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 $F = m\frac{\partial^2 x}{\partial^2 t^2} = -\frac{\partial V}{\partial x}$. 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 $\Psi = N e^{i(kx-\omega t)}$ (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. $\hat{p} = -i\hbar\partial\Psi/\partial x$. 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

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

$\Psi(x,t)$ now has a probablilisic 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 $< A >= \int \Psi^* \hat{A}\Psi dx$. $< x >= \int \Psi^* x\Psi dx$, $< p >= \int \Psi^*.(-i\hbar\partial\Psi/\partial x)dx...$

Anything we can observe HAS to be real ie $< A >=< A >^*$ 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

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

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.

Any arbitrary sum of eigenfunctions also is a solution of the Schroedinger equation so the general solution is $\psi(x) = \sum_n A_n\psi_n(x)$. This itself has to be normalised so $\int \psi(x)^*\psi(x)dx = 1$ which means that $\sum_n A_n^2 = 1$ 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 A_n^2 for a normalised wavefunction. So there is probability A_n^2 to measure energy E_n. This is not the same as the expectation value $< E >= \sum_n A_n^2 E_n$

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

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

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

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

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 $\psi_{nx,ny,nz}(x, y, z) = \psi_{nx}(x)\psi_{ny}(y)\psi_{nz}(z)$ where each direction has its own quantum number eg infinite square well potential, and 3D harmonic potential. Volume integral is $\int\int\int\psi^*\psi dxdydz$.

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 $V(r) = -Ze/4\pi\epsilon_0 r$. For ANY spherically symmetric radial potential where $V(x, y, z) = V(r)$ then the Schroedinger equation separates into 3 separate equations, 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 $\Theta(\theta)\Phi(\phi)$ are the same for any potential and are the eigenequations of the angular momentum operators. Volume integral is $\int\int\int\psi^*\psi r^2\sin\theta drd\theta d\phi$.

2.3 Angular momentum

In 3D we can have angular momentum $\underline{L} = \underline{r}\times\underline{p}$ This looks bad initially - trying to constrain momentum and position. but do it in cartesian coordinates and it becomes clear that $L_x = (yp_z - zp_y) = -i\hbar(y\partial/\partial z - z\partial/\partial y)$. so

its position along one axis, and momentum along another so OK (Hermitian). Its when we try to constrain combinations of these we run into trouble.

$$LxLy = (yp_z - zp_y)(zp_x - xp_z) = yp_zzp_x - yp_zxp_z - zp_yzp_x + zp_yxp_z$$

These won't commute - 1st and 4th term have p_z and z. so we cannot simultaneously measure all the components of $\underline{L}$.

But we can know $L^2 = L_x^2 + L_y^2 + L_z^2$ together with ONE of the angular momentum components as $[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$. we choose L^2 and L_z as $L_z = -i\hbar\partial/\partial\phi$ has a simpler form than L_x, L_y.

2.4   Eigenfunctions of L^2 and L_z

The eigenequation is $L_z\Phi_m = m\hbar\Phi_m$ where the eigenvalue has been split into $m\hbar$ for convienience. so $-i\hbar\partial\Phi_m/\partial\phi = m\hbar\Phi_m$ so $\partial\Phi_m/\partial\phi = im\Phi_m$ or $\Phi_m = (2\pi)^{-1/2}e^{im\phi}$ (normalised). Satisfied for any value of m (not necessarily integer). But in order to be single valued need $\Phi_m(0) = \Phi_m(2\pi)$ so $m = 0, \pm 1, \pm 2 \ldots$. So Eigenvalues of L_z are $0, \pm\hbar, \pm 2\hbar \ldots$.

L^2 and L_z share a common set of eigenfunctions. call them $Y_{lm}(\theta\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$ It has to be separable as $L_zY_{lm}(\theta\phi) = m\hbar\Theta_{lm}(\theta)\Phi_m(\phi) = m\hbar Y_{lm}(\theta\phi)$. But these are also eigenfunctions of L^2 so our next eigenequation is $L^2Y_{lm}(\theta\phi) = l(l+1)\hbar^2Y_{lm}(\theta\phi)$ where again the $\hbar^2$ is for convienience. Fight through a lot of algebra and the solutions are Legendre polynomials of order l for $m = 0$ and associated Legendre polymonials for $m \neq 0$. Associated legendre polynomials are given by the mth derivative so the $l+1$ derivitive will vanish so a given l we can have $m = -l, -l+1, \ldots 0, 1, 2 \ldots l$. Normalise so $\int\int Y_{lm}(\theta\phi)\sin\theta d\theta d\phi = 1$

2.5   Radial eigenfunctions

$[H, L^2] = 0$ and $[H, L_z] = 0$. So these all share a common set of eigenfunctions and we can measure energy, total angular momentum and angular momentum about one axis simultaneously as the wavefunction is separable $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$. so eigenfunctions of L^2 and L_z are also eigenfunctions of H for a central potential. so all we need to get now are $R_{nl}(r)$ with corresponding $E_n = -13.6/n^2$ eV where $n = 1, 2, \ldots$. These are laguerre polynomials for $l = 0$ and assocaiated laguerre polynomials for $l \neq 0$

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where again the associated laguerre polynomials are derivatives so only exist for $l = 0, 1, 2 \ldots n - 1$. And so we get the wavefunctions and spectrum of hydrogen. If the system is in state ψ_{nlm} then we can calculate any observable such as $< r >= \int \int \int \psi_{nlm}^* r \psi_{nlm} r^2 \sin \theta dr d\theta d\phi$.

2.6 Spin

The E_n from ψ_{nlm} above explain *most* of what we see in hydrogen. But not all. Fermions also have spin angular momentum, $\underline{S}$. This is an angular momentum so we can measure S^2 and S_z together. $S_z \psi = m_s \hbar \psi$ while $S^2 \psi = s(s+1)\hbar^2 \psi$ and $m_s = -s \ldots s$. $s = \frac{1}{2}$ for fermions so m_s can take values $\pm \frac{1}{2}$

if we have electron spin, we have a small additional potential that comes from the associated magnetic moment interacting with the electronstartic field of the nucleus. This is very difficult to solve exactly but its only a small perturbation to the exact solutions for the $1/r$ potential. so we use...

3 Perturbation theory

3.1 nondegenerate

Before we had $H^0 \psi_n^0 = E_n^0 \psi_n^0$. Now we have $H = H^0 + \lambda H'$. Now we have corrections to the energy $E \approx E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2$ and to the wavefunction $\psi_n \approx \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2$. $H\psi_n = E_n \psi_n$ so

$$(H^0 + \lambda H')(\psi_0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \ldots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots)(\psi_0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \ldots)$$

zeroth order (no λ) $H^0 \psi_n^0 = E_n^0 \psi_n^0$ (as before) but 1st order tells us something new: $H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$. multiply by $(\psi_n^0)^*$ and integrate to get $E_n^1 = \int (\psi_n^0)^* H' \psi_n^0 dx$ These are often amazingly accurate!

1st order correction to the wavefunction is a lot less impressively accurate $\psi_n^1 = \sum_l c_l \psi_l^0$ for $l \neq n$ where $c_l = -\frac{1}{E_l^0 - E_n^0} \int \psi_l^{0*} H' \psi_n^0 dx$. We CAN'T use this if the energy levels are degenerate - though we can often get away with it by if the perturbation which commutes with all the other operators (see below)

2nd order correction to the energy is $E_n^2 = \int \psi_n^{0*} H' \psi_n^1 dx$.

3.2 Degenerate perturbation theory

A perturbation to the potential, H', breaks the symmetry so also has the potential to break some of the degeneracies. A n-fold degeneracy means there are n states, ψ_a^0, $\psi_b^0 \ldots$ which give the same energy E^0. Say we have 2. Any linear combination $\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0$ also gives the same energy E^0 (eg spin)

typically the perturbation H' breaks the degeneracy, so that E^0 splits into two, with the difference in energy increasing as λ goes from $0 \to 1$. when we turn off the pertubation, the upper states goes back to a unique α, β while the lower states goes back to another unique α, β. we find these 'good' unperturbed states from the matrix equation

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

where $W_{ij} = \int \psi_i^{0*} H' \psi_j^0 dx$ and i, j is one of a, b. solve by subtracting, and then inverting the matrix.

If we happen to choose the 'good' basis wavefunctions from the start then we CAN use non-degenerate perturbation theory - which is a lot easier. so thats why we use total angular momentum in hydrogen $\underline{J} = \underline{L} + \underline{S}$ This can takes values $|l - s| < j < l + s$ in integer steps. J^2 has eigenvalues $j(j+1)\hbar^2$, and the corresponding $-j < m_j < j$ in integer steps, while J_z has eigenvalues $m_j\hbar$. so we use quantum numbers n, l, j, m_j and then our wavefunctions are the 'good' wavefunctions and we can use non-degenerate perturbation theory for our perturbation $H_{so}^1 \propto \underline{S}.\underline{L}$ (spin orbit coupling).