PC2232 Physics for Electrical Engineers
Lecture 7: Schrödinger Equation

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Schrödinger Equation for Free Particle

- Like Maxwell's equations, the Schrödinger equation for a quantum particle is usually expressed in differential form.
- For a free nonrelativistic particle with mass m, the wavefunction of three-dimensional position $\boldsymbol{r} \in \mathbb{R}^3$ is

$$\boxed{i\hbar \frac{\partial \psi(\boldsymbol{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\boldsymbol{r}, t).} \tag{1}$$

  Note that this is somewhat different from the EM-wave equation. We are neglecting spin here.
- $\hbar = h/(2\pi)$, where $h \approx 6.626 \times 10^{-34}$ Js is Planck's constant.
- A useful solution is the sinusoidal plane-wave solution:

$$\psi(\boldsymbol{r}, t) = \tilde{\psi} \exp\left(i\boldsymbol{k} \cdot \boldsymbol{r} - i\omega t\right). \tag{2}$$

  Again ω and $\boldsymbol{k}$, a real vector, are related. Let k be the magnitude of $\boldsymbol{k}$. Putting this solution into the Schrödinger equation,

$$i\hbar \frac{\partial \psi(\boldsymbol{r}, t)}{\partial t} = i\hbar(-i\omega)\tilde{\psi} \exp\left(i\boldsymbol{k} \cdot \boldsymbol{r} - i\omega t\right) = \hbar\omega\tilde{\psi} \exp\left(i\boldsymbol{k} \cdot \boldsymbol{r} - i\omega t\right), \tag{3}$$

$$\nabla^2 \psi(\boldsymbol{r}, t) = -k^2 \tilde{\psi} \exp\left(i\boldsymbol{k} \cdot \boldsymbol{r} - i\omega t\right), \tag{4}$$

$$\boxed{\hbar\omega = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m}.} \tag{5}$$

Correspondence with Classical Physics

- A wavefunction that oscillates in time $\propto \exp(-i\omega t)$ is associated with a classical energy

$$\boxed{E = \hbar\omega.} \tag{6}$$

- A wavefunction that oscillates in space $\propto \exp(i\boldsymbol{k}\cdot\boldsymbol{r})$ is associated with a classical momentum

$$\boxed{\boldsymbol{p} = \hbar\boldsymbol{k}.} \tag{7}$$

- The plane-wave solution $\exp(i\boldsymbol{k}\cdot\boldsymbol{r} - i\omega t)$ has definite energy and definite momentum. It is nonzero everywhere in space and time however.
- The relation $\hbar\omega = \hbar^2 k^2/(2m)$ implies that

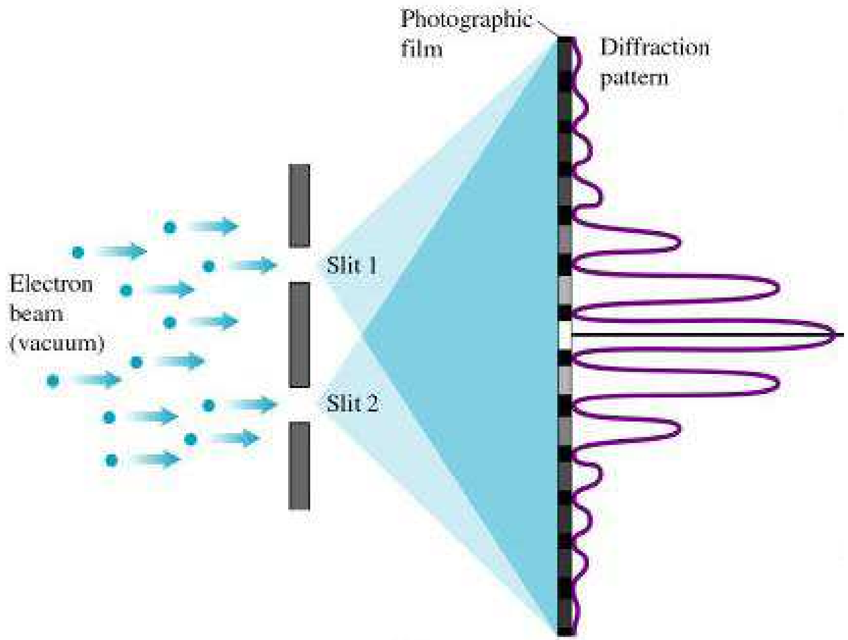
$$E = \frac{p^2}{2m}, \tag{8}$$

where p is the magnitude of $\boldsymbol{p}$. This agrees with the classical relation for the energy of a nonrelativistic free particle (all kinetic energy).
- The wavelength (**de Broglie wavelength**) is

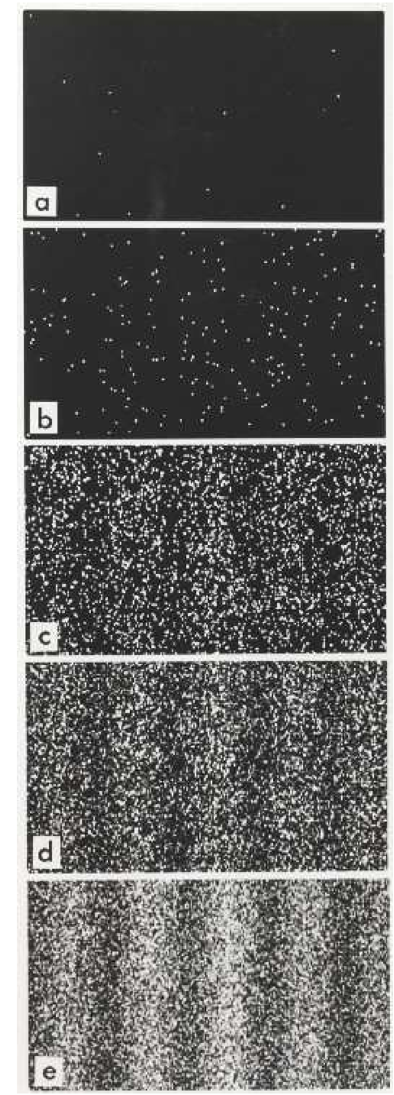
$$\boxed{\lambda = \frac{2\pi}{k} = \frac{2\pi\hbar}{p} = \frac{h}{p}.} \tag{9}$$

It associates the classical particle property (momentum) to a wave property (wavelength).

- This means that small particles like electrons can experience diffraction and interference too:



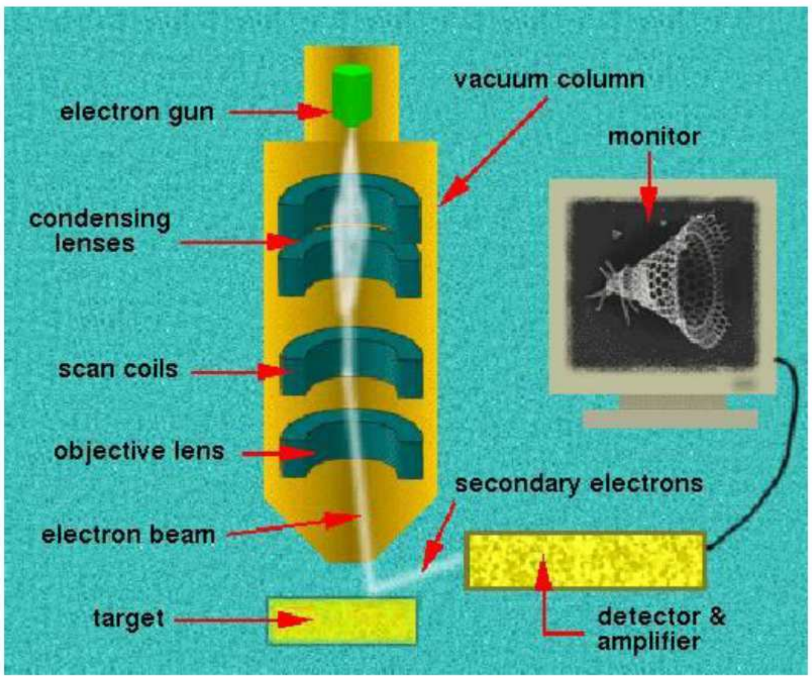
- This is known as **wave-particle** duality: the electron will diffract and interfere like waves if you are not looking, but if you measure its position, there is a wavefunction collapse and the outcome reveals that the electron is at a single position.
- Interference pattern $\propto |\psi(x,t)|^2$ is revealed after multiple measurements.



http://www.learningwithat
Tonomura *et al.*, Am. J. Phys. **57**, 117 (1989).

Electron Microscopes

- The resolution of microscopes using electrons as waves can be a lot higher than optical microscopes because electron wavelength can be much smaller.
- Suppose that an electron is accelerated by a voltage $V = 1$ kV. What is its wavelength? $p = \sqrt{2mE}$, $E = eV$, $e = 1.6 \times 10^{-19}$ C, $m = 9.11 \times 10^{-31}$ kg, $\lambda = h/p \sim 4 \times 10^{-11}$ m. Compare with optical wavelength ~ 500 nm.
- Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM):

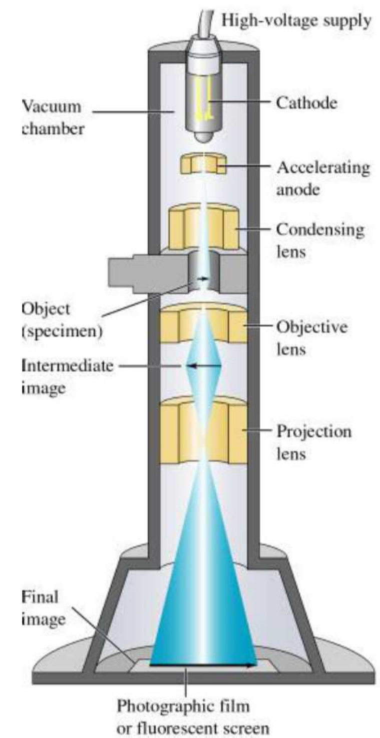


http://www.mos.org/sln/sem/

See the animation on the working principle of a Scanning Electron Microscope

- 1986 Physics Nobel Prize
- Ernst Ruska

"for his fundamental work in electron optics, and for the design of first electron microscope"



http://www.iflscience.com/technology/some-spectacular-sem-images-microscopic-world
http://legacy.mos.org/sln/sem/sem.mov

*General Solution

- Given an initial condition $\psi(\boldsymbol{r}, 0)$, the solution for $\psi(\boldsymbol{r}, t)$ can be obtained by Fourier-transform techniques:

$$\psi(\boldsymbol{r}, t) = \int_{\text{all space}} d^3\boldsymbol{r}_0 \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} \exp\left(\frac{im}{2\hbar t}|\boldsymbol{r} - \boldsymbol{r}_0|^2\right) \psi(\boldsymbol{r}_0, 0). \tag{10}$$

  The propagator is

$$\psi(\boldsymbol{r}, t|\boldsymbol{r}_0, 0) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} \exp\left(\frac{im}{2\hbar t}|\boldsymbol{r} - \boldsymbol{r}_0|^2\right). \tag{11}$$

- Note how this is mathematically similar to Fresnel diffraction, except that here t plays the role of optical axis z, and the integral is 3D rather than 2D.

- Our main interest here is how the energies of electrons depend on positively charged nuclei in atoms, molecules, solids, etc.
- Since electrons are much lighter than nuclei in general, we can assume that the nuclei don't move. The nuclei would then in general impose an electrostatic potential $U(\boldsymbol{r})$ to an electron.
- The Schrödinger equation for an electron becomes

$$\boxed{i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\boldsymbol{r})\right]\psi(\boldsymbol{r},t).} \tag{12}$$

- We are going to focus on solutions with definite frequencies and definite energies $E = \hbar\omega$:

$$\psi(\boldsymbol{r},t) = \tilde{\psi}(\boldsymbol{r})\exp\left(-i\omega t\right), \tag{13}$$

$$\boxed{\hbar\omega\tilde{\psi}(\boldsymbol{r}) = E\tilde{\psi}(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\boldsymbol{r})\right]\tilde{\psi}(\boldsymbol{r}).} \tag{14}$$

  This is called a time-independent Schrödinger equation.
- For simplicity, we are also going to assume $U(\boldsymbol{r}) = U(x)$, $\frac{\partial\psi}{\partial y} = 0$ and $\frac{\partial\psi}{\partial z} = 0$. Then ψ doesn't depend on y and z, and we obtain a (1+1)D Schrödinger equation:

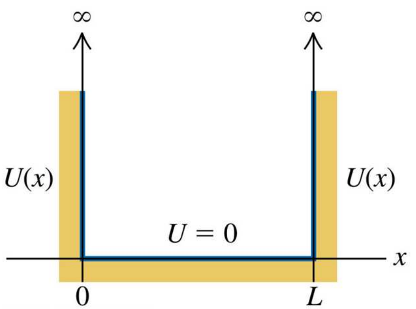
$$\boxed{E\tilde{\psi}(x) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right]\tilde{\psi}(x).} \tag{15}$$

I will omit the tilde for brevity from now on.

Examples of Potential

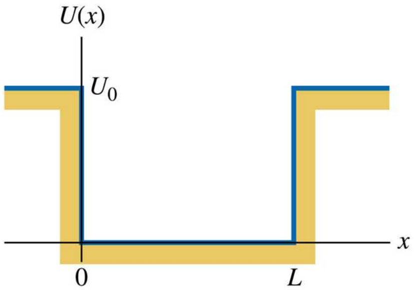
- Infinite Square Well:

$$U(x) = \begin{cases} 0, & 0 \le x \le L, \\ \infty, & x < 0 \text{ or } x > L. \end{cases} \tag{16}$$



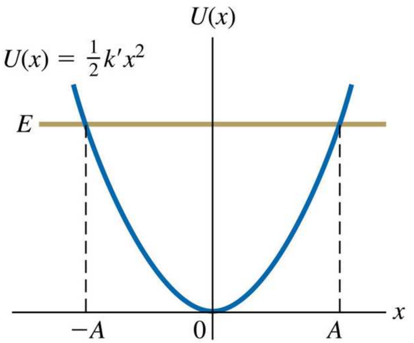
- Finite Square Well:

$$U(x) = \begin{cases} 0, & 0 \le x \le L, \\ U_0, & x < 0 \text{ or } x > L. \end{cases} \tag{17}$$



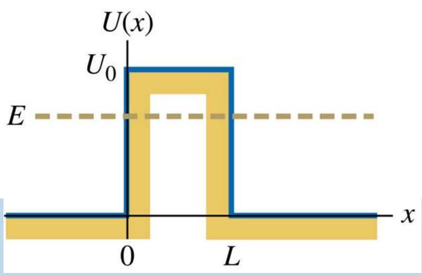
- Harmonic Well:

$$U(x) = \frac{1}{2}\kappa x^2, \tag{18}$$



- Barrier:

$$U(x) = \begin{cases} U_0, & 0 \le x \le L, \\ 0, & x < 0 \text{ or } x > L. \end{cases} \tag{19}$$



Infinite Square Well

- If $U(x) = \infty$, $\psi(x)$ must be zero there.

$$\psi(x) = 0 \text{ for } x < 0 \text{ or } x > L. \tag{20}$$

- Inside $0 \leq x \leq L$, the free-particle equation holds (omitting the tilde for brevity),

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) \text{ for } 0 \leq x \leq L. \tag{21}$$

General solution for $E > 0$: $A\sin(kx) + B\cos(kx)$, A and B arbitrary (or $a\exp(jkx) + b\exp(-jkx)$ if you wish)

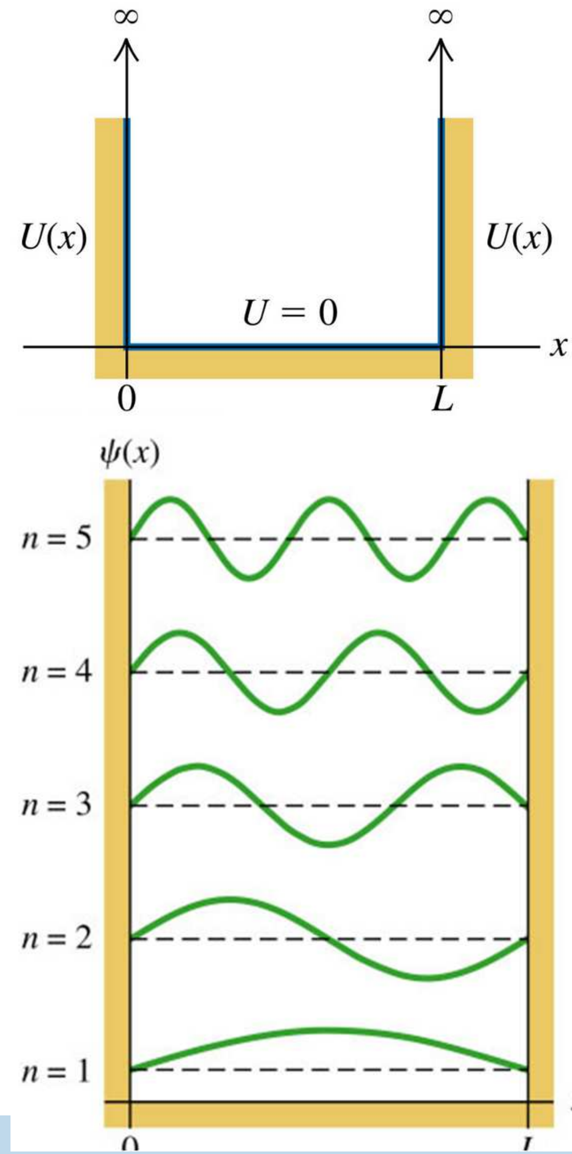
$$\psi(x) = A\sin(kx), \quad E = \frac{\hbar^2 k^2}{2m}. \tag{22}$$

We choose the sine solution only because $\psi(0) = 0$.

- A can be determined by normalization condition.
- Boundary condition at $x = L$ leads to quantized k:

$$\boxed{kL = \pi n, \quad n = 1, 2, \ldots} \tag{23}$$

- (No $E < 0$ solution exists that can satisfy the boundary conditions)



Quantized Momentum and Energy

- Note $\psi(x) \propto (e^{ikx} - e^{-ikx})/(2i)$. The momentum can have two values $+k$ and $-k$, corresponding to two plane waves. Here momentum is **quantized**, and the lowest momentum has nonzero magnitude:

$$k(n=1) = \frac{\pi}{L}. \tag{24}$$

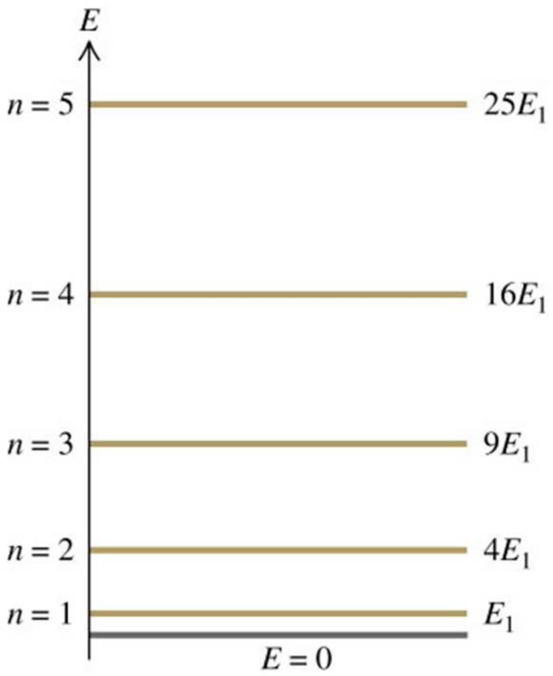
- Energy can be obtained by substituting the standing-wave solution into the Schrödinger equation:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2}, \quad n = 1, 2, 3, \ldots \tag{25}$$

  Energy is also **quantized**.
- The lowest energy (called **ground-state energy** or **zero-point energy**) is nonzero because of nonzero momentum:

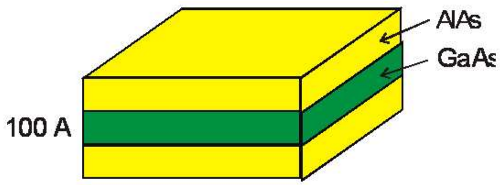
$$E(n=1) = \frac{\hbar^2 \pi^2}{2mL^2}. \tag{26}$$

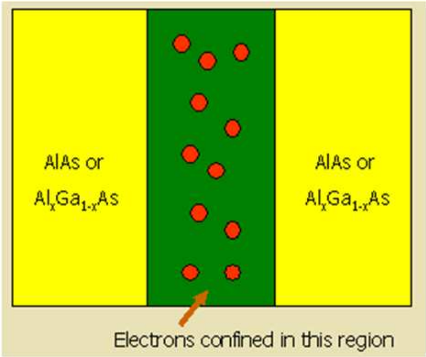
- Note that the energy $E = \hbar\omega$ here depends on the integer n quadratically. This is not the same as the optical frequencies of standing waves in an optical cavity.
- Here we see why quantum mechanics is called **quantum**: energy and momentum exist only in discrete levels for standing waves.

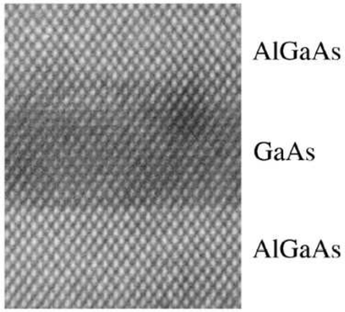


*Quantum Well

- Many lasers and light-emitting diodes (LEDs) are made from quantum well structures in semiconductors:







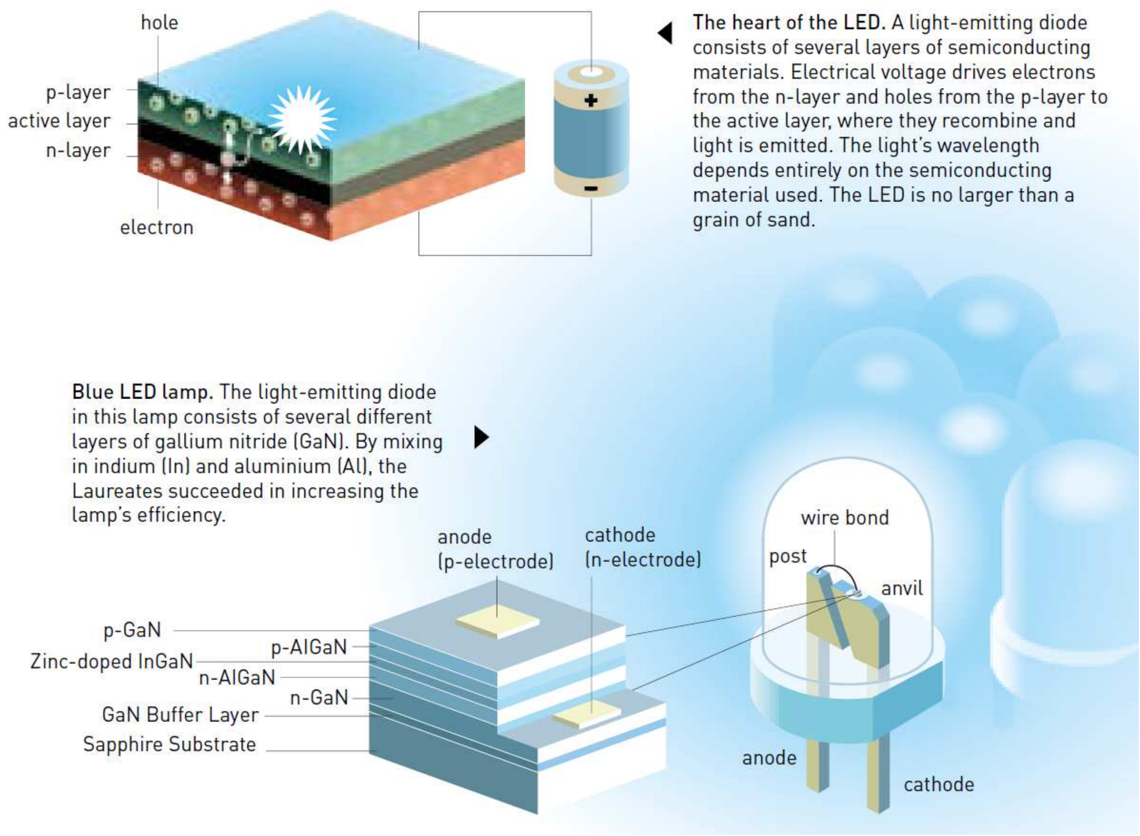
- Electrons are confined inside the layer with thickness along x. Energy is

$$E(k_x, k_y, k_z) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right), \qquad k_x(n) = \frac{\hbar^2\pi^2 n^2}{2mL^2}, \quad n = 1, 2, \ldots \tag{27}$$

  k_x is discrete because of the potential, although the electrons can still move freely in the $y - z$ plane and k_y and k_z can have continuous values (we neglected k_y and k_z earlier).
- The electrons in such a layer is called a two-dimensional electron gas.

*Blue LEDs

- 2014 Nobel Prize in Physics: Isamu Akasaki, Hiroshi Amano and Shuji Nakamura, “for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources.”
- Quantum well structure :



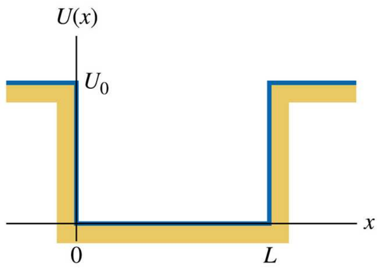
`http://www.nobelprize.org/nobel_prizes/physics/laureates/2014/popular.html`

- Electrons (and holes) are trapped inside the active layer (quantum well) for efficient generation of light.
- We'll learn more about electrons, holes, LEDs, etc. later.

Finite Square Well

- For a more realistic model of quantum well, consider a square well with finite potential walls:

$$U(x) = \begin{cases} 0, & 0 \le x \le L, \\ U_0, & x < 0 \text{ or } x > L. \end{cases} \tag{28}$$



- First consider $x < 0$:

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U_0\psi(x), \quad x < 0. \tag{29}$$

If we'd like a normalizable solution, $\exp(jkx)$ or $\exp(-jkx)$ or $\sin(kx)$ or $\cos(kx)$ won't work. Instead, consider $E < U_0$, that is, energy below U_0:

$$(E - U_0)\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}. \tag{30}$$

When $E - U_0 < 0$, the general solution is $C\exp(\alpha x) + D\exp(-\alpha x)$. For the final solution to be normalizable, we'd like it to decay exponentially away from the wall in the limit $x \to -\infty$. This leaves

$$\psi(x) = C\exp(\alpha x), \quad x < 0, \qquad E = U_0 - \frac{\hbar^2\alpha^2}{2m}, \quad (E < U_0) \tag{31}$$

Finite Square Well

- Similarly, for $x > L$, we'd like the solution to decay exponentially for $x \to \infty$ for it to be normalizable:

$$\psi(x) = G\exp(-\alpha x), \quad x > L. \tag{32}$$

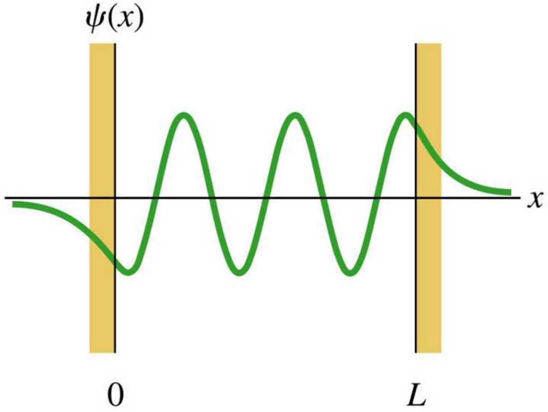
- Inside the well, we can assume sinusoidal solutions:

$$\psi(x) = A\sin(kx) + B\cos(kx), \quad 0 \leq x \leq L, \qquad E = \frac{\hbar^2 k^2}{2m}, \quad (E > 0). \tag{33}$$

- Thus we have

$$\psi(x) = \begin{cases} C\exp(\alpha x), & x < 0, \\ A\sin(kx) + B\cos(kx), & 0 \leq x \leq L, \\ G\exp(-\alpha x), & x > L. \end{cases} \tag{34}$$

Here is one possible solution:



We can write α and k as

$$E = \frac{\hbar^2 k^2}{2m} = U_0 - \frac{\hbar^2 \alpha^2}{2m}, \tag{35}$$

$$k = \frac{\sqrt{2mE}}{\hbar}, \qquad \alpha = \frac{\sqrt{2m(U_0 - E)}}{\hbar}, \tag{36}$$

- We still need to find C, A, B, G.

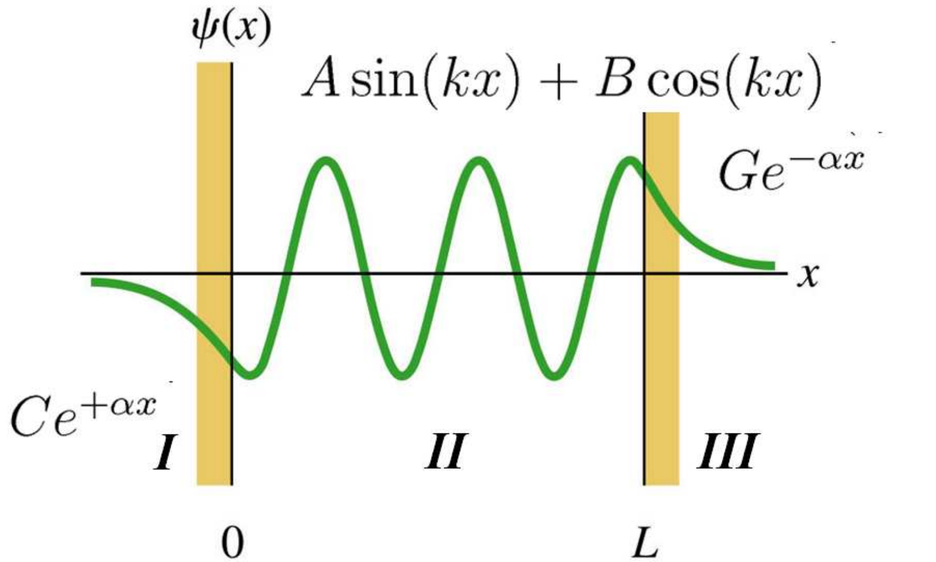
- Since E, U_0, ψ are all finite, for the Schrödinger equation to hold, $\frac{\partial \psi}{\partial x}$ and $\frac{\partial^2 \psi}{\partial x^2}$ cannot be infinite.
- Finite $\frac{\partial \psi}{\partial x}$ means that $\psi(x)$ must be continuous everywhere:

$$\psi(x+\Delta x) - \psi(x) = \Delta x \frac{\partial \psi}{\partial x} \to 0. \tag{37}$$

  Similarly, finite $\frac{\partial^2 \psi}{\partial x^2}$ means that $\frac{\partial \psi}{\partial x}$ must be continuous everywhere.
- This implies that we have to match the solutions in different regions at the boundaries:

$$\boxed{\psi_I(0) = \psi_{II}(0)} \qquad \boxed{\psi_{III}(L) = \psi_{II}(L)}$$

$$\boxed{\left.\frac{d\psi_I(x)}{dx}\right|_{x=0} = \left.\frac{d\psi_{II}(x)}{dx}\right|_{x=0}} \qquad \boxed{\left.\frac{d\psi_{III}(x)}{dx}\right|_{x=L} = \left.\frac{d\psi_{II}(x)}{dx}\right|_{x=L}}$$



Boundary Conditions for Finite Square Well

- Matching boundary conditions at $x = 0$:

$$C = B, \qquad \alpha C = kA. \tag{38}$$

$$\psi(x) = \begin{cases} C\exp(\alpha x), & x < 0, \\ \frac{\alpha C}{k}\sin(kx) + C\cos(kx), & 0 \le x \le L, \\ G\exp(-\alpha x), & x > L. \end{cases} \tag{39}$$

- At $x = L$:

$$\frac{\alpha C}{k}\sin(kL) + C\cos(kL) = Ge^{-\alpha L}, \qquad \alpha C\cos(kL) - kC\sin(kL) = -\alpha G e^{-\alpha L}. \tag{40}$$

The first equation gives us $G = Ce^{\alpha L}[\frac{\alpha}{k}\sin(kL) + \cos(kL)]$, so only C is unknown but it can be determined by normalization condition. Combining the two equations gives

$$\frac{\alpha C}{k}\sin(kL) + C\cos(kL) = -C\cos(kL) + \frac{kC}{\alpha}\sin(kL), \tag{41}$$

$$2C\cos(kL) = \left(\frac{k}{\alpha} - \frac{\alpha}{k}\right) C\sin(kL), \tag{42}$$

$$2\cot(kL) = \frac{k}{\alpha} - \frac{\alpha}{k}. \tag{43}$$

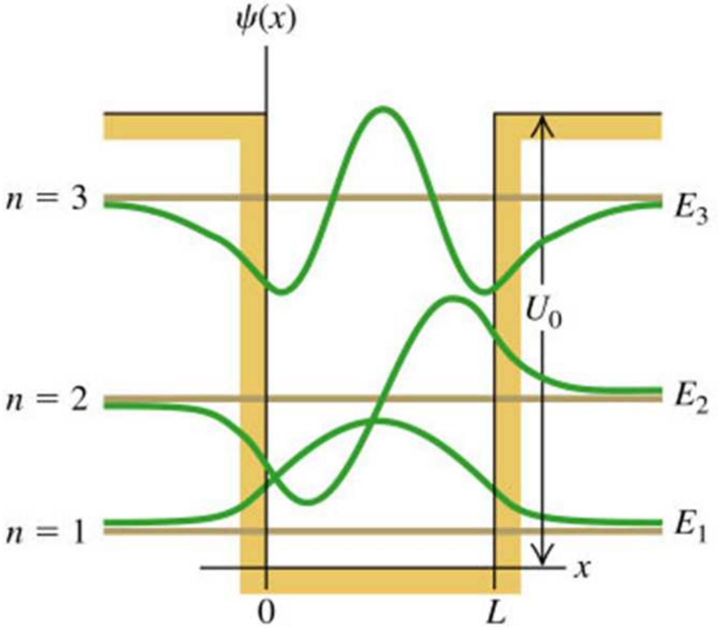
Remember that k and α depend on E according to Eq. (36).

- In terms of E,

$$2\cot\left(\frac{\sqrt{2mE}}{\hbar}L\right) = \sqrt{\frac{E}{U_0 - E}} - \sqrt{\frac{U_0 - E}{E}}. \quad (44)$$

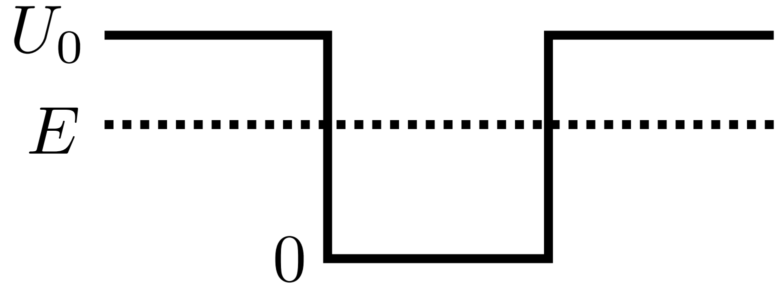
  Analytic solution is not possible in general. It has to be solved numerically (e.g., plot left-hand side with respect to E, plot right-hand side with respect to E in the same plot, and find intersections).
- If $U_0 \to \infty$ (infinite square well), solution is possible only if $\alpha \to \infty$ and $\sin(kL) = 0$, $kL = \pi n$, as expected.
- In general, only a finite number of discrete E's can satisfy this equation.
- PhET/sims/bound-states
- Here is an example with $U_0 = 6(\pi^2\hbar^2/2mL^2)$ (U_0 is 6 times the ground-state energy for an infinite square well)

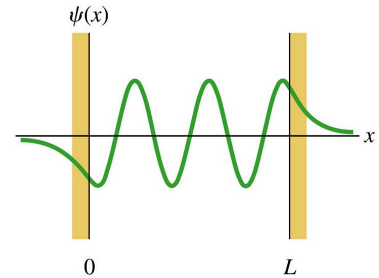
$$U_0 = 6E_\infty = 6\left(\frac{h^2}{8mL^2}\right)$$



Bound States

- We have assumed solutions such that E must lie in $0 \le E \le U_0$.





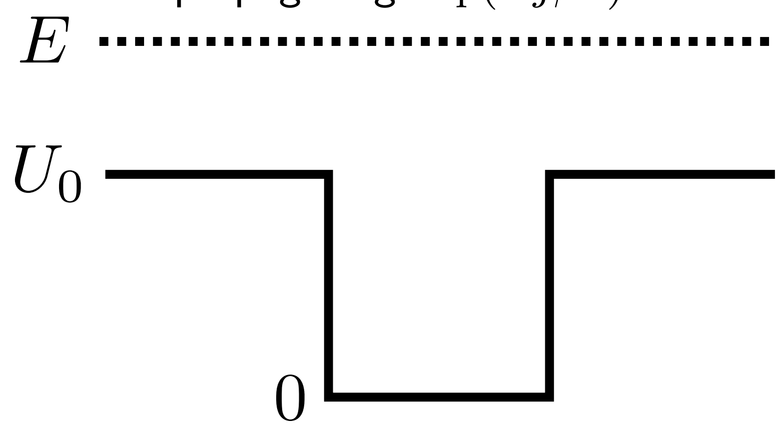
- The solutions decay exponentially away from the well, oscillate inside the well, are normalizable, and have discrete energies. They are called **bound states**.
- Another way of thinking about bound states in a square well is **total internal reflection**. Inside the well, the wavefunction consists of a right-propagating wave and a left-propagating wave:

$$\psi \propto Ae^{ikx} + Be^{-ikx}. \tag{45}$$

- When a wave impinges on a wall, the energy E is not high enough for the transmitted wave to be propagating. Instead, the transmitted wave is **evanescent** and decays exponentially. The wave is then totally reflected back into the well.
- The bound-state solution is really a special case of multiple (infinite) reflections of waves off the two walls, with a simple time-dependence $e^{-i\omega t}$.

Scattering States

- It is also possible to find solutions with $E > U_0$, but we won't have evanescent solutions outside the the well. Instead, we will have propagating $\exp(\pm j\beta x)$ solutions there.



- The $\exp(\pm j\beta x)$ solutions are not normalizable in general, can have arbitrary energies above U_0, and are sometimes called **scattering states**.
- The scattering states are useful for studying transmission and reflection of traveling waves. Think of these states as representing a stream of quantum particles.
- No solution exists for $E < U_0$.

Suggested Problems

- Suppose that $\psi(\boldsymbol{r}, t)$ is a solution of Schrödinger equation. What about $e^{i\theta}\psi(\boldsymbol{r}, t)$, where θ is a constant that doesn't depend on $\boldsymbol{r}$ and t? Does θ affect the probability distribution of any observable?
- Given $\psi_0(\boldsymbol{r}, t)$, which is a solution of

$$i\hbar\frac{\partial \psi_0}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi_0 + U(\boldsymbol{r})\psi_0, \tag{46}$$

solve

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + U(\boldsymbol{r})\psi + E_0\psi, \tag{47}$$

where E_0 is a constant. If $\psi_0 \propto e^{-j\omega_0 t}$ and $\psi \propto e^{-j\omega t}$, how are their frequencies and energies related?
- Consider a plane-wave solution

$$\psi(\boldsymbol{r}, t) \propto \exp(i\boldsymbol{k}\cdot\boldsymbol{r} - i\omega t). \tag{48}$$

The energy is $E = \hbar\omega$, and momentum is $\hbar\boldsymbol{k}$. Given the relativistic energy-momentum relation $E^2 = p^2c^2 + m^2c^4$ and assume that $E \geq 0$, write down the relation between ω and the magnitude of $\boldsymbol{k}$. Assume the Newtonian limit $p^2c^2 \ll m^2c^4$ and express E as a quadratic function with respect to p. Show that E is a sum of rest energy and kinetic energy. Write ω as a function of k in this limit. Show that, if we consider only the excess energy above the rest energy, we get back the dispersion relation from the free-particle Schrödinger equation.

Suggested Problems (continued)

- infinite square well: Find the constant A through normalization condition.
- If $L = 100$ Angstrom for an infinite square well, what is the groud-state energy for an electron (in electron-volt eV)?
- 3D infinite square well: What are the wavefunctions, the permitted momenta and energies for a 3D infinite square well (box) with widths L_x, L_y, L_z?
-