x^2 + y^2 < R^2$.

Since $B = 0$ outside the cylinder we might guess that the magnetic field has no effect on the particle! In Quantum mechanics this is wrong! Although $B = 0$ it is $\vec{A}$ that enters Schrödinger's equation and not $\vec{B}$! Let us calculate $\vec{A}$ outside the cylinder. For simplicity, let us assume that the magnetic field has cylinderical symmetry, although this is not imperative. We have:

$$\Phi = \int \vec{B} \cdot dA = \oint \vec{A} \cdot d\vec{s} \Longrightarrow \vec{A} = \frac{\Phi}{2\pi r}\hat{\theta}.$$

Here $\hat{\theta}$ is a unit vector in the angular direction and $r = \sqrt{x^2 + y^2}$. So now we can find $\psi(x, y, z, t)$ that satisfies Schrödinger's equation with this $\vec{A}$. On the otherhand, we can pick a gauge transformation:

$$\Lambda = -\frac{\Phi}{2\pi}\theta.$$

We can then define: $\widetilde{\psi} = e^{\frac{iq}{\hbar c}\Lambda}\psi = e^{\frac{iq\Phi}{2\pi\hbar c}\theta}\psi$ and $\widetilde{\psi}$ satisfies the free Schrödniger equation because: $\widetilde{A} = A + \vec{\nabla}\Lambda = 0$. So, it seems that $\vec{B}$ has no effect on the particle after all. But this is wrong! $\widetilde{\psi}$ is not a single-valued function of θ. Its boundary conditions are:

$$\widetilde{\psi}(\theta = 2\pi) = e^{\frac{iq\Phi}{\hbar c}}\widetilde{\psi}(\theta = 0).$$

In other words: A particle that passes the region with flux Φ from the right picks up a phase relative to a particle passing from the left. The phase is:

$$\frac{q\Phi}{\hbar c}.$$

If Φ is an integer multiple of

$$\Phi_0 = \frac{2\pi\hbar c}{q}$$

then there is no phase difference. The quantity:

$$\frac{2\pi\hbar c}{|e|} = 4.135 \times 10^{-7} Gauss - cm^2$$

is called the *fundamental unit of magnetic flux.*

Physics 505
Week 9, Nov 18, 1999
Ori Ganor

Perturbation Theory

48 Diagonalizing a 2×2 matrix

We start with:

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

and add a small correction:

$$V = \begin{pmatrix} V_{11} & V_{12} \\ V_{12}^* & V_{22} \end{pmatrix}$$

The exact eigenvalues of $H = H_0 + V$ are:

$$\frac{E_1 + V_{11} + E_2 + V_{22} \pm \sqrt{(E_1 + V_{11} - E_2 - V_{22})^2 + 4|V_{12}|^2}}{2}$$

Let us assume $E_1 < E_2$. For small V we can expand:

$$E_1' = E_1 + V_{11} - \frac{|V_{12}|^2}{E_2 - E_1} + O(V)^3, \qquad E_2' = E_2 + V_{22} + \frac{|V_{12}|^2}{E_2 - E_1} + O(V)^3.$$

49 An $n \times n$ matrix

Now take the Hilbert space of n-component vectors such that the operators are $n \times n$ matrices. Take:

$$H_0 = \begin{pmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & \cdots & 0 \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \cdots & E_n \end{pmatrix}$$

and a small correction:

$$V = \begin{pmatrix} V_{11} & V_{12} & \dots & V_{2n} \\ V_{21} & V_{22} & \dots & V_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ V_{n1} & V_{n2} & \dots & V_{nn} \end{pmatrix}$$

An eigenstate for the j^{th} energy level is given by:

$$\psi = \begin{pmatrix} a_1 \\ \vdots \\ a_{j-1} \\ 1 \\ a_{j-1} \\ \vdots \\ a_n \end{pmatrix}.$$

We assume that the a_k's are small and of the order of V. Note that ψ is not normalized. We can defer normalizing it till the end. Let us look for the correction to the ground state:

$$\psi = \begin{pmatrix} 1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}.$$

We can try to solve:

$$(H_0 + V)\psi = (E_1 + \delta_1)\psi$$

To first order in V (and keep in mind that a_j and δ are also of the order of V) we find the equations:

$$\begin{aligned} E_1 + V_{11} &= E_1 + \delta_1, \\ V_{21} + E_2 a_2 &= E_1 a_2, \\ &\vdots \\ V_{n1} + E_n a_n &= E_1 a_n, \end{aligned}$$

The solution is:

$$\delta_1 = V_{11}, \qquad a_j = \frac{V_{j1}}{E_1 - E_j}$$

Now we try to keep corrections of order $O(V)^2$. We do this by writing:

$$(H_0 + V)\psi = (E_1 + V_{11} + \delta_2)\psi$$

and setting $a_j = \frac{V_{j1}}{E_1 - E_j} + b_j$. We now treat δ_2 and b_j as quantities of order $O(V)^2$. We find the equation for the first element:

$$E_1 + V_{11} + \sum V_{1j} \frac{V_{j1}}{E_1 - E_j} = E_1 + V_{11} + \delta_2$$

This implies:

$$\delta_2 = \sum \frac{|V_{1j}|^2}{E_1 - E_j}.$$

For the second element we find:

$$\begin{aligned}(E_1 + V_{11})\frac{V_{21}}{E_1 - E_2} + E_1 b_2 &= V_{21} + (E_2 + V_{22})\frac{V_{21}}{E_1 - E_2} \\ &\quad + E_2 b_2 + \sum_{j=2}^{n} V_{2j}\frac{V_{j1}}{E_1 - E_j}\end{aligned}$$

From this equation we can find b_2.

To summarize, we found that up to second order in V, the energy of the k^{th} level is:

$$E'_k = E_k + V_{kk} + \sum_{j \neq k} \frac{|V_{jk}|^2}{E_k - E_j} + O(V)^3$$

50 The correction to the ground state

Note that if $V_{11} = 0$ the correction to the ground state is always negative. There is a good reason for that. The ground state energy E'_1 can be defined as the minimum of $\langle\psi|\hat{H}|\psi\rangle$ over all possible (normalized) states $|\psi\rangle$. To see this expand $|\psi\rangle$ in the basis of eigenstates of $\hat{H}$:

$$|\psi\rangle = \sum_n c_n |n\rangle \Longrightarrow \langle\psi|\hat{H}|\psi\rangle = \sum_n |c_n|^2 E'_n \geq E'_1.$$

In our case, we can choose

$$|\psi\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \Longrightarrow E_1 = \langle\psi|\hat{H}|\psi\rangle \geq E'_1.$$

51 The secular equation

The arguments above fail if there are two eneries such that $E_j - E_l$ is small (of the order of V).

In particular if $E_k = E_l$ for two different states $k \neq l$, we get a zero in the denominator for one of the terms in the correction to the energy of the k^{th} state:

$$E_k + V_{kk} + \sum_{j \neq k} \frac{|V_{jk}|^2}{E_k - E_j} + O(V)^3.$$

Thus, we have to reconsider all our arguments. **What is the assumption that was wrong in this case?** The wrong assumption is that all a_j's are small. To see why this assumption is wrong, let us consider the case $E_2 = E_1$ first. Then, to first order any vector of the form:

$$\psi = \begin{pmatrix} v_1 \\ v_2 \\ 0 \\ \vdots \\ 0 \end{pmatrix}.$$

is an eigenstate. There is no guarantee that after we add V to H_0, the eigenstate will be of the form:

$$\psi = \begin{pmatrix} 1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$$

(with small a_j's.) However, if all other energy levels E_k are different from E_1 and E_2 and moreover, all differences $E_k - E_1$ (and therefore also $E_k - E_2$) are much bigger than the order of magnitude of V, we can expect the exact eigenstate to be of the form:

$$\psi = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ a_3 \\ \vdots \\ a_n \end{pmatrix},$$

with $a_3, \ldots$ small (of the order of V) but α_1 and α_2 need not be small!

Our first task is to find α_1 and α_2 and from there we will proceed as before. To first order we can ignore all the a_j's. We are left with the equation:

$$\begin{pmatrix} E_1 + V_{11} & V_{12} \\ V_{12}^* & E_2 + V_{22} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \begin{pmatrix} E\alpha_1 \\ E\alpha_2 \end{pmatrix}$$

We find:

$$E = \frac{E_1 + V_{11} + E_2 + V_{22} \pm \sqrt{(E_1 + V_{11} - E_2 - V_{22})^2 + 4|V_{12}|^2}}{2}$$

Note that the square root is of the order of V. We can also set:

$$\alpha_1 = 1, \qquad \alpha_2 = -\frac{E_1 + V_{11} - E}{V_{12}} = \frac{E_2 - E_1 + V_{22} - V_{11} \pm \sqrt{(E_1 + V_{11} - E_2 - V_{22})^2 + 4|V_{12}|^2}}{2V_{12}}$$

In general α_2 is of the order of 1. We see that we get two states with energies that are close to E_1 (and hence E_2) up to $O(V)$ corrections. The two states have different α_2's (according to which of the $(\pm)$ signs we choose). If $E_1 = E_2$ we say that the states are initially *degenerate*. In this case, generically, E_1' will be different from E_2' after we include the perturbation. The difference will be:

$$E_1' - E_2' = \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}$$

We say that the perturbation "lifts" the degeneracy.

52 Polarizability – the Stark effect

As an example of second order perturbation theory Let us discuss what happens to an atom in a small external electric field. An atom with n electrons is described by a very complicated Schrödinger equation with the Hamiltonian operator:

$$\hat{H}_0 = \sum \frac{\vec{p}_i^2}{2m} + \sum_i \frac{Ze^2}{|\vec{r}_i|} - \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

(There are small, relativistic corrections to this, like spin-orbit interaction, that we will disregard at the moment.) The wave-function of the electrons is $\psi(\vec{r}_1, \ldots, \vec{r}_n, \sigma_1, \ldots, \sigma_n)$ where $\sigma_1, \ldots, \sigma_n$ are the spins. In general, Schrödinger's equation is too complicated to solve exactly. We will discuss later in the course various features of the solutions. For now, we just need the general statement that the operator of (orbital) angular momentum:

$$\hat{L} = \sum_i \vec{r}_i \times \vec{p}_i$$

commutes with the Hamiltonian and is therefore conserved. The term *conserved* means that its expectation value in any state does not change with time. Since $\hat{L}_z$ and $\hat{L}^2$ commute with each other and with the Hamiltonian we can find eigenstates of $\hat{H}$ that are also eigenvalues of $\hat{L}_z$ and $\hat{L}^2$. For a

given value of $\hat{L}_z$ and $\hat{L}^2$ there can be several (in general an infinite number of) states. We denote the states by $|nlm\rangle$. Their energy is E_{nl}. We have:

$$\hat{L}^2|nlm\rangle = \hbar^2 l(l+1)|nlm\rangle, \qquad \hat{L}_z|nlm\rangle = \hbar m|nlm\rangle, \qquad \hat{H}|nlm\rangle = E_{nl}|nlm\rangle.$$

How do we know that E_{nl} doesn't depend on m? Because we can check that

$$|nl, m+1\rangle = \frac{1}{\hbar\sqrt{(l-m)(l+m+1)}}\hat{L}_+|nlm\rangle$$

has the same energy as $|nlm\rangle$, since $[\hat{L}_+, \hat{H}] = 0$.

Let us also recall another fact from our study of angular momentum. We defined a vector to be any collection of three operators $\hat{v}_i$ $(i = 1, 2, 3)$ with the commutation relations:

$$[\hat{L}_i, \hat{v}_j] = i\hbar \sum_k \epsilon_{ijk}\hat{v}_k.$$

We then argued that all the matrix elements $\langle n'l'm'|\hat{v}_i|nlm\rangle$ for fixed n, n', l, l' are related to each other by known factors. Note that what we are saying now is a stronger statement than what we said before. Now we are talking about a multiparticle system.

We have not shown this but the coefficients of proportionality can actually be determined. The result is as follows:

$$\langle nlm|\hat{v}_z|n'lm\rangle = C_{n'nl}m, \qquad \langle n(l+1)m|\hat{v}_z|n'lm\rangle = D_{n'nl}\sqrt{l^2 - m^2}.$$

Here C and D are constants that depend only on n, n' and l but not on m.

Now we can ask what happens if we turn on a small electric field. This is described by the perturbation:

$$V = -\vec{\mathcal{E}} \cdot \vec{d}, \qquad \vec{d} = -|e| \sum \vec{r}_i$$

We can take $\vec{\mathcal{E}}$ to be in the z-direction in which case

$$\hat{V} = -\mathcal{E}\hat{d}_z.$$

Now we can calculate the first order correction in perturbation theory to the energy levels. At first it seems that this is degenerate perturbation theory. We need to diagonalize the $(2l+1) \times (2l+1)$ matrix with matrix elements:

$$\langle nlm'|\hat{V}|nlm\rangle.$$

However, $\hat{d}$ is a vector operator. Thus $\langle nlm'|\hat{V}|nlm\rangle = 0$ unless $m = m'$. So the matrix is always diagonal. We can actually say more! $\langle nlm|\hat{V}|nlm\rangle = 0$ as well! This is because of *parity*. Parity, $\hat{P}$, is another operator that commutes with the Hamiltonian. It acts on the wave-function as follows:

$$\hat{P} : \psi(\vec{r}_1, \ldots, \vec{r}_n, \sigma_1, \ldots, \sigma_n) \mapsto \psi(-\vec{r}_1, \ldots, -\vec{r}_n, \sigma_1, \ldots, \sigma_n).$$

It commutes with the Hamiltonian and with $\hat{L}_z$ and $\hat{L}^2$ (Why?). Therefore, the energy eigenstates $|nlm\rangle$ can be taken to have definite parity. Let us calculate a few properties of P. First we need to know that $\hat{P}^\dagger = \hat{P}$. This is because:

$$\begin{aligned}\langle \hat{P}a|b\rangle &= \sum_{\sigma_i} \int \prod d^3\vec{r}_i \psi_a(-\vec{r}_1, \ldots, -\vec{r}_n, \sigma_1, \ldots, \sigma_n)^* \psi_b(\vec{r}_1, \ldots, \vec{r}_n, \sigma_1, \ldots, \sigma_n) \\ &= \sum_{\sigma_i} \int \prod d^3\vec{r}_i \psi_a(\vec{r}_1, \ldots, \vec{r}_n, \sigma_1, \ldots, \sigma_n)^* \psi_b(-\vec{r}_1, \ldots, -\vec{r}_n, \sigma_1, \ldots, \sigma_n) = \langle a|\hat{P}b\rangle.\end{aligned}$$

Next we need to know that: $\hat{P}\hat{d}_z\hat{P} = -\hat{d}_z$. This is easy to check on wave-functions. Now suppose $\hat{P}|nlm\rangle = (-1)^P|nlm\rangle$. We can calculate

$$\langle nlm|\hat{d}_z|nlm\rangle = -\langle nlm|\hat{P}\hat{d}_z\hat{P}|nlm\rangle = -\langle \hat{P}^\dagger nlm|\hat{d}_z|\hat{P}nlm\rangle = -\langle nlm|\hat{d}_z|nlm\rangle.$$

So $\langle nlm|\hat{d}_z|nlm\rangle = 0$.

The conclusion is that to first order of perturbation theory there is no correction to the energy levels of the atom.

What happens to second order? In principle, we should worry again about secular perturbation theory (i.e. having degenerate states). However, $\hat{d}_z$ has nonzero matrix elements only between states with the same m. Thus, effectively we need to diagonalize a matrix which is a small perturbation of a matrix with distinct eigenvalues. (There is an exception to that case, which is the hydrogen atom where there are degenerate energy levels with the same m. We will not discuss this today.) We thus have to calculate:

$$\sum_{n'l'} \frac{|\langle n'l'm|\hat{V}|nlm\rangle|^2}{E_{nl} - E_{n'l'}} = \mathcal{E}^2 \sum_{n'l'} \frac{|\langle n'l'm|\hat{d}_z|nlm\rangle|^2}{E_{nl} - E_{n'l'}}$$

Now recall that $\langle n'l'm|\hat{d}_z|nlm\rangle = 0$ unless $|l - l'| = 0, 1$. We obtain

$$\begin{aligned}\sum_{n'l'} \frac{|\langle n'l'm|\hat{d}_z|nlm\rangle|^2}{E_{nl} - E_{n'l'}} &= \sum_{n'} \frac{|\langle n'(l+1)m|\hat{d}_z|nlm\rangle|^2}{E_{nl} - E_{n'(l+1)}} \\ &\quad + \sum_{n'} \frac{|\langle n'lm|\hat{d}_z|nlm\rangle|^2}{E_{nl} - E_{n'l}} + \sum_{n'} \frac{|\langle n'(l-1)m|\hat{d}_z|nlm\rangle|^2}{E_{nl} - E_{n'(l-1)}}\end{aligned}$$

Using the expressions above for the matrix elements of $\hat{d}_z$, we see that the result is of the form:

$$\Delta E_{nl} = -\frac{1}{2}\mathcal{E}^2(a_{nl} + b_{nl}m^2)$$

Here, a_{nl} and b_{nl} are numbers that can be calculated numerically. Moreover, the correction to the ground state energy is of the form:

$$-\frac{1}{2}\alpha\mathcal{E}^2, \qquad \alpha \geq 0.$$

What does α mean? Recall from classical EM that a dielectric material in an electric field becomes polarized with the polarization being $\vec{P} = (\epsilon - \epsilon_0)\vec{\mathcal{E}}$. If we gradually increase the electric field, we recall that the energy increases by $dE = -\vec{P} \cdot d\vec{\mathcal{E}}$. Thus, the energy of a material with polarizabilty $(\epsilon - \epsilon_0)$ is $-\frac{1}{2}(\epsilon - \epsilon_0)\mathcal{E}^2$.

What we just did is calculate the dielectric constant of a material from first principles!

53 Force between atoms

Consider two atoms that are very far apart at a distance R. What is the force between them? If we think about atoms as spherically symmetric balls of electron charge, then there shouldn't be any electric field outside them and there shouldn't be any force! However, in QM the story is different!

Let us take $\hat{H}_0$ as the part of the Hamiltonian that describes the non-interacting atoms. Now, each atom has a dipole electric moment operator. Call them $\vec{d}$ and $\vec{d'}$. The electric field away from a dipole moment is:

$$\mathcal{E} = -\frac{3(\vec{d} \cdot \vec{r})\vec{r} - (r^2)\vec{d}}{r^5}$$

The potential energy of the interaction between two dipole moments is:

$$-d' \cdot \mathcal{E} = \frac{3(\vec{d} \cdot \vec{r})(\vec{d'} \cdot \vec{r}) - r^2(\vec{d} \cdot \vec{d'})}{r^5}$$

Now let us take $\vec{r}$ in the z-direction. We see that the perturbation is:

$$\hat{V} = -\frac{1}{R^3}(\hat{d}_x\hat{d}'_x + \hat{d}_y\hat{d}'_y - 2\hat{d}_z\hat{d}'_z).$$

As before, the first order correction to the energy is zero because the expectation value of $\hat{d}_x$, $\hat{d}_y$ and $\hat{d}_z$ (as well as $\hat{d}'_x$, $\hat{d}'_y$ and $\hat{d}'_z$) are zero in a given energy state of each atom. Suppose both atoms are in their ground state. We denote this by $|0,0\rangle$. Let $|n,n'\rangle$ be the state where the first atom is in state $|n\rangle$ (a collective name for all quantum numbers) and the second is in state $|n'\rangle$. We have:

$$\langle n,n'|\hat{V}|n,n'\rangle = \frac{1}{R^3}(\langle n|\hat{d}_x|n\rangle\langle n'|\hat{d}'_x|n'\rangle + \langle n|\hat{d}_y|n\rangle\langle n'|\hat{d}'_y|n'\rangle - 2\langle n|\hat{d}_z|n\rangle\langle n'|\hat{d}'_z|n'\rangle).$$

Now we can write the correction to the energy of the two atoms as:

$$\Delta E = -\frac{1}{R^6}\sum_{n\neq 0}\sum_{n'\neq 0}\frac{1}{E_n + E'_{n'} - E_0 - E'_0}|\langle n|\hat{d}_x|n\rangle\langle n'|\hat{d}'_x|n'\rangle + \langle n|\hat{d}_y|n\rangle\langle n'|\hat{d}'_y|n'\rangle - 2\langle n|\hat{d}_z|n\rangle\langle n'|\hat{d}'_z|n'\rangle|^2$$

We see that in general, the force is attractive and falls off as $1/R^7$. We have derived the formula for van Der Waals forces.

Physics 505
Week 10, Nov 30, 1999
Ori Ganor

Time dependent Perturbation Theory

54 The problem

We wish to solve:

$$i\hbar\frac{\partial\Psi}{\partial t} = (\hat{H}_0 + \hat{V}(t))\Psi.$$

Let us assume that $\hat{H}_0$ is independent of time. We search for a solution in the form of a sum:

$$\Psi = \sum_k a_k(t)\Psi_k e^{-\frac{i}{\hbar}E_k t}.$$

Here Ψ_k are the eigenfunctions of $\hat{H}_0$ with energy E_k. We find:

$$i\hbar\sum_k a'_k(t)\Psi_k e^{-\frac{i}{\hbar}E_k t} = \sum_m a_m(t)e^{-\frac{i}{\hbar}E_m t}\hat{V}\Psi_m = \sum_{km} a_m(t)e^{-\frac{i}{\hbar}E_m t}\langle k|\hat{V}|m\rangle\Psi_k$$

It follows that:

$$i\hbar a'_k(t) = \sum_m e^{-\frac{i}{\hbar}(E_m - E_k)t}a_m(t)V_{km}(t), \qquad V_{km}(t) \equiv \langle k|\hat{V}(t)|m\rangle.$$

Now we can solve order by order. To zeroth order, we assume that all a_k's are constant. For example, we can assume that the system is in a particular state $|j\rangle$ in which case $a_k(0) = \delta_{kj}$. We are then looking for a solution of the form:

$$a_k(t) = \delta_{kj} + b_k(t).$$

We treat $b_k(t)$ as $O(V)$ and neglect corrections which are $O(V)^2$. We find:

$$i\hbar b_k'(t) = e^{-\frac{i}{\hbar}(E_j - E_k)t} V_{kj}(t) + O(V)^2$$

The solution is:

$$\Longrightarrow b_k(t) = -\frac{i}{\hbar}\int_0^t dt' e^{-\frac{i}{\hbar}(E_j - E_k)t'} V_{kj}(t')$$

Let us denote:

$$\omega_{kj} = \frac{1}{\hbar}(E_k - E_j).$$

We find:

$$b_k(t) = -\frac{i}{\hbar}\int_0^t dt' e^{i\omega_{kj}t'} V_{kj}(t').$$

55 Periodic driving force

Now let us take:

$$\hat{V} = \hat{U}e^{-i\omega t} + \hat{U}^\dagger e^{i\omega t}$$

We integrate and find

$$b_k(t) = -\frac{e^{i(\omega_{kj} - \omega)t} - 1}{\hbar(\omega_{kj} - \omega)} U_{kj} - \frac{e^{i(\omega_{kj} + \omega)t} - 1}{\hbar(\omega_{kj} + \omega)} U_{jk}^*$$

This implies that small perturbations create a certain probability to change to another state (state k). The probability $|b_k(t)|^2$, to find the particle in state $|k\rangle$ is oscillating with time. In nature, there are many transitions, due to small perturbations, that do not seem to be oscillating with time. We see that the denominator of the equation for b_k is zero if $\omega_{kj} = \omega$. How should we treat this case?

56 transitions to the continuum

Let us suppose that $E_k - E_j - \hbar\omega$ is small. It is sufficient to consider only the term with denominator $\omega_{kj} - \omega$ and neglect the term with $\omega_{kj} + \omega$. We find:

$$|b_k|^2 = \frac{4}{\hbar^2}|U_{kj}|^2 \frac{\sin^2 \frac{(\omega_{kj}-\omega)t}{2}}{(\omega_{kj}-\omega)^2}$$

Suppose there is a continuum of states E_k. Let us consider $|b_k(t)|^2$ as a function of E_k. A larger and larger portion of this curve (of $|b_k|^2$ as a function of E_k) becomes localized around $E_k = E_j + \hbar\omega$ as t increase. Note also that:

$$\int_{-\infty}^{\infty} \frac{\sin^2(xt)}{x^2} dx = \pi t.$$

So the total area under the curve increase linearly with t. Let $P_k(t)$ be the probability to be in the state $|k\rangle$ at time t. when t is large, we can write this as:

$$P_k(t) = \frac{t^2}{\hbar^2}|U_{kj}|^2 I((\omega_{kj}-\omega)t),$$

where $I(x) = \frac{4\sin^2\frac{x}{2}}{x^2}$. As time goes by, $I((\omega_{kj}-\omega)t)$ becomes localized around $\omega_{kj} = \omega$. So, the vast majority of the probability is localized around states $|k\rangle$ with $\omega_{kj} = \omega$. We can therefore write:

$$\frac{d}{dt}P_k(t) = \frac{2\pi}{\hbar}|U_{kj}|^2 \delta(E_k - E_j - \hbar\omega).$$

What does this mean in practice?

57 Transitions to the continuum

The continuum is made of non-normalizable states as we have seen in the second week. In the derivation above we actually assume that $|k\rangle$ is normalized. That's because we wrote:

$$\hat{V}|m\rangle = \sum_k |k\rangle\langle k|\hat{V}|m\rangle$$

If $|k\rangle$ is normalized as:

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

We have to replace the sum with an integral:

$$\hat{V}|m\rangle = \int dk |k\rangle\langle k|\hat{V}|m\rangle.$$

(How do we know this? Multiply each side by $\langle k'|$ and check what we get!) Now we know that at time t the state of the system has a piece that can be written as:

$$\int_{k-\epsilon}^{k+\epsilon} dk' b_{k'}(t) e^{-\frac{i}{\hbar}E_{k'}t}\Psi_{k'}$$

What is the probability to be in a state in the continuum between $|k-\epsilon\rangle$ to $|k+\epsilon\rangle$? It should be:

$$\left|\int_{k-\epsilon}^{k+\epsilon} dk' b_{k'}(t) e^{-\frac{i}{\hbar}E_{k'}t}\Psi(k')\right|^2 = \int_{k-\epsilon}^{k+\epsilon} dk' |b_{k'}(t)|^2$$

This becomes:

$$\frac{2\pi t}{\hbar}\int_{k-\epsilon}^{k+\epsilon} |U_{kj}|^2 \delta(E_k - E_j - \hbar\omega)dk$$

The integral can be performed by changing variables from k to E_k. We find

$$\int \delta(E_k - E_j - \hbar\omega)dk = \int \left|\frac{dE_k}{dk}\right|^{-1} \delta(E_k - E_j - \hbar\omega)dE_k = \left|\frac{dE_k}{dk}\right|^{-1}.$$

As time goes by, the probability does not continue to increase linearly. Rather, $a_j(t)$ starts decreasing too and what happens in effect is that $a_j(t)$ decreases exponentially with time. The rate of growth of $b_k(t)$ starts decreasing exponentially too because $a_j(t)$ decreases.

58 Finite width

We have seen that the probability for transition to states near $|k\rangle$ increases linearly as

$$P \sim \frac{\Gamma}{\hbar}t,$$

with

$$\Gamma = 2\pi|\langle k|\hat{U}|i\rangle|^2 \left|\frac{dE_k}{dk}\right|^{-1}$$

This means that the probability to stay in the initial state $|i\rangle$ must decrease linearly. Eventually, when $t \sim \hbar\Gamma^{-1}$ we will find that $a_j(t)$ is far from 1 and

the approximation ceases to be valid. What really happens? It turns out that:

$$|a_j(t)|^2 \sim e^{-\frac{\Gamma}{\hbar}t}$$

and therefore

$$a_j(t) \sim e^{-\frac{\Gamma}{2\hbar}t}$$

All the previous equations can be modified quickly by replacing:

$$E_j \longrightarrow E_j - i\Gamma.$$

Thus,

$$b_k(t) = -\frac{e^{i(\omega_{kj}-\omega)t-\frac{\Gamma}{\hbar}t}-1}{\hbar(\omega_{kj}-\omega)+i\Gamma}U_{kj} - \frac{e^{i(\omega_{kj}+\omega)t-\frac{\Gamma}{\hbar}t}-1}{\hbar(\omega_{kj}+\omega)+i\Gamma}U^*_{jk}$$

Now we can take the limit $t \to \infty$ and find that for ω_{kj} near ω:

$$|b_k(\infty)|^2 \longrightarrow \frac{|U_{kj}|^2}{(E_k - E_j - \hbar\omega)^2 + \Gamma^2}.$$

This function is peaked around $E_k = E_j + \hbar\omega$ and the peak has a width of size Γ.

59 Summary

1. A perturbation of the form $\hat{V} = \hat{U}e^{-i\omega t} + \hat{U}^\dagger e^{i\omega t}$ can cause transitions from a state $|i\rangle$ to a state $|f\rangle$ if $\langle f|\hat{U}|i\rangle$ or $\langle f|\hat{U}^\dagger|i\rangle$ are nonzero.

2. If state $|f\rangle$ is in the continuum then, as time increases, a larger and larger portion of the transitions is going into states with E_f near $E_i \pm \hbar\omega$. the transition probability increases linearly with time at first.

3. After a long time, the probability to stay in $|i\rangle$ decreases exponentially to zero and the probability to be in any state $|f\rangle$ reaches a constant limit.

To calculate the probability for transition from state $|i\rangle$ to state $|f\rangle$ in the continuum, we have to:

1. Choose an orthonormal basis for the continuum and label it by a continuous variable $|k\rangle$.

2. Make sure that the wave-functions are normalized such that: $\langle k'|k\rangle = \delta(k-k')$.

3. The probability of transition from $|i\rangle$ to a state $|k\rangle$ with $E_k = E_i + \hbar\omega$ is given by the *golden rule*:

$$\frac{dP}{dt} = \frac{2\pi}{\hbar}|\langle k|\hat{U}|i\rangle|^2 \left|\frac{dE_k}{dk}\right|^{-1}.$$

4. As $t \to \infty$ the probability to remain in state $|i\rangle$ decreases exponentially. The probability to end up in state $|k\rangle$ is:

$$|b_k(\infty)|^2 \longrightarrow \frac{|\langle k|\hat{U}|i\rangle|^2}{(E_k - E_j - \hbar\omega)^2 + \Gamma^2}.$$

where

$$\Gamma = 2\pi|\langle k|\hat{U}|i\rangle|^2 \left|\frac{dE_k}{dk}\right|^{-1}$$

is the "width" of the state $|i\rangle$.

60 The continuum – an example

This is a problem from the general exams of 1997. We start with the potential $V = -\lambda\delta(x)$. Let us denote:

$$\alpha = \frac{m\lambda}{\hbar^2}$$

The energy levels fall into three classes:

- A bound state with energy

$$E_0 = -\frac{\hbar^2\alpha^2}{2m} = \frac{m\lambda^2}{2\hbar^2}$$

and wave function:

$$\psi_0(x) = \sqrt{2\alpha}e^{-\alpha|x|}.$$

- Odd wave-functions with energy

$$E_k = \frac{\hbar^2 k^2}{2m},$$

and wave-function:

$$\psi_k^{(-)} = \sin kx.$$

- Even wave-functions with energy

$$E_k = \frac{\hbar^2 k^2}{2m},$$

and wave-function:

$$\psi_k^{(+)} = \cos(k|x| + \delta_k), \qquad \tan\delta_k = \frac{\alpha}{k}.$$

Now let us check the normalization:

$$\begin{aligned}
\int \psi_0(x)^* \psi_k^{(-)}(x) dx &= 0, \\
\int \psi_0(x)^* \psi_k^{(+)}(x) dx &= \frac{a\cos\delta_k - k\sin\delta_k}{a^2+k^2} = 0,
\end{aligned}$$

To check the normalization in the continuum we will use:

$$\int e^{i(k-k')x} dx = 2\pi\delta(k-k').$$

This implies:

$$\int \sin kx\ \sin k'x dx = -\frac{1}{4}\int \left(e^{ikx} - e^{-ikx}\right)\left(e^{ik'x} - e^{-ik'x}\right) dx = \pi(\delta(k-k') - \delta(k+k')).$$

We can actually assume that $k, k' > 0$. In which case we find

$$\int \sin kx\ \sin k'x dx = \pi\delta(k-k').$$

As for $\psi^{(+)}$, we need to express it as:

$$\psi_k^{(+)}(x) = \int f_k(u) e^{iux} du.$$

Then we can write:

$$\begin{aligned}
\int \psi_k^{(+)}(x)^* \psi_{k'}^{(+)}(x) dx &= \int f_k(u)^* e^{-iux} f_{k'}(v) e^{ivx} dx du dv \\
&= 2\pi \int f_k(u)^* f_{k'}(v)\delta(u-v) du dv = 2\pi \int f_k(u)^* f_{k'}(u) du.
\end{aligned}$$

To find the Fourier tranform we need the Fourier transform of a step function.
We observe:

$$\begin{aligned}
\theta(x) &= \frac{1}{2\pi i}\lim_{\epsilon\to 0}\int \frac{1}{k-i\epsilon} e^{ikx} dk, \\
\theta(-x) &= -\frac{1}{2\pi i}\lim_{\epsilon\to 0}\int \frac{1}{k+i\epsilon} e^{ikx} dk.
\end{aligned}$$

Here:

$$\theta(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0 \end{cases}$$

Now we can write:

$$\begin{aligned} \cos(k_0|x| + \delta) &= \frac{1}{2}(e^{ik_0x+i\delta} + e^{-ik_0x-i\delta})\theta(x) + \frac{1}{2}(e^{-ik_0x+i\delta} + e^{ik_0x-i\delta})\theta(-x) \\ &= \frac{1}{4\pi i}\int \left(\frac{e^{i\delta}}{k - k_0 - i\epsilon} + \frac{e^{-i\delta}}{k + k_0 - i\epsilon} - \frac{e^{i\delta}}{k + k_0 + i\epsilon} - \frac{e^{-i\delta}}{k - k_0 + i\epsilon} \right) e^{ikx} dk. \end{aligned}$$

So:

$$f_k(u) = \frac{1}{4\pi i}\int \left(\frac{e^{i\delta_k}}{u - k - i\epsilon} + \frac{e^{-i\delta_k}}{u + k - i\epsilon} + \frac{e^{i\delta_k}}{u + k + i\epsilon} + \frac{e^{-i\delta_k}}{u - k + i\epsilon} \right).$$

Using the integrals:

$$\begin{aligned} \int \frac{du}{(u - a - i\epsilon)(u - b - i\epsilon)} &= 0, \\ \int \frac{du}{(u - a + i\epsilon)(u - b + i\epsilon)} &= 0, \\ \int \frac{du}{(u - a + i\epsilon)(u - b - i\epsilon)} &= \frac{2\pi i}{b - a + 2i\epsilon}, \end{aligned}$$

and the equations:

$$\begin{aligned} \sin(\delta_k - \delta_{k'}) &= \frac{a(k' - k)}{\sqrt{(a^2 + k^2)(a^2 + k'^2)}}, \\ \sin(\delta_k + \delta_{k'}) &= \frac{a(k' + k)}{\sqrt{(a^2 + k^2)(a^2 + k'^2)}}, \end{aligned}$$

We can find the normalization:

$$\int \psi_k^{(+)}(x)^* \psi_{k'}^{(+)}(x) dx = \pi\delta(k - k').$$

61 Example of time-dependent perturbation theory

The problem from the generals of 1997 continues as follows. We turn on a small perturbation $V(t) = U\hat{x}\cos\omega t$. Find the rate of transition in the first order approximation.

In our case:

$$\hat{U} = \frac{1}{2} U \hat{x}.$$

$\hat{U}$ can only induce transitions to the odd states with wavefunction $\psi_k^{(-)}$. This is because:

$$\int \psi_k^{(+)}(x) x \psi_0(x) dx = 0.$$

We now have to calculate $\langle k|\hat{U}|i\rangle$. We have to normalize $|k\rangle$ to have wavefunction $\frac{1}{\sqrt{\pi}} \sin kx$ so that $\langle k'|k\rangle = \delta(k - k')$. We calculate:

$$\langle k|\hat{U}|i\rangle = \sqrt{\frac{2\alpha}{\pi}} U \int x \sin kx e^{-\alpha|x|} dx = \frac{\sqrt{2} k \alpha^{3/2} U}{\sqrt{\pi}(k^2 + \alpha^2)^2}.$$

Therefore:

$$|\langle k|\hat{U}|i\rangle|^2 = \frac{2|U|^2 k^2 \alpha^3}{\pi(k^2 + \alpha^2)^4}.$$

$$\left|\frac{dE_k}{dk}\right|^{-1} = \frac{m}{\hbar k}.$$

$$\frac{dP}{dt} = \frac{2\pi}{\hbar} |\langle k|\hat{U}|i\rangle|^2 \left|\frac{dE_k}{dk}\right|^{-1} = \frac{4m|U|^2 k \alpha^3}{\hbar^2 (k^2 + \alpha^2)^4}.$$

Physics 505
Week 11, Dec 2, 1999
Ori Ganor

Scattering

62 Classical

Classically, we find the deflection angle, θ, as a function of the impact parameter, b. We then find $b(\theta)$. To interpret experiments, we need to calculate the cross-section:

$$d\sigma = 2\pi b db = 2\pi b(\theta) \frac{db}{d\theta} d\theta.$$

63 Perturbation theory – Born aproximation

We start with the state $|\vec{k}\rangle$ and wish to find the rate of transitions to states $|\vec{k}'\rangle$. The result is:

$$\frac{dP}{dt} = \frac{2\pi}{\hbar}|\langle\vec{k}'|\hat{U}|i\rangle|^2 \int \delta(E_{k'} - E_k) d^3\vec{k}'.$$

Let us take $\vec{k}'$ to be within a small $d\Omega$ of angular region. Then

$$\begin{aligned}\int \delta(E_{k'} - E_k) d^3\vec{k}'. &= \int \delta(E_{k'} - E_k) k'^2 dk' d\Omega \\ &= \frac{\sqrt{2}m^{3/2}}{\hbar^3} \int \delta(E_{k'} - E_k) E_{k'}^{1/2} dE_{k'} d\Omega = \frac{\sqrt{2}m^{3/2}}{\hbar^3} E_k^{1/2} d\Omega \\ &= \frac{mk}{\hbar^2} d\Omega.\end{aligned}$$

We find:

$$\frac{dP}{dt} = \frac{2\pi mk}{\hbar^3}|\langle\vec{k}'|\hat{U}|i\rangle|^2 d\Omega$$

The cross-section is related to the rate after dividing by the flux:

$$\frac{\hbar k}{m} d\sigma = \frac{dP}{dt},$$

so:

$$d\sigma = \frac{2\pi m^2}{\hbar^4}|\langle\vec{k}'|\hat{U}|i\rangle|^2 d\Omega$$

What is $\langle\vec{k}'|\hat{U}|i\rangle$? For $|i\rangle$ we choose the wave-function:

$$|i\rangle \to e^{ikz}.$$

This is normalized so that the rate of "particles" going through area A is $\frac{\hbar k}{m} A = vA$. Recall that the normalization for the final state, $|f\rangle$, should be:

$$\langle\vec{k}''|\vec{k}'\rangle = \delta^{(3)}(\vec{k}'' - \vec{k}') = \delta(k_x'' - k_x')\delta(k_y'' - k_y')\delta(k_z'' - k_z').$$

This means that we should take:

$$|\vec{k}'\rangle \to \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}'\cdot\vec{r}}$$

The normalization of $(2\pi)^{3/2}$ is because we are in 3D and not 1D. We find:

$$d\sigma = \frac{m^2}{4\pi^2\hbar^4} \left| \int U(\vec{r}) e^{i(\vec{k}' - \vec{k})\cdot\vec{r}} \right|^2 d\Omega$$

64 Beyond perturbation theory

We are looking for a solution to the time-independent Schrödinger's equation, that far away from the scattering center, that is, for $r \to \infty$, behaves as:

$$\psi(\vec{r}) \longrightarrow f(\theta,\phi)\frac{e^{ikr}}{r} + e^{ikr\cos\theta}, \qquad \frac{\hbar^2 k^2}{2m} = E.$$

The differential cross-section will then be:

$$\frac{d\sigma}{d\Omega} = |f(\theta,\phi)|^2.$$

So for a spherically symmetric potential:

$$d\sigma = 2\pi \sin\theta |f(\theta)|^2 d\theta.$$

65 Born aproximation and Green's functions

We seek a solution in the form:

$$\psi = \psi^{(0)} + \psi^{(1)}, \qquad \psi^{(0)} = e^{i\vec{k}\cdot\vec{R}}$$

We need to solve:

$$\nabla\psi^{(1)} + k^2\psi^{(1)} = \frac{2mU}{\hbar^2}\psi^{(0)}.$$

We find:

$$\psi^{(1)}(\vec{R}) = -\frac{m}{2\pi\hbar^2}\int U(\vec{r})\frac{e^{i(\vec{k}\cdot\vec{r}+k|\vec{R}-\vec{r}|)}}{|\vec{R}-\vec{r}|}d^3\vec{r}.$$

We can write approximately:

$$|\vec{R}-\vec{r}| \approx \vec{R} - \vec{r}\cdot\vec{n}, \qquad \vec{n} \equiv \frac{\vec{R}}{|\vec{R}|}.$$

We find:

$$\psi^{(1)}(\vec{R}) \approx -\frac{m}{2\pi\hbar^2}\frac{e^{ik|\vec{R}|}}{|\vec{R}|}\int U(\vec{r})e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}d^3\vec{r},$$

where $\vec{k}' = k\vec{n}$. Thus:

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int U(\vec{r})e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}d^3\vec{r},$$

To find the region of applicability of the Born approximation, we must require $|\psi^{(1)}| \ll |\psi^{(0)}|$. (See Landau+Lifshitz p153.) Let us assume that a is a typical

size over which U is different from zero. If ka is not large, we can estimate the integral as:

$$|\psi^{(1)}(\vec{R})| \sim \frac{m|U|a^2}{\hbar^2}|\psi^{(0)}|, \qquad |\vec{R}| \sim a.$$

(a^3 is an estimate for $d^3\vec{r}$ and a^{-1} is an estimate for $|\vec{R}-\vec{r}|$ at points inside the potential. If $ka \gg 1$ the oscillating factor damps the integral. We then obtain the estimate:

$$|\psi^{(1)}| \sim \frac{mUa}{\hbar^2 k}$$

The conclusion is that the approximation is good when either of the two condition holds:

$$|U(r)| \ll \frac{\hbar^2}{mr^2},$$

or

$$|U(r)| \ll \frac{\hbar k}{mr}$$

66 Spherical waves

Recall that the solutions to Schrödinger's equation with definite angular momentum can be written as:

$$\psi(r,\theta,\phi) = R_{k,l}(r)Y_{lm}(\theta,\phi),$$

where:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_l}{dr}\right) + \left[k^2 - \frac{l(l+1)}{r^2} - \frac{2m}{\hbar^2}U(r)\right]R_l = 0.$$

The asymptotic form of the function R_l can be found by writing:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_l}{dr}\right) = \frac{1}{r}\frac{d^2}{dr^2}\left(rR_l\right).$$

Let us first set $U = 0$ and solve. For $l = 0$ we find:

$$\frac{d^2}{dr^2}\left(rR_0\right) = k^2 r R_0.$$

The solution is:

$$R_0 = A\frac{\sin(kr+\delta)}{r}.$$

The boundary condition is that $R_0(0)$ is finite and that sets $\delta = 0$. The normalization that we pick is:

$$\int \psi^*_{k'l'm'} \psi_{klm} r^2 dr \, \sin\theta \, d\theta \, d\phi = \delta_{ll'} \delta_{mm'} \delta(k' - k).$$

This sets:

$$R_{k0} = \sqrt{\frac{2}{\pi}} \frac{\sin kr}{r}.$$

One can show that

$$R_{kl} = (-1)^l \sqrt{\frac{2}{\pi}} \frac{r^l}{k^l} \left(\frac{1}{r} \frac{d}{dr} \right)^l \frac{\sin kr}{r} = \sqrt{\frac{k}{r}} J_{l+\frac{1}{2}}(kr).$$

where J is the Bessel function. For large r the asymptotic behavior is:

$$R_{kl} \approx \sqrt{\frac{2}{\pi}} \frac{\sin(kr - \frac{1}{2} l\pi)}{r}.$$

Since e^{ikz} is also an eigenstate of the free Schrödinger equation with the same energy it should be possible to write:

$$e^{ikz} = e^{ikr\cos\theta} = \sum_l C_l R_{k0}(r) Y_{l0}(\theta, \phi).$$

(Note that only $m = 0$ appears.) The coefficients can be found by comparing the coefficients of $(r\cos\theta)^n$. The result is:

$$e^{ikz} = \sum_{l=0}^{\infty} (-i)^l (2l+1) P_l(\cos\theta) \left(\frac{r}{k} \right)^l \left(\frac{1}{r} \frac{d}{dr} \right)^l \frac{\sin kr}{r}$$

How does this expansion behave for large r?

$$e^{ikz} \approx \frac{1}{kr} \sum_{l=0}^{\infty} i^l (2l+1) P_l(\cos\theta) \sin(kr - \frac{1}{2} l\pi).$$

Now let us turn on the potential $U(r)$. The solution R_{kl} will, in general, behave asymptotically (when $r \to \infty$) as:

$$R_{kl} \approx \frac{\sin(kr - \frac{1}{2} l\pi + \delta_l)}{r}.$$

The *phase shift*, δ_l, can only be determined from the boundary condition at $r = 0$ and therefore requires the knowledge of $U(r)$. Now we are looking for a solution of the form:

$$\psi = \sum A_l R_{kl} P_l(\cos\theta)$$

that for large r can also be written as:

$$\psi \to e^{ikz} + f(\theta)\frac{e^{ikr}}{r}.$$

We can calculate

$$\psi - e^{ikz} \to \frac{1}{kr}\sum P_l(\cos\theta)\left\{A_l \sin(kr - \frac{1}{2}l\pi + \delta_l) - i^l(2l+1)\sin(kr - \frac{1}{2}l\pi)\right\}$$

This must represent an outgoing wave. We can write the term in brackets as:

$$\frac{1}{2i}e^{i(kr-\frac{1}{2}l\pi)}[A_l e^{i\delta_l} - i^l(2l+1)] - \frac{1}{2i}e^{i(kr-\frac{1}{2}l\pi)}[A_l e^{-i\delta_l} - i^l(2l+1)]$$

and we find: $A_l = i^l(2l+1)e^{i\delta l}$. Thus:

$$f(\theta) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)[e^{2i\delta_l} - 1]P_l(\cos\theta).$$

Using:

$$2\pi\int_0^\pi P_l^2(\cos\theta)\sin\theta d\theta = \frac{4\pi}{2l+1},$$

we can find the total cross-section:

$$\sigma = 2\pi\int_0^\pi |f(\theta)|^2 \sin\theta d\theta = \frac{4\pi}{k^2}\sum(2l+1)\sin^2\delta_l.$$

Physics 505
Week 12, Dec 7, 1999
Ori Ganor

Atoms

67 Attractive Coulomb field

The potential energy is:

$$U = -\frac{Ze^2}{r}.$$

The wave-functions are of the form $\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$. The function R satisfies:

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} - \frac{l(l+1)}{r^2}R + \frac{2m}{\hbar^2}\left(E + \frac{Ze^2}{r}\right)R = 0.$$

We make a linear change of variables:

$$r = A\rho.$$

We find:

$$R'' + \frac{2}{\rho}R' - \frac{l(l+1)}{\rho^2}R + \frac{2mA^2E}{\hbar^2}R + \frac{2mZAe^2}{\hbar^2\rho}R = 0.$$

We choose A such that:

$$\frac{2mA^2E}{\hbar^2} = -\frac{1}{4} \Longrightarrow A = \frac{\hbar}{2\sqrt{-2mE}}.$$

We also denote:

$$\lambda = \frac{2mZAe^2}{\hbar^2} = \frac{Ze^2}{\hbar}\sqrt{\frac{m}{-2E}}.$$

Thus:

$$E = -\frac{mZ^2e^4}{2\hbar^2\lambda^2}.$$

Now we find the equation:

$$R'' + \frac{2}{\rho}R' + \left[-\frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]R = 0.$$

where $R' = dR/d\rho$.

In order to guess the solution it is usually useful to find the asymptotic behavior for large and small ρ. For large ρ we are left with:

$$R'' \approx \frac{1}{4}R \Longrightarrow R \sim e^{\pm\frac{1}{2}\rho}.$$

To find the behavior for small ρ we try a Taylor series:

$$R = \sum_{k=0}^{\infty} a_k \rho^{k+\alpha}$$

From the coefficient of a_0 we find:

$$\alpha(\alpha-1) + 2\alpha = l(l+1) \Longrightarrow \alpha = l, -(l+1).$$

Only $\alpha = l$ satisfies the boundary conditions at $\rho = 0$. Thus $R \sim \rho^l$ for small ρ. We now make the substitution:

$$R = \rho^l e^{-\frac{1}{2}\rho} P(\rho).$$

P satisfies:

$$\rho P'' + (2l + 2 - \rho)P' + (\lambda - l - 1)P = 0.$$

It turns out that the solutions of this differential equation that are finite at $\rho = 0$ behave like e^ρ at infinity, unless $\lambda = n$ is a positive integer and $n \geq l + 1$. In that case, there is a solution that is a polynomial of degree $n - l - 1$. It is called the *generalized Laguerre polynomial* and is denoted by $L_{n+l}^{2l+1}(\rho)$. It is given by:

$$\frac{(n+l)!}{(n-l-1)!} e^\rho \frac{d^{n+l}}{d\rho^{n+l}} \left(z^{n-l-1} e^{-z} \right).$$

The final result, with normalization, is:

$$R_{nl}(\rho) = -\frac{1}{n^2} \sqrt{\frac{(n-l-1)!}{[(n+l)!]^3}} e^{-\frac{1}{2}\rho} \rho^l L_{n+l}^{2l+1}(\rho).$$

They are normalized such that:

$$\int R_{nl}^2 \rho^2 d\rho = 1.$$

Let us denote:

$$a = \frac{\hbar^2}{2mZe^2}.$$

We will write down the first few:

$$\begin{aligned} R_{10} &= 2a^{-3/2} e^{-\frac{r}{a}}, \\ R_{20} &= \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{r}{2a}\right) e^{-\frac{r}{2a}}, \\ R_{21} &= \frac{1}{2\sqrt{6}} a^{-3/2} \frac{r}{a} e^{-\frac{r}{2a}}. \end{aligned} \tag{6}$$

They are normalized such that:

$$\int R_{nl}^2 r^2 dr = 1.$$

One can also calculate:

$$\langle r^k \rangle = \int_0^\infty r^{k+2} R_{nl}^2 dr.$$

It turns out that:

$$\langle \frac{r}{a} \rangle = \frac{1}{2}[3n^2 - l(l+1)], \qquad \langle \frac{a}{r} \rangle = \frac{1}{n^2}.$$

(See Landau+Lifshitz for more details)

The energy in this case is independent of l and is given by:

$$E_n = -\frac{mZ^2e^4}{2\hbar^2 n^2}.$$

For Hydrogen ($Z = 1$) the lowest energy level is:

$$E_1 = -13.6eV$$

68 The Atom

The energy levels of atoms with more than one electron cannot be solved exactly. Let us first describe the Hamiltonian. We consider an atom with n electrons and nuclear charge Z. (For neutral atoms $Z = n$ but we will also consider ions.) Neglecting relativistic effects the Hamiltonian is just:

$$\hat{H} = \frac{1}{2m_e}\sum_{i=1}^{n}\vec{p}_i^2 - Ze^2\sum_{i=1}^{n}\frac{1}{|\vec{r}_i|} + e^2\sum_{i<j}^{n}\frac{1}{|\vec{r}_i - \vec{r}_j|}.$$

The total angular momentum:

$$\vec{L} = \sum \vec{r}_i \times \vec{p}_i$$

commutes with $\hat{H}$. The energy levels can be characterized by the total angular momentum, which we denote by L, such that:

$$\vec{L}^2|L\rangle = \hbar^2 L(L+1)|L\rangle.$$

States with $L = 0$ are denoted by "S". States with $L = 1$ are denoted by "P". And so on. The values $L = 0, 1, 2, \ldots, 10$ are denoted by:

$$S, P, D, F, G, H, I, K, L, M, N.$$

If the electrons were not identical particles, we would get a degeneracy of 2^n states for each energy level, because there are 2^n values for the spins states. However, we have seen for the case of two electrons, that the spin-variables and position variables can be separated and the wave-functions can be written as:

$$\psi = \phi(\vec{r}_1, \vec{r}_2)\chi(\sigma_1, \sigma_2).$$

If ϕ is symmetric then χ has to be antisymmetric and vice versa. We also saw that anti-symmetric χ's correspond to states with total spin $S = 0$ (there is one such state) and symmetric χ's correspond to states with total spin $S = 1$ (three such states). Thus, for $n = 2$ electrons, states with $S = 0$ have to come with symmetric orbital wave-functions and states with $S = 1$ have to come with anti-symmetric orbital wave-functions. Thus, the degeneracy of 2^n states for non-identical particles is much smaller for identical particles. In this special case of $n = 2$ we have seen that the degeneracy due to the spin variables is only $(2S + 1)$. This turns out to be true for any n, though the details are more complicated. First, the total value of S can take integer values from $0, 1, \ldots \frac{n}{2}$ for even n and half-integer values $\frac{1}{2}, \frac{3}{2}, \ldots, \frac{n}{2}$ for odd n. The wave-functions of the form:

$$\phi(\vec{r}_1, \cdots, \vec{r}_n)\chi(\sigma_1, \ldots, \sigma_n)$$

do not give all the states for $n > 2$. There are more states that cannot be separated like that. However, it is still true that the value of the total spin S, together with the requirement of identical fermions has some implications on the behavior of the wave-function under interchange of $\vec{r}_i$ with $\vec{r}_j$. For example, for $n = 3$ all the states with $S = \frac{3}{2}$ satisfy:

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \sigma_1, \sigma_2, \sigma_3) = -\psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \sigma_1, \sigma_2, \sigma_3) = \cdots$$

and are completely antisymmetric in $\vec{r}_1, \vec{r}_2, \vec{r}_3$. There are $2S+1 = 4$ degenerate states. It turns out (without proof) that wave-functions with total $S = \frac{1}{2}$ can be chosen so as to satisfy

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \sigma_1, \sigma_2, \sigma_3) = -\psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \sigma_1, \sigma_2, \sigma_3)$$

but, in general,

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \sigma_1, \sigma_2, \sigma_3) \neq -\psi(\vec{r}_3, \vec{r}_2, \vec{r}_1, \sigma_1, \sigma_2, \sigma_3).$$

Instead, they can be chosen to satisfy (dropping the σ_i variables that do not change):

$$\psi(\vec{r}_1, \vec{r}_3, \vec{r}_2) + \psi(\vec{r}_3, \vec{r}_2, \vec{r}_1) = \psi(\vec{r}_1, \vec{r}_2, \vec{r}_3).$$

The point is that in general we can look for solutions to Schrödinger's equation, supplemented with extra conditions that determine the behavior of the

wave-functions under interchange of $\vec{r}_i$ with $\vec{r}_j$. This behavior is in general more complicated that just being symmetric or antisymmetric. (It is a mathematical theory known as Young Diagrams.) Because the electrons are identical fermions, one finds that different values of the total spin S have different behavior under interchange. Thus, the energy levels can also be labeled by the total spin S. This is usually denoted by a superscript to the left of the letter that denotes L. Thus, ${}^2P$ denotes a state with $L = 1$ and $S = \frac{1}{2}$. ${}^3P$ denotes a state with $L = 1$ and $S = 1$. There are $(2L+1)(2S+1)$ states in the multiplet.

69 The Shell model

This model explains the basic properties of the periodic table. One of the most important properties of atoms is the *ionization energy*, that is, the energy that is required in order to release one electron. It is given by the difference in energies of the ground state of an atom with nucleus of charge Z and $n = Z$ electrons and the energy of the ground state of an atom with nucleus of charge Z and $n = Z - 1$ electrons. The ionization energy is the highest for He (approximately 25eV). In general it is very large for the inert gases:

$$He, Ne, A, Kr, Xe$$

and is small for the Alkali metals:

$$Li, Na, K, Rb, Cs, \ldots$$

The pattern of filling of shells is as follows (see Landau+Lifshitz):

$1s$				2	electrons
$2s$,	$2p$			8	electrons
$3s$,	$3p$			8	electrons
$4s$,	$3d$,	$4p$		18	electrons
$5s$,	$4d$,	$5p$		18	electrons
$6s$,	$4f$,	$5d$,	$6p$	32	electrons
$7s$,	$6d$,	$5f$			electrons

The heuristic explanation for why $4s$ gets filled before $3d$ is that in higher d states $\langle r \rangle$ is smaller. Thus the electrons in higher d states penetrate closer

into the previously filled shells and the repulsion with those electrons in the filled shell is stronger.

Suppose we are given the electron configuration (i.e. we know how many electrons are in each shell). How do we determine L and S? The electrons in a complete shell add up to a total angular momentum and a total spin of zero. However, The electrons in an incomplete shell can still add up to a nonzero value of S and L. For example, in a configuration $1s^2 2s^2 2p^2$ the two electrons in $2p^2$ can have values of m ranging from $-1, 0, 1$ and spin values ranging from $-\frac{1}{2}, +\frac{1}{2}$. If both spins are aligned in the same direction we have a total of $S = 1$. The orbital wave-function should be antisymmetric. The symmetric combinations are:

$$\frac{1}{\sqrt{2}}(|10\rangle - |01\rangle), \frac{1}{\sqrt{2}}(|1,-1\rangle - |-1,1\rangle), \frac{1}{\sqrt{2}}(|0,-1\rangle - |-1,0\rangle).$$

All these states have $L = 1$. If the total spin is $S = 0$ we have three symmetric combinations of m as follows:

$$|11\rangle, \frac{1}{\sqrt{2}}(|10\rangle+|01\rangle), \frac{1}{\sqrt{2}}(|1,-1\rangle+|-1,1\rangle), |00\rangle, \frac{1}{\sqrt{2}}(|0,-1\rangle+|-1,0\rangle), |-1,-1\rangle.$$

It turns out that 5 linear combinations of these states have $L = 2$ and one linear combination has $L = 0$. So we have the possibilities ${}^1S$ and ${}^1D$. So we have the three possibilities:

$${}^1S,\ {}^1D,\ {}^3P.$$

Which one has the lowest energy?

Hund's Rule: Among allowed states with the same configuration, the state with largest possible value of S and the state with the maximal value of L, for this given S, has lowest energy. In our case, this is ${}^3P$.

70 Relativistic effects

- Spin-orbit interaction:

$$\hat{V} = -\frac{|e|}{mc}\vec{S}\cdot\vec{p}\times\vec{\mathcal{E}} = \frac{Ze^2}{m^2c^2r^3}\vec{L}\cdot\vec{S}$$

- Correction to the kinetic energy:

$$E = \frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}} = mc^2 + \frac{1}{2}mv^2 - \frac{1}{2c^2}mv^4 + \cdots$$

- Spin-Spin interactions.

When is it necessary to include relativistic effects? Let us first estimate the velocity of the electron in the ground state of the hydrogen-like atom.

$$\langle v^2 \rangle = \frac{2}{m}\langle \hat{H} + \frac{Ze^2}{r} \rangle = \frac{Z^2 e^4}{\hbar^2}.$$

The ratio of v/c can therefor be estimated:

$$\frac{v}{c} \sim Z\frac{e^2}{\hbar c}.$$

The quantity $\frac{e^2}{\hbar c}$ is called *the find structure constant.* It has the approximate value of $1/137$. We see that for $Z = 1$ the relativistic corrections are small. However, the electrons in inner shells of, say, Uranium ($Z = 92$) move at speeds comparable to the speed of light and the relativistic theory (Dirac's equation) should be used for them.

There is another reason why we should include relativistic effects even if they are small. Relativistic effects can cause degenerate energy levels to split. For example, the n^{th} level of the hydrogen atom has a degeneracy of $2n^2$ because $l = 0 \ldots n-1$ and there are two values for the spin. The spin orbit interaction can, in principle, split it into $2n$ levels. The extra correction to the energy will be:

$$\frac{Ze^2}{m^2c^2}\langle r^{-3} \rangle_{n,l} \langle L \cdot S \rangle.$$

Here:

$$\langle L \cdot S \rangle = \frac{1}{2}\langle (\hat{L}+\hat{S})^2 - \hat{L}^2 - \hat{S}^2 \rangle$$

The operator $\hat{J} = \hat{L} + \hat{S}$ is conserved, unlike $\hat{L}$ and $\hat{S}$ separately. The operators $\hat{J}^2$ and $\hat{L}^2$ (and of course $\hat{S}^2$) are also conserved. The values for $\hat{J}^2$ turn out to be $j(j+1)$ with $j = l \pm \frac{1}{2}$. Thus:

$$\langle L \cdot S \rangle = \frac{1}{2}(j(j+1) - l(l+1) - \frac{3}{4}) = \pm\frac{1}{2}l.$$

This means that E could in principle depend on n, l and j. In practice, the correction from this term adds up with the other relativistic correction $-\frac{1}{2c^2}mv^4$ and the energy levels of hydrogen depend on j but still do not depend on l. Since j can take values from $\frac{1}{2}$ up to $(n-1)+\frac{1}{2} = n-\frac{1}{2}$, the n^{th} level of hydrogen is split into n levels with distinict energies.

Physics 505
Week 13, Dec 14, 1999
Ori Ganor

The Quasi-Classical Approximation

See Landau+Lifshitz for a good reference.

71 Equations of motion on average

Let us discuss the 1D time independent Hamiltonian:

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + U(\hat{x}).$$

We have seen that the classical Newton's equation is satisfied on average (Ehrenfest's laws):

$$m\frac{d^2}{dt^2}\langle\hat{x}\rangle_t = \frac{d}{dt}\langle\hat{p}\rangle_t = \frac{i}{\hbar}\langle[\hat{H},\hat{p}]\rangle = -\langle U'(\hat{x})\rangle = \langle F(\hat{x})\rangle.$$

Why doesn't that imply that the average of the position, $\langle\hat{x}\rangle_t$, has a classical trajectory? Because we have to remember that:

$$\langle F(\hat{x})\rangle \neq F(\langle\hat{x}\rangle).$$

72 The classical limit

In this class, we would like to study under what conditions the classical approximation is valid. We would also like to describe more concretely the relation between the wave-function and the classical trajectory in the classical limit.

The starting point is to note that the classical approximation, roughly speaking, is correct when the deBroglie wave-length is small. In this case, the phase of the wave-function fluctuates quickly.

We wish to perform an expansion in $\hbar$. The constant $\hbar$ is dimensionful, so what we mean by an expansion in $\hbar$ is really that $\hbar$ will multiply functions like $\frac{1}{xp}$ with the opposite dimensions as $\hbar$ and these functions will be small.

The strategy is to look for a solution:

$$\psi = e^{\frac{i}{\hbar}\phi}, \qquad \phi = \phi_0 + \hbar\phi_1 + \hbar^2\phi_2 + \cdots$$

Putting this in Schrödinger's equation we find the 0^{th} order equation:

$$\frac{1}{2m}\phi_0'^2 + U = E \Longrightarrow \phi_0(x) = \pm\int\sqrt{2m(E-U(x))}dx.$$

We will denote the classical momentum at point x by:

$$p(x) = \sqrt{2m(E-U(x))}.$$

Then,

$$\phi_0(x) = \pm\int^x p(y)dy.$$

Let us continue with the eapproximation. The next order is:

$$-\frac{i}{2m}\phi_0'' + \frac{1}{m}\phi_0'\phi_1' = 0.$$

Therefor,

$$\phi_1' = i\frac{p'}{2p} \Longrightarrow \phi_1 = \frac{1}{2}\log|p|.$$

So at this order we find the real solutions:

$$\psi = \frac{C_0}{\sqrt{|p|}}\sin\left[\frac{1}{\hbar}\int^x p(y)dy + \theta\right].$$

The meaning of this approximation is as follows. The quantity $\frac{p}{\hbar}$ is, locally, the wave-number $k = \frac{2\pi}{\lambda}$, associalted with the deBroglie wavelength. The integral $\frac{1}{\hbar}\int^x p(y)dy$ is the generalization of kx when p varies. The factor of $\sqrt{|p|}$ also has a nice interpretation. It makes $|\psi|^2$ proportional to $\frac{1}{|p|}$. This means that the probability to find the particle between x and $x+dx$ is inversely proportional to the velocity. This is what we expect classically.

To check when the approximation is valid, we have to require:

$$|\phi_0'| \gg \hbar |\phi_1'|.$$

(We put the derivative since ϕ_0 and ϕ_1 themselves have undetermined integration constants.) We find:

$$|p| \gg \hbar \frac{|p'|}{|p|} \Longrightarrow \left|\frac{d\lambda}{dx}\right| \ll 1.$$

Here λ is the deBroglie wavelength calculated from $p(x)$ (which, in turn, is calculated from $U(x)$).

73 The WKB approximation

What about the regions of x for which $E < U$? These are the regions were classically, the particle can never be. Nevertheless, we can try to do the same procedure in those regions as well. In these regions $p(x)$ is imaginary. We can write:

$$p(x) = i\alpha(x), \qquad \alpha(x) = \sqrt{2m(U-E)}.$$

The approximation is valid as long as: $\hbar|\alpha'(x)| \ll \alpha(x)^2$. The wavefunction decays exponentially as:

$$\frac{C_1}{\sqrt{\alpha}} e^{-\int^x \alpha(y)dy}$$

This is called the WKB approxiamtion.

74 The turning point

Suppose we have a potential U such that $U < E$ for $x < 0$ and $U > E$ for $x > 0$. Classically, $x = 0$ is a *turning point*. That is a point where the particle will turn back. Can we use the same formula for the wave-function on both sides of the turning point?

We can calculate the condition for validity explicitly in terms of U:

$$\frac{dp}{dx} = \frac{d}{dx}\sqrt{2m(E-U)} = -\frac{m}{p}\frac{dU}{dx} = \frac{mF}{p}.$$

So, in terms of the force, the quasi-classical approximation is valid if (see Landau+Lifshitz):

$$\left|\frac{m\hbar F}{p^3}\right| \ll 1.$$

We see that the approximation always fails at the turning point where $p = 0$.

What can we do? suppose the approximation holds for x that is negative enough and also for x that is positive engouh. We can then write:

$$\psi(x) \approx \begin{cases} \frac{C_0}{\sqrt{|p|}} \sin\left[-\frac{1}{\hbar}\int_x^0 p(y)dy + \theta\right] & \text{for } x < 0 \\ \frac{C_1}{\sqrt{\alpha}} e^{-\int_0^x \alpha(y)dy} & \text{for } x > 0 \end{cases}$$

Can we find the relation between C_0 and C_1? Can we find θ? For this purpose, we obviously need to analyze the region near $x \approx 0$. Let us assume that near that region the force F is constant.

75 Constant force

Let us take $U = -Fx$. The exact solution is given in terms of the Airy function as:

$$\psi(x) = A\Phi(\xi), \qquad \xi = \left(\frac{2mF}{\hbar^2}\right)^{1/3}(x + \frac{E}{F}).$$

It is given by:

$$\Phi(\xi) = \frac{1}{2\sqrt{\pi}} \int_{-\infty}^{\infty} \cos(u\xi + \frac{1}{3}u^3)du.$$

We can also define it as:

$$\Phi(\xi) = \frac{1}{2\sqrt{\pi}} \int_{-i\infty}^{i\infty} e^{u\xi - \frac{1}{3}u^3}.$$

We can make the integrand divergent by deforming slightly to give u a small negative real part.

This wave-function is not normalizable. We can check by integration by parts that:

$$\Phi''(\xi) = \xi\Phi(\xi).$$

ψ then satisfies Schrödinger's equation. It can be checked from the saddle approximation that the asympotic behavior of Φ is (see Landau+Lifshitz,

appendix (b)):

$$\Phi \approx \begin{cases} \frac{1}{2}\xi^{-\frac{1}{4}} e^{-\frac{2}{3}\xi^{\frac{3}{2}}} & \text{for } \xi \to -\infty \\ |\xi|^{-\frac{1}{4}} \sin(\frac{2}{3}|\xi|^{\frac{3}{2}} + \frac{1}{4}\pi) & \text{for } \xi \to \infty \end{cases}$$

Let us set $E = 0$ and substitute in $\psi(x)$. This means that the wave-function behaves as:

$$\Psi \approx \begin{cases} \frac{1}{2}\left(\frac{2mF}{\hbar^2}\right)^{-\frac{1}{12}} x^{-\frac{1}{4}} \exp\left\{\frac{2\sqrt{2mFx^3}}{3\hbar}\right\} & \text{for } x \to -\infty \\ \left(\frac{2mF}{\hbar^2}\right)^{-\frac{1}{12}} |x|^{-\frac{1}{4}} \sin(\frac{2\sqrt{2mF|x|^3}}{3\hbar} + \frac{1}{4}\pi) & \text{for } x \to \infty \end{cases}$$

Comparing to the classical approximation we find:

$$p(x) = \sqrt{2mFx}, \qquad \int_x^0 p(x)dx = \frac{2}{3}\sqrt{2mF|x|^3}.$$

Comparing with the classical two limiting cases of the classical approximation we can state the summary.

76 Summary

If the turning point is at $x = 0$ then the approximate expressions for the wave-function, away from the turning point, are:

$$\psi(x) \approx \begin{cases} \frac{C}{\sqrt{|p|}} \sin\left[\frac{1}{\hbar}\int_x^0 p(y)dy + \frac{1}{4}\pi\right] & \text{for } x < 0 \\ \frac{C}{2\sqrt{\alpha}} e^{-\int_0^x \alpha(y)dy} & \text{for } x > 0 \end{cases}$$

77 Bohr's quantization rule

Suppose there are two turning points a and b. Let us take p to be the positive root of $\sqrt{2m(E-U)}$. The wave function would behave, on the one hand, as:

$$\frac{C}{\sqrt{p}} \sin\left[\frac{1}{\hbar}\int_x^b p(y)dy + \frac{1}{4}\pi\right].$$

On the other hand, it would behave as:

$$\frac{C'}{\sqrt{p}} \sin\left[\frac{1}{\hbar}\int_a^x p(y)dy - \frac{1}{4}\pi\right].$$

In order for both expressions to be consistent we need:

$$\frac{1}{\hbar}\int_a^b p(x)dx = (n + \frac{1}{2})\pi, \qquad C = (-1)^n C'.$$

This is Bohr's quantization condtion. This is an implicit equation for E.

78 Example: Harmonic oscillator

For a harmonic oscillator we find:

$$p(x) = \sqrt{2mE - mkx^2}.$$

$$b = \sqrt{\frac{2E}{k}}, \qquad a = -\sqrt{\frac{2E}{k}}.$$

$$\int_a^b p(x)dx = 2E\sqrt{\frac{m}{k}}\int_{-1}^{1}\sqrt{1-x^2}dx = \frac{E}{\omega}\pi.$$

Bohr's quantization condition implies:

$$\frac{E}{\omega} = \hbar(n + \frac{1}{2}).$$

As we know, this is also true exactly!

79 Quasi-Classical scattering

80 Hamilton Jacobi eqaution