

5 Formalism

5.1 Commutator algebra

we saw $[A, B] = AB - BA = -[B, A]$ and that this is NOT necessarily equal to zero i.e operators do not have to commute. and they will NOT commute if we are trying to simultaneously measure position and momentum. $[x, p] = i\hbar$. we obviously have $[A, A] = 0$.

$$[A+B, C] = (A+B)C - C(A+B) = AC + BC - CA - CB = [A, C] + [B, C]$$

$$[AB, C] = ABC - CAB = ABC - ACB + ACB - CAB = A[B, C] + [A, C]B$$

$$[A, BC] = ABC - BCA = ABC - BAC + BAC - BCA = [A, B]C + B[A, C]$$

e.g $[H, x]$ its always good to give this a wavefunction to see what we are doing so

$$\begin{aligned} [H, x]\psi &= [p^2/2m + V(x), x]\psi = [p^2/2m, x]\psi + [V(x), x]\psi = 1/2m[p^2, x] \\ &= 1/2m(p[p, x] + [p, x]p) = 1/2m(p \cdot -i\hbar + -i\hbar p)\psi = -2i\hbar/2mp\psi = -i\hbar/mp\psi \end{aligned}$$

take away the test wavefunction and we have $[H, x] = -(i\hbar/m)p$. similarly all operators A, B which commute share a common set of eigenfunctions - we can prove this. let $Af_n = a_n f_n$. then

$[A, B] = 0$ implies $ABf_n - BAf_n = 0$. so $A(Bf_n) = a_n(Bf_n)$ but this means that $Bf_n \propto f_n$ i.e. $Bf_n = b_n f_n$ so $A(Bf_n) = a_n(Bf_n)$ so $A(b_n f_n) = a_n b_n f_n$ in other words $[A, B] = 0$ implies that A and B SHARE common eigenfunction f_n .

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

5.2 generalized statistical interpretation

if you measure an observable $Q(x, p)$ on a particle in state $\Psi(x, t)$ then you are certain to get one of the eigenvalues of the Hermitian operator Q . If the

particle is bound then the spectrum of Q is discrete, so there are eigenvalues q_n associated with eigenfunctions f_n .

Eigenfunctions have the property that they are orthonormal so $\int f_n^* f_m dx = \delta_{nm}$. They are also complete in that they span the space so any arbitrary function $\Psi(x, t)$ can be written as a linear sum of them $\Psi(x, t = 0) = \sum_n c_n f_n(x)$. Then the probability of measuring q_n is $|c_n|^2$ where $c_n = \int f_n^* \Psi(x, t = 0) dx$. Upon measurement the wavefunction 'collapses' into the state f_n . Any further measurement will always return the value q_n .

The observable energy only has a deterministic value if the system is in one of these eigenstates of the Hamiltonian ψ_n , at which point the energy is E_n . If it's not one of the eigenstates, if it has instead some arbitrarily shaped wavefunction ψ , then this can be expanded out as a sum of all the different eigenstates so $\psi = \sum_n c_n \psi_n$. But then the outcome is NOT deterministic. The systems can only be on ONE of the states. We don't know which one, we only know the probability as we know the average energy is

$$\begin{aligned} \langle E \rangle &= \int \psi^* H \psi dV = \int \sum_n c_n^* \psi_n^* H \left(\sum_m c_m \psi_m \right) dV = \sum_n c_n^* \sum_m c_m \int \psi_n^* E_m \psi_m dV \\ &= \sum_n c_n^* \sum_m c_m E_m \delta_{nm} = \sum_n (c_n)^2 E_n \end{aligned}$$

the only way this works is if each state n has probability of c_n^2 of being observed.

If we prepare many identical copies of the system, i.e. all having the same initial state wavefunctions ψ then the probability we measure the energy is E_n is c_n^2 but we can't tell WHICH system will give us which energy.

Probability is at the heart of quantum mechanics. It is inherently non-deterministic, a statistical theory.

6 Schroedinger in 3D

so far we have stuck in only 1D. but we will need to go to 3D to treat a lot of physical situations like of electrons in atoms. again we can use our operator approach.

6.1 cartesian coordinates

if we are in 3D, then $E = T + V$ but kinetic energy can now have components in all 3 directions. so $T = p_x^2/2m$ was what we had when the motion was just along the x axis. so now in 3D we have total squared momentum to use in kinetic energy is given by $p^2 = p_x^2 + p_y^2 + p_z^2$. Hence

$$H = \frac{p^2}{2m} + V(x, y, z, t) = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(x, y, z, t)$$

$$i\hbar \frac{\partial}{\partial t} = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right)^2 + \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial y} \right)^2 + \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial z} \right)^2 + V(x, y, z, t)$$

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

so our 3D Schroedinger equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V(x, y, z, t) \Psi$$

where $\Psi = \Psi(x, y, z, t)$. We can write this more compactly in vector form by recognising that $\underline{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ so $\Psi(x, y, z, t) = \Psi(\underline{r}, t)$ and $V(x, y, z, t) = V(\underline{r}, t)$. Then

$$i\hbar \frac{\partial \Psi(\underline{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\underline{r}, t) + V(\underline{r}, t) \Psi(\underline{r}, t)$$

and we can use the same separation of variables techniques to show that as long as the potential is NOT dependent on time then the equation is separable in time and space as $\Psi_n(\underline{r}, t) = \psi_n(\underline{r}) e^{-iE_n t/\hbar}$ where the time independent equation to solve is

$$\frac{-\hbar^2}{2m} \nabla^2 \psi_n(\underline{r}) + V \psi_n(\underline{r}) = E_n \psi_n(\underline{r})$$

or going back explicitly to cartesian coordinates

$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2 \psi_n}{\partial x^2} + \frac{\partial^2 \psi_n}{\partial y^2} + \frac{\partial^2 \psi_n}{\partial z^2} \right) + V(x, y, z) \psi_n = E \psi_n(x, y, z)$$

This is separable into $\psi_n(x, y, z) = X(x)Y(y)Z(z)$ if $V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$.

$$\frac{-\hbar^2}{2m} \left(YZ \frac{\partial^2 X}{\partial x^2} + XZ \frac{\partial^2 Y}{\partial y^2} + XY \frac{\partial^2 Z}{\partial z^2} \right) + (V_x + V_y + V_z)XYZ = EXYZ$$

divide by XYZ to get

$$\left(\frac{-\hbar^2}{2mX} \frac{\partial^2 X}{\partial x^2} + V_x \right) + \left(-\frac{\hbar^2}{2mY} \frac{\partial^2 Y}{\partial y^2} + V_y \right) + \left(-\frac{\hbar^2}{2mZ} \frac{\partial^2 Z}{\partial z^2} + V_z \right) = E$$

these three groups are each dependent only on x, y and z respectively so NONE of them can depend on x,y or z - they must be constants which we'll call E_x, E_y, E_z . Then we get the three equations

$$\frac{-\hbar^2}{2m} \frac{\partial^2 X(x)}{\partial x^2} + V_x X(x) = E_x X(x)$$

$$\frac{-\hbar^2}{2m} \frac{\partial^2 Y(y)}{\partial y^2} + V_y Y(y) = E_y Y(y)$$

$$\frac{-\hbar^2}{2m} \frac{\partial^2 Z(z)}{\partial z^2} + V_z Z(z) = E_z Z(z)$$

and $E_x + E_y + E_z = E$