

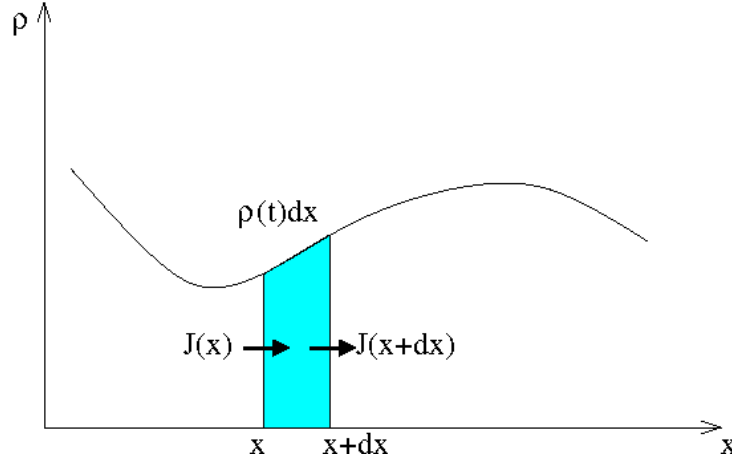
Second Year Quantum Mechanics - Handout 1

Probability density and current density

Paul Dauncey, 18 Oct 2011

1 Classical gas flow

Imagine a cloud of gas moving from left to right. The gas density is given by $\rho(x, t)$ and is denoted by the curve in the figure. Consider an elementary spatial interval x to $x + dx$. The



definition of the density means that the amount of gas within this elementary spatial interval at time t is $\rho(x, t) dx$. At time $t + dt$, it is $\rho(x, t + dt) dx$. Using a Taylor series

$$\rho(x, t + dt) = \rho(x, t) + \frac{\partial \rho}{\partial t} dt \quad (1)$$

so the change in time dt in the amount of gas within this interval of width dx is

$$\Delta \rho dx = [\rho(x, t + dt) - \rho(x, t)] dx = \frac{\partial \rho}{\partial t} dx dt \quad (2)$$

For a classical gas, then the only way we can change the amount of gas in the interval is for it to flow in or out through the boundaries of the interval. This requires it to have a net velocity described by a gas “current density” $J(x, t)$ (in analogy with charge density and charge current density in electromagnetism). This is also often called the “flux” of gas particles. The current density is defined such that the amount of gas flowing *into* the interval dx during the time interval dt across the left hand boundary at x is $J(x, t) dt$. Hence, the amount flowing *out* of the right hand boundary during the same time is $J(x + dx, t) dt$. Again, using a Taylor series, the net amount flowing into the interval is given by

$$\Delta J dt = [J(x, t) - J(x + dx, t)] dt = \left[J(x, t) - J(x, t) - \frac{\partial J}{\partial x} dx \right] dt = -\frac{\partial J}{\partial x} dx dt \quad (3)$$

We assume the total amount of gas is conserved, so the change in the amount of gas within the elementary spatial interval dx during the time dt must be equal to the net amount of gas flowing into dx during time dt . Hence

$$\frac{\partial \rho}{\partial t} dx dt = -\frac{\partial J}{\partial x} dx dt \quad (4)$$

which implies

$$\frac{\partial \rho}{\partial t} + \frac{\partial J}{\partial x} = 0 \quad (5)$$

If we had worked in three dimensions, the current density would have been a vector \mathbf{J} , since the gas velocity is a vector and gas molecules can leave a volume in any direction. The resulting equation would have been

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0 \quad (6)$$

This is a *continuity equation*; it essentially expresses conservation of the gas. The gas disappearing from one place, and reappearing somewhere else, does so by virtue of a current (flux) flowing so there is no net loss or gain of gas.

It is straightforward to show the total amount of gas is conserved. Assuming the densities go to zero as x goes to infinity (or else the gas can escape and the total amount will then not be conserved), then the rate of change of the total amount of gas is

$$\frac{d}{dt} \left(\int_{-\infty}^{\infty} \rho dx \right) = \int_{-\infty}^{\infty} \frac{\partial \rho}{\partial t} dx = - \int_{-\infty}^{\infty} \frac{\partial J}{\partial x} dx = - [J]_{-\infty}^{\infty} = 0 \quad (7)$$

The equivalent in three dimensions uses Gauss's divergence theorem

$$\frac{d}{dt} \left(\int_{-\infty}^{\infty} \rho d^3r \right) = \int_{-\infty}^{\infty} \frac{\partial \rho}{\partial t} d^3r = - \int_{-\infty}^{\infty} \nabla \cdot \mathbf{J} d^3r = - \int_S \mathbf{J} \cdot d\mathbf{S} = 0 \quad (8)$$

where $d\mathbf{S}$ is the normal to the surface enclosing the volume, i.e. the surface at infinity, and so this final integral gives zero.

Note, continuity is a stronger constraint than simply conservation of the total amount of gas; it says the gas cannot instantaneously cease to exist at one position and simultaneously appear at a different position. Besides anything else, relativity would not allow this, as two simultaneous events in one frame are not simultaneous in any others. The gas has to flow between the two.

2 Quantum probability flow

Now take the time dependent Schrödinger equation and its complex conjugate

$$i\hbar \left(\frac{\partial \psi}{\partial t} \right) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} \right) + V\psi, \quad -i\hbar \left(\frac{\partial \psi^*}{\partial t} \right) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi^*}{\partial x^2} \right) + V\psi^* \quad (9)$$

These equations contain derivatives so we need to be careful about what they are differentiating, hence the explicit brackets above. Multiplying by ψ^* in the first case and ψ in the second gives

$$i\hbar \psi^* \left(\frac{\partial \psi}{\partial t} \right) = -\frac{\hbar^2}{2m} \psi^* \left(\frac{\partial^2 \psi}{\partial x^2} \right) + \psi^* V\psi, \quad -i\hbar \left(\frac{\partial \psi^*}{\partial t} \right) \psi = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi^*}{\partial x^2} \right) \psi + \psi^* V\psi \quad (10)$$

Subtracting one equation from the other gives

$$i\hbar \left[\psi^* \left(\frac{\partial \psi}{\partial t} \right) + \left(\frac{\partial \psi^*}{\partial t} \right) \psi \right] = \frac{\hbar^2}{2m} \left[\left(\frac{\partial^2 \psi^*}{\partial x^2} \right) \psi - \psi^* \left(\frac{\partial^2 \psi}{\partial x^2} \right) \right] \quad (11)$$

Now the bracket on the left hand side of this equation is simply

$$\left[\psi^* \left(\frac{\partial \psi}{\partial t} \right) + \left(\frac{\partial \psi^*}{\partial t} \right) \psi \right] = \frac{\partial (\psi^* \psi)}{\partial t} \quad (12)$$

The right hand side bracket can be rearranged using the identity

$$\frac{\partial}{\partial x} \left[\left(\frac{\partial \psi^*}{\partial x} \right) \psi - \psi^* \left(\frac{\partial \psi}{\partial x} \right) \right] = \left(\frac{\partial^2 \psi^*}{\partial x^2} \right) \psi - \psi^* \left(\frac{\partial^2 \psi}{\partial x^2} \right) \quad (13)$$

Hence, rearranging gives

$$\frac{\partial(\psi^*\psi)}{\partial t} + \frac{\partial}{\partial x} \left\{ \frac{i\hbar}{2m} \left[\left(\frac{\partial \psi^*}{\partial x} \right) \psi - \psi^* \left(\frac{\partial \psi}{\partial x} \right) \right] \right\} = 0 \quad (14)$$

Now compare equation 14 with equation 5. The latter equation concerned the motion of a gas. What is the “gas” of interest in quantum mechanics? According to our interpretation of the wavefunction the *probability* of finding a particle in a particular place is the key quantity. It therefore makes sense to make the identification $\rho \equiv \psi^*\psi = |\psi|^2$ where ρ is now a probability density. If this is to be the case then we are forced to make the identification of a quantity J which must be a “probability current density” (or “probability flux”) as

$$J = \frac{i\hbar}{2m} \left[\left(\frac{\partial \psi^*}{\partial x} \right) \psi - \psi^* \left(\frac{\partial \psi}{\partial x} \right) \right] \quad (15)$$

Note, the two terms within the bracket are complex conjugates of each other. Writing $\psi^*(\partial\psi/\partial x) = a + ib$, then clearly $(\partial\psi^*/\partial x)\psi = a - ib$. Hence, the difference is $-2ib$, i.e. purely imaginary, and the i at the front of the above expression then ensures $J = \hbar b/m$ is real. This may seem somewhat abstract so let us see what it implies for a free particle traveling from left to right. Putting the free particle wavefunction $\psi = Ae^{-i(\omega t - kx)}$ into equation 15 gives

$$\begin{aligned} J &= \frac{i\hbar}{2m} \left[\frac{\partial(A^*e^{i(\omega t - kx)})}{\partial x} Ae^{-i(\omega t - kx)} - A^*e^{i(\omega t - kx)} \frac{\partial(Ae^{-i(\omega t - kx)})}{\partial x} \right] \\ &= \frac{i\hbar}{2m} \left[-ikA^*e^{i(\omega t - kx)} Ae^{-i(\omega t - kx)} - ikA^*e^{i(\omega t - kx)} Ae^{-i(\omega t - kx)} \right] \\ &= \frac{i\hbar}{2m} (-2ik|A|^2) = \frac{\hbar k}{m}|A|^2 \end{aligned} \quad (16)$$

But $|A|^2 = \rho$ so

$$J = \frac{\hbar k}{m}|A|^2 = \frac{\hbar k}{m}\rho = \frac{p}{m}\rho = v\rho \quad (17)$$

This is exactly the behaviour you would expect; a given current (of particles or of probability) can be maintained by a high density moving slowly or a low density moving quickly.

This analysis alerts us to take care in the scattering problems we will get onto soon, i.e. problems where we wish to know the transmission coefficient for a particular type of barrier, where the transmission coefficient is the ratio of the numbers of particles which pass through the barrier to the number that are incident on the barrier. The continuity equation tells us that the transmission coefficient is given by the transmitted current divided by the incident current, i.e. by $J_t/J_i = k_t|\psi_t|^2/k_i|\psi_i|^2$, and not simply by $|\psi_t|^2/|\psi_i|^2$. (Here the subscripts t and i denote *transmitted* and *incident*.) It is worth noting that there is usually a partial reflection at a boundary so that the total wavefunction on the incident side of a barrier is comprised of an incident and a reflected part. In order to calculate the transmission coefficient it is necessary to identify which part of the expression for this wavefunction describes “incident” particles and to use only this part of the wavefunction in calculating the transmission coefficient. A barrier may have some complicated shape but one thing is clear; if k is the same on both sides of the barrier, which is the case if the potential V is the same on both sides, then the extra factor drops out, but if k is different on either side of the barrier then an extra factor of k_t/k_i must be taken into account.

3 Three dimensions

For future reference, the three-dimensional version of the probability current is

$$\mathbf{J} = \frac{i\hbar}{2m} [(\nabla\psi^*)\psi - \psi^*(\nabla\psi)] \quad (18)$$

As we will see later, the momentum “operator” $\hat{\mathbf{p}}$ is $-i\hbar\nabla$ so the above can be written as

$$\mathbf{J} = \frac{1}{m} \frac{[\psi^*(\hat{\mathbf{p}}\psi) + (\hat{\mathbf{p}}\psi)^*\psi]}{2} = \frac{1}{m} \mathcal{R}e(\psi^*\hat{\mathbf{p}}\psi) \quad (19)$$

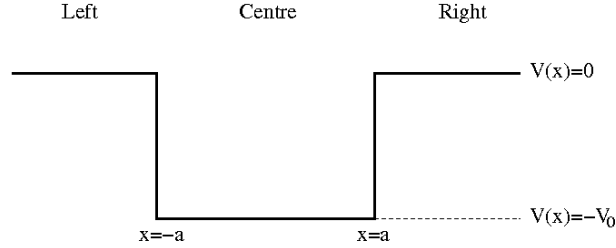
You can think of the real part of $\psi^*\hat{\mathbf{p}}\psi$ as roughly the momentum density, so dividing this by m gives the velocity density, i.e. the generalised equivalent of $\mathbf{v}\rho$.

Second Year Quantum Mechanics - Handout 2

The finite square well and barrier

Paul Dauncey, 20 Oct 2011

1 The finite square well bound states



The potential is shown above. Solutions of the TISE with $-V_0 < E < 0$ are

$$\begin{aligned} u_L &= A \exp(ik_L x) + B \exp(-ik_L x), & k_L^2 &= 2mE/\hbar^2 \\ u_C &= C \exp(ik_C x) + D \exp(-ik_C x), & k_C^2 &= 2m(E + V_0)/\hbar^2 \\ u_R &= F \exp(ik_R x) + G \exp(-ik_R x), & k_R^2 &= 2mE/\hbar^2 = k_L^2 \end{aligned}$$

Since $E < 0$, then $k_L = k_R$ are imaginary; put $k_L = k_R = i\gamma$. Also put $k_C = k$. Hence

$$\begin{aligned} u_L &= A \exp(-\gamma x) + B \exp(\gamma x) & u \text{ finite at } x = -\infty : & A = 0 \\ u_C &= C \exp(ikx) + D \exp(-ikx) \\ u_R &= F \exp(-\gamma x) + G \exp(\gamma x) & u \text{ finite at } x = +\infty : & G = 0 \end{aligned}$$

Imposing boundary conditions involves ensuring a smooth join between the real exponential functions in the classically forbidden regions and the complex oscillatory function in the well itself. Clearly such a smooth join can only be achieved for a restricted set of values of γ and k (see figure 1).

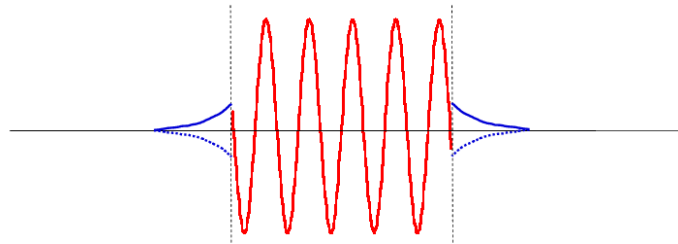


Figure 1: Schematic. The complex oscillatory function in the middle (real part only shown) does not join smoothly on to the exponential parts outside the well because the wrong value of k has been used.

Boundary conditions at $x = -a$ give

$$u \text{ continuous} \quad B \exp(-\gamma a) = C \exp(-ika) + D \exp(ika) \quad (1)$$

$$u' \text{ continuous} \quad \gamma B \exp(-\gamma a) = ik[C \exp(-ika) - D \exp(ika)] \quad (2)$$

Boundary conditions at $x = +a$ give

$$u \text{ continuous} \quad F \exp(-\gamma a) = C \exp(ika) + D \exp(-ika) \quad (3)$$

$$u' \text{ continuous} \quad -\gamma F \exp(-\gamma a) = ik[C \exp(ika) - D \exp(-ika)] \quad (4)$$

These are four *homogeneous* simultaneous equations. Formally they are consistent only if the determinant of the coefficients is zero. Including also the requirement of normalisation, then they can be solved for the five unknowns B, C, D, F and E , since $k = k(E)$ and $\gamma = \gamma(E)$. This constrains γ and k giving a discrete set of eigenvalues E . Simplifying the equations gives

$$(1) + (3) \quad \rightarrow \quad (B + F) \exp(-\gamma a) = (C + D)[\exp(-ika) + \exp(ika)] \quad (5)$$

$$(1) - (3) \quad \rightarrow \quad (B - F) \exp(-\gamma a) = (C - D)[\exp(-ika) - \exp(ika)] \quad (6)$$

$$(2) + (4) \quad \rightarrow \quad \gamma(B - F) \exp(-\gamma a) = ik(C - D)[\exp(-ika) + \exp(ika)] \quad (7)$$

$$(2) - (4) \quad \rightarrow \quad \gamma(B + F) \exp(-\gamma a) = ik(C + D)[\exp(-ika) - \exp(ika)] \quad (8)$$

The coefficients B and F control the size of the exponentially decaying parts in the classically forbidden regions. Since the potential is symmetric we should expect $|u|^2$ to be symmetric (i.e. why should there be a greater probability of finding the particle on one side of the well than on the other?). These considerations lead to the requirement that $B = \pm F$ (see figure 2).

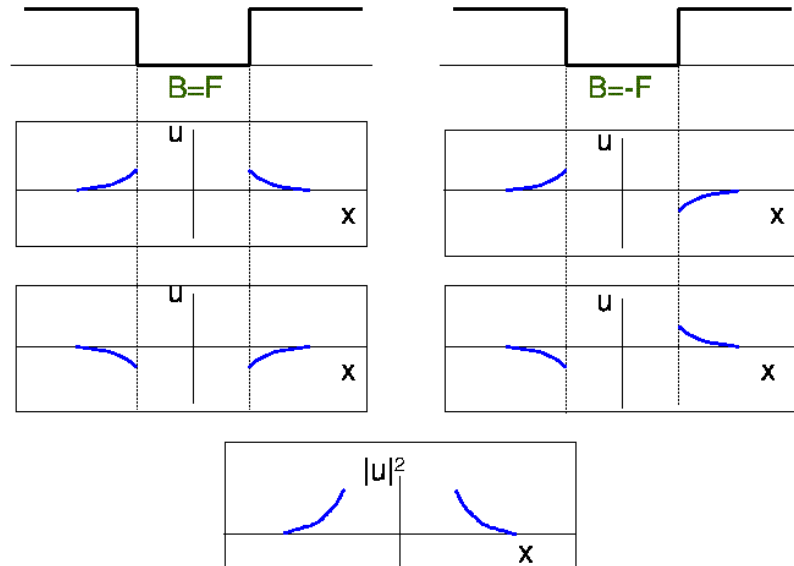


Figure 2: All four situations generate the same symmetrical $|u|^2$.

Solution I

$$\begin{aligned} B = F \quad \text{so } C = D \quad \text{to satisfy eqn's (6)(7)} & \quad \rightarrow B = F = C = D = 0 \\ \text{and } B = -F \quad \text{so } C = -D \quad \text{to satisfy eqn's (5)(8)} & \end{aligned}$$

So $u_L = u_C = u_R = 0$ a TRIVIAL (empty) solution which cannot be normalised.

Solution II

$$\begin{aligned}
 B = F, \quad \text{so} \quad C = D & \quad \text{thus satisfying eqn's (6)(7).} \\
 \text{Subst. into (5)} \quad 2B \exp(-\gamma a) = 2C \cdot 2 \cos ka \\
 C = \frac{B \exp(-\gamma a)}{2 \cos ka} \\
 \text{and (8)/(5)} \rightarrow \underline{\gamma = k \tan ka}
 \end{aligned}$$

$$u_L = B \exp(\gamma x), \quad u_C = \frac{B \exp(-\gamma a)}{\cos ka} \cos kx, \quad u_R = B \exp(-\gamma x)$$

These (by inspection) are EVEN PARITY solutions.

Solution III

$$\begin{aligned}
 B = -F, \quad \text{so} \quad C = -D & \quad \text{thus satisfying eqn's (5)(8).} \\
 \text{Subst. into (6)} \quad 2B \exp(-\gamma a) = 2C \cdot -2i \sin ka \\
 C = \frac{B \exp(-\gamma a)}{-2i \sin ka} = \frac{iB \exp(-\gamma a)}{2 \sin ka} \\
 \text{and (7)/(6)} \rightarrow \gamma = \frac{ik2 \cos ka}{-i2 \sin ka} \rightarrow \underline{\gamma = -k \cot ka}
 \end{aligned}$$

$$u_L = B \exp(\gamma x), \quad u_C = -\frac{B \exp(-\gamma a)}{\sin ka} \sin kx, \quad u_R = -B \exp(-\gamma x)$$

These (by inspection) are ODD PARITY solutions.

In both cases, the value of B is fixed by normalisation.

Eigenvalues: The energy of the state relative to the bottom of the well is $\Delta E = E + V_0$, so that the relationships between γ , K and ΔE are

$$k^2 = \frac{2m\Delta E}{\hbar^2} : \quad \gamma^2 = \frac{2m}{\hbar^2}(V_0 - \Delta E) \quad \text{which combine to give} \quad k^2 + \gamma^2 = \frac{2mV_0}{\hbar^2} \quad (9)$$

$$\gamma = k \tan ka \quad \text{even parity solutions,} \quad \gamma = -k \cot ka \quad \text{odd parity solutions} \quad (10)$$

These equations cannot be solved analytically. Graphical solutions are obtained by plotting γ versus k . Eqn (9) is a circle, which intercepts the tangent curves of eqn (10) to give the eigenvalues for the even parity states. Intersections with the cotangent curves of eqn (10) give the eigenvalues for the odd parity states. Note that γ is only defined for positive values, otherwise solutions $\rightarrow \infty$ as $x \rightarrow \pm\infty$. Note also that exchanging k for $-k$ does not affect the wavefunctions so we need only plot the positive quadrant.

Numerical solutions can also be obtained from the above equations. For the even parity solutions, then $\gamma^2 = k^2 \tan^2 ka$ so

$$k^2 + \gamma^2 = k^2 + k^2 \tan^2 ka = k^2 \left(1 + \frac{\sin^2 ka}{\cos^2 ka} \right) = k^2 \left(\frac{\cos^2 ka + \sin^2 ka}{\cos^2 ka} \right) = \frac{k^2}{\cos^2 ka} = \frac{2mV_0}{\hbar^2}$$

so

$$\cos ka = \pm \frac{\hbar}{a\sqrt{2mV_0}} ka$$

which can then be solved numerically for ka . Note, squaring the initial equation introduces extra solutions so be careful to ensure the correct sign is chosen for the particular solution needed; this can be done by inspection. A similar manipulation can be made for the odd parity states to give

$$\sin ka = \pm \frac{\hbar}{a\sqrt{2mV_0}} ka$$

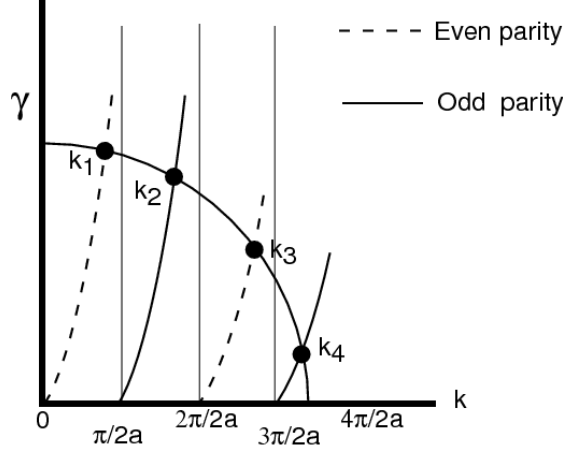


Figure 3: Plot of γ vs k : only the positive quadrant is relevant. The intersections of the curves give the k -values, from which the energy eigenvalues E_n are obtained.

2 The finite square well unbound states

Solutions of the energy eigenvalue equation with $E > 0$ are, as before

$$\begin{aligned} u_L &= A \exp(ik_L x) + B \exp(-ik_L x), & k_L^2 &= 2mE/\hbar^2 \\ u_C &= C \exp(ik_C x) + D \exp(-ik_C x), & k_C^2 &= 2m(E + V_0)/\hbar^2 \\ u_R &= F \exp(ik_R x) + G \exp(-ik_R x), & k_R^2 &= 2mE/\hbar^2 = k_L^2 \end{aligned}$$

In this case, as $E > 0$, all the k values are real. Take $k_L = k_R = k$ and consider an experiment with particles incident from the left: i.e. $G = 0$. Boundary conditions at $x = -a$ give

$$\begin{aligned} u \text{ continuous} \quad A \exp(-ika) + B \exp(ika) &= C \exp(-ik_C a) + D \exp(ik_C a) & (11) \\ u' \text{ continuous} \quad ik[A \exp(-ika) - B \exp(ika)] &= ik_C[C \exp(-ik_C a) - D \exp(ik_C a)] & (12) \end{aligned}$$

Boundary conditions at $x = +a$ give

$$u \text{ continuous} \quad F \exp(ika) = C \exp(ik_C a) + D \exp(-ik_C a) \quad (13)$$

$$u' \text{ continuous} \quad ikF \exp(ika) = ik_C[C \exp(ik_C a) - D \exp(-ik_C a)] \quad (14)$$

Hence, the boundary conditions (continuity of u and u') yield four equations. Including the normalisation, this gives five equations for the six “unknowns” A, B, C, D, F and E , so there are *no constraints*. One constant remains free and the eigenvalues are unrestricted. Hence the energy can take a *continuous* range of the values and particles are free. This is in contrast to the bound state above, where there is one fewer unknown, resulting in constraints that yield the discrete eigenvalues.

We want to calculate the reflection and transmission coefficients for the particle flux,

$$R = \frac{|B|^2}{|A|^2} : \quad T = \frac{|F|^2}{|A|^2} : \quad (\text{velocity factors in flux cancel.})$$

However, as $R + T = 1$, then calculating T is sufficient.

$$\text{Eliminate } C, D : \quad (13) + (14)/ik_C \rightarrow 2C \exp(ik_C a) = \left(1 + \frac{k}{k_C}\right) F \exp(ika)$$

$$(13) - (14)/ik_C \rightarrow 2D \exp(-ik_C a) = \left(1 - \frac{k}{k_C}\right) F \exp(ika)$$

$$\text{Eliminate } B : \quad (11) + (12)/ik \rightarrow 2A \exp(-ika) = \left(1 + \frac{k_C}{k}\right) C \exp(-ik_C a) + \left(1 - \frac{k_C}{k}\right) D \exp(ik_C a)$$

Hence

$$\begin{aligned} A &= \frac{1}{4} \left(1 + \frac{k_C}{k}\right) \left(1 + \frac{k}{k_C}\right) F \exp(2ika) \exp(-2ik_C a) + \frac{1}{4} \left(1 - \frac{k_C}{k}\right) \left(1 - \frac{k}{k_C}\right) F \exp(2ika) \exp(2ik_C a) \\ &= F \exp(2ika) \left[\frac{(k + k_C)^2}{4kk_C} \exp(-2ik_C a) - \frac{(k - k_C)^2}{4kk_C} \exp(2ik_C a) \right] \end{aligned}$$

Hence

$$\frac{F}{A} = \frac{4kk_C \exp(-2ika)}{(k + k_C)^2 \exp(-2ik_C a) - (k - k_C)^2 \exp(2ik_C a)}$$

This means the transmission coefficient is

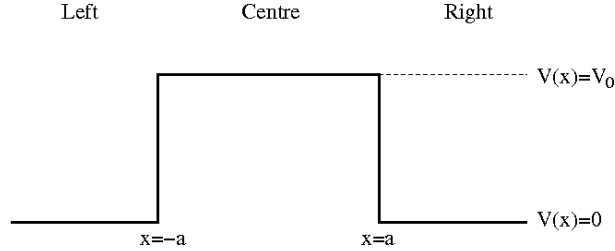
$$\begin{aligned} T &= \frac{|F|^2}{|A|^2} = \frac{16k^2 k_C^2}{(k + k_C)^4 + (k - k_C)^4 - 2(k + k_C)^2 (k - k_C)^2 \cos(4k_C a)} \\ &= \frac{8k^2 k_C^2}{k^4 [1 - \cos(4k_C a)] + k_C^4 [1 - \cos(4k_C a)] + 2k^2 k_C^2 [3 + \cos(4k_C a)]} \end{aligned}$$

Note, when $\cos(4k_C a) = 1$, then $T = 1$ and so the well becomes perfectly transparent. This occurs when

$$4k_C a = 2n\pi \quad \text{so} \quad k_C = \frac{n\pi}{2a}$$

which correspond to the wavenumbers for an infinite square well.

3 The finite square barrier



The potential is shown above. The case for $E > V_0$ is identical to the above except $-V_0 \rightarrow V_0$. This changes the value of E for which k_C gives $T = 1$ but the calculation is identical.

The case for $0 < E < V_0$ is similar, but the wavefunction within the barrier is exponential rather than oscillatory. This means we can replace k_C with $i\gamma$ above to get the solution up to when we take the modulus squared, which is when we need to know whether we are dealing with real or imaginary values. Hence, the equation becomes

$$\frac{F}{A} = \frac{4ik\gamma \exp(-2ika)}{(k + i\gamma)^2 \exp(2\gamma a) - (k - i\gamma)^2 \exp(-2\gamma a)}$$

This means the transmission coefficient is

$$\begin{aligned} T &= \frac{|F|^2}{|A|^2} = \frac{16k^2 \gamma^2}{(k^2 + \gamma^2)^2 \exp(4\gamma a) + (k^2 + \gamma^2)^2 \exp(-4\gamma a) - (k + i\gamma)^4 - (k - i\gamma)^4} \\ &= \frac{16k^2 \gamma^2}{(k^2 + \gamma^2)^2 \exp(4\gamma a) + (k^2 + \gamma^2)^2 \exp(-4\gamma a) - 2(k^4 - 6k^2 \gamma^2 + \gamma^4)} \end{aligned}$$

Note, T is very sensitive to the value of γa . If $\gamma a \ll 1$ then $\exp(\pm 4\gamma a) \approx 1 \pm 4\gamma a$ and so

$$\begin{aligned} T &\approx \frac{16k^2\gamma^2}{(k^2 + \gamma^2)^2(1 + 4\gamma a) + (k^2 + \gamma^2)^2(1 - 4\gamma a) - 2(k^4 - 6k^2\gamma^2 + \gamma^4)} \\ &\approx \frac{16k^2\gamma^2}{2(k^2 + \gamma^2)^2 - 2(k^4 - 6k^2\gamma^2 + \gamma^4)} = \frac{16k^2\gamma^2}{16k^2\gamma^2} = 1 \end{aligned}$$

The product $\gamma a \sim \sqrt{(V_0 - E)}a$. Hence, if $V_0 - E$ or a are very small the tunneling probability can be large. Conversely, if $\gamma a \gg 1$ then the denominator is dominated by the $\exp(4\gamma a)$ term so

$$T \approx \frac{16k^2\gamma^2}{(k^2 + \gamma^2)^2 \exp(4\gamma a)} = \frac{16k^2\gamma^2}{(k^2 + \gamma^2)^2} \exp(-4\gamma a) = \frac{16E(V_0 - E)}{V_0^2} \exp(-4\gamma a)$$

T varies much more rapidly due to the exponential factor than the $E(V_0 - E)/V_0^2$ term. An example is the mean lifetime of α -decaying nuclei, which range from $\mu\text{s} \rightarrow 10^9$ years for a factor ~ 2 in $(V_0 - E)$.

Second Year Quantum Mechanics - Handout 3

The simple harmonic oscillator

Paul Dauncey, 25 Oct 2011

1 Definition of variables

The TISE for the simple harmonic oscillator is

$$\hat{H}u_n = -\frac{\hbar^2}{2m} \frac{d^2 u_n}{dx^2} + \frac{m\omega^2}{2} x^2 u_n = E_n u_n$$

For more convenient variables, define

$$y = \sqrt{\frac{m\omega}{\hbar}} x, \quad \alpha_n = \frac{2E_n}{\hbar\omega}$$

so the equation becomes

$$\frac{d^2 u_n}{dy^2} + (\alpha_n - y^2) u_n = 0$$

2 Solutions

We look for solutions of the form

$$u_n = A_n H_n e^{-y^2/2}$$

where H_n is a polynomial in y and A_n is a normalisation constant. With this, then

$$\frac{du_n}{dy} = \frac{dH_n}{dy} A_n e^{-y^2/2} - y H_n A_n e^{-y^2/2} = \frac{dH_n}{dy} A_n e^{-y^2/2} - y u_n$$

and so

$$\frac{d^2 u_n}{dy^2} = \frac{d^2 H_n}{dy^2} A_n e^{-y^2/2} - y \frac{dH_n}{dy} A_n e^{-y^2/2} - u_n - y \frac{du_n}{dy} = A_n e^{-y^2/2} \left[\frac{d^2 H_n}{dy^2} - 2y \frac{dH_n}{dy} + (y^2 - 1) H_n \right]$$

Hence, dropping the overall $A_n e^{y^2/2}$ factor, the eigenvalue equation becomes

$$\frac{d^2 H_n}{dy^2} - 2y \frac{dH_n}{dy} + (\alpha_n - 1) H_n = 0$$

The H_n are called Hermite polynomials. The simplest is a constant, i.e. $H_0 = 1$, so the derivatives are zero and

$$(\alpha_0 - 1) = 0 \quad \text{so} \quad \alpha_0 = 1$$

The next is first order polynomial in y , i.e. $H_1 = 2y$. Hence

$$-4y + 2(\alpha_1 - 1)y = 2(\alpha_1 - 3)y = 0$$

To hold for all y , then $\alpha_1 = 3$.

3 The Hermite polynomials

The recursion relation for the Hermite polynomials is

$$H_{n+1} = 2yH_n - 2nH_{n-1}$$

so knowing the first two, H_0 and H_1 , then all the higher polynomials can be calculated. The first few Hermite polynomials are given by

$$\begin{aligned}H_0(y) &= 1 \\H_1(y) &= 2y \\H_2(y) &= 2yH_1 - 2H_0 = 4y^2 - 2 \\H_3(y) &= 2yH_2 - 4H_1 = 8y^3 - 12y\end{aligned}$$

Higher order Hermite polynomials can be found by repeated application of the recursion relation.

4 Normalised harmonic oscillator eigenstates

The normalised eigenstates are given in terms of the Hermite polynomials by

$$u_n(y) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(y) e^{-y^2/2}$$

The corresponding eigenstates and eigenvalues in terms of the original variables are

$$\begin{aligned}u_0 &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}, & E_0 &= \frac{1}{2}\hbar\omega \\u_1 &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} x e^{-m\omega x^2/2\hbar}, & E_1 &= \frac{3}{2}\hbar\omega \\u_2 &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2}} \left(\frac{2m\omega}{\hbar} x^2 - 1\right) e^{-m\omega x^2/2\hbar}, & E_2 &= \frac{5}{2}\hbar\omega \\u_3 &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{m\omega}{3\hbar}} x \left(\frac{2m\omega}{\hbar} x^2 - 3\right) e^{-m\omega x^2/2\hbar}, & E_3 &= \frac{7}{2}\hbar\omega\end{aligned}$$

Second Year Quantum Mechanics - Handout 4

The Ehrenfest theorem

Paul Dauncey, 10 Nov 2011

1 Operator properties

We need to establish some general properties of operators we will use. Firstly, it is important to note that if \hat{A} and \hat{B} are Hermitian operators, this does not mean the product $\hat{A}\hat{B}$ is necessarily Hermitian. An operator is Hermitian if it satisfies

$$\int \psi^* \hat{A} \phi dx = \int (\hat{A} \psi)^* \phi dx$$

where the integral is over all space. Consider

$$\int \psi^* \hat{A} \hat{B} \phi dx = \int \psi^* \hat{A} (\hat{B} \phi) dx = \int (\hat{A} \psi)^* \hat{B} \phi dx = \int [\hat{B} (\hat{A} \psi)]^* \phi dx = \int (\hat{B} \hat{A} \psi)^* \phi dx \quad (1)$$

The commutator is

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

so the above can be written as

$$\int \psi^* \hat{A} \hat{B} \phi dx = \int (\hat{A} \hat{B} \psi)^* \phi dx - \int ([\hat{A}, \hat{B}] \psi)^* \phi dx$$

The product $\hat{A}\hat{B}$ is therefore only Hermitian if \hat{A} and \hat{B} commute, which is not true in general.

However, there are two forms of a product of Hermitian operators \hat{A} and \hat{B} which are always Hermitian. From the above, it is clear that by inverting the original order of the operators, then

$$\int \psi^* \hat{B} \hat{A} \phi dx = \int (\hat{B} \hat{A} \psi)^* \phi dx \quad (2)$$

Hence, adding equation 2 to 1 gives

$$\int \psi^* (\hat{A}\hat{B} + \hat{B}\hat{A}) \phi dx = \int [(\hat{B}\hat{A} + \hat{A}\hat{B}) \psi]^* \phi dx = \int [(\hat{A}\hat{B} + \hat{B}\hat{A}) \psi]^* \phi dx$$

This combination is therefore Hermitian; it is called the anticommutator of the operators and is written as

$$\hat{A}\hat{B} + \hat{B}\hat{A} = \{\hat{A}, \hat{B}\}$$

Furthermore subtracting equation 2 from 1 and multiply throughout by i gives

$$\int \psi^* i(\hat{A}\hat{B} - \hat{B}\hat{A}) \phi dx = \int i[(\hat{B}\hat{A} - \hat{A}\hat{B}) \psi]^* \phi dx = \int [i(\hat{A}\hat{B} - \hat{B}\hat{A}) \psi]^* \phi dx$$

where taking the i inside the complex conjugation gives the critical sign change. Hence i times the commutator is also Hermitian. Therefore, when taking products of Hermitian operators, then one or other of these forms is normally be used. Note, if the commutator is zero, the first reduces to

$$\{\hat{A}, \hat{B}\} = 2\hat{A}\hat{B}$$

while if the anticommutator is zero, the second reduces to

$$i[\hat{A}, \hat{B}] = 2i\hat{A}\hat{B}$$

so that it is normal to use one of

$$\frac{1}{2}\{\hat{A}, \hat{B}\} \quad \text{or} \quad \frac{i}{2}[\hat{A}, \hat{B}]$$

One other point to note is that, as stated above, for a wavefunction ψ , then a Hermitian operator by definition satisfies

$$\int \psi^* \hat{A} \psi dx = \int (\hat{A} \psi)^* \psi dx = \left[\int (\hat{A} \psi) \psi^* dx \right]^*$$

and since the RHS is the complex conjugate of the LHS, this must be real. However, this does not mean that for every x position

$$\psi^* \hat{A} \psi = (\hat{A} \psi)^* \psi$$

Nor does it mean that $\psi^* \hat{A} \psi$ (or $(\hat{A} \psi)^* \psi$) is always real. In general, as they are complex conjugates of each other, these terms have imaginary components which have opposite signs for these two expressions.

$$\mathcal{R}e[\psi^* \hat{A} \psi] = \mathcal{R}e[(\hat{A} \psi)^* \psi], \quad \mathcal{I}m[\psi^* \hat{A} \psi] = -\mathcal{I}m[(\hat{A} \psi)^* \psi]$$

Over all space, the imaginary parts integrate to zero, so as to cancel out in the Hermitian condition equation. Hence, to get the part at each x which contributes to the overall integral, we can take the real part or can add the complex conjugate and divide by two, i.e.

$$\mathcal{R}e[\psi^* \hat{A} \psi] = \mathcal{R}e[(\hat{A} \psi)^* \psi] = \frac{1}{2}[\psi^* \hat{A} \psi + (\hat{A} \psi)^* \psi]$$

2 Quantum mechanics without measurements

One of the wierd things about quantum mechanics is that the process of making a measurement does not obey the Schrödinger equation. This sometimes makes seeing the physics in the Schrödinger equation more difficult. It is instructive to get a clearer idea of what is going on to consider the (unreal) world where “measurements” in the quantum mechanics sense do not exist, i.e. the system is not disturbed and continues to obey the Schrödinger equation. There is then no particle-like behaviour as the wavefunction does not collapse to a point; the system acts as pure waves, rather in the same way that classical electromagnetism is about waves. In this case, then we would see real densities (i.e. intensities) of fields, energy, momentum, etc, spread throughout space, just as for electromagnetism. An alternative classical comparison would be to an ideal gas of classical particles, where we can ask how many particles are at each position, what their energy and momentum are, etc. There would be no probabilities and so these densities would be (in principle) measurable in fine detail.

Consider an operator \hat{Q} with no explicit time dependence. We assume the density of whatever variable this operator represents is given by

$$\psi^* \hat{Q} \psi$$

As stated above, in general this is not real and we could use the procedure above to make it so, but will ignore this complication until the end for simplicity. For this density, then

$$\frac{\partial(\psi^* \hat{Q} \psi)}{\partial t} = \left(\frac{\partial \psi^*}{\partial t} \right) (\hat{Q} \psi) + \psi^* \left(\hat{Q} \frac{\partial \psi}{\partial t} \right)$$

Using the Schrödinger equation and its complex conjugate

$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \psi, \quad \frac{\partial \psi^*}{\partial t} = \frac{i}{\hbar} (\hat{H} \psi)^*$$

then

$$\frac{\partial(\psi^* \hat{Q} \psi)}{\partial t} = \frac{i}{\hbar} [(\hat{H} \psi)^* (\hat{Q} \psi) - \psi^* (\hat{Q} \hat{H} \psi)]$$

This can be manipulated to give

$$\begin{aligned} \frac{\partial(\psi^* \hat{Q} \psi)}{\partial t} &= \frac{i}{\hbar} [(\hat{H} \psi)^* (\hat{Q} \psi) - \psi^* (\hat{Q} \hat{H} \psi) + \psi^* (\hat{H} \hat{Q} \psi) - \psi^* (\hat{H} \hat{Q} \psi)] \\ &= \frac{i}{\hbar} [(\hat{H} \psi)^* (\hat{Q} \psi) - \psi^* (\hat{H} \hat{Q} \psi) + \psi^* ([\hat{H}, \hat{Q}] \psi)] \end{aligned}$$

Consider the first two terms on the RHS. Since $\hat{H} = \hat{T} + \hat{V}$, and $\hat{V} = V$ is real and so cancels out, then they are

$$\begin{aligned} \frac{i}{\hbar} [(\hat{H} \psi)^* (\hat{Q} \psi) - \psi^* (\hat{H} \hat{Q} \psi)] &= \frac{i}{\hbar} [(\hat{T} \psi)^* (\hat{Q} \psi) - \psi^* (\hat{T} \hat{Q} \psi)] \\ &= -\frac{i\hbar}{2m} \left[\left(\frac{\partial^2 \psi^*}{\partial x^2} \right) (\hat{Q} \psi) - \psi^* \left(\frac{\partial^2 (\hat{Q} \psi)}{\partial x^2} \right) \right] \\ &= -\frac{i\hbar}{2m} \frac{\partial}{\partial x} \left[\left(\frac{\partial \psi^*}{\partial x} \right) (\hat{Q} \psi) - \psi^* \left(\frac{\partial (\hat{Q} \psi)}{\partial x} \right) \right] \\ &= -\frac{1}{2m} \frac{\partial}{\partial x} [(\hat{p} \psi)^* (\hat{Q} \psi) + \psi^* (\hat{p} \hat{Q} \psi)] \end{aligned}$$

Hence

$$\frac{\partial(\psi^* \hat{Q} \psi)}{\partial t} + \frac{\partial}{\partial x} \left\{ \frac{1}{2m} [(\hat{p} \psi)^* (\hat{Q} \psi) + \psi^* (\hat{p} \hat{Q} \psi)] \right\} = \frac{1}{\hbar} \psi^* (i[\hat{H}, \hat{Q}] \psi) \quad (3)$$

We showed above that i times a commutator is Hermitian so the operator on the RHS corresponds to an observable. However, this equation is not necessarily real so we need to take the complex conjugate and add to remove the imaginary parts. Writing

$$\rho_Q = \frac{1}{2} [\psi^* (\hat{Q} \psi) + (\hat{Q} \psi)^* \psi]$$

and

$$J_Q = \frac{1}{4m} [(\hat{p} \psi)^* (\hat{Q} \psi) + \psi^* (\hat{p} \hat{Q} \psi) + (\hat{Q} \psi)^* (\hat{p} \psi) + (\hat{p} \hat{Q} \psi)^* \psi]$$

then this becomes

$$\frac{\partial \rho_Q}{\partial t} + \frac{\partial J_Q}{\partial x} = \frac{1}{2\hbar} \left\{ \psi^* (i[\hat{H}, \hat{Q}] \psi) + (i[\hat{H}, \hat{Q}] \psi)^* \psi \right\}$$

The meaning of J_Q may seem hard to interpret. Consider the integral, where it can be manipulated using the Hermitian properties of the operators

$$\begin{aligned} \int J_Q dx &= \frac{1}{4m} \int (\hat{p} \psi)^* (\hat{Q} \psi) + \psi^* (\hat{p} \hat{Q} \psi) + (\hat{Q} \psi)^* (\hat{p} \psi) + (\hat{p} \hat{Q} \psi)^* \psi dx \\ &= \frac{1}{4m} \int \psi^* (\hat{p} \hat{Q} \psi) + \psi^* (\hat{p} \hat{Q} \psi) + \psi^* (\hat{Q} \hat{p} \psi) + (\hat{Q} \psi)^* (\hat{p} \psi) dx \\ &= \frac{1}{4m} \int 2\psi^* (\hat{p} \hat{Q} \psi) + 2\psi^* (\hat{Q} \hat{p} \psi) dx \\ &= \frac{1}{m} \int \psi^* \frac{1}{2} \{\hat{p}, \hat{Q}\} \psi dx \end{aligned}$$

Hence, under the integral, it is seen to be equal to the anticommutator, which we showed was a Hermitian operator. Hence, we can consider J_Q to be an observable as well. Physically, it

is $\{\hat{p}/m, \hat{Q}\}/2 = \{\hat{v}, \hat{Q}\}/2$ and so is something like a vQ term, i.e. the current density for the variable.

This should all look similar to the form of the equation discussed in Handout 1, i.e. the continuity equation. If the commutator is zero, then this is indeed a continuity equation and the total amount of the variable

$$\int_{-\infty}^{\infty} \rho_Q dx = \langle Q \rangle$$

is a constant. In fact, the calculation in Handout 1 is seen to be a special case of this for the “particle number” (or “normalisation”) operator $\hat{Q} = \hat{N} = 1$, for which

$$\rho_N = \frac{1}{2}(\psi^* \psi + \psi \psi^*) = \psi^* \psi$$

and

$$J_N = \frac{1}{4m} [(\hat{p}\psi)^* \psi + \psi^* (\hat{p}\psi) + \psi^* (\hat{p}\psi) + (\hat{p}\psi)^* \psi] = \frac{1}{2m} [(\hat{p}\psi)^* \psi + \psi^* \hat{p}\psi] = \frac{\rho_p}{m}$$

so

$$\frac{\partial \rho_N}{\partial t} + \frac{\partial J_N}{\partial x} = 0$$

since clearly $[\hat{H}, 1] = 0$. As an aside; if we think in terms of quantum mechanics measurements, then this very simple operator has an eigenvalue given by

$$\hat{N}\psi = \psi = \lambda\psi$$

so clearly $\lambda = 1$ is the only allowed value. This is why one particle is always found when a measurement of the total number of particles is made and hence why we need to normalise wavefunctions.

Note that if ψ happens to be an eigenstate of the operator \hat{Q} , so $\hat{Q}\psi = q\psi$, then the density and current density reduce to

$$\rho_Q = q\rho_N, \quad J_Q = qJ_N$$

E.g. in terms of a classical gas, this would be the case where every particle carries the same amount of the variable (e.g. momentum) and so the density of the variable is simply the same as the particle density multiplied by that common value.

Let us see whether the other operators we have are conserved or not. For $\hat{Q} = x$, then

$$[\hat{H}, x] = -\frac{i\hbar}{m}\hat{p}$$

so

$$\frac{\partial \rho_x}{\partial t} + \frac{\partial J_x}{\partial x} = \frac{1}{2m} [\psi^* (\hat{p}\psi) + (\hat{p}\psi)^* \psi] = \frac{\rho_p}{m}$$

For the case of $\hat{Q} = \hat{p}$, then

$$[\hat{H}, \hat{p}] = i\hbar \frac{dV}{dx} = -i\hbar F$$

where F is the force, so

$$\frac{\partial \rho_p}{\partial t} + \frac{\partial J_p}{\partial x} = \rho_F$$

Hence, momentum is conserved when there is no force. For $\hat{Q} = \hat{H}$, then clearly

$$[\hat{H}, \hat{H}] = 0$$

so

$$\frac{\partial \rho_H}{\partial t} + \frac{\partial J_H}{\partial x} = 0$$

and energy is conserved.

3 The Ehrenfest theorem

Taking equation 3 and integrating over all space gives

$$\int \frac{\partial(\psi^* \hat{Q} \psi)}{\partial t} dx + \int \frac{\partial}{\partial x} \left\{ \frac{1}{2m} [(\hat{p}\psi)^* \hat{Q} \psi + \psi^* \hat{p} \hat{Q} \psi] \right\} dx = \frac{i}{\hbar} \int \psi^* [\hat{H}, \hat{Q}] \psi dx$$

For any quantity J

$$\int_{-\infty}^{\infty} \frac{\partial}{\partial x} \{J\} dx = [J]_{-\infty}^{\infty} = 0$$

assuming J goes to zero at infinity, which is the case as wavefunctions have this behaviour. Also, since the integral is over space, the time derivative can be taken outside to give

$$\int \frac{\partial(\psi^* \hat{Q} \psi)}{\partial t} dx = \frac{d(\int \psi^* \hat{Q} \psi dx)}{dt}$$

and so in terms of expectation values

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

This looks very similar to the classical Hamilton equation of motion for a variable using the Poisson bracket defined in Lecture 1

$$\frac{dQ}{dt} = \{Q, H\}$$

This is therefore the basis of the Ehrenfest theorem: *The equations of motion for the expectation values of observables are the same as the equations of motion for their classical counterparts.*

The connection between the Poisson brackets and commutators is sometimes taken as a postulate of quantum mechanics and they are said to be generally exchangeable as

$$[\hat{A}, \hat{B}] \leftrightarrow i\hbar\{\hat{A}, \hat{B}\} \quad \text{or equivalently} \quad \{\hat{A}, \hat{B}\} \leftrightarrow -\frac{i}{\hbar}[\hat{A}, \hat{B}]$$

to go between quantum and classical mechanics. Note, do not confuse the classical Poisson bracket with the quantum anticommutator; they use the same notation but are very different things.

For the above operators

$$\begin{aligned} \frac{d\langle \hat{N} \rangle}{dt} &= \frac{i}{\hbar} \langle [\hat{H}, \hat{N}] \rangle = 0 \\ \frac{d\langle \hat{x} \rangle}{dt} &= \frac{i}{\hbar} \langle [\hat{H}, \hat{x}] \rangle = \frac{1}{m} \langle \hat{p} \rangle \\ \frac{d\langle \hat{p} \rangle}{dt} &= \frac{i}{\hbar} \langle [\hat{H}, \hat{p}] \rangle = -\left\langle \frac{dV}{dx} \right\rangle \\ \frac{d\langle \hat{H} \rangle}{dt} &= \frac{i}{\hbar} \langle [\hat{H}, \hat{H}] \rangle = 0 \end{aligned}$$

The classical equivalents of these four equations are: the number of particles remains unchanged, the velocity is p/m , the rate of change of momentum is equal to the force $F = -dV/dx$ (i.e. Newton's second law), and the energy is a constant (as we are considering conservative systems), respectively.

Second Year Quantum Mechanics - Handout 5

The Uncertainty Principle

Paul Dauncey, 14 Nov 2011

The goal is to derive the Uncertainty Principle from the postulates of quantum mechanics. To do this firstly requires some mathematical tools; specifically the Schwarz inequality.

1 The Schwarz inequality

In the following, all integrals should be understood as running over the whole x axis; the explicit $\pm\infty$ limits are omitted for clarity. Consider the expression

$$\int \left| f \left(\int |g|^2 dx \right) - g \left(\int g^* f dx \right) \right|^2 dx. \quad (1)$$

This must be greater than or equal to zero since the integrand is nowhere negative. This is true because the integrand is the square of the modulus of a complex function, say $\alpha(x) + i\beta(x)$, and the modulus squared of this function is $\alpha^2 + \beta^2$ which is a function that is positive or zero everywhere. We now expand the modulus squared in the above equation as the function times its complex conjugate

$$\int \left[f \left(\int |g|^2 dx \right) - g \left(\int g^* f dx \right) \right] \times \left[f^* \left(\int |g|^2 dx \right) - g^* \left(\int f^* g dx \right) \right] dx \geq 0$$

We now multiply out the square brackets giving

$$\begin{aligned} & \int \left[f f^* \left(\int |g|^2 dx \right)^2 - f^* g \left(\int |g|^2 dx \int g^* f dx \right) \right. \\ & \left. - g^* f \left(\int f^* g dx \int |g|^2 dx \right) + g g^* \left(\int f^* g dx \int g^* f dx \right) \right] dx \geq 0 \end{aligned}$$

and remembering that definite integrals like $\int g^* f dx$ are simply numbers, not functions, this gives

$$\begin{aligned} & \int |f|^2 dx \left(\int |g|^2 dx \right)^2 - \int f^* g dx \int |g|^2 dx \int g^* f dx \\ & - \int g^* f dx \int f^* g dx \int |g|^2 dx + \int |g|^2 dx \int f^* g dx \int g^* f dx \geq 0. \end{aligned}$$

Now the last two terms are equal and opposite so they cancel and the other two terms have a common positive factor $\int |g|^2 dx$ which cancels giving

$$\int |f|^2 dx \int |g|^2 dx - \int f^* g dx \int g^* f dx \geq 0$$

or

$$\int |f|^2 dx \int |g|^2 dx - \left| \int f^* g dx \right|^2 \geq 0$$

so

$$\int |f|^2 dx \int |g|^2 dx \geq \left| \int f^* g dx \right|^2, \quad (2)$$

which is the Schwarz inequality. Note we started by saying that equation 1 was always positive or zero. The equality sign in equation 2 holds when equation 1 is zero. This happens when

$f \propto g$, i.e. when $f = \lambda g$ where λ is any complex number. This can be shown as follows; if $f = \lambda g$ then equation 1 becomes

$$\int \left| \lambda g \left(\int |g|^2 dx \right) - g \left(\int \lambda g^* g dx \right) \right|^2 dx = \int \left| \lambda g \left(\int |g|^2 dx \right) - \lambda g \left(\int |g|^2 dx \right) \right|^2 dx = 0$$

The equivalent result can be found using equation 2. For $f = \lambda g$, the LHS becomes

$$\int |\lambda g|^2 dx \int |g|^2 dx = |\lambda|^2 \int |g|^2 dx \int |g|^2 dx = |\lambda|^2 \left(\int |g|^2 dx \right)^2$$

while the RHS becomes

$$\left| \int \lambda^* g^* g dx \right|^2 = |\lambda|^2 \left| \int g^* g dx \right|^2 = |\lambda|^2 \left(\int |g|^2 dx \right)^2$$

and hence both sides are equal for this case.

2 Proof of the Uncertainty Principle

If a number of measurements of the quantity represented by an operator \hat{Q} are made then the average result is equal to the expectation value

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

In any single measurement the deviation of the actual result from the average is represented by an eigenvalue of the operator

$$\hat{Q}' = \hat{Q} - \langle \hat{Q} \rangle$$

Now clearly $\langle \hat{Q} \rangle$, being an expectation value, is real, so we need to show that if \hat{Q} is Hermitian then $\hat{Q} + k$, where k is a real number, is also Hermitian. Consider

$$\begin{aligned} \int \psi_1^* (\hat{Q} + k) \psi_2 dx &= \int \psi_1^* \hat{Q} \psi_2 dx + \int k \psi_1^* \psi_2 dx = \int (\hat{Q} \psi_1)^* \psi_2 dx + \int (k \psi_1)^* \psi_2 dx \\ &= \int [(\hat{Q} \psi_1)^* + (k \psi_1)^*] \psi_2 dx = \int (\hat{Q} \psi_1 + k \psi_1)^* \psi_2 dx = \int [(\hat{Q} + k) \psi_1]^* \psi_2 dx \end{aligned}$$

Hence $\hat{Q} + k$ is Hermitian, which means \hat{Q}' is a Hermitian operator. We will want to work with the *variance*, i.e. the mean square, rather than the deviation and this can be defined as the expectation value of \hat{Q}'^2

$$\Delta q^2 = \int \psi^* (\hat{Q} - \langle \hat{Q} \rangle)^2 \psi dx = \int \psi^* \hat{Q}'^2 \psi dx$$

We can apply the Hermitian condition to our expression for Δq^2 giving

$$\Delta q^2 = \int \psi^* \hat{Q}' \hat{Q}' \psi dx = \int (\hat{Q}' \psi)^* \hat{Q}' \psi dx = \int |\hat{Q}' \psi|^2 dx$$

Similarly for measurements of another observable represented by \hat{R} we have

$$\Delta r^2 = \int |\hat{R}' \psi|^2 dx$$

where $\hat{R}' = \hat{R} - \langle \hat{R} \rangle$. Now consider the product

$$\Delta q^2 \Delta r^2 = \int |\hat{Q}'\psi|^2 dx \int |\hat{R}'\psi|^2 dx \geq \left| \int (\hat{Q}'\psi)^* (\hat{R}'\psi) dx \right|^2 \quad (3)$$

where we have used the Schwarz inequality (equation 2) with $f \equiv \hat{Q}'\psi$ and $g \equiv \hat{R}'\psi$. Now using the Hermitian property of \hat{Q}' again the integral on the RHS of equation 3 is

$$I = \int (\hat{Q}'\psi)^* \hat{R}'\psi dx = \int \psi^* \hat{Q}' \hat{R}'\psi dx$$

In order to make a connection with the commutator $[\hat{Q}, \hat{R}]$ we write this as

$$\begin{aligned} I &= \int \psi^* \hat{Q}' \hat{R}'\psi dx = \frac{1}{2} \left(\int \psi^* (\hat{Q}' \hat{R}' + \hat{R}' \hat{Q}')\psi dx - \int \psi^* (\hat{R}' \hat{Q}' - \hat{Q}' \hat{R}')\psi dx \right) \\ &= \int \psi^* \frac{1}{2} \{\hat{Q}', \hat{R}'\}\psi dx - i \int \psi^* \frac{i}{2} [\hat{Q}', \hat{R}']\psi dx \end{aligned} \quad (4)$$

We know from the lectures that the operators $i[\hat{Q}', \hat{R}']/2$ and $\{\hat{Q}', \hat{R}'\}/2$ are Hermitian. But the integrals on the RHS of equation 4 are just expectation values of these operators. The expectation values of Hermitian operators are real so we can write $I = a - ib$ where a and b are real and are given by

$$\begin{aligned} a &= \int \psi^* \frac{1}{2} \{\hat{Q}', \hat{R}'\}\psi dx \\ b &= \int \psi^* \frac{i}{2} [\hat{Q}', \hat{R}']\psi dx \end{aligned}$$

We are actually interested in $|I|^2$, which is

$$|I|^2 = I^* I = (a + ib)(a - ib) = a^2 + b^2$$

so that

$$|I|^2 = \left\{ \left(\int \psi^* \frac{1}{2} \{\hat{Q}', \hat{R}'\}\psi dx \right)^2 + \left(\int \psi^* \frac{i}{2} [\hat{Q}', \hat{R}']\psi dx \right)^2 \right\}$$

However, note

$$[\hat{Q}', \hat{R}'] = (\hat{Q} - \langle Q \rangle)(\hat{R} - \langle R \rangle) - (\hat{R} - \langle R \rangle)(\hat{Q} - \langle Q \rangle) = \hat{Q}\hat{R} - \hat{R}\hat{Q} = [\hat{Q}, \hat{R}]$$

and

$$\{\hat{Q}', \hat{R}'\} = (\hat{Q} - \langle Q \rangle)(\hat{R} - \langle R \rangle) + (\hat{R} - \langle R \rangle)(\hat{Q} - \langle Q \rangle) = \{\hat{Q}, \hat{R}\} - 2\hat{Q}\langle R \rangle - 2\hat{R}\langle Q \rangle + 2\langle Q \rangle\langle R \rangle$$

which gives an expectation value

$$\langle \{\hat{Q}', \hat{R}'\} \rangle = \langle \{\hat{Q}, \hat{R}\} \rangle - 2\langle Q \rangle\langle R \rangle$$

so we have

$$\Delta q^2 \Delta r^2 \geq \left(\left\langle \frac{1}{2} \{\hat{Q}, \hat{R}\} \right\rangle - \langle Q \rangle\langle R \rangle \right)^2 + \left(\left\langle \frac{i}{2} [\hat{Q}, \hat{R}] \right\rangle \right)^2 \quad (5)$$

This is the general form for the Uncertainty Principle. The inequality becomes an equality only in the special case where

$$\hat{Q}'\psi = \lambda \hat{R}'\psi \quad (6)$$

which is a feature of the Schwarz inequality.

Since both terms are real and positive then as

$$\Delta q^2 \Delta r^2 \geq a^2 + b^2$$

it is clear that the uncertainty product is bigger than either term by itself, i.e.

$$\Delta q^2 \Delta r^2 \geq a^2 = \left(\left\langle \frac{1}{2} \{ \hat{Q}, \hat{R} \} \right\rangle - \langle Q \rangle \langle R \rangle \right)^2 \quad \text{and} \quad \Delta q^2 \Delta r^2 \geq b^2 = \left(\left\langle \frac{i}{2} [\hat{Q}, \hat{R}] \right\rangle \right)^2$$

There are cases where one of a or b is zero, so these expressions can then be simplified. For the inequality to be an equality in these cases, we require both that $\hat{Q}'\psi = \lambda \hat{R}'\psi$ and that $a = 0$ or $b = 0$.

Let us now take the specific example of $\hat{Q} \equiv \hat{x}$ and $\hat{R} \equiv \hat{p}$. We know the commutator is always non-zero so consider the inequality

$$\begin{aligned} \Delta x^2 \Delta p^2 &\geq \left\langle \frac{i}{2} [\hat{x}, \hat{p}] \right\rangle^2 \\ \Delta x^2 \Delta p^2 &\geq \left(\int \psi^* \frac{i}{2} \hbar \psi \, dx \right)^2 \\ \Delta x^2 \Delta p^2 &\geq \frac{\hbar^2}{4} \left(\int \psi^* \psi \, dx \right)^2 \\ \Delta x^2 \Delta p^2 &\geq \frac{\hbar^2}{4} \\ \Delta x \Delta p &\geq \frac{\hbar}{2} \end{aligned}$$

This is a common form of the Uncertainty Principle. For this to be an equality, then we need

$$\left(\left\langle \frac{1}{2} \{ \hat{x}, \hat{p} \} \right\rangle - \langle x \rangle \langle p \rangle \right)^2 = 0 \quad \text{i.e.} \quad \left\langle \frac{1}{2} \{ \hat{x}, \hat{p} \} \right\rangle = \langle x \rangle \langle p \rangle$$

as well as

$$\hat{x}'\psi = \lambda \hat{p}'\psi \quad \text{i.e.} \quad (\hat{x} - \langle x \rangle)\psi = \lambda(\hat{p} - \langle p \rangle)\psi$$

These two conditions are indeed satisfied for some wavefunctions.

Second Year Quantum Mechanics - Handout 6

Perturbation Theory

Paul Dauncey, 22 Nov 2011

1 General concept

In classical and quantum mechanics alike there exist very few problems that can be solved exactly. Often we need to resort to approximation techniques and perturbation theory is one of the most popular. It was originally developed within the framework of classical mechanics but is now extensively used in quantum mechanics. In quantum mechanics we are very often interested in finding the energies of the bound states in a given potential. We proceed by assuming that the Hamiltonian can be split up into two parts

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (1)$$

The first part, \hat{H}_0 , is the Hamiltonian of a problem that can be solved exactly to find energy eigenvalues and eigenfunctions, i.e.

$$\hat{H}_0 u_n = E_n u_n \quad (2)$$

The second part, \hat{H}' , is the small perturbation. We might, for instance, assume \hat{H}_0 to be the Hamiltonian for a infinite square well. Now this may be used as an idealised model for certain ‘quantum well’ semiconductor devices. As an example of a perturbation we might assume that a device has been manufactured with a small slope at the bottom of the well (see figure 1). We might expect the energy eigenfunctions of the perturbed system to be similar to those of the unperturbed system. Intuitively we might guess that any differences should manifest themselves as an increased amplitude for finding the particle on the left hand side of the well. We might also expect the energy levels to be raised a bit in the perturbed well. A similar problem is set on Problem Sheet 8. Although we may have this specific example in mind, the methods are completely general.

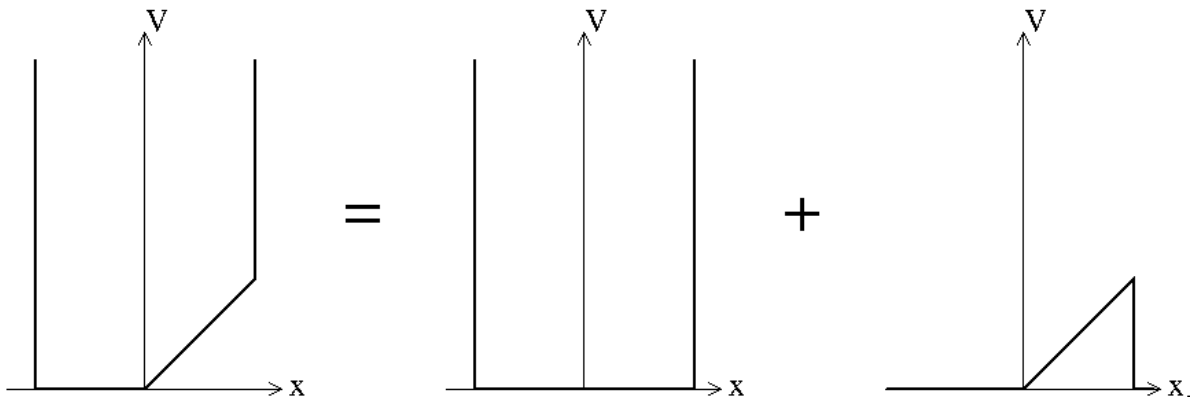


Figure 1: A perturbed infinite square well potential, shown as the sum of a normal infinite square well potential and a perturbing potential.

We assume that the eigenfunctions u_n corresponding to the eigenvalues E_n of \hat{H}_0 form a complete orthonormal set. So if u_m and u_n are members of that set then we have

$$\int u_m^* u_n dx = \delta_{mn} \quad (3)$$

The full eigenvalue problem we want to solve is given by the time independent Schrödinger equation

$$\hat{H}U_n = \mathcal{E}_n U_n \quad (4)$$

where we use U_n to mean the true energy eigenfunctions of the perturbed system. We should expect the perturbation to shift the energy levels according to

$$\mathcal{E}_n = E_n + E_n^{(1)} \quad (5)$$

where $E_n^{(1)}$ is a small shift in the n^{th} energy level. The meaning of the superscript (1) is made clear below. Now in general the energy levels of a system are given by the expectation value of the Hamiltonian. It is therefore tempting to use the wavefunctions u_n to calculate the expectation value of the perturbation Hamiltonian \hat{H}' to give us a value for $E_n^{(1)}$.

$$E_n^{(1)} = \int_{-\infty}^{\infty} u_n^* \hat{H}' u_n dx = \langle H' \rangle_n \quad (6)$$

We know this will not give us exactly the right answer since we have used the unperturbed wavefunctions. If the perturbation is small we might expect this approach to give reasonable results, assuming the change in the wavefunctions due to the perturbation is small.

It turns out that this approach works very well for a large class of problems. Furthermore, as shown below, equation (6) can be put on a much firmer footing. The next section also outlines the method by which it can be shown that the total wavefunction is modified according to

$$U_n = u_n + u_n^{(1)} \quad (7)$$

where $u_n^{(1)}$ is the correction to the wavefunction, and is given by

$$u_n^{(1)} = \sum_{m \neq n} \left(\frac{\int_{-\infty}^{\infty} u_m^* \hat{H}' u_n dx}{E_n - E_m} \right) u_m \quad (8)$$

The perturbed wavefunction can therefore be expressed as a superposition of the unperturbed wavefunctions.

2 Mathematical derivation

Our starting point will be to write down “perturbation expansions” for the eigenfunctions and eigenvalues. We assume that the perturbed energy level \mathcal{E}_n is much closer to E_n than to any other unperturbed level. We then write

$$U_n = u_n + u_n^{(1)} + u_n^{(2)} + \dots \quad (9)$$

and

$$\mathcal{E}_n = E_n + E_n^{(1)} + E_n^{(2)} + \dots \quad (10)$$

The numbers in brackets denote the “order” of the correction term in question. The terms on the right hand sides of equations (9) and (10) are therefore progressively smaller as the order increases. Substituting these expansions into equation (4) and using equation (1) we have

$$(\hat{H}_0 + \hat{H}')(u_n + u_n^{(1)} + u_n^{(2)} + \dots) = (E_n + E_n^{(1)} + E_n^{(2)} + \dots)(u_n + u_n^{(1)} + u_n^{(2)} + \dots) \quad (11)$$

Multiplying out the brackets in equation (11) we can simplify the resulting equation by grouping the terms by *order*. Terms like $\hat{H}_0 u_n$ on the left hand side and $E_n u_n$ on the right hand side are obviously zero order terms. The $\hat{H}' u_n$ term on the left hand side is clearly a first order term since it has the “small” bit of the Hamiltonian acting on a zero order wavefunction. However, $\hat{H}_0 u_n^{(1)}$ is also a first order term since the zero order Hamiltonian here acts on a “small” bit of wavefunction. By similar reasoning, on the right hand side the terms $E_n u_n^{(1)}$ and $E_n^{(1)} u_n$ are both first order. Second order terms arise in a number of ways. Looking at the right hand side, clearly terms like $E_n u_n^{(2)}$ and $E_n^{(2)} u_n$ are second order, but so too is the term $E_n^{(1)} u_n^{(1)}$ since here something “very small” is generated by the product of two “small” things. The next crucial step in perturbation theory is to insist that the sum of all the terms of a given order on the left hand side of equation (11) must balance out the sum of all the terms of the same order on the right hand side. We can then split equation (11) up into separate, simpler equations for the different orders. In zero order we have, rather unsurprisingly

$$\hat{H}_0 u_n = E_n u_n \quad (12)$$

which is identical to equation (2). In first order we have

$$\hat{H}_0 u_n^{(1)} + \hat{H}' u_n = E_n u_n^{(1)} + E_n^{(1)} u_n \quad (13)$$

In second order we have

$$\hat{H}_0 u_n^{(2)} + \hat{H}' u_n^{(1)} = E_n u_n^{(2)} + E_n^{(1)} u_n^{(1)} + E_n^{(2)} u_n \quad (14)$$

We could, in principle continue on up to third order and beyond but we will not do so here.

The perturbation expansions can be justified by considering a more intuitive, iterative approach to the problem. The perturbation causes some small changes to both the energy eigenvalues and the eigenfunctions. We would write $U_n = u_n + u_n^{(1)}$ and $\mathcal{E}_n = E_n + E_n^{(1)}$. If we substitute these expressions into the time independent Schrödinger equation (equation (4)) we could attempt to find solutions for $E_n^{(1)}$ and $u_n^{(1)}$. We would find the solutions don't work without “throwing away” some small terms. We would then find solutions for $E_n^{(1)}$ and $u_n^{(1)}$ but we would know that our total energies and wavefunctions were still only approximate, since we had thrown away some terms. We could then attempt to get an even better solution by going back to the beginning and writing down $U_n = [u_n + u_n^{(1)}] + u_n^{(2)}$ and $\mathcal{E}_n = [E_n + E_n^{(1)}] + E_n^{(2)}$. Substituting these into the time independent Schrödinger equation, we would then discover that solutions for $E_n^{(2)}$ and $u_n^{(2)}$ could only be found if third order terms were ignored. This process could, of course, be iterated infinitely. In effect this procedure amounts to writing down the perturbation expansions of equations (9) and (10) *and* adding the condition that we equate terms of the same order on either side of the Schrödinger equation.

Let us set about using equation (13) to find the first order correction to the energy. In our calculation we will need to use the fact that \hat{H}_0 is Hermitian. The Hermitian condition for \hat{H}_0 is given by

$$\int_{-\infty}^{\infty} u_a^* \hat{H}_0 u_b dx = \int_{-\infty}^{\infty} (\hat{H}_0 u_a)^* u_b dx \quad (15)$$

We proceed by multiplying equation (13) by u_n^* and integrating over all space. This gives

$$\int_{-\infty}^{\infty} u_n^* (\hat{H}_0 - E_n) u_n^{(1)} dx + \int_{-\infty}^{\infty} u_n^* (\hat{H}' - E_n^{(1)}) u_n dx = 0 \quad (16)$$

Using the Hermitian condition along with equation (2) so that

$$\int_{-\infty}^{\infty} u_n^* \hat{H}_0 u_n^{(1)} dx = \int_{-\infty}^{\infty} (\hat{H}_0 u_n)^* u_n^{(1)} dx = E_n \int_{-\infty}^{\infty} u_n^* u_n^{(1)} dx \quad (17)$$

and the orthonormality condition, equation (3), then equation (16) reduces to

$$E_n^{(1)} = \int_{-\infty}^{\infty} u_n^* \hat{H}' u_n dx = \langle H' \rangle_n \quad (18)$$

Equation (18) is the result we were looking for. It tells us that we find the first order correction to the energy by calculating the expectation value of the perturbation Hamiltonian using the zero order eigenfunction. Let us now try to calculate the second order correction to the energy. To do this we use equation (14). Again we multiply by u_n^* and integrate over all space giving

$$\int_{-\infty}^{\infty} u_n^* (\hat{H}_0 - E_n) u_n^{(2)} dx + \int_{-\infty}^{\infty} u_n^* (\hat{H}' - E_n^{(1)}) u_n^{(1)} dx - E_n^{(2)} \int_{-\infty}^{\infty} u_n^* u_n dx = 0 \quad (19)$$

We again use the Hermitian condition (equation (15)) and orthonormality (equation (3)) to yield

$$E_n^{(2)} = \int_{-\infty}^{\infty} u_n^* (\hat{H}' - E_n^{(1)}) u_n^{(1)} dx \quad (20)$$

This is the second order correction to the energy. Notice however, that it contains the first order correction to the eigenfunction. Therefore, in order to calculate $E_n^{(2)}$ explicitly we will first have to calculate the first order correction to the wavefunction. Since the eigenfunctions u_n form a complete set we can expand any arbitrary wavefunction in terms of this basis. In particular we can write down an expansion of $u_n^{(1)}$ as

$$u_n^{(1)} = \sum_{m \neq n} a_{nm}^{(1)} u_m \quad (21)$$

where we exclude $m = n$ as this is the original eigenstate. To find the values of the $a_{nm}^{(1)}$ we substitute equation 21 into equation 13 which gives

$$(\hat{H}_0 - E_n) \sum_m a_{nm}^{(1)} u_m + (\hat{H}' - E_n^{(1)}) u_n = 0 \quad (22)$$

Multiplying by u_l^* and integrating over all space gives

$$a_{nl}^{(1)} (E_l - E_n) + \int_{-\infty}^{\infty} u_l^* \hat{H}' u_n dx - E_n^{(1)} \delta_{nl} = 0 \quad (23)$$

where we have used $\hat{H}_0 u_l = E_l u_l$ and $\int u_l^* u_n dx = \delta_{nl}$. The a_{nl} are only for $n \neq l$, for which we have

$$a_{nl}^{(1)} = \frac{\int_{-\infty}^{\infty} u_l^* \hat{H}' u_n dx}{E_n - E_l} \quad (24)$$

$$u_n^{(1)} = \sum_{m \neq n} \left(\frac{\int_{-\infty}^{\infty} u_m^* \hat{H}' u_n dx}{E_n - E_m} \right) u_m \quad (25)$$

Substituting this back into equation (20) gives an expression for $E_n^{(2)}$ in terms of things we can calculate. The integral $\int_{-\infty}^{\infty} u_m^* \hat{H}' u_n dx$ is called a *matrix element*. You will encounter these again next term when you calculate transition rates between states.

Second Year Quantum Mechanics - Handout 7

Wavefunctions in spherical polar coordinates

Paul Dauncey, 6 Dec 2011

Many important problems are best treated using spherical polar coordinates rather than Cartesian coordinates. The relationship between these two coordinate systems is shown in figure 1.

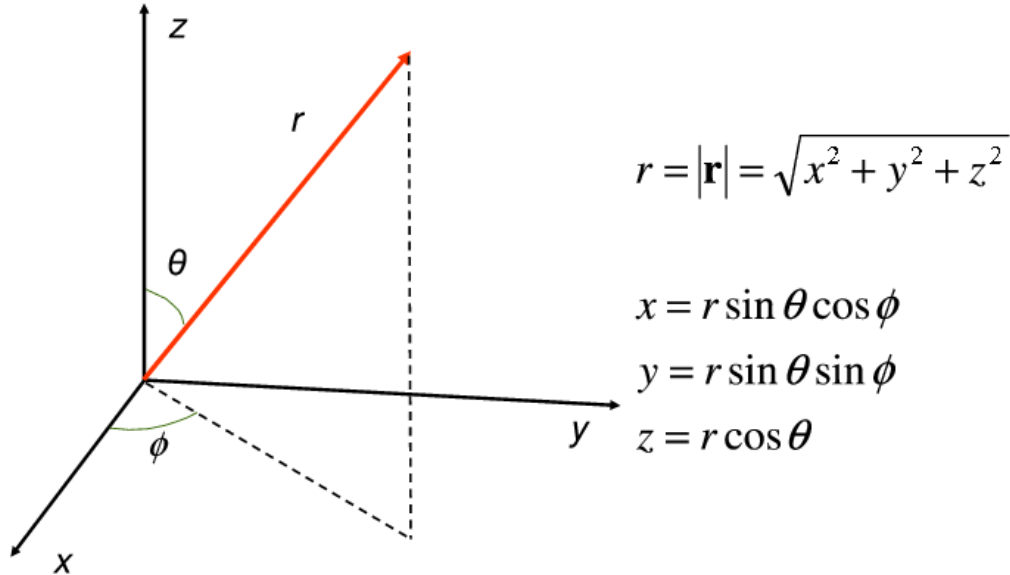


Figure 1: The relationship between spherical polar coordinates and Cartesian coordinates.

In the lectures we will see that the 3D time independent Schrödinger equation is a partial differential equation in r , θ and ϕ . For central potentials, i.e. where $V(\mathbf{r}) = V(r)$, a separation of variables can be achieved by writing the wavefunction $u(\mathbf{r}) = R(r)\Theta(\theta)\Phi(\phi)$. The resulting Φ equation is straightforward

$$-i\hbar \frac{d\Phi}{d\phi} = m_l \hbar \phi \quad \text{so} \quad \Phi(\phi) = A e^{im_l \phi}$$

where A is a normalisation constant, and the imposition of boundary conditions leads to the constraint that m_l must be an integer.

The equation for Θ turns out to be the associated Legendre equation which can be solved by series methods. The special case of $m_l = 0$ leads to the Legendre equation. This is easier to solve than the full problem for arbitrary m_l so we will outline the approach below. The solution to the full problem (the associated Legendre equation) is more complicated. The solution can be found in textbooks on mathematics.

For the $m_l = 0$ case we have the basic Legendre equation. We set $\cos \theta = \epsilon$ and $P(\epsilon) = \Theta(\theta)$ which gives

$$\frac{d}{d\epsilon} \left[(1 - \epsilon^2) \frac{dP}{d\epsilon} \right] + cP = 0 \tag{1}$$

where c is the separation constant. We attempt a series solution

$$P = \sum_{p=0}^{\infty} a_p \epsilon^p$$

We start by differentiating P giving

$$\frac{dP}{d\epsilon} = \sum_{p=0}^{\infty} a_p p \epsilon^{p-1}$$

The first term in equation 1 is then

$$\begin{aligned} \frac{d}{d\epsilon} \left[(1 - \epsilon^2) \frac{dP}{d\epsilon} \right] &= \frac{d}{d\epsilon} \sum_{p=0}^{\infty} [a_p p \epsilon^{p-1} - a_p p \epsilon^{p+1}] \\ &= \sum_{p=2}^{\infty} a_p p (p-1) \epsilon^{p-2} - \sum_{p=0}^{\infty} a_p p (p+1) \epsilon^p \\ &= \sum_{p'=0}^{\infty} a_{p'+2} (p'+2)(p'+1) \epsilon^{p'} - \sum_{p=0}^{\infty} a_p p (p+1) \epsilon^p \end{aligned}$$

where, in the last step, we have defined $p' = p - 2$. Note that in the second to last line the first summation begins from $p = 2$. This is because the $p = 0$ and $p = 1$ terms vanish. With the change of index from p to p' the summation must run from $p' = 0$. Now p and p' are just indices of summation so we can write them both as say p . If we do this and insert the resulting expression in equation 1 we get

$$\sum_{p=0}^{\infty} [a_{p+2}(p+2)(p+1) - a_p p (p+1) + a_p c] \epsilon^p = 0$$

This can only be true if the coefficient of each power of ϵ is zero which leads to

$$\begin{aligned} 0 &= a_{p+2}(p+2)(p+1) - a_p p (p+1) + a_p c \\ &= a_{p+2}(p+2)(p+1) - a_p [p(p+1) - c] \end{aligned}$$

which leads to the recurrence relation

$$\frac{a_{p+2}}{a_p} = \frac{p(p+1) - c}{(p+1)(p+2)}.$$

Now $a_{p+2}/a_p \rightarrow p/(p+2)$ as $p \rightarrow \infty$. This is the same recurrence relation as we find for the two series

$$\frac{1}{2} + \frac{1}{4} + \frac{1}{6} + \frac{1}{8} + \dots \quad (2)$$

and

$$\frac{1}{1} + \frac{1}{3} + \frac{1}{5} + \frac{1}{7} + \dots \quad (3)$$

Both of these series are divergent. However, at the points where $\epsilon = \pm 1$ we have $\epsilon^p = \pm 1$ regardless of the value of p and, for $p \rightarrow \infty$, P is simply one of the above series. P is therefore divergent at the extreme ends of its range i.e. where $\cos \theta = \epsilon = \pm 1$.

If the series solution for P is to remain bounded at the ends of its range then the series must not be infinite but must terminate at some maximum value of p , say l . This constraint gives the condition $a_{l+2}/a_l = 0$ which in turn gives $c = l(l+1)$. Furthermore, since the recurrence relation links the $(p+2)$ term to the p term we have to insist that either $a_0 = 0$ when l is odd or $a_1 = 0$ when l is even. With these constraints we have

$$P_l(\epsilon) = \sum_{p=0}^l a_p \epsilon^p$$

It remains to fix the values of a_0 and a_1 for the cases when they are not equal to zero. For applications in quantum mechanics where we use these functions as elements of the full three-dimensional wavefunction it doesn't really matter what values we choose since the entire wavefunction will be normalised at the end of the whole process. Conventionally the coefficients a_0 and a_1 are chosen so that the function P has the value $+1$ when $\epsilon = 1$. The special functions that are solutions of the Legendre equation with no singularities are called the Legendre polynomials. The first few Legendre polynomials are given by

$$\begin{aligned} P_0(\cos \theta) &= 1 &= 1 \\ P_1(\cos \theta) &= \epsilon &= \cos \theta \\ P_2(\cos \theta) &= \frac{1}{2}(3\epsilon^2 - 1) &= \frac{1}{2}(3 \cos^2 \theta - 1) \\ P_3(\cos \theta) &= \frac{1}{2}(5\epsilon^3 - 3\epsilon) &= \frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta) \end{aligned}$$

For the general case where $m_l \neq 0$ the θ equation becomes the associated Legendre equation whose solutions are

$$P_l^{|m_l|}(\epsilon) = (1 - \epsilon^2)^{|m_l|/2} \frac{d^{|m_l|} P_l(\epsilon)}{d\epsilon^{|m_l|}}$$

If we take the explicit example of $l = 1$ and $m_l = 2$ it is clear that the $|m_l|^{\text{th}}$ derivative of $P_l(\epsilon)$, i.e. the 2nd derivative in this example, is zero since $P_l(\epsilon)$ is a polynomial of order l . This means that the wavefunction would become zero everywhere if $|m_l| > l$. The result is that there is a link between the quantum numbers l and m_l and it can be expressed as

$$-l \leq m_l \leq l$$

The first few associated Legendre polynomials are given in table 1.

$$\begin{aligned} P_0^0(\cos \theta) &= 1 \\ P_1^0(\cos \theta) &= \cos \theta \\ P_1^1(\cos \theta) &= (1 - \cos^2 \theta)^{\frac{1}{2}} = \sin \theta \\ P_2^0(\cos \theta) &= \frac{1}{2}(3 \cos^2 \theta - 1) \\ P_2^1(\cos \theta) &= 3(1 - \cos^2 \theta)^{1/2} \cos \theta = 3 \sin \theta \cos \theta \\ P_2^2(\cos \theta) &= 3(1 - \cos^2 \theta) = 3 \sin^2 \theta \end{aligned}$$

Table 1: Explicit formulæ for the first few (associated) Legendre polynomials $P_l^{|m_l|}$.

With these, we can finally put together a full angular solution for θ and ϕ . Once these have been normalised they are called the *spherical harmonics*. The first few spherical harmonics are given in table 2.

$$\begin{aligned}
Y_{00} &= \sqrt{\frac{1}{4\pi}} \\
Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos \theta \\
Y_{1\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} \\
Y_{20} &= \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \\
Y_{2\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi} \\
Y_{2\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}
\end{aligned}$$

Table 2: Explicit formulæ for the first few spherical harmonics Y_{lm_l} .

Solutions of the radial equation can only be found when an explicit form for the potential has been stipulated. The first example you will encounter (next term, Applications of Quantum Mechanics) will be the hydrogen atom for which the potential is given by

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

The radial equations for hydrogen are give in table 3. For these functions $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.29 \times 10^{-11}$ m, which is known as the Bohr radius. Z is the number of positive charges located at the nucleus. For hydrogen $Z = 1$, but other systems can behave exactly like hydrogen. For instance, “hydrogen-like helium” is a helium nucleus (containing two protons) with a single attached electron. The system is not electrically neutral - it is an ion - but apart from the fact that $Z = 2$ for this system, the calculations are exactly the same as for hydrogen. It turns out that the energies scale as Z^2 times the hydrogen energies, so the electron is much more tightly bound in these systems than in hydrogen.

$$\begin{aligned}
R_{10}(r) &= 2 \left(\frac{Z}{a_0}\right)^{3/2} e^{-(Zr/a_0)} \\
R_{20}(r) &= 2 \left(\frac{Z}{2a_0}\right)^{3/2} \left(1 - \frac{Zr}{2a_0}\right) e^{-(Zr/2a_0)} \\
R_{21}(r) &= \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-(Zr/2a_0)} \\
R_{30}(r) &= 2 \left(\frac{Z}{3a_0}\right)^{3/2} \left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2r^2}{27a_0^2}\right) e^{-(Zr/3a_0)} \\
R_{31}(r) &= \frac{4\sqrt{2}}{9} \left(\frac{Z}{3a_0}\right)^{3/2} \left(1 - \frac{Zr}{6a_0}\right) \left(\frac{Zr}{a_0}\right) e^{-(Zr/3a_0)} \\
R_{32}(r) &= \frac{4}{27\sqrt{10}} \left(\frac{Z}{3a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-(Zr/3a_0)}
\end{aligned}$$

Table 3: Explicit formulæ for the first few “hydrogen-like” radial wave functions $R_{nl}(r)$.