Time Dependent Quantum Chemistry

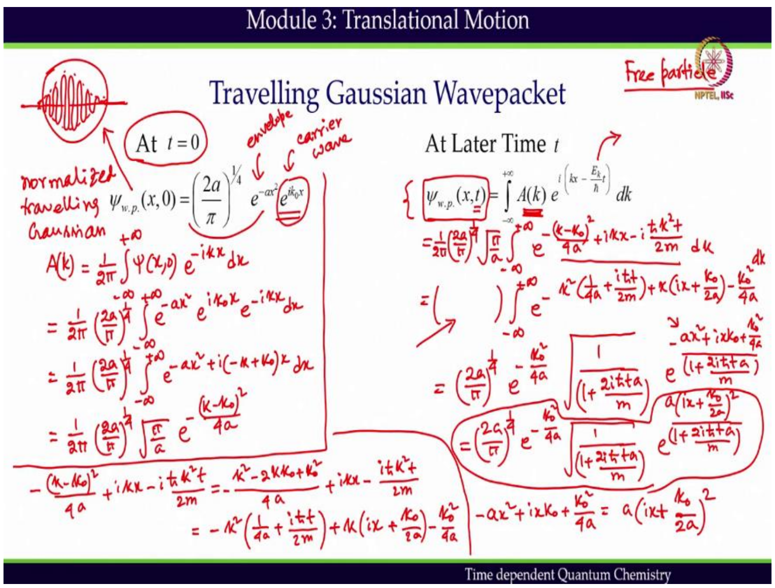
Professor Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru

Module: 03 Lecture: 19

Travelling Gaussian Wavepacket

Welcome back to module 3, we are continuing the discussion on how to represent a particle in quantum mechanics. And we are trying to find out the analytical solution to the wave packet dynamics. And we have so for seen, if I have a Stationary Wavepacket, Gaussian Wavepacket, how it should behave as a function as the time progresses, the shape of the Gaussian, how it is changing, we have seen that it is broadening and the amplitude also decreasing.

(Refer Slide Time: 01:06)



So, next we will move to Traveling Gaussian. The Gaussian which will travel as a function of time. Now, as I mentioned before our traveling gaussian in this analytical approach, I just remind that , I need the initial gaussian wave function at t equals 0.

Because from that I can find out A(k) and then I can insert that function A(k) function and I can get the wave function which the wavepacket, how does it look like at a different time, this time dependent wavepacket I can find out. Now, it is just one example with the Gaussian function if we start with Gaussian function we can get this analytical solution, but this does not mean that for every situation I will be able to get an analytical solution and these are the things which will learn very soon, but so, far we are talking about free particle. Free particle which means that the particle is not experiencing any potential. So, previously I told already this is the Normalized Traveling Gaussian.

$$\psi_{w.p,}(x,0)=\left(\frac{2a}{\pi}\right)^{\frac{1}{4}}e^{-ax^2}e^{ik_0x}$$

This part is the Gaussian function and it is traveling, this part is contributing to this movement and we have seen that this is the envelope function and this is the carrier wave of the Wavepacket. So, this is called carrier wave of the Wavepacket and this is the envelope function. So, what we did before we will first find out A(k).

Because that is the way we are going to work on we need this A(k) and with the help of Dirac delta function, we have seen that

$$A(k)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\psi(x,0)e^{-ikx}dx$$

So, let us plug that in this initial Gaussian Wavepacket.

$$=\frac{1}{2\pi}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}}\int_{-\infty}^{\infty}e^{-ax^2}e^{ik_0x}e^{-ikx}dx$$

I can plug that in and I can get this. You can remember that k0 was the average of all k. So, in order to get this initial Wavepacket. How does this Wavepacket look like?

I have an envelope function and then carrier wave. So, this is what initial wavepacket is which is nothing but the particle in quantum mechanics. A particle in quantum mechanics is the localized matter wave and this is localized in space. So, we should view particle as this, this is just an example.

It can be Gaussian, it can be some other shapes, shape can change, but it should look like this and k0 was kind of average of all ks. So, k1 + k 2 + k 3 like this all components and here because it is minus infinity to plus infinity we have to add them and then add the total number. So, that was the k the meaning of k0 it was the average of all this that is the and that is the k represented by the carrier wave.

The reason why we take the Gaussian shape is because the integration would be much simpler to deal with otherwise integration is we need to use numerical method to integrate it.

$$A(k) = \frac{1}{2\pi}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \int_{-\infty}^{\infty} e^{-ax^2 + i(-k+k_0)x} dx$$

$$= \frac{1}{2\pi}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \sqrt{\frac{\pi}{a}} e^{-\frac{(k-k_0)^2}{4a}}$$

And this is A(k) then I will be able to plug this in here and I can get the wave function A(k) is write down the constants first.

$$\psi_{w.p,}(x,t) = \int_{-\infty}^{\infty} A(k) e^{i\left(kx - \frac{E_k t}{\hbar}\right)} dk$$

$$= \frac{1}{2\pi}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \sqrt{\frac{\pi}{a}} \int_{-\infty}^{\infty} e^{-\frac{(k-k_0)^2}{4a} + ikx - i\frac{\hbar k^2 t}{2m}} dk$$

Remember E_k we had a value E_k and E_k was used to be this is the kinetic energy of the particle and the kinetic energy of the particle was given previously.

So, we can use that E_k value and we can reduce this equation to following. So, this is the integration we have to perform analytically to get them final Wavepacket. Now, if we look at this expression.

The exponentiation this can be reduced very easily we can reduce it in the following way

$$-\frac{(k-k_0)^2}{4a} + ikx - i\frac{\hbar k^2 t}{2m} = -\frac{k^2 - 2kk_0 + k_0^2}{4a} + ikx - i\frac{\hbar k^2 t}{2m}$$

$$= -k^2\left(\frac{1}{4a} + \frac{i\hbar t}{2m}\right) + k\left(ix + \frac{k_0}{2a}\right) - \frac{k_0^2}{4a}$$

$$-ax^2 + ixk_0 + \frac{k_0^2}{4a} = a\left(ix + \frac{k_0}{2a}\right)^2$$

So, this can be used in this exponentiation and if we do that, then I have all these constant parts and then I am not writing

$$\psi_{w.p,}(x,t) = \frac{1}{2\pi}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \sqrt{\frac{\pi}{a}} \int_{-\infty}^{\infty} e^{-k^2\left(\frac{1}{4a} + \frac{i\hbar t}{2m}\right) + k(ix + \frac{k_0}{2a}) - \frac{k_0^2}{4a}} dk$$

$$= \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-\frac{k_0^2}{4a}} \sqrt{\frac{1}{\left(1 + \frac{2i\hbar t a}{m}\right)}} e^{\frac{-ax^2 + ixk_0 + \frac{k_0^2}{4a}}{\left(1 + \frac{2i\hbar t a}{m}\right)}}$$

This is the exponential function we have.

The terms in exponential can be modified as-

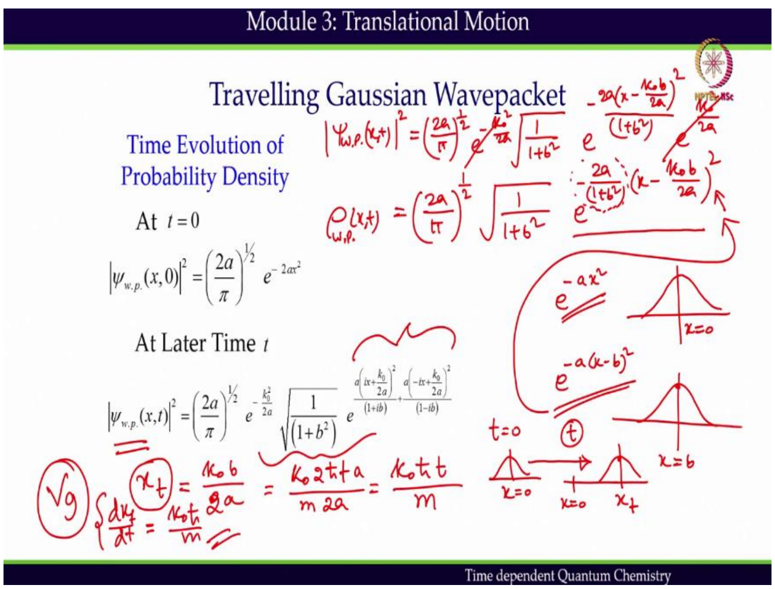
$$-ax^2 + ixk_0 + \frac{k_0^2}{4a} = a\left(ix + \frac{k_0}{2a}\right)^2$$

So, if we plug in this result in the above equation we got-

$$\psi_{w.p,}(x,t) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-\frac{k_0^2}{4a}} \sqrt{\frac{1}{\left(1+\frac{2i\hbar ta}{m}\right)}}\, e^{\frac{a(ix+\frac{k_0}{2a})^2}{\left(1+\frac{2i\hbar ta}{m}\right)}}$$

So, this is the final expression we get for the wave function with this final expression once we get the final expression we know we are interested in the density because the wave function is not going to give any meaning until I convert it to the density and then look at the density how the density is changing. So, we have got the final expression for the wave function and we are going to check the density how the density is changing.

(Refer Slide Time: 15:56)



Because density is something which can be connected to the experimental observable, and when you look at the density in order to find out the density what will do, we will assume that again as we did before $\frac{2\hbar ta}{m} = b$.

We will assume that and if we assume that, then I will be able to write down the density in this following form.

And the reason why I can write down the density is in volume form because I get this wave function this Wavepacket (x,t) Wavepacket as follows, it is going to be

$$\psi_{w.p,}(x,t)=\left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-\frac{k_0^2}{4a}}\sqrt{\frac{1}{(1+ib)}}e^{\frac{a(ix+\frac{k_0}{2a})^2}{(1+ib)}}$$

So, this is the wave function we get and from that wave function I can find out the density. And once we get this density we can rewrite this expression for the density as follows we will rewrite this part, this part we have to simplify here and we will follow this simplification

$$\frac{a\left(ix+\frac{k_0}{2a}\right)^2}{(1+ib)}+\frac{a\left(-ix+\frac{k_0}{2a}\right)^2}{(1-ib)}=\frac{a}{(1+b^2)}\left[(1-ib)\left(ix+\frac{k_0}{2a}\right)^2+1+ib)\left(-ix+\frac{k_0}{2a}\right)^2\right]$$

$$=\frac{a}{(1+b^2)}\left[-2x^2+\frac{2bxk_0}{a}+\frac{2k_0^2}{4a^2}\right]$$

$$=-\frac{2a}{(1+b^2)}\left[x^2-\frac{bxk_0}{a}-\frac{k_0^2}{4a^2}\right]$$

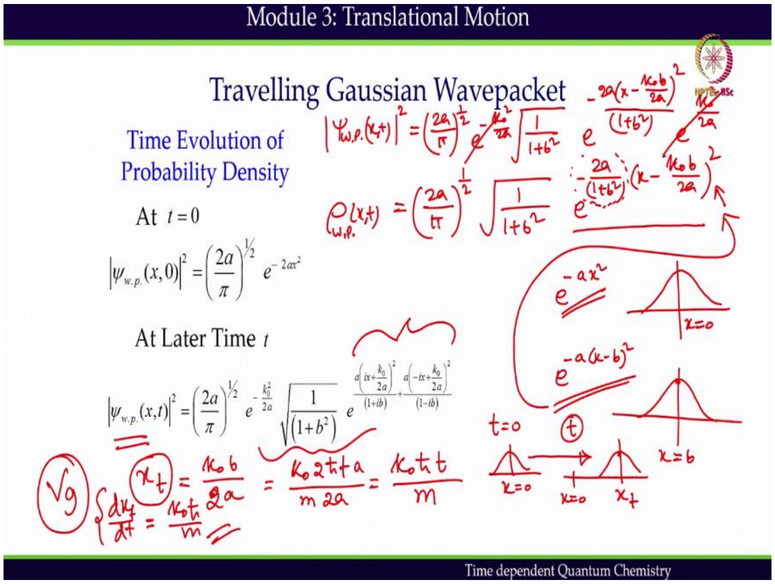
$$=-\frac{2a}{(1+b^2)}\left[x^2-2x\frac{bk_0}{a}+\left(\frac{bk_0}{2a}\right)^2-\left(\frac{bk_0}{2a}\right)^2-\frac{k_0^2}{4a^2}\right]$$

$$=-\frac{2a}{(1+b^2)}\left[\left(x-\frac{bk_0}{2a}\right)^2-\frac{k_0^2}{4a^2}(1+b^2)\right]$$

$$=\frac{2a}{(1+b^2)}\left(x-\frac{bk_0}{2a}\right)^2+\frac{k_0^2}{2a}$$

So, we get this simplification and we can plug this in here and we will get.

(Refer Slide Time: 22:20)



We will finally get this form this Wavepacket form we have simplified this part we will get this

$$|\psi_{w.p,}(x,t)|^2 = \left(\frac{2a}{\pi}\right)^{\frac{1}{2}} e^{-\frac{k_0^2}{2a}} \sqrt{\frac{1}{1+b^2}} e^{-\frac{a\left(ix+\frac{k_0}{2a}\right)^2}{(1+ib)}} e^{-\frac{a\left(-ix+\frac{k_0}{2a}\right)^2}{(1-ib)}}$$

$$|\psi_{w.p,}(x,t)|^2 = \left(\frac{2a}{\pi}\right)^{\frac{1}{2}} e^{-\frac{k_0^2}{2a}} \sqrt{\frac{1}{1+b^2}} e^{-\frac{2a\left(x-\frac{k_0 b}{2a}\right)^2}{\left(1+b^2\right)}} e^{\frac{k_0^2}{2a}}$$

So, this part will cancel out each other and finally, I get a simplified form of this big expression as.

$$\rho_{w.p.}(x,t) = \left(\frac{2a}{\pi}\right)^{\frac{1}{2}} \sqrt{\frac{1}{1+b^2}} e^{-\frac{2a\left(x-\frac{k_0 b}{2a}\right)^2}{\left(1+b^2\right)}}$$

So, I get this final expression for this $\rho_{w.p.}(x,t)$. And one thing I would like to now.

So, this expression, this initial part is constant and then you have x square. So, what I have right now is the Wavepacket which is having a Gaussian shape again, but there is a difference. And the difference is if I had e^{-ax^2}, this is a Gaussian function which is centered at x equals 0.

But if I have $e^{-a(x-b)^2}$, then this Gaussian function will be centered at x equals b is just shifted from the center position x equals 0 to x equals b. And that is the meaning of this function, this Gaussian function and similar Gaussian function we have here. So, what we see here is that the center of the Gaussian is changing in this case.

And the center of the Gaussian will be represented by x_t,

$$x_t = \frac{k_0 b}{2a} = \frac{k_0 2\hbar ta}{2ma} = \frac{k_0 \hbar t}{m}$$

We can see that it is if I use the b value, previously, we have used the b value and a value we know that a value both are known. So, in the end, what I get the center of the Gaussian is t dependent ,What we observe here, this x_t is the center of the Gaussian. The Gaussian is now is shifting.

So, at t equals 0, I started with the Gaussian which was centered at x equals 0. Now, at different time, let us say a t time the Gaussian is not centered at x equals 0 anymore. It is centered at this point, which is x_t point. So, it shows that the Gaussian is traveling over time on the x-axis, on the x-axis is slowly traveling and center of the Gaussian is traveling.

And if x t the center of the Gaussian is traveling like this way, then I can find out dx_t/dt center of the Gaussian center of the envelope is changing, envelope function is propagating. Now, because dx_t/dt is finding out the velocity of the envelope, velocity of the envelope is given by the group velocity.

$$V_g = \frac{dx_t}{dt} = \frac{k_0 \hbar}{m}$$

That is the definition we have given velocity of the envelope in a Wavepacket is given by group velocity .What we observe here is that Wavepacket that particle which is represented by the Wavepacket is now traveling with this k naught h cut by m group velocity.

Have observed that the particle which started with a position at x equals 0, the center of the Gaussian started with x equals 0, it is now propagating along x-axis as a function of time and we have found that the group velocity is represented by the velocity of the wavepacket. So, we will stop here and we will meet again in this module. We will continue this module in the next session.