

The Quantum Mechanics note.

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15 October, 2020

1 Basic

The de'Broglie Wavelength is the reason why all this waves and stuff will appear in the next few pages, over-frequently, for that, we tell very first,

$$\lambda = \frac{h}{p} \quad (1)$$

And we will define,

$$\hbar = \frac{h}{2\pi} \quad (2)$$

As we do this, we will have to write \hbar so many times that,

$$\lambda = \frac{2\pi\hbar}{p} \quad (3)$$

Energy will be central to our analysis.

$$T = \frac{\hbar^2 k^2}{2m} \quad (4)$$

$$E = \hbar\omega \quad (5)$$

Schrodinger's equation for a Free Particle stands out to be,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t} \quad (6)$$

The Wave Function in general can be anything, from the Euler's Equation,

$$e^{i\theta} = \cos \theta + i \sin \theta \quad (7)$$

$$\Psi = \Psi(x, t) = A e^{i(kx - \omega t)} \quad (8)$$

For a particle, the $\psi^2(x, t)dx$ is the probability $P(x)$ that the particle is at any t , between x and $x + dx$,

$$P(x) = \Psi^2 dx$$

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The normalization persists here, for all the area possible, the particle must be somewhere.

$$\int_{-\infty}^{\infty} \Psi^2(x, t) dx = 1 \quad (9)$$

Be careful the square of the wave function can only be taken using Complex Conjugate, where the sign of i has to be reversed,

$$\Psi^2 = \Psi^* \Psi = (A^* e^{-i(kx-\omega t)})(A e^{i(kx-\omega t)})$$

Theorem 1. *Now if we can renormalize the function, then it will be possible to find the constants that we are assuming. Superposition of waves does satisfy Schrodinger's Equation.*

The Potential Energy can be introduced in it,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U(x) \Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (10)$$

The total Energy in the system turns out to be,

$$-\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x)\psi = E\psi \quad (11)$$

Let us have,

$$\psi = A_1 e^{ikx} + A_2 e^{-ikx} \quad (12)$$

So, is it valid? And what is the total energy that it has? **Solution:** We will input this in the Energy formula above, then,

$$-\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x)\psi = E\psi \quad (13)$$

$$-\frac{\hbar}{2m} [(ik)^2 A_1 e^{ikx} + (ik)^2 A_2 e^{-ikx}] = E\psi \quad (14)$$

$$-\frac{\hbar}{2m} [-k^2 A_1 e^{ikx} - k^2 A_2 e^{-ikx}] = E\psi \quad (15)$$

$$\frac{\hbar k^2}{2m} \psi = E\psi \quad (16)$$

$$\frac{\hbar k^2}{2m} = E \quad (17)$$

For validity, we input this in the Schrodinger equation and that will also validate it.

Further: We can see that the energy is $E = \frac{\hbar k^2}{2m}$ which is just the Kinetic Energy. Also note the wave function is in the form,

$$\psi = \sum A_i e^{\pm ikx}$$

This on the other hand validates the reason for having the *Stationary wave function*.

2 Potetial Wells

For the unidimentional boundary, the wave function for a well should have this property,

$$\Psi(0) = \Psi(L) = 0 \quad (18)$$

If there is box, and that has ∞ potential outside (impossible to go there.)

The wavefunction of the well should support this boundary condition. And the Ae^{ikx} does not satisfy this.

From the Superposition theorem,

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (19)$$

This actually works to be honest. Using the Euler's theorem,

$$\psi = A(\cos kx + i \sin kx) + B(\cos(-kx) + i \sin(-kx)) \quad (20)$$

That becomes

$$\begin{aligned} &= A \cos kx + A i \sin kx + B \cos kx + B i \sin kx \\ &= (A + B) \cos kx + i(A - B) \sin kx \end{aligned}$$

With the Boundary Conditions above, $x = 0, \psi = 0$

$$\therefore A + B = 0 \quad A = -B$$

$$\begin{aligned} &= 2iA \sin kx \\ &= C \sin kx \quad [C = 2iA] \\ \text{For, } x = L, \psi &= 0 \\ \therefore \sin kx &= \sin n\pi \\ kx = n\pi &\rightarrow \frac{2\pi}{\lambda}x = n\pi \\ \therefore \frac{2x}{\lambda} = n &\rightarrow \frac{2L}{\lambda} = n \\ \lambda &= \frac{2L}{n} \\ k = \frac{2\pi}{\lambda} &= \frac{n\pi}{L} \end{aligned}$$

$$\begin{aligned} \psi &= C \sin kx \\ \psi &= C \sin \frac{n\pi}{L}x \end{aligned}$$

Doing the math has been worth it, because, we used the boundary conditions to radically simplify the $\sum A_i e^{\pm i k x}$ to a simple $C \sin \frac{n\pi}{L}x$. So, wave function of a particle in a box (or well) is,

$$\psi = C \sin \frac{n\pi}{L}x \quad (21)$$

And, we also have an important description,

$$k = \frac{n\pi}{L} \quad (22)$$

If there is *no potential energy in the well*, $U(x, y) = 0$ then,

$$E = T = \frac{\hbar^2 k^2}{2m} \quad (23)$$

And because, inside the box, this k is *changed to something dependent on boundary*,

$$E = \frac{\hbar^2 n^2 \pi^2}{2mL^2} \quad (24)$$

So, there will be energy states depending on the $n \in \mathbb{Z}$, there will eminently be a change in the energy in a quantized fashion. This energy of particle inside box of certain shape and certain particle mass tells us that,

$$E = \left(\frac{\hbar^2 \pi^2}{2mL^2} \right) n^2 = \alpha n^2 \quad \rightarrow \quad E = \alpha n^2 \quad (\text{Particle in Box}) \quad (25)$$

This α is easy to find out, because, at $n = 1$ the $E = (\alpha)1^2 \rightarrow E_0 = \alpha$ Super-interestingly, there also is another cool fact, as we know $p = \hbar k$ thus,

$$p = \hbar k = \hbar \left(\frac{n\pi}{L} \right) = \frac{nh}{2L} \quad (26)$$

Recalling that $\hbar = h/2\pi$. Also recall Bohr started out using the fact,

$$mvr = n\hbar \quad (n \in \mathbb{Z}^+) \quad (27)$$

So, let me write again for sake of the LaTeX that,

$$\phi = C \sin \frac{n\pi}{L} x \quad (28)$$

By normalization, we can tell that the *particle must be inside the box at any point, so mathematically*

$$\int_0^L |\psi|^2 dx = 1 \quad (29)$$

So, generally,

$$\int_0^L C^2 \sin^2 \frac{n\pi x}{L} dx = 1 \quad (30)$$

As we can put the formula of $\sin^2 \theta = \frac{1 - \cos 2\theta}{2}$ found from that same formula $e^{i\theta} = \cos \theta + i \sin \theta$. Simplifying the above thing for a bit more,

$$C = \sqrt{\frac{2}{L}} \quad (31)$$

This finalizes,

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (32)$$

3 Bound States

You are asked to do some random algebra to, again writing the Schrodinger,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U(x) = E\Psi \quad (33)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{2m(E - U)\Psi}{\hbar^2}$$

$$\Psi = Ce^{kx} + De^{-kx}$$

4 The Harmonic Oscillator

The total energy is,

$$E = \frac{1}{2} \kappa A^2 \quad (34)$$

And the Force should be,

$$F = \kappa x \quad (35)$$

Let us assume that the oscillation takes places in this way,

$$\omega = \sqrt{\frac{\kappa}{m}} \quad (36)$$

Now let a oscillator move from a high level to a lower level, then it turns down on energy, as it should *emit a photon*, $E = hf$

$$hf = 2\pi\hbar \left(\frac{\omega}{2\pi} \right) = \hbar\omega \quad (37)$$

Note, this above won't be exact. Now, we can dare to write the Schrodinger's equation in the way,

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{2m(\frac{1}{2}\kappa x^2 - E)\Psi}{\hbar^2} \quad (38)$$

This has some kind of equation has to have a solution with some broad analysis that I am not gonna do here (as I am lazy), it turns out that

$$E_n = (n + \frac{1}{2})\hbar\sqrt{\frac{\kappa}{m}} \quad (39)$$

Here the ground energy level is denoted by the $n = 0$ not $n = 1$!

Okay I have gained some energy this morning to do this stuff.

Let the x be enough large. Then, $1/2\kappa x^2 - E$ is positive. The function ψ and $\frac{\partial^2 \psi}{\partial x^2}$ have same *positive* sign.

We have to keep in mind that **Quantum Mechanics will allow some penetration from the amplitude anyway**. But this will ensure that for $|x| \gg 1$ $\psi \Rightarrow 0$.

Let us take a point x that is outside the amplitude $x = A$. Now, there is a slope of the ψ at that place that is $\frac{\partial \psi}{\partial x}$ at that place.

1. Let the slope be positive and increasing. Then, $\frac{\partial^2 \psi}{\partial x^2}$ is also positive. But this blows up at high x so *it is not feasible*.
2. Let the slope be negative but increasing. Then, $\frac{\partial^2 \psi}{\partial x^2}$ is positive, but it will also blow up.
3. Let the slope be negative but increasing so that it does not gain altitude but tries to become parallel to x axis. When the $x \gg 1$ than the slope doesn't yet change too much and turn to go to zero.
4. Let the slope be negative but keeps decreasing in altitude. It turns out come down to x axis. And blow off at lower negative ∞ .

This qualitative discussion suggests how the boundary conditions as $|x| \rightarrow \infty$ determine the possible energy levels for the quantum mechanical harmonic oscillator.

It turns out that these boundary conditions are satisfied if the E is equal to E_n .

$$E_n = \left(n + \frac{1}{2} \right) \hbar \sqrt{\frac{\kappa}{m}} = \left(n + \frac{1}{2} \right) \hbar\omega \quad (40)$$

(I kind of love the way using snippets in LaTeX)

5 Comparing Quantum and Newtonian Oscillator

The wave functions of the levels $n = 0, 1, 2, \dots$ are called *Hermite Functions*.

The harmonic wave function for the $n = 0$ is,

$$\psi(x) = Ce^{-\sqrt{m\kappa}x^2/2\hbar} \quad (41)$$

Keep in mind that,

$$\int_{-\infty}^{\infty} e^{-a^2x^2} dx = \frac{\sqrt{\pi}}{a} \quad (42)$$

We can also verify for this wave function that it has the total energy of $E_0 = \frac{1}{2}\hbar\omega$. How much energy does the Hermite Function of the Harmonic Oscillator Pertain? **Solution:** The Hermite Wave Function for the state $n = 0$ is,

$$\psi = Ce^{-\sqrt{m\kappa}x^2/2\hbar} \quad (43)$$

Let us call,

$$\frac{\sqrt{m\kappa}}{2\hbar} = \alpha^2 \quad (44)$$

So, this becomes,

$$\psi = Ce^{-\alpha^2x^2} \quad (45)$$

The Schrodinger equation is,

$$-\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x)\psi = E\psi \quad (46)$$

Now, putting required stuff into it,

$$-\frac{\hbar}{2m} \left(\frac{\partial^2}{\partial x^2} (Ce^{-\alpha^2x^2}) \right) + \left(\frac{1}{2}\kappa x^2 \right) (Ce^{-\alpha^2x^2}) = E (Ce^{-\alpha^2x^2}) \quad (47)$$

Hopefully this should melt down to tell that,

$$E = \frac{1}{2}\hbar\omega \quad (48)$$

We can determine the amplitude from the Energy, though in Quantum Mechanical Oscillators the particle has well possibility to go off the amplitude zone. Not a problem at all. We kind of need to again redefine the definition of the Amplitude.

6 For more dimensions

The Kinetic Energy

$$K = \frac{P_x^2}{2m} + \frac{P_y^2}{2m} + \frac{P_z^2}{2m} \quad (49)$$

For more dimensions,

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (50)$$

$$\int_{-\infty}^{\infty} \psi \psi^* dV = \iiint_{-\infty}^{\infty} |\psi|^2 dx dy dz \quad (51)$$

The question is to find some relevant wave function that can nicely satisfy the three dimension, the simplest one is this one below,

$$\psi = X(x) Y(y) Z(z) = \psi(x)\psi(y)\psi(z) \quad (52)$$

some kind off. This system helps to write the stuff in such a manner,

$$\sum_i -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x_i)}{\partial x_i^2} = E_x \psi(x) \quad (53)$$

Thanks to Allah we can now write the simple three dimension form of the *Particle in the box* case without any problem

$$Q_i(q_i) = C_i \sin \frac{n_i \pi q_i}{L} \quad (54)$$

The i indece is for the coordinate. So,

$$\psi = C \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L} \quad (55)$$

For this kind of symmetry, the energy is also trascalbe,

$$E_x = \frac{n_x^2 \pi^2 \hbar^2}{2mL^2} \quad (56)$$

Total energy is also quite interesting,

$$E = \frac{(n_x^2 + n_y^2 + n_z^2) \pi^2 \hbar^2}{2mL^2} \quad (57)$$

These can give rise to degenerate states. And from the renormalized method, we can tell that,

$$C = \sqrt{\frac{8}{L^3}} \quad (58)$$

7 The Schrodinger Equation for the *Hydrogen Atom*

We can take the classical formula ofr the job,

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad (59)$$

And we have to write the equation of course in the *Polar system*,

$$\psi = \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (60)$$

And then something happens,

$$\begin{aligned} -\frac{\hbar^2}{2m_r r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(\frac{\hbar^2 l(l+1)}{2m_r r^2} + U(r) \right) R(r) &= E R(r) \\ \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left(l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) &= 0 \\ \frac{d\Phi(\phi)}{d\phi^2} + m_l^2 \Phi(\phi) &= 0 \end{aligned}$$

This tooke me some snippeting so a longer time either. Never mind.

7.1 Angular Momentum and Orbital

Magnitude of the Orbital Angular Momentum is,

$$L = \sqrt{l(l+1)}\hbar \quad (61)$$

And the component of the angular momentum on any of the axis is given by,

$$L_z = m_l \hbar \quad (62)$$

And,

$$m_l = 0, \pm 1, \pm 2, \dots \quad (63)$$

Some conditions

$$l_{max} = n - 1 \quad m_l \leq l \quad (64)$$

Then this particle can even have some intrinsic *Spin Angular Momentum* and that has (for electron),

$$S = \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1 \right)} \hbar = \sqrt{\frac{3}{4}} \hbar \quad (65)$$

Any component on any axis will be, *for electron only*,

$$S_z = m_s \hbar \quad \left[m_s = \pm \frac{1}{2} \right] \quad (66)$$

7.2 States and Quantum Numbers

There are orbit numbers n and this determines the states for Energy.

There is the angular momentum that determines so level of *motion*, l .

This angular momentum requires the magnetic quantum number m_l .

These $l, m_l, n \in \mathbb{Z}^+$.

This angular momentum is also quite a bit of thing that we have to keep in measure. Now, this angular momentum keeps track of the motion of the particle, and where is it : here or there.

8 The Atomic Stuff

These angular momentum has some various *Quantized* momentum.

- $l = 1$ is s
- $l = 2$ is p
- $l = 3$ is d
- $l = 4$ is f

There is the number of shell named.

- $n = 1$ is K
- $n = 2$ is L
- $n = 3$ is M
- $n = 4$ is N

These are just kind of the states that are possible that can be taken by the electrons and by the Schrodinger's equation. For the Hydrogen this usually works. I don't yet know the interpretation for many electron, as the electrons are interacting with themselves.

This angular momentum helps in positions. These angular momentum, shells, spin, everything makes up the wave function.

And wave function is just the positions stuff.

I am having some problem accepting and the 4 quantum number stuff, but not a fact.

High angular momentum cause electron move somewhere else. So, this will obviously cause terror in the atom anyway.

There can be some feasible states that are inside the quantum levels.

These electron tend to make the most of the interactions in the atom and that is why the place where this electron is - is very important to define in usual sense.

And in general we can assume that there in no electric interactinos of hte electron and this is trivial to consider for the mean time. These take various shape as the dumbbells, and we can take advantage of the shapes in

8.1 Electrons taking states

Electrons in the atoms will take possible states that are present. They will keep filling the states until they reach the saturation that no states (feasible states) remain. So, for an atom that will have n rooms, and per every room there is s number of states, then there will be ns amount of electrons in the atom (around the nuclues)

Let us go for the first states, $n = 1$ and $n \geq l$, so l can take only $l = 0$ angular momentum. Now, $m_l = 0$ too. The spin of electron can be $1/2$ or $-1/2$. So, there are only 2 possible states, the number of states in the anularlr momentum room and magnetic qunatum number room is just 1. Also in the shell, the room is 1. But in the single room, two spins can be taken.

So the shell $n = 1$ can keep 2 electrons. $l = 0$ so comes an s . We tell that,

$$1s^2 \tag{67}$$

For the shell $n = 2$, the angular momentum state can be $l = 0, 1$. And the magnetic quantum $m_l = -1, 0, 1$. Spins taken are $1/2$ and $-1/2$. So, for $l = 0$ there are 1×2 states (each magnetic

quantum number can have up spin or down spin). so total 2 state. And the $l = 1$ there are 3×2 states, so 6 states. Total states in the $n = 2$ are $2 + 6 = 8$ states.

We tell,

$$1s^2 2s^2 2p^6 \quad (68)$$

Explaining, I shall count the number of states in each of the Orbital (angular momentum calculation each) to find states. Each of the states will be filled with an electron, so the number of states also defines the number of electrons.

$$\begin{array}{ll} 1s^2 & (n = 1, l = 0, m_l = 0) \quad (n = 1, n(l) = 1, n(m_l) = 1, n(s) = 2) \\ 2s^2 & (n = 2, l = 0, m_l = 0) \quad (n = 1, n(l) = 1, n(m_l) = 1, n(s) = 2) \\ 2p^6 & (n = 2, l = 1, m_l = -1, 0, 1) \quad (n = 1, n(l) = 1, n(m_l) = 3, n(s) = 2) \end{array}$$