Quantum Physics 1

Notes-7

The Square Well

(A particle in an escape-proof box)

Solving the Schrodinger Equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x,t)\Psi(x,t)=i\hbar\frac{\partial\Psi}{\partial t}$$

If the potential energy is independent of time, then we can start solving this equation using the separation of variables technique:

- Assume that $\Psi(x,t)=\psi(x)f(t)$

$$-f(t)\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)f(t)=i\hbar\psi(x)\frac{\partial \mathrm{f(t)}}{\partial t}$$

$$-\frac{1}{\psi(x)}\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=i\hbar\frac{1}{f(t)}\frac{\partial \mathrm{f(t)}}{\partial t}$$

And the only way the two sides can be equal for a x and t is if they are equal to a constant (which we will call *E*)

Solving the Schrodinger Equation

$$-\frac{1}{\psi(x)}\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t}=E$$

Solving $i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t}=E$, $\frac{df(t)}{f(t)}=-i\frac{E}{\hbar}dt$ and integrating both sides:

$$\ln\big(f(t)\big)-\ln\big(f(0)\big)=-i\frac{E}{\hbar}t$$

$$f(t)=Ce^{-i\frac{E}{\hbar}t}=Ce^{-i\omega t}$$

And the left hand side:

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

Is known as the time-independent Schrodinger Equation

Solution for $\psi(x)$ for constant V(x)

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi(x) = 0$$

And setting $k^2 = \frac{2m}{\hbar^2}(E - V)$ for $E > V$

$$\frac{\partial^2\psi(x)}{\partial x^2} + k^2\psi(x) = 0$$

Which has solutions:

$\psi(x) = Ae^{ikx}$and Be^{-ikx}

So the overall solution is:

$\Psi(x, t) = Ae^{-i(kx+\omega t)} + B\ e^{i(kx-\omega t)}$

Traveling waves!

Particle in a well with infinite walls

- $V(x) = 0\ for\ 0 < x < L$ and infinity for $|x| > L$.
- Inside the well:
  $\Psi(x,t) = (Ae^{-i(kx)} + B\ e^{i(kx)})\ e^{-i\omega t}$
- Boundary conditions:

$\psi(x) = 0\ at\ x = 0\ and\ x = L$

$\psi(0) = 0\ \rightarrow\ A + B = 0$ so $-A = B$

$\psi(x) = A(e^{-i(kx)} - e^{i(kx)}) = -Asin(kx)$

$\psi(L) = 0\ \rightarrow\ Asin(ka) = 0\ \rightarrow\ ka = n\pi$

$k_n = n\frac{\pi}{a}$ where n is an integer. (quantization)

Particle in a well

$k^2 = \frac{2m}{\hbar^2}E \quad and \quad k^2 = \frac{n^2\pi^2}{L^2}$ so

$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2} = \frac{h^2 n^2}{8mL^2}$ (quantized)

Another way of finding this result:

λ that meets the boundary conditions must be such that $\frac{n\lambda_n}{2} = L$ and since $p = \frac{h}{\lambda}$ and $E = \frac{p^2}{2m}$ we have $E = \frac{h^2 n^2}{8mL^2}$.

The formal TISE approach allows us to deduce a lot more physics.

Particle in a well with infinite walls

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- Inside the well:
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$\psi(x) = A(e^{-i(kx)} - e^{i(kx)}) = -Asin(kx)$

$\psi(L) = 0\ \rightarrow\ Asin(kL) = 0\ \rightarrow\ kL = n\pi$

$k_n = n\frac{\pi}{L}$ where n is an integer. (quantization)

Normalization

Normalization requires that

$$P[0, L] = 1 = \int_0^L A^2 \sin^2 \frac{n\pi x}{L} \, dx$$

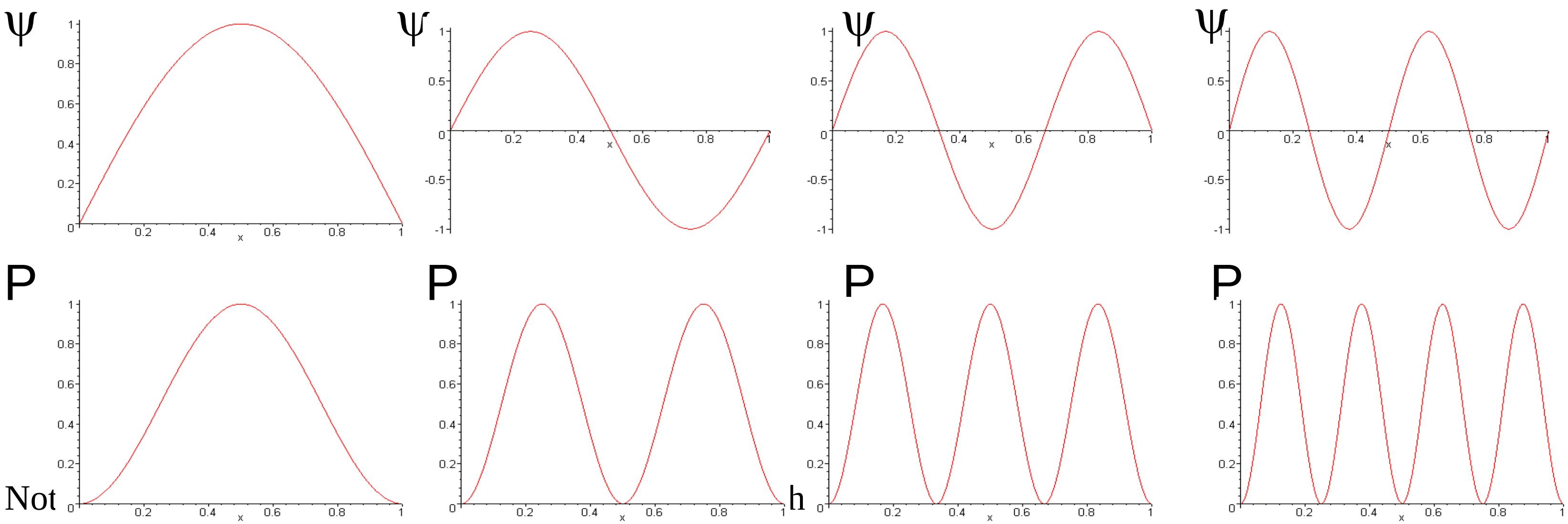
which leads to $A = \sqrt{\frac{2}{L}}$.

Particle in a well

$$k^2 = \frac{2m}{\hbar^2}E \quad and \quad k^2 = \frac{n^2\pi^2}{L^2}$$ so

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2} = \frac{h^2 n^2}{8mL^2}$$ (quantized)

$$\Psi(x,t) = \sqrt{\frac{2}{L}}\, sin\left(\frac{n\pi x}{L}\right) e^{\frac{iE_n t}{\hbar}}$$



Square well centered at x=0

- If we center the square well at x=0 so that it extends from –L/2 to L/2, then the general solutions remain the same but the boundary conditions change.
- $E_n, k_n, and\ A$ remain unchanged.
- The solutions are then the same as those found in the text.

$$\psi_n(x) = A\cos\left(\frac{n\pi x}{L}\right) for\ n = odd$$

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right) for\ n = even$$

Square well continued

- Next: Compute momentum distribution, averages and standard deviations of position, momentum, and energy.

- We will just do the computations for the even states $(\cos\left(\frac{n\pi x}{L}\right))$ of the well centered at 0 because the arithmetic is easier. We can generalize for the odd states.

Expectation values of position

$$\langle x\rangle = \int \Psi^* x\Psi dx = \frac{2}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} x cos^2\left(\frac{n\pi x}{L}\right) dx = 0$$

(Why didn't I have to carry out the integration?)

$$\langle x^2\rangle = \frac{2}{L}\int_{-L/2}^{L/2} x^2 \cos^2\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{1}{L}\int_{-L/2}^{L/2} x^2 (1 - \cos\left(\frac{2n\pi x}{L}\right)) dx$$

$$= \frac{1}{L}\left(\frac{x^3}{3} - \int_{-\frac{L}{2}}^{\frac{L}{2}} x^2 \cos\left(\frac{2n\pi x}{L}\right)\right) = L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$

$$\sigma_x = \frac{L}{2n\pi}\left(\frac{n^2\pi^2}{3} - 2\right)^{\frac{1}{2}}$$ (=0.18, 0.26, 0.279, 0.283…0.289)

Momentum in the square well

$$\Psi(x,t) = \sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right)e^{i\omega t}$$

$$\Phi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\Psi(x,0)e^{-ipx/\hbar}dx = \frac{1}{\sqrt{L\pi\hbar}}\int_{-L/2}^{L/2}\cos\left(\frac{n\pi x}{L}\right)e^{ipx/\hbar}dx$$

$$= \frac{1}{\sqrt{L\pi\hbar}}\int_{-L/2}^{L/2}\cos\left(\frac{n\pi x}{L}\right)(\cos(px/\hbar) + i\sin(px/\hbar))dx$$

$$= \frac{1}{\sqrt{L\pi\hbar}}\int_{-L/2}^{L/2}\cos\left(\frac{n\pi x}{L}\right)\cos(\frac{px}{\hbar})dx$$

$$= \frac{1}{2\sqrt{L\pi\hbar}}\int_{-L/2}^{L/2}\left[\cos\left(\left(\frac{n\pi}{L}-\frac{p}{\hbar}\right)x\right) + \cos\left(\left(\frac{n\pi}{L}+\frac{p}{\hbar}\right)x\right)\right]dx$$

$$= \frac{1}{2\sqrt{L\pi\hbar}}\left[\frac{\sin\left(\left(\frac{n\pi}{L}-\frac{p}{\hbar}\right)x\right)}{\left(\left(\frac{n\pi}{L}-\frac{p}{\hbar}\right)\right)} + \frac{\sin\left(\left(\frac{n\pi}{L}+\frac{p}{\hbar}\right)x\right)}{\left(\left(\frac{n\pi}{L}+\frac{p}{\hbar}\right)\right)}\right]_{-L/2}^{L/2}$$

$$= \frac{1}{\sqrt{L\pi\hbar}}\left[\frac{\sin\left(\left(\frac{n\pi}{L}-\frac{p}{\hbar}\right)\frac{L}{2}\right)}{\left(\left(\frac{n\pi}{L}-\frac{p}{\hbar}\right)\right)} + \frac{\sin\left(\left(\frac{n\pi}{L}+\frac{p}{\hbar}\right)\frac{L}{2}\right)}{\left(\left(\frac{n\pi}{L}+\frac{p}{\hbar}\right)\right)}\right]$$

Momentum in square well

$$\Phi(p) = \frac{L}{2}\frac{1}{\sqrt{L\pi\hbar}}\left[\frac{\sin\left(\left(\frac{n\pi}{L}-\frac{p}{\hbar}\right)\frac{L}{2}\right)}{\left(\left(\frac{n\pi}{L}-\frac{p}{\hbar}\right)\frac{L}{2}\right)} + \frac{\sin\left(\left(\frac{n\pi}{L}+\frac{p}{\hbar}\right)\frac{L}{2}\right)}{\left(\left(\frac{n\pi}{L}+\frac{p}{\hbar}\right)\frac{L}{2}\right)}\right]$$

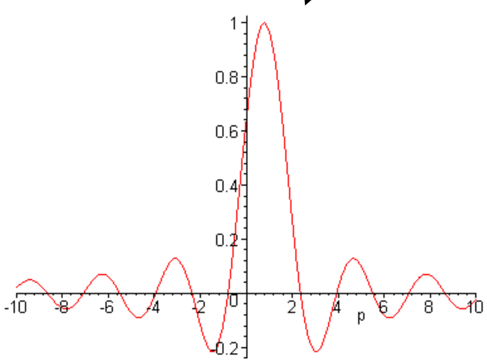
$$\Phi(p) = \sqrt{\frac{L}{4\pi\hbar}}\left[\frac{\sin\left(\left(\frac{n\pi}{2}-\frac{L}{2\hbar}p\right)\right)}{\left(\frac{n\pi}{2}-\frac{L}{2\hbar}p\right)} + \frac{\sin\left(\frac{n\pi}{2}+\frac{L}{2\hbar}p\right)}{\left(\frac{n\pi}{2}+\frac{L}{2\hbar}p\right)}\right]$$

$$A(k)=\sqrt{\frac{L}{4\pi\hbar}}\left[\frac{\sin\left(\left(\frac{n\pi}{2}-\frac{kL}{2}\right)\right)}{\left(\frac{n\pi}{2}-\frac{kL}{2}\right)} + \frac{\sin\left(\frac{n\pi}{2}+\frac{kL}{2}\right)}{\left(\frac{n\pi}{2}+\frac{kL}{2}\right)}\right]$$

Momentum in square well

One part of the momentum distribution looks like this

The other looks like this



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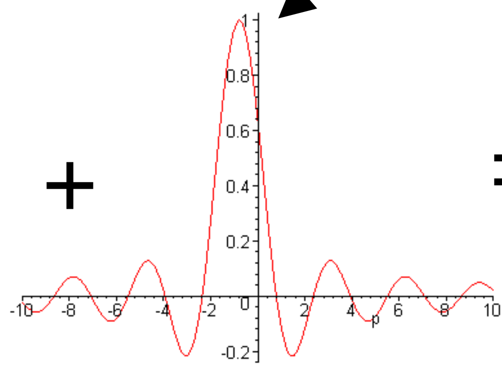

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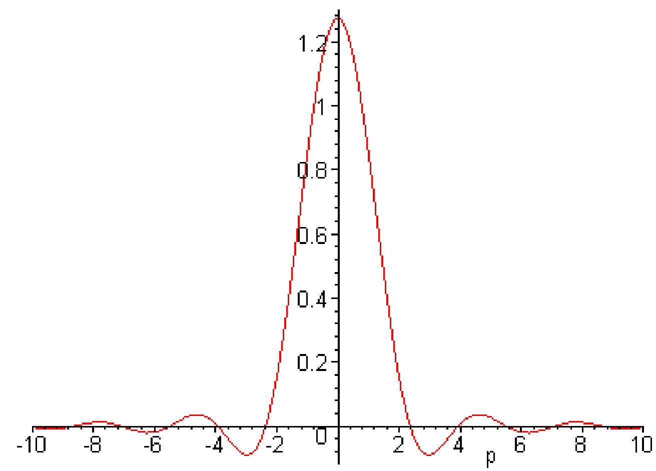


peaked at $p = \pm\hbar\pi/L$
for the ground state

The sum

Momentum in square well

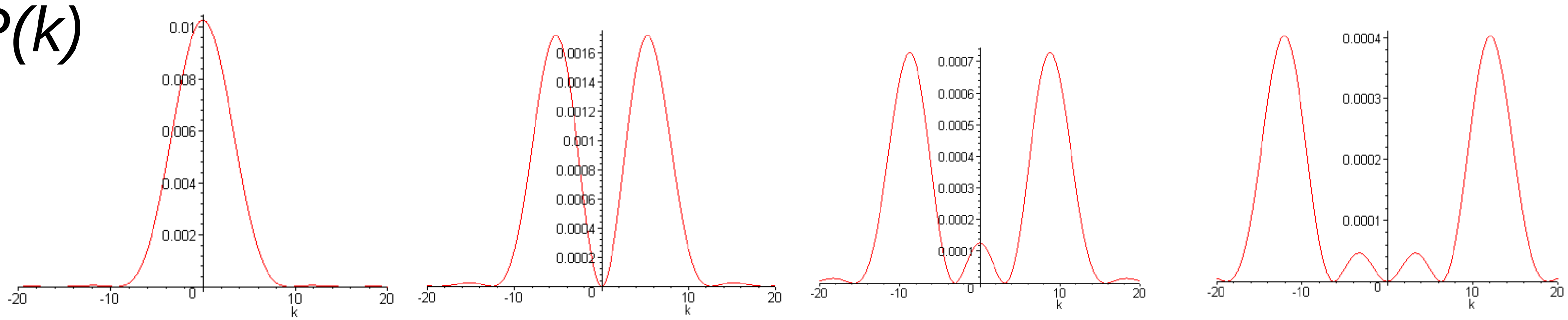
Now to calculate expectation value of momentum,

$$\langle \mathrm{p} \rangle = \int_{-\infty}^{\infty} \Phi^* p \Phi dp = \int_{-\infty}^{\infty} \sqrt{\frac{L}{4\pi\hbar}} \left[\frac{\sin\left(\left(\frac{n\pi}{2} - \frac{L}{2\hbar} p\right)\right)}{\left(\frac{n\pi}{2} - \frac{L}{2\hbar} p\right)} + \frac{\sin\left(\frac{n\pi}{2} + \frac{L}{2\hbar} p\right)}{\left(\frac{n\pi}{2} + \frac{L}{2\hbar} p\right)} \right]^2 p dp$$

(We don′t really want to calculate this awful thing, so let′s think about symmetry. We note that Φ is symmetric about $p = 0$. This means that $p\Phi$ is an odd function, and therefore the integral is zero.)

$$\langle p \rangle = 0$$

P(k)



Expectation values for the square well: Momentum

$$\langle p_x \rangle = \int_{-a}^{a} \Psi^*(x,t)\hat{p}_x \Psi(x,t)dx = \int_{-a}^{a} \Psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi(x,t)dx$$

$$= \frac{-i\hbar 2}{L}\int_{-a}^{a} \cos\left(\frac{n\pi x}{L}\right)\frac{\partial}{\partial x}\left(\cos\left(\frac{n\pi x}{L}\right)\right)dx$$

$$= \frac{-i\hbar n 2\pi}{L^2}\int_{-a}^{a} \cos\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx = \frac{-i\hbar n 2\pi}{L^2}\int_{-a}^{a} u\,du = 0$$

$$\langle p_x^2 \rangle = -\int_{-a}^{a} \Psi^*(x,t)\left(\hbar^2\frac{\partial^2}{\partial x^2}\right)\Psi(x,t)dx = \frac{\hbar^2\pi^2 n^2}{L^3}\int_{-a}^{a} \cos^2\left(\frac{n\pi x}{L}\right)dx$$

$$\langle p_x^2 \rangle = \frac{\hbar^2\pi^2 n^2}{L^3}\frac{L}{2} = \frac{\hbar^2\pi^2 n^2}{2L^2}$$

Expectation values in the square well: Momentum uncertainty

We just found that $\langle p \rangle = 0$ and $\langle p_x^2 \rangle = \frac{\hbar^2 \pi^2 n^2}{2L^2}$.

The standard deviation of the momentum is thus

$$\sigma_p = \frac{\hbar \pi n}{\sqrt{L}}$$

Particle in a box
Expectation value and uncertainty in energy

The kinetic energy operator is: $\hat{T} = \dfrac{\hat{p}^2}{2m}$.

Since we previously solved for $\left\langle p_n^2 \right\rangle$ we can easily solve for $\langle T \rangle$.

$$\left\langle T_n \right\rangle = \frac{\left\langle p_n^2 \right\rangle}{2m} = \frac{1}{2m}\left(\frac{n\pi\hbar}{L}\right)^2$$

The lowest allowed state has n=1,

so expectation value of the kinetic energy is always > zero.

Another remarkable observation is that: $\left\langle T^2 \right\rangle - \left\langle T \right\rangle^2 = 0.$

There is no uncertainty in the energy!

Particle in a box – Probability current

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) e^{-i\omega_n t}$$

$$j(x,t) \equiv \frac{-i\hbar}{2m}\left[\Psi^* \frac{\partial}{\partial x}\Psi - \Psi \frac{\partial}{\partial x}\Psi^*\right]$$

$$= \frac{-i\hbar}{2m}\frac{2}{L}\left[k \sin k_n\, x \sin k_{nx} - k \sin k_n\, x \sin k_{nx}\right]$$

$$= 0$$

everywhere in the box.

NOTE: The probability current is zero for any real space function.

Orthogonality of eigenfunctions $\psi_n(x)$

When $n \neq n'$

$$\int_{-\frac{a}{2}}^{\frac{a}{2}} \cos\frac{n\pi x}{a}\cos\frac{n'\pi x}{a}\,dx = 0$$

$$\int_{-\frac{a}{2}}^{\frac{a}{2}} \sin\frac{n\pi x}{a}\cos\frac{n'\pi x}{a}\,dx = 0$$

$$\int_{-\frac{a}{2}}^{\frac{a}{2}} \sin\frac{n\pi x}{a}\sin\frac{n'\pi x}{a}\,dx = 0$$

Completeness

Any physically admissible wavefunction can be expanded in the complete set of eigenfunctions, provided that the wavefunction obeys the same boundary conditions as the eigenfunctions.

$$\psi(x) = \sum_i c_i \psi_i$$

We find the coefficients using orthogonality!

$$\int \psi(x)\psi_n(x)dx = \int \sum_i c_i \psi_i \psi_n \, dx = c_i$$