

1 Basics - in 1D

1.1 Time dependent Sch. equation and operators

In the heart of classical mechanics in 1D we have Newton $F = ma$. For conservative forces $F = m \frac{\partial^2 x}{\partial t^2} = -\frac{\partial V}{\partial x}$. we can get $x(t)$ if we know the potential and some boundary conditions. All other dynamical quantities follow eg $v(t) = dx/dt$, $p = mv$, $KE = mv^2/2 = p^2/2m$ etc

In quantum mechanics we also need the potential but we look for the wave function $\Psi(x, t)$ as wave particle duality means that particles are 'wavy'. We can't know position and momentum simultaneously $\Delta x \Delta p \geq \hbar/2$. We can't get velocity, etc from dx/dt as there is no well defined $x(t)$. Waves in free space have $\Psi = Ne^{i(kx - \omega t)}$ (left to right), and $p = \hbar k$. $\partial\Psi/\partial x = Nike^{i(kx - \omega t)} = ik\Psi$. This gets us to operators $\hat{p}\Psi = \frac{\hbar}{i}\partial\Psi/\partial x$ i.e. $\hat{p} = -i\hbar\partial/\partial x$. Then we can get $KE = p^2/2m = -\hbar^2/2m\partial^2/\partial x^2$. Total energy (Hamiltonian) $\hat{H} = KE + PE = p^2/2m + V$. But for waves we also know that total energy $E = \hbar\omega$. $\partial\Psi/\partial t = -i\omega\Psi$ hence $E = \hbar/(-i)\partial/\partial t = i\hbar\partial/\partial t$ Hence we get Schroedingers equation in 1D which we solve for Ψ from boundary conditions

$$E\Psi = i\hbar \frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2\Psi}{\partial x^2} + V\Psi = \hat{H}\Psi \quad \text{where } \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \quad (1)$$

$\Psi(x, t)$ now has a probabilistic interpretation - probability of finding particle between a and b at time t is $\int_a^b |\Psi(x, t)|^2 dx$. Thus it has to normalise to unity over all space $\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1$. $|\Psi(x, t)|^2$ is the probability density.

1.2 Observables

We now get all other dynamical quantities, A , by writing it in operator form \hat{A} - replace any quantity involving p by \hat{p} . Then the expectation value from any measurement is $\langle A \rangle = \int \Psi^* \hat{A} \Psi dx$. $\langle x \rangle = \int \Psi^* x \Psi dx$, $\langle p \rangle = \int \Psi^* (-i\hbar\partial/\partial x) \Psi dx$...

Anything we can observe HAS to be real ie $\langle A \rangle = \langle A \rangle^*$ so $\int \Psi^* (\hat{A}\Psi) dx = \int \Psi \hat{A}^* \Psi^* dx = \int (\hat{A}\Psi)^* \Psi dx$ Any operator which has this property is termed Hermitian. Only Hermitian operators can represent observables. The Hamiltonian is forced to be Hermitian by virtue of conservation of probability! so energy is always a real observable.

1.3 Time independent Schroedinger equation

We can split the time dependent sch equation up into a time and spatial part IF the potential is NOT time dependent. So for $V(x, t) = V(x)$ we get $\Psi(x, t) = \psi(x)T(t)$ where $T(t) = e^{-iEt/\hbar}$ and $\psi(x)$ satisfies

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

So we solve this EIGENVALUE equation (operator acting on a function returns a function multiplied by a number) to get $\psi(x)$.

If the particle is bound then its a standing wave. There are only so many ways to fit this into the potential so the solutions are quantised. This gives a series of possible solutions (eigenfunctions) $\psi_n(x)$ all of which satisfy the time independent Schroedinger equation, each with their own quantised eigenenergy E_n . We normalise each one so that $\int \psi_n(x)^* \psi_n(x) dx = 1$ and then these form an orthonormal basis so $\int \psi_n(x)^* \psi_m(x) dx = \delta_{nm}$ i.e. 1 when $n = m$ (as we normalised it to itself) and 0 otherwise. These form a basis set, so any arbitrary wavefunction $\psi(x)$ can be decomposed into a sum of eigenfuctions so $\psi(x) = \sum_n c_n \psi_n(x)$ where $c_n = \int \psi_n^* \psi(x) dx$. since the wavefunctions are normalised than $\sum_n c_n^2 = 1$ When we measure the system we force it to pick ONE of the possible eigenfunctions, $\psi_n(x)$. The probability that it picks ψ_n is c_n^2 for a normalised wavefunction. So there is probability c_n^2 to measure energy E_n . This is not the same as the expectation value $\langle E \rangle = \sum_n c_n^2 E_n$

we saw examples of these eigenfunctions - infinite square well potential ($0 < x < L$: $\psi_n(x) \propto \sin n\pi x/L$ $n = 1, 2 \dots$), harmonic potential $\frac{1}{2}\kappa x^2$ $\psi_n(x) \propto e^{-\alpha^2 x^2/2} H_n(\alpha x)$, $n = 0, 1, 2 \dots$ where H_n are Hermite polynomials and $n = 0$ means there is a zero point energy).

The full time dependent solution is $\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$.

1.4 Commutators

We can only observe quantities simultaneously to arbitrary accuracy if they commute ie the commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$ eg $[x, p_x]\psi = x(p_x\psi) - p_x(x\psi) = i\hbar!$ The measurement of x disturbs the wavefunction for the measurement of p. Alternatively, measuring p disturbs the wavefunction for measuring x. $[\hat{A}, \hat{B}] = 0$ means that \hat{A}, \hat{B} share common eigenfunctions f , so $Af = af$, and $Bf = bf$ and measuring one does not disturb the wavefunction for the other.

2 Schroedinger in 3D

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi = E\Psi$$

Normalisation is now over the entire volume so that $\int \psi^* \psi dV = 1$

2.1 Cartesians

$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. If the potential is separable so $V(x, y, z) = V_x(x)V_y(y)V_z(z)$ then we just have 3 time independent Schroedinger equations to solve for the 3 coordinates, for $\psi_{n_x, n_y, n_z}(x, y, z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$ where each direction has its own quantum number eg infinite square well potential, and 3D harmonic potential. Volume integral is $\int \int \int \psi^* \psi dx dy dz$.

In 2D or 3D there is much more room. and any symmetry comes at a price of introducing a degeneracy - same energy but different wavefunction!

2.2 Spherical polars

∇^2 has much more difficult form. But the electrostatic potential $V(x, y, z) = -Ze/4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}$ is not separable in cartesian coordinates but is in spherical polars $V(r) = -Ze/4\pi\epsilon_0r$. For ANY spherically symmetric radial potential where $V(x, y, z) = V(r)$ then the Schroedinger equation separates into 3 separate equations in spherical polar coordinates, one for each of the r, θ, ϕ coordinates, with the potential ONLY appearing in the r equation, not in the θ, ϕ equations due to spherical symmetry. so the wavefunction is $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ where $\Theta(\theta)\Phi(\phi) = Y(\theta, \phi)$ are the same for any potential and are the simultaneous eigenfunctions of the angular momentum operators L^2 and L_z . $L^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$ and $L_z Y_{lm} = m\hbar Y_{lm}$ where $m = -l, -l+1, \dots, l-1, l$. We can measure L^2 and L_z simultaneously to infinite accuracy (they commute, share eigenfunctions) but NOT all the individual components as $[L_x, L_y] = i\hbar L_z$.

When we solve for Hydrogen we get a further condition that $l = 0 \dots n-1$ which is SPECIFIC to a $1/r$ potential.

Volume integral is $\int_0^{2\pi} \int_0^\pi \int_0^\infty \psi^* \psi r^2 \sin \theta dr d\theta d\phi$.