Chapter1: Quantum Mechanics

1 Schröedinger Equation

In classical mechanics, we talk about a particle say an electron with a position x and velocity v. In quantum mechanics, particle state is represented by complex waves $\exp(ikx)$ or sum of such waves $\sum_j \exp(ik_j x)$. In complex wave $\exp(ikx)$, k is the wavenumber of the particle. The wave evolves in time as $\exp(i(kx-\omega(k)t))$, $\omega(k)$ is the frequency of the wave and depends on wavenumer k. The dependence $\omega(k)$ is called the dispersion relation of the wave. First postulate of quantum mechanics is that the energy of the wave is $E = \hbar\omega(k)$, where $\hbar$ is a fundamental constant called Planck's constant. Its units are angular momentum and in SI units its value is 6.6×10^{-34}.

Consider a classical particle of mass m moving with velocity v in frame O'. It kinetic energy is $\frac{1}{2}mv^2$. If no work is done on the system with a force then this energy is conserved. Furthermore this is conserved in all frames of reference. The kinetic energy in frame O in which the frame O' moves with velocity u is $E(u) = \frac{1}{2}m(v+u)^2$. For infinitesimal u, $E(u) \sim \frac{1}{2}mv^2 + mvu$ and since energy is conserved in this new frame $mv = \frac{dE}{du}$ is conserved. This quantity $\frac{dE}{du}$ is called momentum. Using this interpretation of momentum, we can calculate the momentum of the complex wave. For this, we develop a little bit of theory of relativity.

1.1 Relativity

Consider lab frame O and a frame O' , moving with respect to lab frame with velocity v.

Then the space time increment $(\Delta x, \Delta t)$ in O, corresponds to $(\Delta x', \Delta t')$ in O'. The phase increment of the light wave in both frames is the same.

Then

$$k\Delta x - \omega\Delta t = k'\Delta x' - \omega'\Delta t' \tag{1}$$

$$k(\Delta x - c\Delta t) = k'(\Delta x' - c\Delta t'). \tag{2}$$

For light travelling in opposite direction

$$k'(\Delta x + c\Delta t) = k(\Delta x' + c\Delta t'). \tag{3}$$

The two relations give

$$(c\Delta t)^2 - \Delta x^2 = (c\Delta t')^2 - \Delta x'^2. \tag{4}$$

For $\Delta x' = 0$, we have, $\Delta x = v\Delta t$ and this gives

$$\Delta t = \frac{\Delta t'}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{5}$$

This is called time dilation. Furthermore

$$\frac{k'}{k} = \frac{1 - \frac{v}{c}}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{6}$$

Then combining Eq. (2. 3, 6), we get

$$\begin{bmatrix} \Delta x \\ c\Delta t \end{bmatrix} = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \begin{bmatrix} 1 & \frac{v}{c} \\ \frac{v}{c} & 1 \end{bmatrix} \begin{bmatrix} \Delta x' \\ c\Delta t' \end{bmatrix} \tag{7}$$

For a rod of length l' in O' we have $(\Delta x', \Delta t') = (l', 0)$, the $l = \Delta x - v\Delta t = l'\sqrt{1 - \frac{v^2}{c^2}}$. This is called length contraction.

For an object moving at velocity in the frame O' at velocity u, for time $\Delta t'$, we have $(\Delta x', \Delta t') = (u\Delta t', \Delta t')$. Then from (Eq. 7), the relative velocity

$$\upsilon = \frac{\Delta x}{\Delta t} = \frac{u + v}{1 + \frac{uv}{c^2}} \tag{8}$$

Consider a electron matter wave with frquency, wavewector (ω, k) and (ω', k') respectively. Then

The phase increment of the matter wave in both frames is the same.

Then

$$k\Delta x - \omega\Delta t = k'\Delta x' - \omega''\Delta t' \tag{9}$$

$$\begin{bmatrix} k & -\frac{\omega}{c} \end{bmatrix} \begin{bmatrix} \Delta x \\ c\Delta t \end{bmatrix} = \begin{bmatrix} k & -\frac{\omega}{c} \end{bmatrix} \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \begin{bmatrix} 1 & \frac{v}{c} \\ \frac{v}{c} & 1 \end{bmatrix} \begin{bmatrix} \Delta x' \\ c\Delta t' \end{bmatrix} = \begin{bmatrix} k' & -\frac{\omega'}{c} \end{bmatrix} \begin{bmatrix} \Delta x' \\ c\Delta t' \end{bmatrix} \tag{10}$$

This gives

$$\begin{bmatrix} k & -\frac{\omega}{c} \end{bmatrix} \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \begin{bmatrix} 1 & \frac{v}{c} \\ \frac{v}{c} & 1 \end{bmatrix} = \begin{bmatrix} k' & -\frac{\omega'}{c} \end{bmatrix} \tag{11}$$

Rewriting this equation we get

$$\begin{bmatrix} k \\ \frac{\omega}{c} \end{bmatrix} = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} \begin{bmatrix} 1 & \frac{v}{c} \\ \frac{v}{c} & 1 \end{bmatrix} \begin{bmatrix} k' \\ \frac{\omega'}{c} \end{bmatrix} \tag{12}$$

Then the energy

$$E(v) = \hbar\omega(v) = \frac{\hbar}{\sqrt{1-\frac{v^2}{c^2}}}(vk' + \omega'). \tag{13}$$

Once again we use our interpretation of momentum and ask what is $\frac{dE(v)}{dv}|_0 = \hbar k'$. Therefore momentum of our complex wave ω', k' is simply

$$\hbar k'.$$

Thus we have two basic results in quantum mechanics the energy is $\hbar\omega$ and momentum $\hbar k$.

Now from classical mechanics $E = \frac{p^2}{2m}$. Then we get $\hbar\omega = \frac{\hbar^2 k^2}{2m}$ or $\omega = \frac{\hbar k^2}{2m}$. Thus my complex wave $\psi(x,t) = \exp(i(kx - \omega t))$ satifies

$$i\hbar\frac{\partial\psi}{\partial t} = (-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}). \tag{14}$$

This equation (14) is called *Schröedinger* equation. It is still true if we have

$$\psi(x,t) = \sum_j \alpha_j \exp(i(k_j x - \omega(k_j)t)).$$

as individual exponential satisfy these equation.

$\psi(x,t)$ is called a wavefunction of electron, it is superposition of plane waves. This is a feature of quantum mechanics, we can be in superposition of states. It satisfies the Schröedinger equation. All we are saying is that if we start with initial state $\psi(x) = \sum_j \alpha_j \exp(ik_j x)$, these ways will evolve by their charateristic energies as $\psi(x,t) = \sum_j \alpha_j \exp(i(k_j x - \omega(k_j)t))$ and $\psi(x,t)$ satisfies the Schröedinger equation.

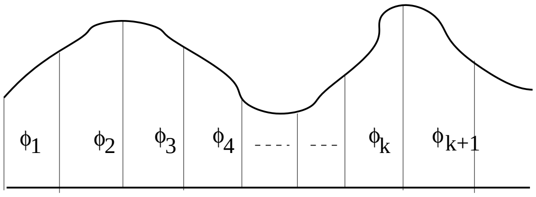

Figure 1: Figure shows how $V(x)$ is decomposed as piecewise constant potential.

Now how does my wavefunction evolve if I have a potential V. Then from classical mechanics $E - V = \frac{p^2}{2m}$, implying $\hbar\omega - V = \frac{\hbar^2 k^2}{2m}$ or my wave satisfies

$$i\hbar\frac{\partial\psi}{\partial t} = (-\hbar\frac{\partial^2}{\partial x^2} + V)\psi. \tag{15}$$

and again same is true if we have superposition of plane waves.

Now how does the evolution of $\psi(x)$ take place when we have $V(x)$. Then we can break $\psi(x)$ into small pieces ϕ_i over which $V(x)$ is contant as V_i. See fig 1. Then each ϕ_i sees a potential V_i. Its evolution will be same if V_i was globally true. Then we can break ϕ into exponentials and conclude it satisfies the equation

$$i\hbar\frac{\partial\phi_i}{\partial t} = (-\hbar\frac{\partial^2}{\partial x^2} + V_i)\phi_i. \tag{16}$$

Then adding them all we get

$$i\hbar\frac{\partial\psi}{\partial t} = (-\hbar\frac{\partial^2}{\partial x^2} + V(x))\psi. \tag{17}$$

Thus we have derived a fundamental equation of quantum mechanics. Wavefunction $\psi(x)$ has a probabilistic interpretation. $\int_a^b |\psi(x)|^2 dx$ gives the probability of finding the particles in the interval $[a, b]$

Lets take sum of such complex waves with k_j centered around k_0. Then using $\Delta k_j = k_j - k_0$, with $\Delta k_j \in [-B, B]$, such that Δk is the spacing between successive Δk_j, we have

$$\begin{aligned} \phi(x) &= \sum_j \exp(ik_j x) = \exp(ik_0 x)\sum_j \exp(i\Delta k_j x) = 2\exp(ik_0 x)\sum_j \cos(\Delta k_j x) & (18) \\ &= 2\exp(ik_0 x)\frac{\sin(Bx)}{\Delta k x} = 2\exp(ik_0 x)\frac{B}{\Delta k}\frac{\sin(Bx)}{Bx}. & (19) \end{aligned}$$

We summarize,

2 Wave Mechanics

lets Recap. The free electron wavefunction is $\psi = \exp(ikx)$. The momentum is $\frac{\hbar}{i}\frac{\partial}{\partial x}$. This gives the kinetic energy $\epsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$, which for $\epsilon = \hbar\omega$ gives,

$$\omega(k) = \frac{\hbar k^2}{2m}. \tag{20}$$

The dispersion is a parabola as shown below in figure 2 A.

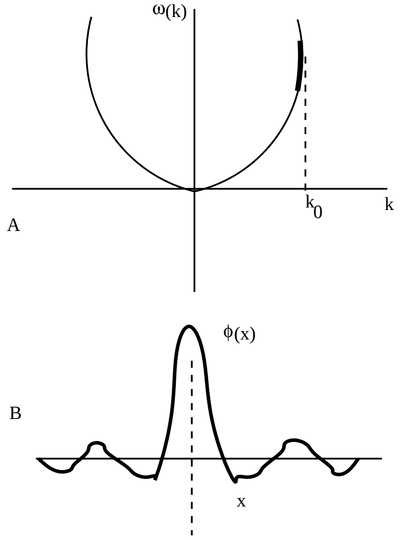

Figure 2: Figure A shows the dispersion $\omega(k)$ vs k for a free electron. Figure B shows a wavepacket centered at k_0.

Now, consider a wavepacket centered at k_0 shown the figure 2 A, B. The packet takes the form

$$\phi(x) = \frac{1}{\sqrt{N}}\sum_j \exp(ik_jx), \quad \phi(x,t) = \frac{1}{\sqrt{N}}\sum_j \exp(-i\omega(k_j)t)\exp(ik_jx), \tag{21}$$

where $\omega(k_j) = \omega(k_0) + \omega'(k_0)\Delta k_j$ where $\Delta k_j = k_j - k_0$. Denote $v_g = \omega'(k_0) = \frac{\hbar k_0}{m}$, as the group velocity. Then

$$\phi(x,t) = \frac{1}{\sqrt{N}}\exp(i(k_0x - \omega(k_0)t))\sum_j \exp(i\Delta k_j(x - v_gt)). \tag{22}$$

The function $f(x) = \frac{1}{\sqrt{N}}\sum_j \exp(i\Delta k_jx) = \frac{2}{\sqrt{N}}\sum_j \cos(\Delta k_jx)$, is centered at origin with width $\propto (\Delta k)^{-1}$ as shown in figure 2 B. Then

$$|\phi(x,t)| = |f(x - v_gt)|, \tag{23}$$

the free electron wavepacket moves with a group velocity v_g.

Now lets apply an electrical field E in the x direction at $t = 0$. Then the Schröedinger equation is

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}(-i\hbar\frac{\partial}{\partial x})^2 + eEx\ \psi. \tag{24}$$

The equation is satisfied by time varying wavevectors $\exp(ik(t)x)$, where $k(t) = k - \frac{eEt}{\hbar}$, with energy (dispersion) $\omega(k(t)) = \frac{\hbar(k(t))^2}{2m} = \frac{\hbar(k-\frac{eEt}{\hbar})^2}{2m}$, so that the wavefunction becomes

$$\exp(-i\int_0^t \omega(k(\tau))\ d\tau)\exp(ik(t)x).$$

The initial wavepacket $\phi(x)$ evolves to $\phi(x,t)$, where,

$$\phi(x) = \frac{1}{\sqrt{N}}\sum_j \exp(ik_j x), \quad \phi(x,t) = \frac{1}{\sqrt{N}}\sum_j \exp(-i\int_0^t \omega(k_j(\tau))d\tau)\exp(ik_j(t)x). \tag{25}$$

The group velocity

$$v_g(t) = \frac{\hbar k(t)}{m} = \frac{\hbar(k - \frac{eEt}{\hbar})}{m}; \quad \frac{dv_g(t)}{dt} = -\frac{eE}{m}. \tag{26}$$

The electron wavepacket simply accelerates the way we know from classical mechanics. Being more pedagogical, we have

$$\begin{aligned}\phi(x,t) &= \frac{1}{\sqrt{N}}\sum_j \exp(-i\int_0^t \omega(k_j(t))\ )\exp(ik_j(t)x) \\ &= \frac{1}{\sqrt{N}}\exp(-i\int_0^t \omega(k_0(t))\ )\exp(ik_0(t)x)\sum_j \exp(i\Delta k_j(x - \int_0^t v_g(\sigma)d\sigma)).\end{aligned} \tag{27}$$

The wavepacket evolves with instantaneous velocity $v_g(t)$.

The above method can be generalized to arbitrary potential. Consider the Schröedinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = (-\frac{\hbar^2}{2m}\frac{\partial}{\partial x^2} - eV(x))\psi. \tag{28}$$

We approximate the potential V by piecewise linear potential such that $V(x) = V(x_i) + V'(x_i)\delta x$, where $\delta x = x - x_i$, as shown in figure 3. We call these regions of linearized potential, cells. We can rewrite the potential in a cell as $V(x) = U(x_i) + V'(x_i)x$

We assume that the wavepacket has large k_0 such that $\Delta k \sim \sqrt{k_0}$ is large and therefore for the wavepacket, $\Delta x \sim (\Delta k)^{-1}$ is small so that it fits well within one cell. Then in this cell, the Schröedinger equation takes the form

$$i\hbar\frac{\partial\psi}{\partial t} = (-\frac{\hbar^2}{2m}\frac{\partial}{\partial x^2} - eV'(x_i)x - eU(x_i))\psi. \tag{29}$$

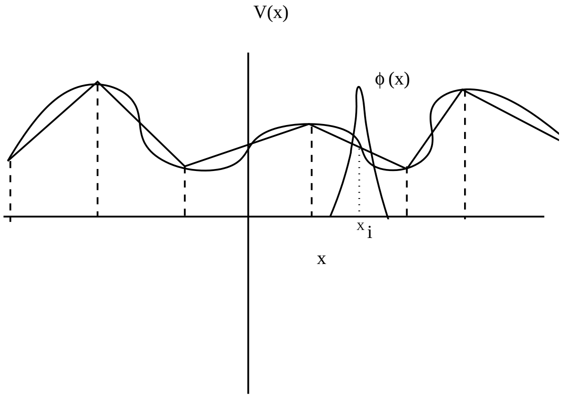

Figure 3: Figure shows linear approximation of potential $V(x)$. The wavepacket $\phi(x)$ is confined to a cell.

Since the wavepacket is confined to a cell, it evolution would be same if the potential we have was not only true in the cell but globally true. This is because the wavepacket doesn't know what the potential is outside the cell, its confined to the cell. Then lets solve the Schröedinger equation with this potential assumed globally true and see how wavepacket evolves.

Then as before for the Schröedinger equation is solved by wavevector $\psi = \exp(ik(t)x)$. Let $x(t)$ denote coordinates of center of wavepacket, then

$$k(t) = k + \frac{e\int_0^t V'(x(\tau))d\tau}{\hbar}, \quad \omega(k(t)) = \frac{\hbar(k + \frac{e\int_0^t V'(x(\tau))d\tau}{\hbar})^2}{2m} - \frac{e\int_0^t U(x(\tau))d\tau}{\hbar}. \tag{30}$$

The group velocity

$$v_g(t) = \frac{\hbar(k + \frac{e\int_0^t V'(x(\tau))d\tau}{\hbar})}{m}; \quad \frac{dv_g(t)}{dt} = \frac{eV'(x(t))}{m}. \tag{31}$$

This is classical mechanics. Therefore at high energies where k_0 is large and wavepacket is well confined, i.e., over the packet width, the second order change of potential is small, $V''(x)\Delta x \ll V'(x)$. A linearized potential is a good approximation and evolution in quantum mechanics mimics classical mechanics.

3 Particle in a Square Well

In this section we solve Schröedinger equation with a special potential. The Schröedinger equation has the form

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{32}$$

$H(x)$ is the Hamiltonian of the system, it is an operator. If we can find eigenfunctions of H call ϕ_i with energies E_i. Then the eigenfunction ϕ_i evolves as $\exp(-i\frac{E_i t}{\hbar})\phi_i(x)$. Given initial wavefunction $\psi(x) = \sum_i \alpha_i \phi_i(x)$, we have $\psi(x,t) = \sum_i \alpha_i \exp(-i\frac{E_i t}{\hbar})\phi_i(x)$. Therefore all the challenge is in finding $\phi_i(x)$. These are called stationary states, eigenfunctions, etc.

Lets take a potential as show in figure 4 which is $-V$ in region II and zero elsewhere.

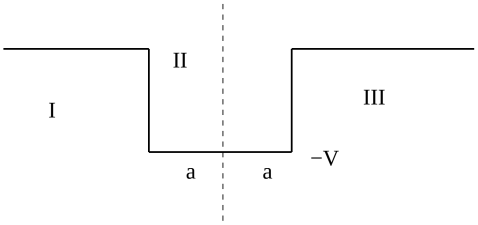

Figure 4: Figure shows a potential well of depth V.

We solve for

$$H\phi = E\phi.$$

We first do it in region II that gives

$$\begin{aligned}(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - V)\phi &= E\phi & (33)\\ -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi &= (E+V)\phi & (34)\end{aligned}$$

then the solution is $\exp(ikx)$ and $\exp(-ikx)$ where $k = \frac{\sqrt{2m(E+V)}}{\hbar}$.

In region I we have solution is $\phi_1 = \exp(k_1 x)$, where $k_1 = \frac{\sqrt{-2mE}}{\hbar}$. E should be negative as solution should die to 0 at $-\infty$. In region III we have solution is $\phi_3 = \exp(-k_1 x)$, as solution should die to 0 at ∞ In region 2, we can say we have a solution $\phi_2 = A\exp(ikx) + B\exp(-ikx)$ we match it to solution in I and III. Then we have

$$\frac{\phi_1'(-a)}{\phi_1(-a)} = \frac{\phi_2'(-a)}{\phi_2(-a)}, \ \frac{\phi_3'(a)}{\phi_3(a)} = \frac{\phi_2'(a)}{\phi_2(a)}. \tag{35}$$

From this we get

$$\frac{\phi_2'(-a)}{\phi_2(-a)} = -\frac{\phi_2'(a)}{\phi_2(a)}. \tag{36}$$

which gives $A = B$ from which we get for $z_0 = \frac{\sqrt{2mV}}{\hbar}$,

$$k_1 = k \tan ka; \tag{37}$$

Let $z = ka$ and $z_0 = \frac{a\sqrt{2mV}}{\hbar}$, with $z < z_0$ from which we get

$$\underbrace{\tan z}_{f_1(z)} = \underbrace{\sqrt{(z_0/z)^2 - 1}}_{f_2(z)} \tag{38}$$

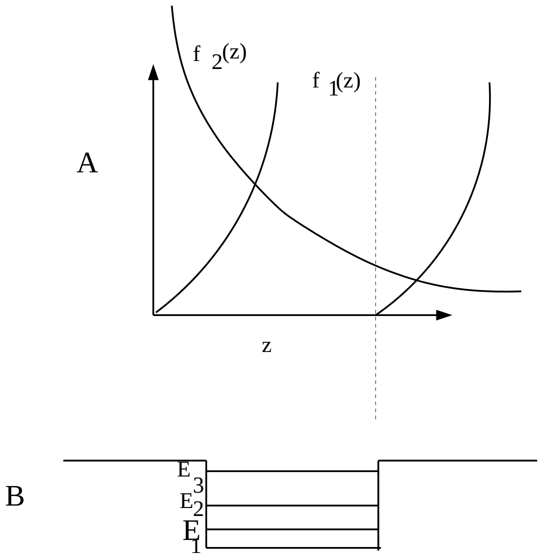

Figure 5: Figure A shows plots of $f_1(z)$ and $f_2(z)$. The energies are depicted in fig B.

When $n\pi < z < (n+1)\pi$, we get n intersections as shown in fig 9A . These are bound solutions. The energies are depicted in fig 9B. Until now we taked about bound states. when total energy $E < 0$. They are like a ball stuck in pit and keeps going back and forth as in Fig. A in 6. There are other states as shown in Fig. A in 6 when $E > 0$, then ball rolls from left crosses the pit and moves to right. Lets find quantum mechanical analog of these scattering states.

Since $E > 0$, we have $k_1 = \frac{\sqrt{2mE}}{\hbar}$. Assume a incident wave (ball) from left $\exp(ik_1x)$, part of which is reflected $R\exp(-ikx)$ and part trnasmiited on right hand side $T\exp(ikx)$. Then we have wavefunction $\exp(ik_1x) + R\exp(-ik_1x)$ in region I and $A\exp(ikx) + B\exp(-ikx)$

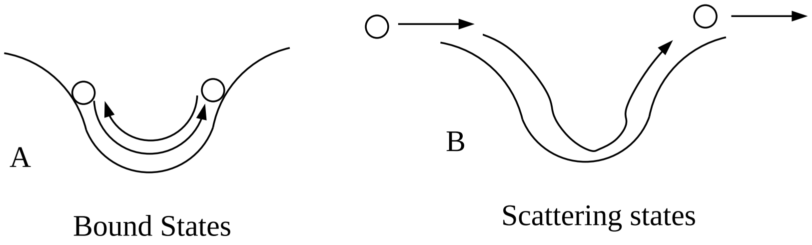

Figure 6: Figure A shows bound states. Figure B shows scattering states

in region II and $T\exp(ikx)$ in region 3. We have 4 boundary conditions

$$\begin{aligned}
\exp(-ik_1a) + R\exp(ik_1a) &= A\exp(-ika) + B\exp(ika). \\
T\exp(ik_1a) &= A\exp(ika) + B\exp(-ika). \\
k_1(\exp(-ik_1a) - R\exp(ik_1a)) &= k(A\exp(-ika) - B\exp(ika)). \\
k_1T\exp(ik_1a) &= k(A\exp(ika) - B\exp(-ika)).
\end{aligned}$$

On solving we get

$$\begin{aligned}
T &= \frac{\exp(-i2k_1a)}{\cos(2ka) - i\frac{k^2+k_1^2}{2kk_1}\sin(2ka)}. \\
R &= -i\frac{k^2-k_1^2}{2kk_1}\sin(2ka)T.
\end{aligned}$$

All energies $E > 0$ are allowed as scattering states.

4 Infinite Square Well

Figure shows an infinite square well which has zero potential in the center and infinite potential $V = \infty$ outside. Let the eigen energy of ϕ be E_0 then $\langle E\rangle = E_0$. But then ϕ cannot have an presence outside center region else $\langle E\rangle = \infty$. Therefore ϕ is confined to center region. ϕ has to be continuous (else its double derivative is ∞^2 which cannot satisfy the Schröedinger equation). Then we look for

$$-\frac{\partial^2\phi}{\partial x^2} = E_0x$$

which gives $\phi_n = \cos(\frac{n\pi x}{2a})$ with energies $E_n = \frac{n^2\pi^2}{(2a)^2}$ or $\phi_n = \sin(\frac{n\pi x}{a})$, with $E_n = \frac{n^2\pi^2}{a^2}$.

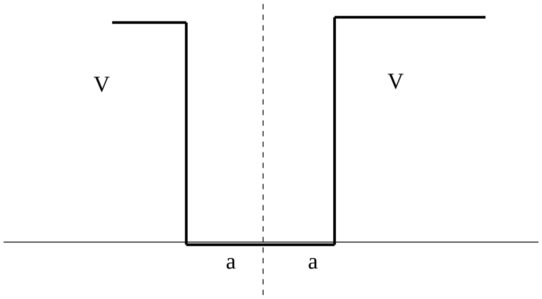

Figure 7: Figure shows an infinite square well.

5 Harmonic Oscillator

Consider Harmonic Oscillator with Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2. \tag{39}$$

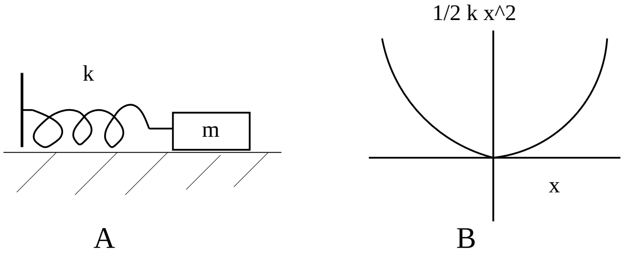

Figure 8: Figure A shows a spring-mass system, a harmonic oscillator. Fig. B shows the quadratic potential

Let $\omega_0^2 = \frac{k}{m}$, be the natural frquency of the oscillator. Then the Hamiltonian takes the form

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 = \frac{1}{2}\hbar\omega_0(\frac{p^2}{m\hbar\omega_0} + \frac{1}{\hbar}m\omega_0 x^2). \tag{40}$$

We can further write it as

$$H = \hbar\omega_0(a^\dagger a + \frac{1}{2}), \tag{41}$$

where

$$a = \sqrt{\frac{m\omega_0}{2\hbar}}x + i\frac{p}{\sqrt{2m\hbar\omega_0}} = X + iP \tag{42}$$

$$a^\dagger = \sqrt{\frac{m\omega_0}{2\hbar}}x - i\frac{p}{\sqrt{2m\hbar\omega_0}} = X - iP, \tag{43}$$

where as before $p = \frac{\hbar}{i}\frac{\partial}{\partial x}$ and we use the commutation relation $[\frac{\partial}{\partial x}, x] = 1$ or $[p, x] = -i\hbar$. Then we get

$$[aa^\dagger] = \hbar\omega_0. \tag{44}$$

Now as before we want to find eigenfunctions of H. The reason for writing H in terms of operator $a, a^\dagger$ is that it helps to find these eigenfunctions. Lets see how. If ϕ is an eigenvector with eigenvale E, then $a\phi$ and $a^\dagger\phi$ are both eigenfunctions with eigenvalues $E - \hbar\omega_0$ and $E + \hbar\omega_0$ respectively.

To see this

$$\hbar\omega_0(a^\dagger a + \frac{1}{2})a\phi = a\hbar\omega_0(a^\dagger a - \frac{1}{2})\phi = (E - \hbar\omega_0)a\phi. \tag{45}$$

$$\hbar\omega_0(a^\dagger a + \frac{1}{2})a^\dagger\phi = a^\dagger\hbar\omega_0(a^\dagger a + \frac{3}{2})\phi = (E + \hbar\omega_0)a^\dagger\phi. \tag{46}$$

Therefore a and $a^\dagger$ are called lowering and raising or annhilation and creation operators respectively. Observe energy has to be positive so we cannot keep lowering the energy. It means there is a ϕ_0 such that

$$a\phi_0 = 0, \tag{47}$$

which gives

$$\frac{\partial\phi_0}{\partial x} = -\frac{m\omega_0}{2\hbar}x\phi_0. \tag{48}$$

This can be integrated to get a unique solution

$$\phi_0(x) = C\exp(-\frac{x^2 m\omega_0}{4\hbar}), \tag{49}$$

with energy $\frac{\hbar\omega_0}{2}$. All other eigenfunctions can be derived by raising ϕ_0 as

$$\phi_1 = a^\dagger\phi_0 = D\ x\exp(-\frac{x^2 m\omega_0}{4\hbar}), \tag{50}$$

with energy $\frac{3\hbar\omega_0}{2}$. These eigenfunctions are called Hermite polynomials

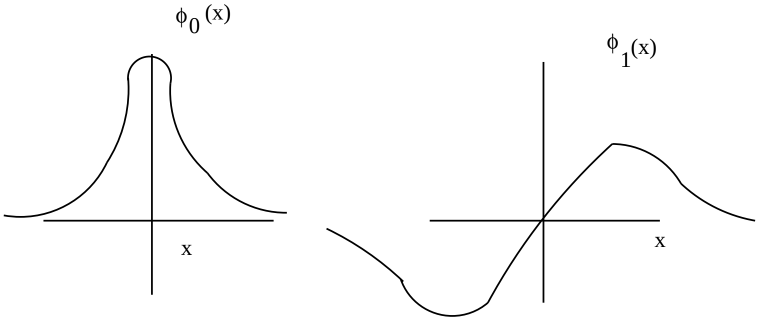

Figure 9: Figure shows first two Hermite polynomials.

6 Hydrogen Atom

In polar coordinates $r = \sqrt{x^2+y^2}$ and $\phi = \tan^{-1}(\frac{y}{x})$.

Then

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} = \cos\phi\frac{\partial}{\partial r} - \frac{\sin\phi}{r}\frac{\partial}{\partial \phi} \\ \frac{\partial}{\partial y} &= \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi} = \sin\phi\frac{\partial}{\partial r} + \frac{\cos\phi}{r}\frac{\partial}{\partial \phi}. \end{aligned}$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial}{\partial \phi^2}.$$

$$\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial}{\partial \phi^2}.$$

Using $R = \sqrt{z^2+r^2}$ and $\theta = \tan^{-1}(\frac{r}{z})$.

$$\begin{aligned} \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} &= \frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\frac{\partial}{\partial \theta^2} + \frac{\cot\theta}{R^2}\frac{\partial}{\partial \theta} + \frac{1}{R^2\sin^2\theta}\frac{\partial}{\partial \phi^2} \\ &= \frac{1}{R^2}\frac{\partial}{\partial R}(R^2\frac{\partial}{\partial R}) + \frac{1}{R^2\sin\theta}\frac{\partial}{\partial \theta}(\sin\theta\frac{\partial}{\partial \theta}) + \frac{1}{R^2\sin^2\theta}\frac{\partial}{\partial \phi^2}. \end{aligned}$$

To Schroedinger Eigenvalue Eq. reals

$$\{\frac{\hbar^2}{2m}(\frac{1}{R^2}\frac{\partial}{\partial R}(R^2\frac{\partial}{\partial R}) + \frac{1}{R^2\sin\theta}\frac{\partial}{\partial \theta}(\sin\theta\frac{\partial}{\partial \theta}) + \frac{1}{R^2\sin^2\theta}\frac{\partial}{\partial \phi^2}) + (E - V(R))\}\psi = 0.$$

$$\{(\frac{\partial}{\partial R}(R^2\frac{\partial}{\partial R})+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})+\frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi^2})+\frac{2mR^2}{\hbar^2}(E-V(R))\}\psi=0.$$

We write the solution $\psi=f(R)Y(\theta,\phi)$.

$$(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})+\frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi^2}+\underbrace{l(l+1)}_{E_1})Y(\theta,\phi)=0. \tag{51}$$

Writing $Y(\theta,\phi)=\Theta(\theta)e^{im\phi}$, we get

$$(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})-\frac{1}{\sin^2\theta}m^2+\underbrace{l(l+1)}_{E_1})\Theta(\theta)=0.$$

For $x=\cos\theta$, the above equation reads

$$(1-x^2)\Theta''-2x\Theta'+(l(l+1)-\frac{m^2}{1-x^2})\Theta=0.$$

The solution Θ_l^m exits for integer l,m satisfying $0\leq|m|\leq l$. For $m\geq 0$

$$\Theta_l^m(x)=\frac{(-1)^m}{2^l l!}(1-x^2)^{\frac{m}{2}}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l.$$

with

$$\Theta_l^{-m}(x)=(-1)^m\frac{(l-m)!}{(l+m)!}\Theta_l^m(x).$$

Then the equation for R gives

$$\frac{\partial}{\partial R}(R^2\frac{\partial f}{\partial R})=(l(l+1)+\frac{2mR^2}{\hbar^2}(V(R)-E))f.$$

Let $u=Rf$, then

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial R^2}+(V+\frac{\hbar^2}{2mR^2}l(l+1))u=Eu,$$

where $V=\frac{-e^2}{4\pi\epsilon_0 r}$. This is one-dimensional Schroedinger equation. Guess a solution of the form $u(r)=R^{l+1}e^{-\frac{R}{a_0}}$. Then twice differentiating R^{l+1} cancels the centrifugal part. Differentiating R^{l+1} and $e^{-\frac{R}{a_0}}$, cancels V, when $\frac{\hbar^2}{m}\frac{l+1}{a_0}=\frac{e^2}{4\pi\epsilon_0}$, i.e,

$$a_0=\frac{(l+1)\hbar^2 4\pi\epsilon_0}{me^2},\quad E=\frac{\hbar^2}{2ma_0^2}.$$

However, we donot have to cancel V immediately. We can add another term

$$u(r) = R^{l+1}e^{-\frac{R}{a_0}} + c_1 R^{l+2}e^{-\frac{R}{a_0}}.$$

Then centrifugal part of second term c_1 can cancel the part of first term obtained by differentiating R^{l+1} and $e^{-\frac{R}{a_0}}$. For this c_1 has to be choosen correct. Now we cancel V by differentiating R^{l+2} and $e^{-\frac{R}{a_0}}$.

Then in general

$$u(r) = R^{l+1}e^{-\frac{R}{a_0}}(1 + \sum_{j=1}^{d} c_j R^j),$$

with $n = l + d + 1$, the principle quantum number. Then

$$\frac{\hbar^2}{m}\frac{n}{a_0} = \frac{e^2}{4\pi\epsilon_0}. \quad a_0 \propto n$$

and

$$\frac{c_j}{c_{j-1}} = \frac{2(l + j - n)a_0^{-1}}{j(2l + j + 1)}.$$

This gives a_0 and finally

$$E = \frac{\hbar^2}{2ma_0^2}, \quad E \propto \frac{1}{n^2}.$$

6.1 Angular Momentum

$$L = r \times p.$$

$$L_x = yp_Z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x.$$

Using $[p_x, x] = -i\hbar$, etc, we have

$$L^2 = L_x^2 + L_y^2 + L_z^2 = R^2(p_x^2 + p_y^2 + p_z^2) - (xp_x + yp_y + zp_z - i\hbar)^2 + \hbar^2.$$

A quick calculation shows

$$xp_x + yp_y + zp_z = -i\hbar R\frac{\partial}{\partial R}.$$

Now substituting for

$$\begin{aligned} p_x^2+p_y^2+p_z^2 &= -\hbar^2(\frac{1}{R^2}\frac{\partial}{\partial R}(R^2\frac{\partial}{\partial R})+\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})+\frac{1}{R^2\sin^2\theta}\frac{\partial}{\partial\phi^2}) && (52)\\ L^2 &= -\hbar^2(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})+\frac{1}{R^2\sin^2\theta}\frac{\partial}{\partial\phi^2}). && (53)\end{aligned}$$

Then from Eq. 51,

$$L^2Y(\theta,\phi)=\hbar^2 l(l+1).$$

and

$$L_zY(\theta,\phi)=-i\hbar\frac{\partial}{\partial\phi}Y(\theta,\phi)=\hbar mY(\theta,\phi).$$

We denote the eigenfunction as Y_{lm}

Observe easily verifiable commutation relations

$$[L_x,L_y]=i\hbar L_z,\quad [L_y,L_z]=i\hbar L_x,\quad [L_z,L_x]=i\hbar L_y. \tag{54}$$

Define $L^-=L_x-iL_y$ and $L^+=L_x+iL_y$. L^- is called lowering operator and L^+ is called raising operator.

$$[L^2,L^\pm]=0,\quad [L_z,L^\pm]=\pm\hbar L^\pm. \tag{55}$$

Then note $[L^2,L^\pm]Y_{lm}=0$ implies $L^2L^\pm Y_{lm}=\hbar^2l(l+1)L^\pm Y_{lm}$ hence $L^\pm Y_{lm}$ is a linear combination of Y_{lm} for different m. Now $[L_z,L^+]Y_{lm}=L^+Y_{lm}$ implying $L_zL^+Y_{lm}=\hbar(m+1)L^+Y_{lm}$ implying $L^+Y_{lm}=a_mY_{l,m+1}$. Similarly $L^-Y_{lm}=b_mY_{l,m-1}$. Then observe $L^+Y_{ll}=0$ and $L^-Y_{l,-l}=0$. Furthermore

$$[L^+,L^-]=2\hbar L_z. \tag{56}$$

Furthermore we get

$$L^+L^-+L^-L^+=2(L^2-L_z^2). \tag{57}$$

Then we get

$$\begin{aligned} L^+L^- &= L^2-L_z^2+\hbar L_z && (58)\\ L^-L^+ &= L^2-L_z^2-\hbar L_z. && (59)\end{aligned}$$

For normalized Y_{lm} we get

$$
\begin{aligned}
b_{lm} &= \hbar\sqrt{l(l+1)-m(m-1)} && (60) \\
a_{lm} &= \hbar\sqrt{l(l+1)-m(m+1)} && (61)
\end{aligned}
$$

We talked about orbitals with principle quantum number n and integer angular momentum number l and z angular momentum l, with $|m| \leq l \leq n-1$. Here l was integer. In principle it can be half integer and is ascribed to an intrinsic angular momentum called spin. We use the quantum number s instead of l. In particular $s = \frac{1}{2}$ is called spin $\frac{1}{2}$ a property of electron. We then have two values of $s_z = \pm\frac{1}{2}$. Then an electron as two set of quantum numbers l, m and s, s_z.

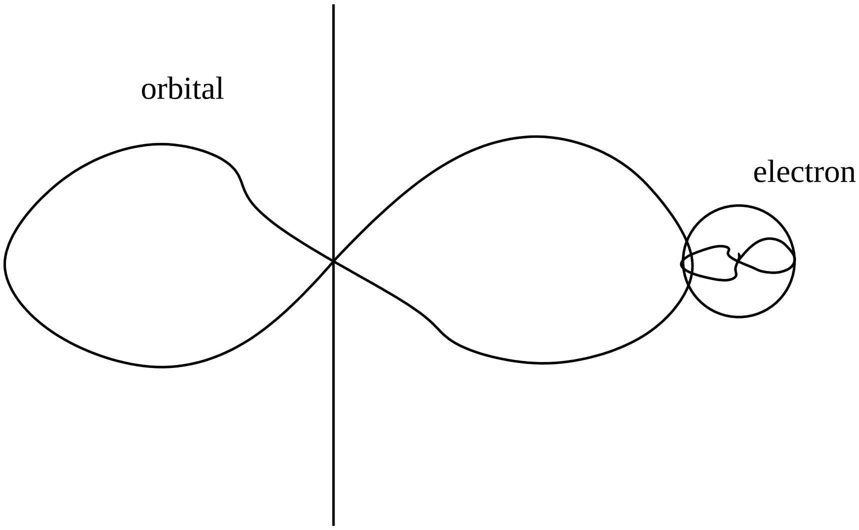

Figure 10: Fig. shows an atomic orbital and an electron with an inner orbital that consitutes its spin angular momentum

7 Fine Structure and Spin orbital coupling

We talked about spin. Lets try to understand the physics of it. You are familiar with earth spinning on its axis. This gives earth a angular momentum. Now imagine our earth was charged. Then spinning will give earth a magnetic moment. Imagine a loop of wire carrying current (circulating charge), then it has a magnetic moment $M = I.A$, where I is the current and A area of the loop, from your basic physics. Now imagine a charge q going around in a loop of radius r, with angular velocity ω. Then it makes $\frac{\omega}{2\pi}$ rotations per sec. The current is then $\frac{q\omega}{2\pi}$ and its magnetic moment is $\mu_S = \frac{q\omega\pi r^2}{2\pi} = \frac{q}{2m}(mvr)$ where $l = mvr$ is the angular momentum. Then $\mu_S = \frac{q}{2m}L$, the ratio $\gamma = \frac{q}{2m}$ is called the gyromagnetic ratio, it relates angular momentum to magnetic moment. For reasons coming from relativity we infact have $\gamma = \frac{q}{m}$.

There is coupling between electron spin and orbital angular momentum. There is coupling Hamiltonian of the form

$$H_1 = \alpha L \cdot S. \tag{62}$$

Let us see how this coupling arises. When electron is at a certain point on its orbital it has a velocity v and momentum p. From perspective of the electron the nucleaus is moving in the opposite direction with same magnitude of velocity. Then from Biot Savart law the moving nucleaus produces a magnetic field on the site of electron given by

$$B = \frac{e\mu_0}{4\pi}\frac{p \times r}{mr^3} = \frac{e\mu_0}{4\pi}\frac{L}{mr^3}. \tag{63}$$

The energy of the electron in this field is

$$B \cdot \mu_S = \gamma B \cdot S = \frac{e^2\mu_0}{4\pi m^2 r^3} L \cdot S. \tag{64}$$

Thus $\alpha = \frac{e^2\mu_0}{4\pi m^2 r^3}$.

In presence of this Hamiltonian our orbitals will change. let us compute how the orbitals change and what are the new energies.

$$L \cdot S = L_z S_z + L_x S_x + L_y S_y = L_z S_z + \frac{L^+ S^- + L^- S^+}{2}. \tag{65}$$

For this define a new operator

$$J^2 = (L+S)^2 = L^2 + S^2 + 2L \cdot S. \tag{66}$$

$$J_z = L_z + S_z, \quad J^{\pm} = L^{\pm} + S^{\pm}. \tag{67}$$

Given l and s, we start with the state $l_z = l$ and $s_z = s$. Denote this state by (l, s). This state is an eigenstate of the operator $L \cdot S$ with eigenvalue l, s and hence it is an eigenstate of J^2 with eigenvalue $j(j+1)$ with $j = l + s$. Now as before we can apply lowering opertor. From last section $J^-(j, j_z) = b(j, j_{z-1})$ with $b = \hbar\sqrt{j(j+1) - j_z(j_z - 1)}$, so by applications of J^- we decrease j_z until it is $-j$. Hence we have constructed $2j$ or $2j+1$ orbitals depending on if j is integer or half integer.

Observe $J^-(l, s) = (l-1, s) + (l, s-1)$. There is another orthogonal state $e_1 = (l-1, s) - (l, s-1)$ which is eigenfunction of J_z with eigenvalue $l + s - 1$ and hence must be an eigenfunction of J^2. We eigevalue of J^2 cannot be $j(j+1)$ as we have exhausted all these vectors as $J^+e_1 = 0$. Only possible value of J^2 is $(j-1)j$, we gain apply lowering operators and go from $j_z = j-1, \dots, -(j-1)$.

Now we consider $J^{-2}(l,s) = (l-2,s) + (l-1,s-1) + (l,s-2)$, which has $J_z = l+s-2$. We have constructed two eigenvectors $J^2 = j(j+1)$ and $J^2 = (j-1)j$. We can form a third eigevector, we can show it has J^2 value $(j-1)(j-2)$, we can again apply lowering operators and construct eigevectors with J^2. Instead of writing J^2 we say this J which in this case has value $j-2$.

We start with one term (l,s). Then $J^-(l,s)$ has two terms, $J^{-2}(l,s)$ has three terms. This process continues till smaller of l, s say s becomes $-s$. Then lowering doesn't increase number of terms. Then starting with $j = l+s$ we go until $j = l-s$. Thus all states can be indexed by $j = l+s, \dots, l-s$ and for a given j we have $j_z = j, \dots, -j$. Thus starting with state $|l, l_z\rangle |s, s-z\rangle$ we have formed state

$$|j, j_z\rangle = \sum_{l_z, s_z} c_{l_z, s_z} |l, l_z\rangle |s, s_z\rangle, \tag{68}$$

where as just told, $j = l+s, \dots, l-s$ and for a given j we have $j_z = j, \dots, -j$.

In the basis $|j, j_z\rangle$, we have $L \cdot S$ is diagonal with eigenvalue $\frac{j(j+1)-l(l+1)-s(s+1)}{2}$. The coeffecients c_{l_z,s_z} are called Clebsch Gordon coeffecients. Fig. (11) shows how $n = 2$, p orbital gets split due to fine structure.

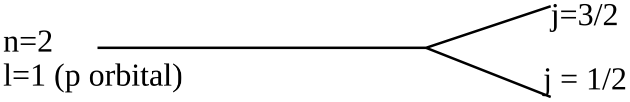

Figure 11: Fig. shows how $n = 2$, p orbital gets split due to fine structure.

As we can see in the figure. A energy level $n = 1, l = 1$ in presence of $L \cdot S$ coupling gets split into two set of orbitals $j = \frac{3}{2}$ with $(j_z = \frac{3}{2}, \dots, -\frac{3}{2})$ and $j = \frac{1}{2}$ with $(j_z = \frac{1}{2}, \dots, -\frac{1}{2})$ with different energies. This is called *fine-structure*. If we estimate how big this is it is $\alpha = \frac{\hbar^2 e^2 \mu_0}{4\pi m_e^2 r^3} \sim 10^2 eV \sim 10^3 GHz$. It arises because the angular momentum of the orbital and the spin of the electron talk to each other.

Electron has a spin, so does the nucleus of the atom. It is called nuclear spin. We denote nuclear spin with I like we denote elctron spin with S. We assume that we again have an interaction between nuclear spin and electron orbital and spin angular momentum as

$$I \cdot (L+S) = I \cdot J. \tag{69}$$

What was between L and S is between I and J so we can define the total angular momentum

$$F = I + J. \tag{70}$$

Given i and j the coupling gives f taking values between $i+j, \ldots, |i-j|$. Thus a j orbital gets split into f orbitals. This is called hyperfine splitting. The eigenvalues of $I \cdot J$ takes one values $\frac{f(f+1)-j(j+1)-i(i+1)}{2}$. Thus if we estimate how much this is, it is $\beta = \frac{\hbar^2 e^2 \mu_0}{4\pi m_e m_p r^3} \sim 1GHz$, where m_p is proton mass which is 10^3 heavier than electrom mass.

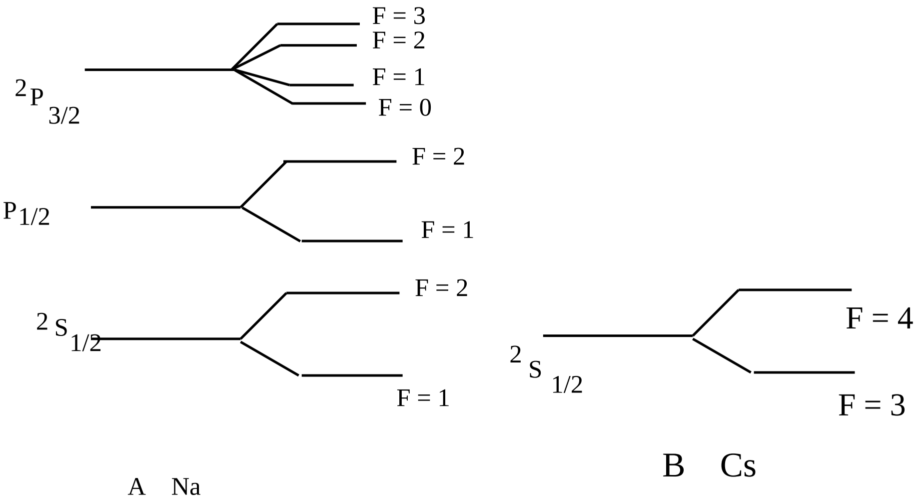

Figure 12: Fig. A shows hyperfine levels for sodium. Fig. B shows hyperfine levels for Cesium

8 Two Level Systems

Consider orbitals ϕ_1 and ϕ_2, with energy E_1 and E_2. Suppose I apply a Electrical field along x direction $E_x \cos \omega t$. Then there is associated potential $V(x) = -exE_x$. Let

$$\langle \phi_1 | V(x) \phi_1 | \rangle = 0, \quad \langle \phi_2 | V(x) | \phi_2 \rangle = 0 \quad \langle \phi_1 | V(x) | \phi_2 \rangle = d \tag{71}$$

Then if we have $\Psi(t) = a(t)\phi_1 + b(t)\phi_2$, then we have Schroedinger equation as

$$i\hbar \frac{d}{dt} \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} E_1 & d\cos\omega t \\ d\cos\omega t & E_2 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} \tag{72}$$

$$\frac{d}{dt} \begin{bmatrix} a \\ b \end{bmatrix} = \frac{-i}{\hbar} \begin{bmatrix} E_1 & d\cos\omega t \\ d\cos\omega t & E_2 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} \tag{73}$$

Let $\Delta E = E_1 - E_2 = \hbar\omega_0$, then

$$\frac{d}{dt}\begin{bmatrix} a \\ b \end{bmatrix} = \frac{-i}{2\hbar}\begin{bmatrix} \Delta E & 2d\cos\omega t \\ 2d\cos\omega t & -\Delta E \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = \frac{-i}{2}\begin{bmatrix} \omega_0 & 2A\cos\omega t \\ 2A\cos\omega t & -\omega_0 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} \tag{74}$$

$$= -i(\omega_0\ \sigma_z + 2A\ \cos\omega t\ \sigma_x)\begin{bmatrix} a \\ b \end{bmatrix} \tag{75}$$

where $d = \hbar A$ and

$$\sigma_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{76}$$

are the Pauli matrices with commutation relation

$$[\sigma_x, \sigma_y] = i\sigma_z, \quad [\sigma_y, \sigma_z] = i\sigma_x, \quad [\sigma_z, \sigma_x] = i\sigma_y \tag{77}$$

Let $x = \begin{bmatrix} a \\ b \end{bmatrix}$ and the above equation is

$$\frac{dx}{dt} = -i(\omega_0\ \sigma_z + 2A\ \cos\omega t\ \sigma_x)x \tag{78}$$

Let us first consider a special case when $\omega = \omega_0$ and now we have $y = \exp(i\omega_o t)x$, then we have

$$\frac{dy}{dt} = -i2A\ \cos\omega_0 t\ (\cos\omega_0 t\sigma_x + \sin\omega_0 t\sigma_y)y = -i\{A\sigma_x + A(\cos 2\omega_0 t\sigma_x + \sin 2\omega_0 t\sigma_y)\}y \tag{79}$$

We assume $A \ll \omega_0$. Then terms rotating at $2\omega_0$ average out giving the evolution

$$\frac{dy}{dt} = -iA\sigma_x y \tag{80}$$

Remember

$$\exp(-i\theta n\cdot\sigma) = \cos\frac{\theta}{2}I - 2i\sin\frac{\theta}{2}n\cdot\sigma \tag{81}$$

Then the solution is

$$y(t) = \exp(-iAt\ \sigma_x)y(0) = \begin{bmatrix} \cos\frac{At}{2} & i\sin\frac{At}{2} \\ i\sin\frac{At}{2} & \cos\frac{At}{2} \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} \cos\frac{At}{2} \\ i\sin\frac{At}{2} \end{bmatrix} \tag{82}$$

when $At = \pi$, we get $\begin{bmatrix} 1 \\ 0 \end{bmatrix} \rightarrow \begin{bmatrix} 0 \\ i \end{bmatrix}$.

We start from initial state ϕ_1 (we are in orbital ϕ_1) and we end up in orbital ϕ_2. By exciting the system with a oscillating field whose frequency is same as the energy difference between the orbitals we can transfer the state of orbital 1 to orbital 2 and viceversa. This is our first and main idea of quatum control.

If $|\omega - \omega_0| \gg A$, we donot get good transfer (we say we are detuned from the transition) . To see this observe in

$$\begin{aligned} \frac{dy}{dt} &= -i2A \ \cos\omega_0 t \ (\cos\omega t\sigma_x + \sin\omega t\sigma_y)y \\ &= -i\{A((\cos(\omega_0 t + \omega t) + \cos(\omega_0 t - \omega t))\sigma_x + ((\sin(\omega_0 t + \omega t) + \sin(\omega_0 t - \omega t))\sigma_y)\}y \end{aligned}$$

All terms oscillate fast and we average to 0. We start in $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and stay , i.e., we start from initial state ϕ_1 (we are in orbital ϕ_1) and we stay in orbital ϕ_1.

In reality we donot have only two orbitals but many orbitals but if we choose our frequency ω as difference of energies of two orbitals ϕ_i and ϕ_j and are detuned from other transitions, we will transfer between ϕ_i and ϕ_j.

We can formalize this, let us assume that we have $\sum_i \alpha_i(t)\phi$, let $x = \begin{bmatrix} \alpha_1 \\ \vdots \\ \alpha_n \end{bmatrix}$ then the Schroedinger equation is of the form

$$\dot{x} = \frac{-i}{\hbar} \begin{bmatrix} \ddots & \dots & \dots & \vdots \\ \vdots & E_i & d_{ij}\cos(\omega t) & \vdots \\ \vdots & d_{ij}\cos(\omega t) & E_j & \vdots \\ \dots & \dots & \dots & \ddots \end{bmatrix} x \tag{83}$$

Choose $\omega = \frac{E_i - E_j}{\hbar}$. Then if we proceed by transformation

$$y = \exp(\frac{it}{\hbar} \begin{bmatrix} E_1 & 0 & 0 & 0 \\ \vdots & \ddots & 0 & 0 \\ 0 & 0 & E_i & \vdots \\ \dots & \dots & \dots & \ddots \end{bmatrix})x \tag{84}$$

Then we have

$$\dot{y} = \left(\frac{-i}{\hbar} \begin{bmatrix} \ddots & \dots & \dots & \vdots \\ \vdots & 0 & \frac{d_{ij}}{2} & \vdots \\ \vdots & \frac{d_{ij}}{2} & & \vdots \\ \dots & \dots & \dots & \ddots \end{bmatrix} + B(t) \right) y \tag{85}$$

where $B(t)$ is rapidly oscillating matrix as all other transitions are detuned from ω and $B(t)$ averages out and we select a transition between i and j provided ofcourse there is a dipole transition between i and j.

8.1 Atomic Clocks and Ramsey Spectroscopy

Atomic clocks are used a time/frequency standards. They help to keep the frequency of a clock very constant. This is done my using the frequency difference between two energy levels as standard. For example in fig. 12 the energy difference between $F = 3$ and $F = 4$ levels of Cesium which is $\omega_0 \sim 9.19GHz$ is used as a standard for atomic clocks. The basic idea is that if the frequency ω with which I irrediate my system is exactly this ω_0, I will get a good transfer, else I won't get a good transfer, so I can adjust my ω so that I get good transfer then I know my $\omega = \omega_0$. This way I make sure if my ω drifts, I can readjust it.

Ramsey spectroscopy is way to make the transfer very sensitive to difference in $\omega - \omega_0$. To understand how this works consider again two levels and recall the two level system equation

$$\frac{dx}{dt} = -i(\omega_0 \ \sigma_z + 2A \ \cos\omega t \ \sigma_x)x \tag{86}$$

Now we have $y = \exp(i\omega_o t)x$, then we have

$$\frac{dy}{dt} = -i((\omega_0 - \omega)\sigma_z + 2A \ \cos\omega t \ (\cos\omega t\sigma_x + \sin\omega t\sigma_y)y = -i\{(\omega_0 - \omega)\sigma_z + A\sigma_x + A(\cos 2\omega_0 t\sigma_x + \sin 2\omega_0 t\sigma_y)\}y \tag{87}$$

We assume $A \ll \omega$. Then terms rotating at 2ω average out giving the evolution

$$\frac{dy}{dt} = -i((\omega_0 - \omega)\sigma_z + A\sigma_x)y \tag{88}$$

Suppose ω is not exactly ω_0, yet $|\omega - \omega_0| \ll A$. Then we switch on A for time T such that $AT = \frac{\pi}{2}$, it is called a $\frac{\pi}{2}$ pulse, then we switch off A and let system evolve for τ units of time and then again do a $\frac{\pi}{2}$ pulse . This is depicted in fig. (13). if there is no τ then ofcourse we jest have a π pulse and transfer $\begin{bmatrix} 1 \\ 0 \end{bmatrix} \rightarrow \begin{bmatrix} 0 \\ 1 \end{bmatrix}$. In presence of τ, the evolution of Eq. (88) is the following

$$\begin{aligned}\begin{bmatrix} 1 \\ 0 \end{bmatrix} & \xrightarrow{A} \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \end{bmatrix} \xrightarrow{\tau} \frac{1}{\sqrt{2}}(\cos(\omega-\omega_0)\tau \begin{bmatrix} 1 \\ i \end{bmatrix} + \sin(\omega-\omega_0)\tau \begin{bmatrix} 1 \\ 1 \end{bmatrix}) \\ & \xrightarrow{A} (\cos(\omega-\omega_0)\tau \begin{bmatrix} 0 \\ i \end{bmatrix} + \frac{1}{\sqrt{2}}\sin(\omega-\omega_0)\tau \begin{bmatrix} 1 \\ 1 \end{bmatrix})\end{aligned}$$

Overlap on the target state $\sqrt{(\cos^2(\omega-\omega_0)\tau + \frac{1}{2}\sin^2(\omega-\omega_0)\tau}$. When $(\omega-\omega_0)\tau = 0$ we have perfect transfer else it is less than 1 and depends on the difference $(\omega-\omega_0)$.

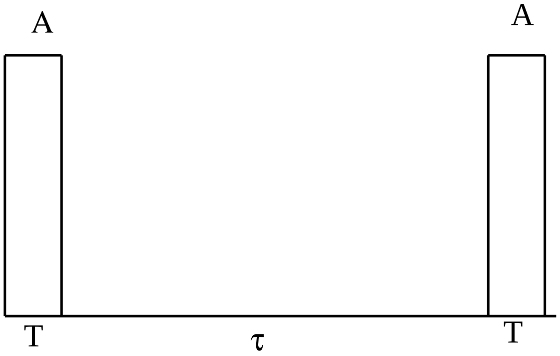

Figure 13: Fig. A shows the Ramsey pulse sequence $\frac{\pi}{2} - \tau - \frac{\pi}{2}$.

9 Perturbation Theory

In quantum mechanics, we are faced with situation that we have a Hamiltonian and we calculate its eigenvalues and eigenvectors (energies and orbitals) and then we perturb the Hamiltonian slightly, this could be say application of electric or magnetic fields. We want to know how does the eigenvalues and eigenvectors change when perturbation is small.

To make matters more concrete suppose I have matrix H_0 whose eigenvalues and eigenvectors I have calculated and I change $H_0 \to H_0 + \lambda H_1$ where λ is a small perturbation. We want to know how does the eigenvalues and eigenvectors change. To fix ideas consider

$$H_0 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

its eigevectors are $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$ with eigenvalues 1 and -1 respectively and I perturb

$$H_0 \to \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + \lambda \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

We can calculate the eigenvalues and eigenvectors they are $\sqrt{1+\lambda^2}$ and $-\sqrt{1+\lambda^2}$ with eigevectors $\begin{bmatrix} \cos\lambda' \\ \sin\lambda' \end{bmatrix}$ and $\begin{bmatrix} -sin\lambda' \\ \cos\lambda' \end{bmatrix}$ respectively where $\lambda' = \frac{\lambda}{1+\lambda^2}$. We can expnad the new eigenvalues and eigenvectors in terms of λ as

$$\sqrt{1+\lambda^2} = 1 + \frac{\lambda^2}{2} - \frac{\lambda^2}{8} + \dots$$

similarly we can expand

$$\begin{bmatrix} \cos\lambda' \\ \sin\lambda' \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \lambda \begin{bmatrix} 0 \\ 1 \end{bmatrix} - \frac{\lambda^2}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \dots$$

what do we find, the new eigenvalues and eigenvectors can be expnaded as a power series in perturbation parameter λ.

Let e_i be eigenvector of H_0 with eigenvalue E_i, after I perturb we can write the new eigenvalues as a power series

$$E_i \to E_i + \lambda E_i' + \lambda^2 E_i'' + \dots \tag{89}$$

$$e_i \to e_i + \lambda e_i' + \lambda^2 e_i'' + \dots \tag{90}$$

lets compute these corrections. We are saying

$$(H_0 + \lambda H_1)(e_i + \lambda e_i' + \lambda^2 e_i'' + \dots) = (E_i + \lambda E_i' + \lambda^2 E_i'' + \dots)(e_i + \lambda e_i' + \lambda^2 e_i'' + \dots) \tag{91}$$

Now just match terms in powers of λ. We get

$$H_0 e_i = E_i e_i \tag{92}$$

$$H_0 e_i' + H_1 e_i = E_i e_i' + E_i' e_i \tag{93}$$

First note $e_i + \lambda e_i' + \lambda^2 e_i'' + \dots$ is a unit vector then this implies that $e_i'^\dagger e$ is imaginary which gives that

$$E_i' = e_i^\dagger H_1 e_i \tag{94}$$

We can expand $e_i' = \sum_j \alpha_{ij} e_j$, where α_{ii} is imaginary as just argued. Then E. (93) gives,

$$H_0 \sum_j \alpha_{ij} e_j + H_1 e_i = E_i \alpha_{ij} e_j + E' e_i \sum_j \alpha_{ij}(E_j - E_i) e_j = (E' - H_1) e_i \tag{95}$$

This gives for $i \neq j$ we have $\alpha_{ij} = \frac{e_j^\dagger H_1 e_i}{E_i - E_j}$. where we assume E_i are non-degenerate. Now

$$H_0 e_i'' + H_1 e_i' = E_i e_i'' + E_i'' e_i + E_i' e_i' \tag{96}$$

This gives

$$E_i'' = e_i^\dagger H_1 e_i' = \sum_{i \neq j} \frac{e_i^\dagger H_1 e_j e_j^\dagger H_1 e_i}{E_i - E_j} \tag{97}$$

Eq. (94 and 97) give the first and second order change of energies. These are important enough to memorize.

10 Zeeman Effect and Chemical shifts

When we calculated fine structure of hydrogen. We saw how starting from the orbitals we get an additional Hamiltonian $L \cdot S$ which gives us the orbitals $|j, j_z\rangle$.

Now suppose we apply external magnetic field say along z direction. In presence of this field we get an aditional Hamiltonain

$$H = \omega_0(L_z + 2S_z) \tag{98}$$

where $\omega_0 = \frac{eB_0}{2m}$. Which we can write as

$$H = \frac{3\omega_0}{2}(L_z + S_z) - \frac{\omega_0}{2}(L_z - S_z) \tag{99}$$

Now observe $L \cdot S$ commutes with $(L_z + S_z)$, so we can take as our Hamiltonian

$$H_0 = \alpha L \cdot S + \frac{3\omega_0}{2}(L_z + S_z) \tag{100}$$

with orbitals $|j, j_z\rangle$. On top of this is the perturbation

$$H_1 = -\frac{\omega_0}{2}(L_z - S_z) \tag{101}$$

Recall Clebsch Gordon Coeffecients

$$|j, j_z\rangle = \sum_{l_z, s_z} c_{l_z, s_z} |l, l_z\rangle |s, s_z\rangle \tag{102}$$

To calculate the first order change in energies $E_i \rightarrow E_i + \langle j, j_z|H'|j, j_z\rangle$

$$\langle j, j_z|H'|j, j_z\rangle = \frac{\omega_0}{2}\sum_{l_z,s_z} c^2_{l_z,s_z}(s_z - l_z) \tag{103}$$

First order change in the eigenvectors is $|j, j_z\rangle \rightarrow |j, j_z\rangle + \sum \alpha_{j',j'_z}|j', j'_z\rangle$

$$\alpha_{j',j'_z} = \frac{\langle j', j'_z|H'|j, j_z\rangle}{E_i - E_j} = \frac{(\sum_{l_z,s_z} c'_{l_z,s_z}\langle l, l_z|\langle s, s_z|)(|\sum_{l_z,s_z} c_{l_z,s_z}(s_z - l_z)|l, l_z\rangle|s, s_z\rangle)}{E_i - E_j} \tag{104}$$

where E_j is energy of $|j', j'_z\rangle$.

Similarly we can calculate second order energy corrections.

Now consider the situation one has a closed shell (inert gas) configuration. Like $1s^2$ or $1s^2 2s^2 2p^6$. Then sum of J_z value on these orbitals is 0. Similarly for J_z and J_y. Then suppose we have a nuclear spin then on nuclear spin site the field produced by closed shells is zero. But if we apply a magnetic field, the orbitals get perturbed. Then it is no longer true that field prduced by closed shells is zero. Thus when we apply a magnetic field, the nuclear spin sees this magnetic field and an additional field due to perturbed orbitals. This additional field gives the phenomenon of chemical shifts in NMR as seen in more detail in next chapter.

11 Excercises

1. Show that if $\Psi_1(x, t)$ and $\Psi_2(x, t)$ are two wavefunctions of Schröedinger equation then

$$\frac{d}{dt}\int_{-\infty}^{\infty} \Psi_2(x, t)^* \Psi_1(x, t) = 0.$$

2. A particle at $t = 0$ is represented by the wavefunction

$$\psi(x) = A(a^2 - x^2), \quad |x| < a \tag{105}$$

$$= 0, \quad otherwise \tag{106}$$

   Find A. Find expected value of x, x^2, p, p^2 at $t = 0$.

3. Recall we said our problem is quantum mechanical when Debroglie wavelength $\lambda = \frac{h}{p}$ is greater than characteristic length at which potential varies. In solid state potential due to atomic nuclei varies at sacle of inter atomic spacing of say $3A^\circ$. Show that at room temperatures ($300K$ electrons in solids are quantum mechanical). You may estimate the velocity of the electron from $\frac{1}{2}mv^2 = \frac{3}{2}kT$.

4. Let $\Psi(x,t)$ be solution to Schröedinger equation. Show that expected value $\langle E\rangle = \langle\Psi, H\Psi\rangle$ stays constant.

5. A particle in an infinite square potential as described has initial wavefunction

$$\Psi(x,0) = A\sin^3\frac{\pi x}{a}, \quad 0 < x < a$$

Find A, $\Psi(x,t)$, $\langle x\rangle$ and $\langle E\rangle$.

6. Find eigen-energies for a half harmonic oscillator with potential

$$V(x) = \frac{1}{2}kx^2, \quad x \geq 0$$

and ∞ for $x < 0$.

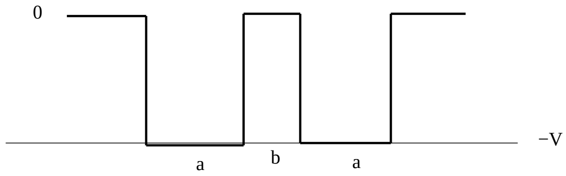

Figure 14: Fig. shows a double well potential.

7. For th double well potential shown in figure, find the ground state and first excited state wavefunction ψ_0 and ψ_1 when $b = 0$, $b \sim a$ and $b \gg a$. Plot the corresponding energies $E_0(b)$ and $E_1(b)$ as function of b.

8. Construct the wavefunction of hydrogen in state $n = 4, l = 3, m = 3$ and express ψ in terms of r, θ, ϕ. Find $\langle r\rangle$. If we measure $L_x^2 + L_y^2$ on this wavefunction, what values can be expect and with what probabaility.

9. Consider the state of a spin $\frac{1}{2}$ nuclei,

$$\chi = A\begin{pmatrix} 1-2i \\ 2 \end{pmatrix}$$

Find A. If we measure S_z what can we expect with what probability. What is $\langle S_z\rangle$. Answer same for S_x, S_y.

10. The combined spatial and spin wavefunction of electron in hydrogen is

$$R_{21}(\frac{1}{\sqrt{3}}Y_{10}\chi^{-}+\frac{2}{\sqrt{3}}Y_{10}\chi^{+}).$$

Find if your measure L^2 what can you expect and with what probability. Same for L_z, S^2, S_z, J^2 and J_z.