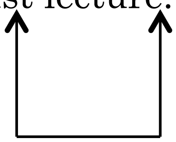
Lecture #3: $|\psi(x,t)|^2$: Motion, Position, Spreading, Gaussian Wavepacket

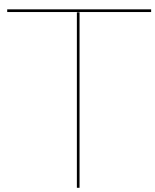
Reading Chapter 1, CTDL, pages 9-39, 50-56, 60-85

Last lecture:



Infinite well

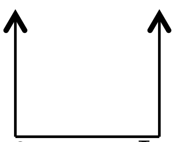
and



Delta-function well

What are the key points?

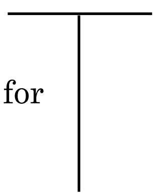
E_n, ψ_n for



$$E_n = n^2\left[\frac{h^2}{8mL^2}\right]$$

$$\psi_n = (2/L)^{1/2}\sin(n\pi x)$$

E, ψ for



$$E = -\frac{ma^2}{2\hbar^2}$$

$$\psi = \left(\frac{ma}{\hbar^2}\right)^{1/2} e^{-ma|x|/\hbar}$$

Do E and ψ for delta function well behave as you expect?

TODAY: Can we construct a $\Psi(x,t)$ for which $|\Psi|^2$ acts like a CM particle, but with correct QM characteristics?

* stationary phase point and its motion
* stationary phase approximation for evaluating an integral with wiggly integrand

Motion *requires* $\Psi(x,t)$ from TDSE! Motion is *encoded* in $\psi(x)$, but we will need to actually observe motion (pages 3-4 thru 3-12).

Our goal is to use a well understood function that appears frequently in quantum mechanics, a normalized Gaussian, as a particle-like quantum mechanical state function, a "Gaussian Wavepacket."

What we want is to know how the time-evolving center position, center amplitude, center velocity, and the width of this wavepacket are encoded in the mathematical expression. This will guide us in constructing particle-like states with chosen properties and in knowing how to recognize these properties in an unfamiliar state function.

From a stationary Gaussian G(x; x_0, Δx) to a moving Gaussian wavepacket |Ψ(x,t)|²

1. $G(x;x_0,\Delta x) = (2\pi)^{-1/2}(\Delta x)^{-1}e^{-(x-x_0)^2/2(\Delta x)^2}$

Normalized: $\int_{-\infty}^{\infty} G(x;x_0,\Delta x)dx = 1$

You can show by evaluating the integral that $G(x;\, x_0,\, \Delta x)$ is normalized to 1.

$\langle x^2 \rangle \equiv \int_{-\infty}^{\infty} G(x;x_0,\Delta x)x^2 dx$ and a similar equation for $\langle x \rangle$.

The width, Δx, the standard deviation of $G(x)$, is the square root of the variance

$$\Delta x = \left[\langle x^2 \rangle - \langle x \rangle^2\right]^{1/2}$$

Finally, we want a function that is normalized to 1 at $t = 0$

$$1 = \int_{-\infty}^{\infty} |\Psi(x,0)|^2 dx$$

$G(x;x_0,\Delta x) = \Psi(x,0)^* \Psi(x,0) = |\Psi(x,0)|^2$

normalized as $\int_{-\infty}^{\infty} |\Psi(x,0)|^2 dx = 1$

$\Psi(x,0) = (2\pi)^{-1/4}(\Delta x)^{-1/2} e^{-(x-x_0)^2/4(\Delta x)^2}$

This is also a Gaussian. Ψ(x,0) is broader and not as tall as $G(x;x_0,\Delta x)$ at $x = x_0$.

2. How do we get to the following complicated-looking textbook function?

spreading and moving with minimum width at $t = 0$

$$\left|\Psi(x,t)\right|^2 = \underbrace{\left(\frac{2}{\pi a^2}\right)^{1/2}\left(1+\frac{4\hbar^2t^2}{m^2a^4}\right)}e^{-\left[\frac{2a^2\left(x-\frac{\hbar k_0}{m}t\right)^2}{a^4+\frac{4\hbar^2t^2}{m^2}}\right]}$$

time-dependent normalization and magnitude. Since probability is conserved, the normalization factor must be t-dependent because the denominator of the exponential factor is t-dependent.

$$\left|\Psi(x,0)\right|^2 = \left(\frac{2}{\pi a^2}\right)^{1/2} e^{-2x^2/a^2}$$

at $t = 0$, by comparison to the normalized Gaussian

$$\left(\frac{2}{\pi a^2}\right)^{1/2} = \left(\frac{1}{2\pi(\Delta x)^2}\right)^{1/2}$$

we have $\Delta x(t = 0) = a/2$.

Now, for motion of the center of the wavepacket, $x_0(t)$, we expect that

$$x_0(t) = x_0(0) + \frac{p_0}{m}t \qquad p_0 \text{ is momentum at } t = 0$$

$$v_0(0) = \frac{p_0(0)}{m} = \frac{\hbar k_0(t)}{m} \qquad v_0 \text{ is velocity at } t = 0,\ k_0 \text{ is the wavenumber, } k = p/\hbar \text{ at } t = 0$$

$$x_0(t) = x_0 + \frac{\hbar k_0(t)}{m}t$$

$\Delta x(0) = a/2.$ Width increases as $|t|$ increases from $t = 0$.

Wavepacket is moving and changing its width. Minimum width is at $t = 0$.

Could shift the t at which minimum width occurs by replacing t by $t' = t + \delta$ in the formula for $\Psi(x,t)$.

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How do we know that the width of the wavepacket is t-dependent? If the value of Ψ at the t-dependent center is changing and $\Psi(x,t)$ is normalized, then the wavepacket must be spreading or contracting. We will have to look at the t-dependent Schrödinger equation to see how the momentum depends on x.

NON-LECTURE

The Fourier transform of a Gaussian is another Gaussian. This means that if you have a wavepacket, $|\Psi(x,0)|^2$, with a Gaussian shape, the momentum distribution of this wavepacket, $|\Phi(p,0)|^2$, will also be a Gaussian. This Gaussian distribution of the momentum will cause the time-dependent spatial shape of the wavepacket to be either stretching or compressing. If the wavepacket shape, $|\Psi(x,t)|^2$, expands as t advances, it compresses as t decreases until it reaches the minimum possible width and then re-expands. The widths, Δx and Δp, are reciprocally related and the minimum uncertainty wavepacket, at the t when $\Delta x \Delta p$ reaches its minimum value, is of particular interest. It is at this instant that the quantum mechanical wavepacket maximally resembles a classical particle.

How do we get from $G(x; x_0, \Delta x)$ to $|\Psi(x,t)|^2$?

Time Dependent Schrödinger Equation (TDSE)

$$\mathbf{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Time Independent Schrödinger Equation (TISE)

$$\mathbf{H}\Psi = E\psi \qquad \text{or} \qquad \mathbf{H}\psi_n = E_n\psi_n$$

Special very useful case: if **H** is independent of time and if we know the solutions to the TISE, hen it is trivial to go from $\{E_n, \psi_n\}$ to $\Psi(x,t)$.

Suppose we create an arbitrary state at $t = 0$. It is always possible to express this arbitrary state as a linear combination of eigenstates of **H**,

$$\psi(x) = \sum_n a_n \psi_n$$

because the set of $\{\psi_n\}$ is "complete". We can convert this $\psi(x)$ to $\Psi(x,t)$ very simply:

$$\Psi(x,t) = \sum_n c_n \psi_n e^{-iE_n t/\hbar}$$

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Show that this satisfies the TDSE:

$$i\hbar\frac{\partial\Psi}{\partial t} = i\hbar\sum_n (-iE/\hbar)c_n\psi_n e^{-iE_nt/\hbar}$$

$$= \sum E_n c_n \psi_n e^{-iE_nt/\hbar}$$

$$\mathbf{H}\Psi = \mathbf{H}\sum_n c_n\psi_n e^{-iE_nt/\hbar}$$

$$= \sum_n E_n c_n \psi_n e^{-iE_nt/\hbar}$$

same, so the TDSE is satisfied

It is clear that $\Psi(x,t)$ "moves", but we still need help in understanding that motion.

(i) $\int_{-\infty}^{\infty}\Psi^*(x,t)\Psi(x,t)dx = 1$
no motion because all $\Delta n \neq 0$ integrals involving $\int_{-\infty}^{\infty}\psi_n^*\psi_{n'}dx = 0$ by orthogonality.

(ii) $\Psi^*(x,t)\Psi(x,t)$ evolves in time if eigenstates that belong to *at least two* different E_n are included.

For example,

$$\Psi_{1,2} = c_1\psi_1 e^{-iE_1t/\hbar} + c_2\psi_2 e^{-iE_2t/\hbar}$$

$$\left|\Psi_{1,2}\right|^2 = |c_1|^2|\psi_1|^2 + |c_2|^2|\psi_2|^2 + c_1^*\psi_1^*c_2\psi_2 e^{iE_1t/\hbar}e^{-iE_2t/\hbar} + c_1\psi_1c_2^*\psi_2^*e^{-iE_1t/\hbar}e^{iE_2t/\hbar}$$

$$\omega_{12} \equiv \left(E_1 - E_2\right)/\hbar$$

$$\left|\Psi_{1,2}\right|^2 = |c_1|^2|\psi_1|^2 + |c_2|^2|\psi_2|^2 + c_1^*c_2\psi_1^*\psi_2 e^{i\omega_{12}t} + c_1c_2^*\psi_1\psi_2^*e^{-i\omega_{12}t}$$

The first two terms are t-independent and the second two terms are t-dependent and their sum is definitely a real number:

$$2\,\mathrm{Re}\left(c_1^* c_2 \psi_1^* \psi_2 e^{i\omega_2 t}\right).$$

Now let us consider the particle in a constant potential.

eigenfunctions $\left\{\psi_k = e^{ikx}, \psi_{-k} = e^{-ikx}\right\}$

$$E_{|k|} = \frac{p^2}{2m} + \underbrace{E_0}_{\substack{\text{arbitrary}\\ \text{zero of}\\ \text{energy}}} = \frac{\hbar^2 k^2}{2m} + E_0$$

$$\frac{E_{|k|} - E_0}{\hbar} \equiv \omega_k$$

$$\Psi_{|k|}(x,t) = e^{-i\omega_k t}\left[Ae^{ikx} + Be^{-ikx}\right]$$
$$= Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)}$$

Stationary phase

$$kx_\phi - \omega t = 0$$

(could choose any constant instead of 0)
x_ϕ is the constant phase point.

$$x_\phi = \frac{\omega t}{k} \qquad \text{A-term}$$

$$x_\phi = -\frac{\omega t}{k} \qquad \text{B-term}$$

phase velocity

$$\frac{dx_\phi}{dt} = v_\phi = \pm\omega / k$$

$$x_\phi(t) = x_\phi(0) \pm \frac{\omega t}{k}$$

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Some arbitrarily chosen constant phase point on $\Psi(x,t)$ moves at a velocity ω/k.

What about $\int_{-\infty}^{\infty}|\Psi(x,t)|^2 dx$?

The t-dependent term integrates to zero due to $\int_{-\infty}^{\infty} e^{\pm 2ikx}dx = 0$.

So there is no motion in $|\Psi(x,t)|^2$, only a constant term and standing waves.

But $\Psi(x,t)$ encodes motion through $\langle \hat{p} \rangle$ and $\langle \hat{x} \rangle$. For example:

$$\left\langle \hat{p}_x \right\rangle = \int_{-\infty}^{\infty} \Psi^* \frac{\hbar}{i}\frac{\partial}{\partial x}\Psi dx$$

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t) = \frac{\hbar}{i}e^{-i\omega_k t}\left[Aike^{ikx} - Bike^{-ikx}\right] = \frac{\hbar}{i}ike^{-i\omega_k t}\left[Ae^{ikx} - Be^{-ikx}\right]$$

Now the whole thing:

$$\frac{\hbar}{i}\Psi^*(x,t)\frac{\partial}{\partial x}\Psi = \hbar k\left[A^* e^{-ikx} + B^* e^{ikx}\right]\left[Ae^{ikx} - Be^{-ikx}\right]$$

Now integrate $\int_{-\infty}^{\infty} dx$

$$\int e^{\pm 2ikx}\, dx = 0$$

$$\langle p \rangle = \hbar k\left[|A|^2 - |B|^2\right]$$

as expected! Motion, just like Classical Mechanics!

To get motion, it is necessary that $|A| \neq |B|$

Now for the payoff.

Consider a superposition of e^{ikx} for many values of k:

$$\Psi(x,0) = \int g(k)e^{ikx}\,dk$$

We can experimentally produce any $g(k)$ we want.

Let $g(k)$ be a Gaussian in k

$$g(k) = e^{-(a^2/4)(k-k_0)^2}$$

But $\int_{-\infty}^{\infty} g(k)e^{ikx}dk$ is the Fourier Transform of a Gaussian in k.

Fourier Transform and Inverse Fourier Transform

$$f(x) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} g(k)e^{ikx}dk \qquad \text{get rid of } k$$

$$g(k) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} f(x)e^{ikx}dx \qquad \text{get rid of } x$$

So let us build $\Psi(x,0)$ as a superposition of e^{ikx}. We can write $g(k)$ in amplitude, argument form:

$$g(k) = |g(k)|\,e^{i\alpha(k)})$$

complex
function
of real variable

We want $|g(k)|$ to be sharply peaked near $k = k_0$, so use a Gaussian

$$|g(k)| = e^{-(a^2/4)(k-k_0)^2}$$

center $k = k_0$
width $\Delta k = 2^{1/2}a$

$$\alpha(k) = \underbrace{\alpha(k_0)}_{\alpha_0} + (k - k_0)\left.\frac{d\alpha}{dk}\right|_{k=k_0}$$ power series expansion

$$g(k) = e^{-(a^2/4)(k-k_0)^2} e^{i\alpha_0} e^{i(k-k_0)\frac{d\alpha}{dk}}$$

$$g(k)e^{ikx} = \underbrace{e^{-(a^2/4)(k-k_0)^2} e^{i\alpha_0}}_{\text{independent of } x} e^{i\left[(k-k_0)\frac{d\alpha}{dk}+kx\right]}$$

rapidly oscillating in x except at a special region of x

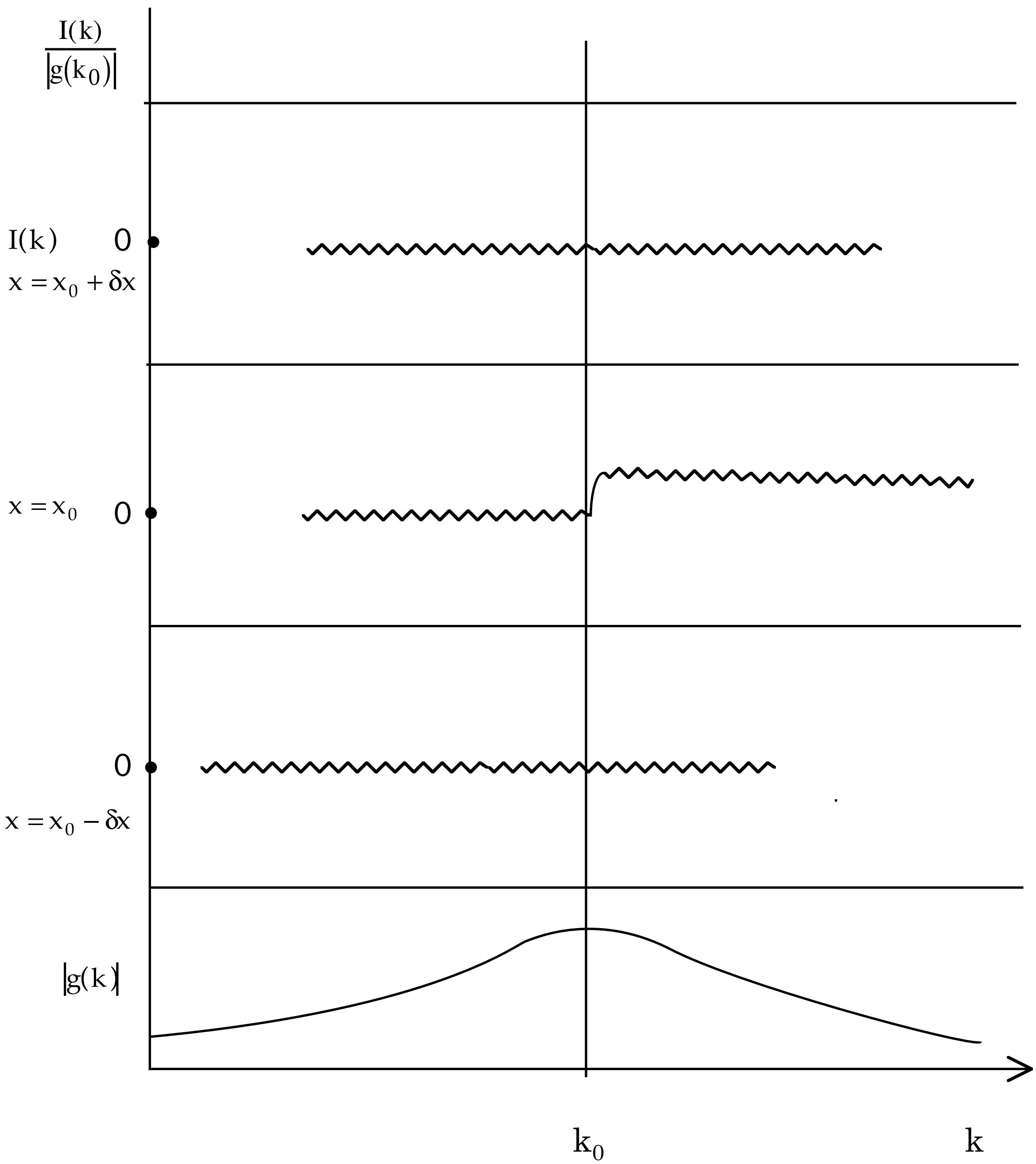
To find the value of x at which the *phase is stationary*, we want at which the phase is stationary, we want

$$\frac{d}{dk}\left[\left(k - k_0\right)\frac{d\alpha}{dk} + kx\right] = 0$$

$$\frac{d\alpha}{dk} + x = 0$$

so if we choose $\left.\frac{d\alpha}{dk}\right|_{k=k_0} = -x_0$ we have stationary phase in k near k_0 and near $x = x_0$. This means that the $\int_{-\infty}^{\infty} g(k)e^{idx}dx$ integral accumulates to its exact value near $x = x_0$.

How does an integral over a rapidly oscillating integrand accumulate? It accumulates near the stationary phase point, x_0.



Integral accumulates near k = k_0 but only when x ≈ x_0.

$I(k) = \int_{-\infty}^{k} f(x,k)\,dk.$ If you examine the integrand and can identify the stationary phase region, you can determine the value of the integral without actually evaluating the integral.
Amaze your friends!

NON-LECTURE

Joel Tellinghuisen, "Reflection and Interference Structure in Diatomic Franck-Condon Factors," J. Mol. Spectrosc. **103**, 455-465 (1984). The figures in this paper show how an integral accumulates at a stationary phase point of the integrand. The stationary phase point, x_{sp}, is the coordinate at which the vibrational wavefunctions for states 1 and 2 have the same classical momentum, $p_{classical}=\left[2m(E-V(x_{sp})\right]^{1/2}$. The stationary phase point is located at the crossing of the V_1 and V_2 potential curves, $V_1(x_{sp})=V_2(x_{sp})$. The semiclassical approximation for calculating vibrational overlap integrals is discussed on pages 278-285 of H. Lefebvre-Brion and R. W. Field, The Spectra and Dynamics of Diatomic Molecules.

$$\Psi(x,0)=\frac{a^{1/2}}{(2\pi)^{3/4}}\int_{-\infty}^{\infty}e^{-(a^2/4)(k-k_0)^2}\underbrace{e^{-i(k-k_0)x_0}}_{\underbrace{e^{-k(x-x_0)}}\,e^{ik_0x_0}}e^{ikx}\,dk$$

This is a δ-function. It causes $\Psi(x,0)$ to be localized near x_0.

So we get $|\Psi|^2$ localized at $x_0(t)$, k_0, $\Delta x(t)$, Δk if $g(k)$ is Gaussian.

$\Delta x = 2^{-1/2}a$
$\Delta k = 2^{1/2}/a$
$\Delta x\Delta k = 1$ at $t = 0$

We have constructed a Gaussian wavepacket, $\Psi(x,t)$, from $\Psi(x,0)$ with localization of $x_0(t)$, $\Delta x(t)$ minimum at $t = 0$, Gaussian in x, Gaussian in k.

We can now ask how this $\Psi(x,t)$ can be modified by features of any time-independent $V(x)$.