Section 5
Analytical Solutions to Free and Bound Electrons

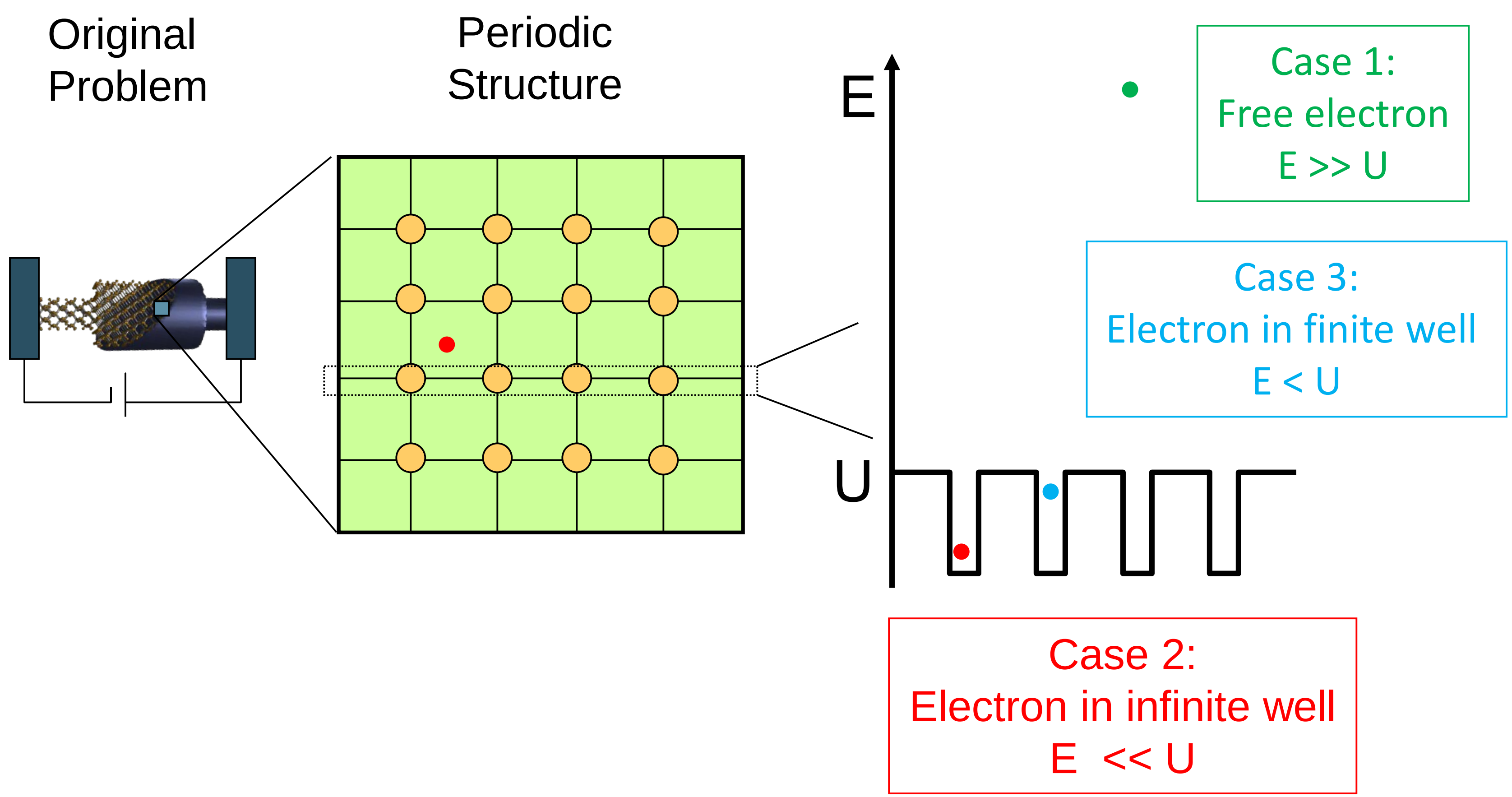
Gerhard Klimeck

gekco@purdue.edu

PURDUE UNIVERSITY

School of Electrical and Computer Engineering

Analytical Solutions to Free and Bound Electrons



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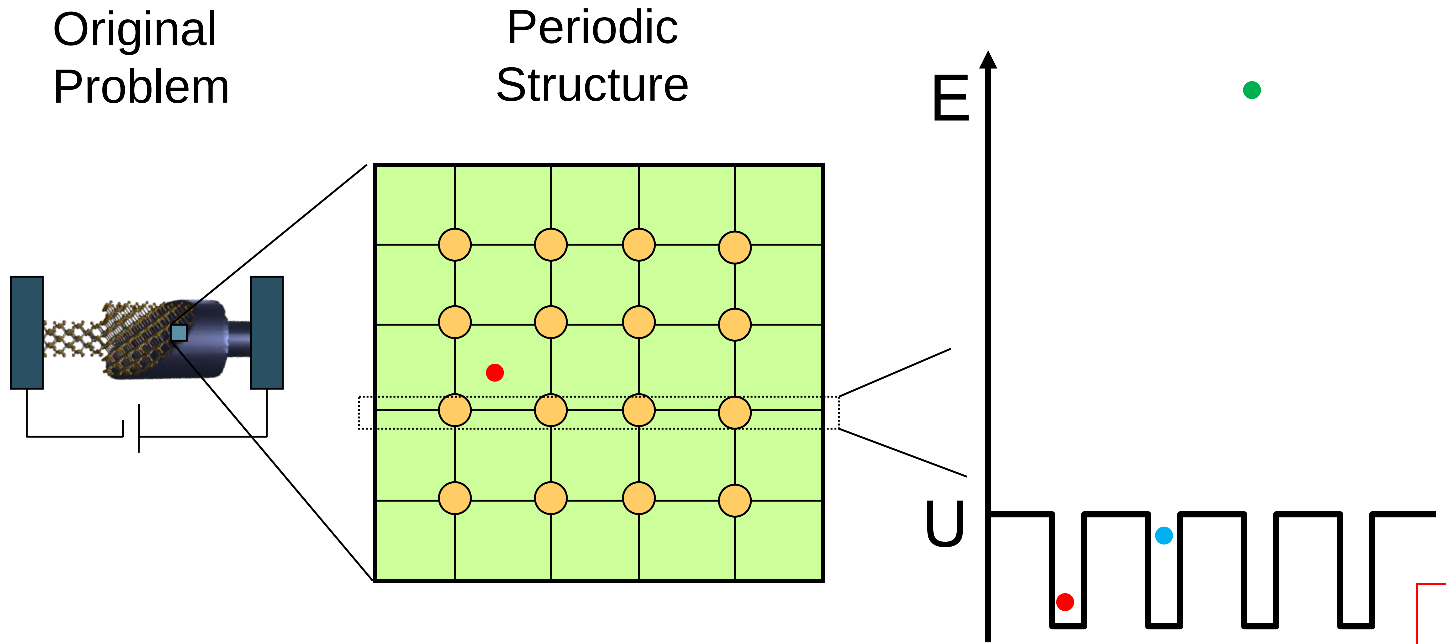

Case 1:
Free electron
E >> U

Case 3:
Electron in finite well
E < U

Case 2:
Electron in infinite well
E << U

- Section 5.1 – Free and Tightly Bound Electrons
  - »Time Independent Schrödinger Equation
  - »(Almost) Free Electrons
  - »Tightly bound electrons – infinite potential well

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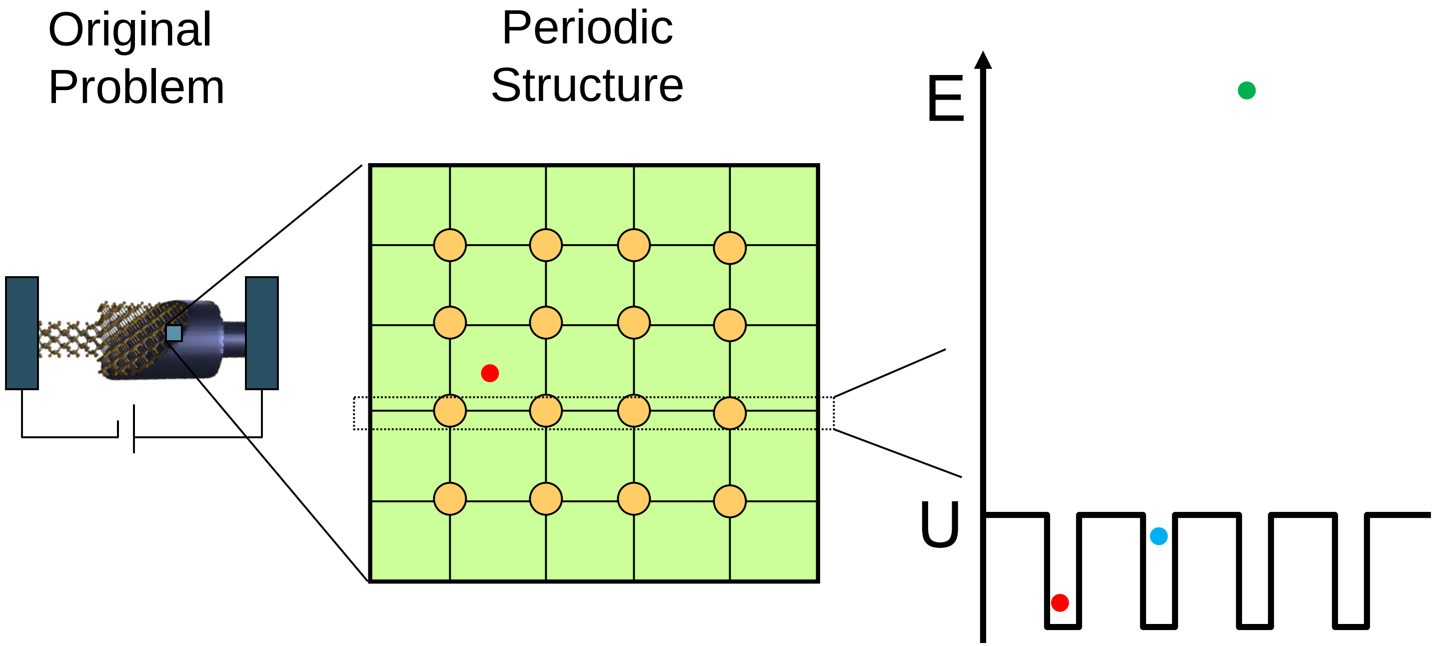
- Section 5.2 - Electrons in a finite potential well

One Video Segment

Reference: Vol. 6, Ch. 2 (pages 29-45)



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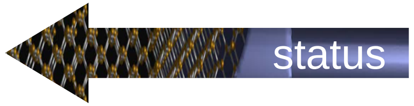

$$-\frac{\hbar^2}{2m_0}\frac{d^2\Psi}{dx^2}+U(x)\Psi=i\hbar\frac{d\Psi}{dt}$$

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- Section 5.2 - Electrons in a finite potential well

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Assume

$$-\frac{\hbar^2}{2m_0}\frac{d^2\Psi}{dx^2}+U(x)\Psi=i\hbar\frac{d\Psi}{dt}$$

$$\Psi(x,t)=\psi(x)\,e^{-iEt/\hbar}$$

$$-e^{-\frac{iEt}{\hbar}}\frac{\hbar^2}{2m_0}\frac{d^2\psi(x)}{dx^2}+e^{-\frac{iEt}{\hbar}}U(x)\psi(x)=i\hbar\frac{-iE}{\hbar}\psi(x)e^{-\frac{iEt}{\hbar}}$$

$$-\frac{\hbar^2}{2m_0}\frac{d^2\psi}{dx^2}+U(x)\psi=E\psi$$

$$\frac{d^2\psi}{dx^2}+\frac{2m_0}{\hbar^2}(E-U)\psi=0$$

Solution Ansatz to the Time-independent Schrödinger Equation

$$\frac{d^2\psi}{dx^2} + \frac{2m_0}{\hbar^2}(E - U)\psi = 0$$

If $E > U$, then ….

$$k \equiv \frac{\sqrt{2m_0\left[E - U\right]}}{\hbar} \qquad \frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \begin{aligned}\psi(x) &= A\sin(kx) + B\cos(kx) \\ &\equiv A_+ e^{ikx} + A_- e^{-ikx}\end{aligned}$$

If $U > E$, then ….

$$\alpha \equiv \frac{\sqrt{2m_0\left[U - E\right]}}{\hbar} \qquad \frac{d^2\psi}{dx^2} - \alpha^2\psi = 0 \qquad \psi(x) = De^{-\alpha x} + Ee^{+\alpha x}$$

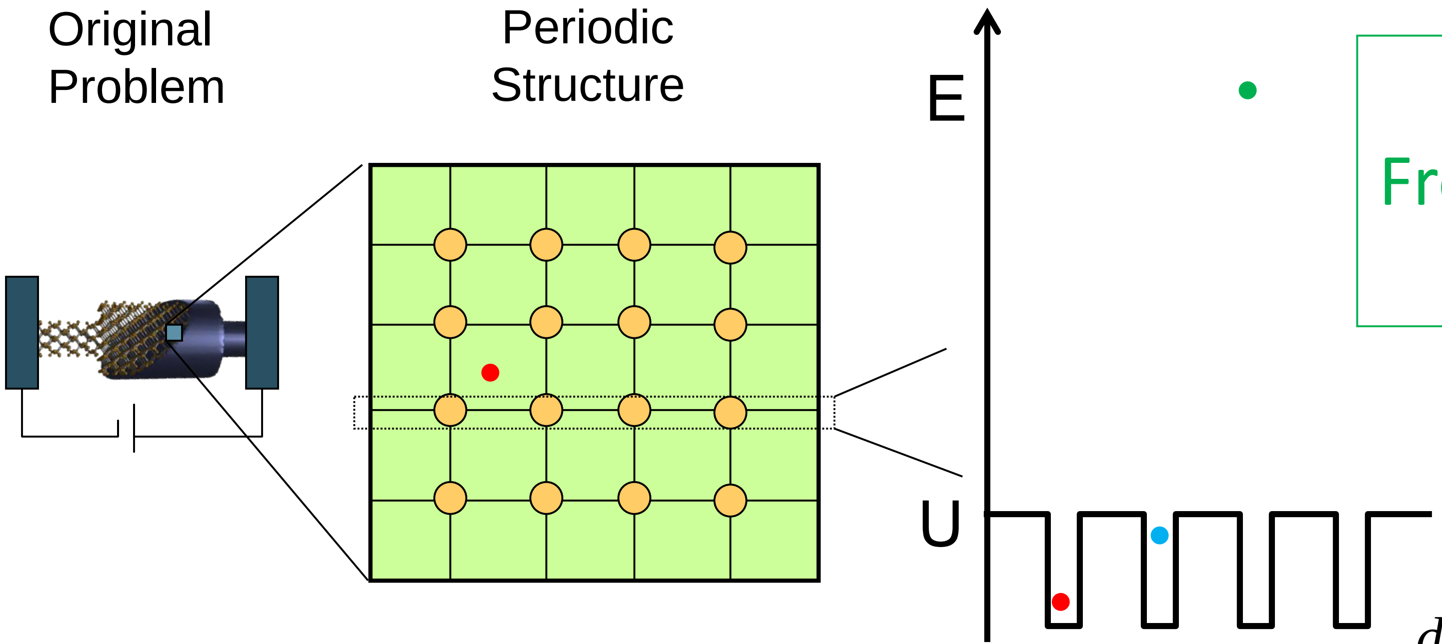
Schrödinger Equation
A Simple Differential Equation

$$\frac{d^2\psi}{dx^2} + \frac{2m_0}{\hbar^2}(E-U)\psi = 0 \qquad -\frac{\hbar^2}{2m_0}\frac{d^2\psi}{dx^2} + U(x)\psi = E\psi \qquad \frac{d^2\psi}{dx^2} + k^2\psi = 0$$

- Obtain U(x) and the boundary conditions for a given problem.
- Solve the 2nd order equation – pretty basic
- Interpret $|\psi|^2 = \psi^*\psi$ as the probability of finding an electron at x
- Compute anything else you need, e.g.,

$$p = \int_0^\infty \Psi^* \left[\frac{\hbar}{i}\frac{d}{dx}\right]\Psi \, dx \qquad E = \int_0^\infty \Psi^* \left[-\frac{\hbar}{i}\frac{d}{dt}\right]\Psi \, dx$$

Analytical Solutions to Free and Bound Electrons



Case 1:
Free electron
E >> U

$$\frac{d^2\psi}{dx^2} + \frac{2m_0}{\hbar^2}(E-U)\psi = 0$$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

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One Video Segment

- Section 5.2 - Electrons in a finite potential well

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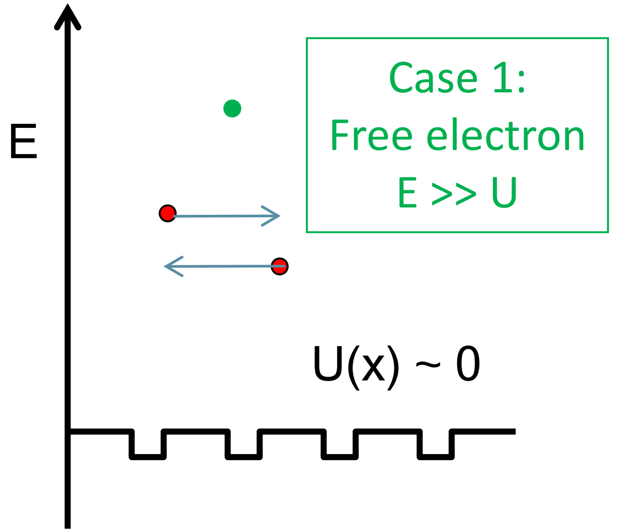
Case 1: Solution for Particles with E>>U

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad k \equiv \frac{\sqrt{2m_0\left[E-U\right]}}{\hbar}$$



1) Solution $\psi(x) = A\sin(kx) + B\cos(kx)$

$$\equiv A_+e^{ikx} + A_-e^{-ikx}$$

2) Boundary condition $\psi(x) = A_+e^{ikx}$ positive going wave

$=A_-e^{-ikx}$ negative going wave

Probability: $|\psi|^2 = \psi\psi^* = |A_+|^2 \, or \, |A_-|^2$

Momentum: $p = \int_0^\infty \Psi^* \left[\frac{\hbar}{i}\frac{d}{dx}\right]\Psi \, dx = \hbar k \text{ or } -\hbar k$

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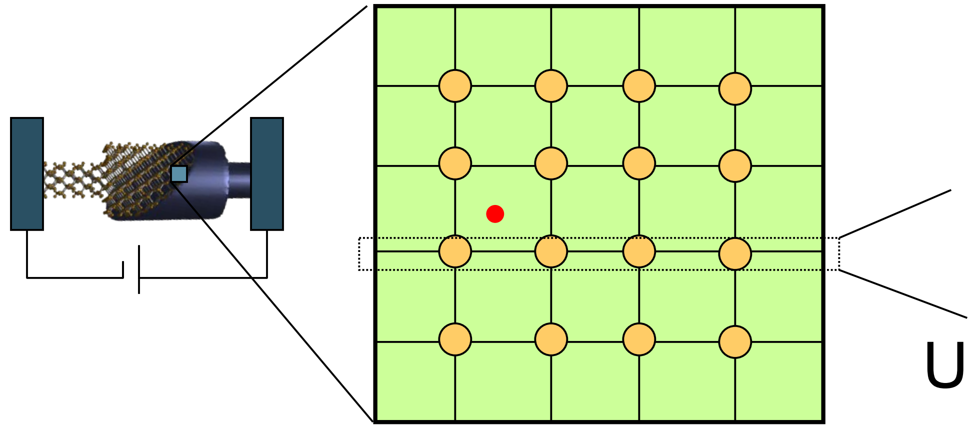

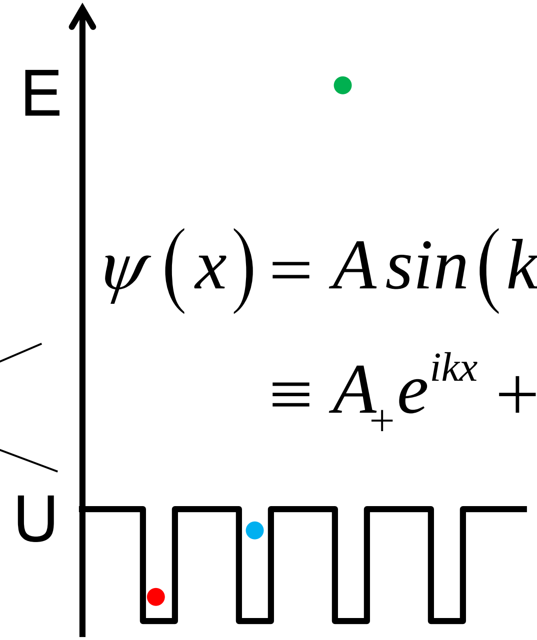

Case 1:
Free electron
E >> U

$$\psi(x) = A\sin(kx) + B\cos(kx)$$
$$\equiv A_+ e^{ikx} + A_- e^{-ikx}$$

Case 2:
Electron in infinite well
E << U

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

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Case 2: Bound State Problems

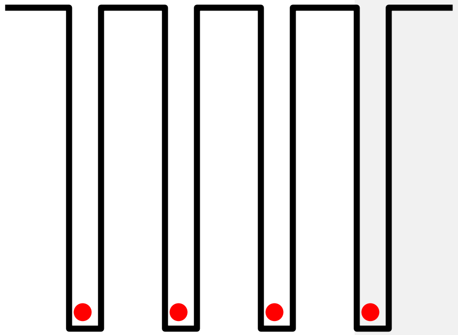
- Mathematical interpretation of Quantum Mechanics(QM)

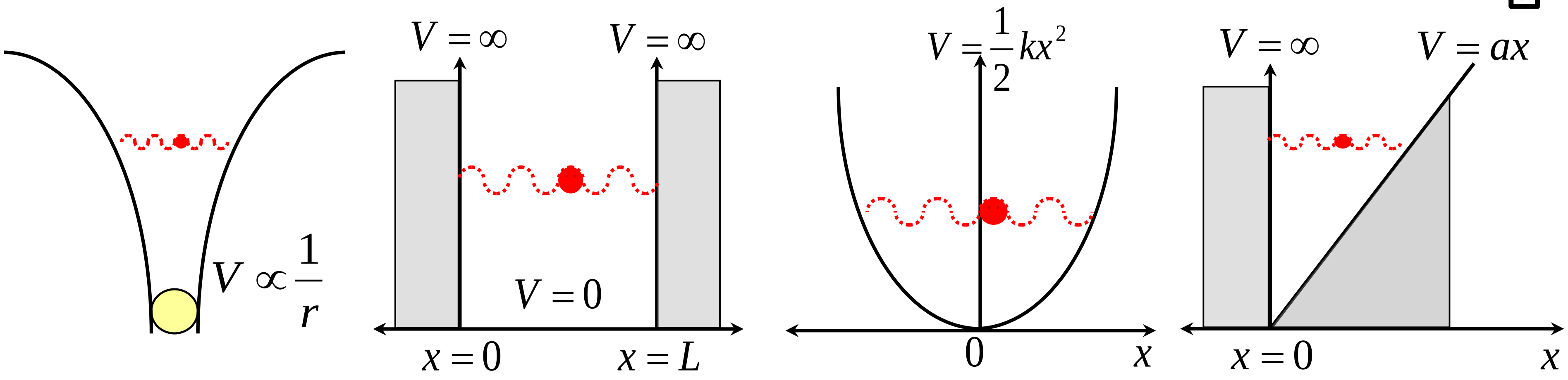
$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+V(x)\psi(x)=E\psi(x)$$

» Only a few number of problems have exact solutions

» They involve specialized functions

Case 2:
Electron in infinite well
E << U





Coulomb Potential by nucleus in an atom | Particle in a box | Harmonic Oscillator | Triangular Potential Well

$\Psi_n(r)=AR_n(r)Y_n(\theta,\varphi)$

$\Psi_n(x)=A\sin(k_n x)$

$\Psi_n(x)=A\frac{1}{\sqrt{2^n n!}}H_n(Bx)e^{-\frac{Cx^2}{2}}$

$\Psi_n(x)=N\mathrm{Ai}(\xi_n)$

1-D Particle in a Box – A Solution Guess

Case 2:
Electron in infinite well
E << U

- (Step 1) Formulate time independent Schrödinger equation

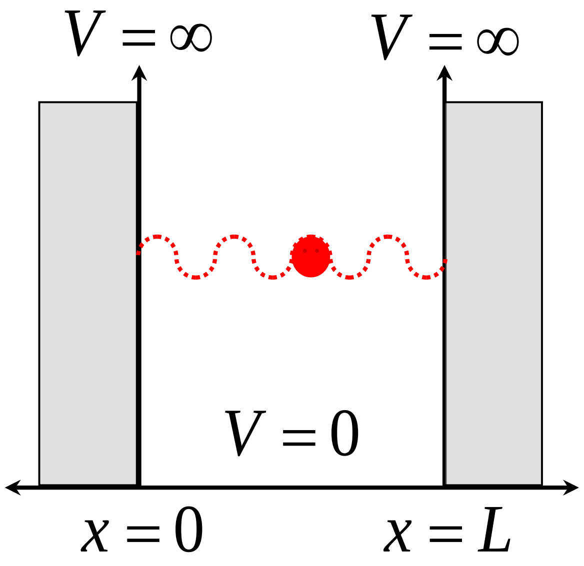
$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+V(x)\psi(x)=E\psi(x) \quad \text{where,} V(x)=\begin{cases}0 & 0<x<L_x\\ \infty & \text{elsewhere}\end{cases}$$

- (Step 2) Use your intuition that the particle will never exist outside the energy barriers to guess,

$$\psi(x)=\begin{cases}0 & 0\le x\le L_x\\ \neq 0 & \text{in the well}\end{cases}$$

- (Step 3) Think of a solution in the well as:

$$\psi_n(x)=A\sin\left(\frac{n\pi}{L_x}x\right),\quad n=1,2,3,\ldots$$

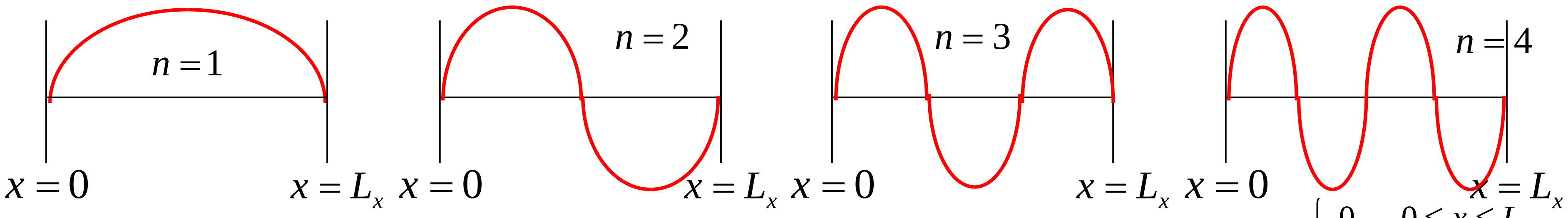


1-D Particle in a Box - Visualization

Case 2:
Electron in infinite well
E << U

- (Step 4) Plot first few solutions

$$\psi_n(x) = A\sin\left(\frac{n\pi}{L_x}x\right), \quad n = 1, 2, 3, \ldots$$



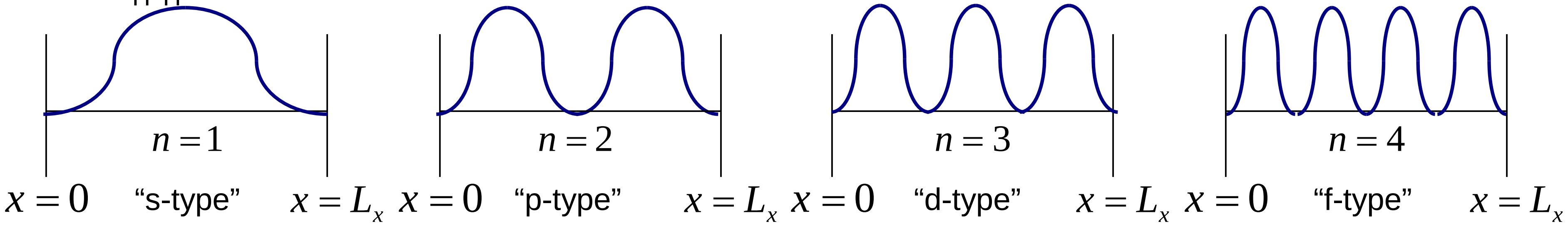
Matches the condition we guessed at step 2!
But what do the NEGATIVE numbers mean?

$$\psi(x) = \begin{cases} 0 & 0 \le x \le L_x \\ \neq 0 & \text{in the well} \end{cases}$$

- (Step 5) Plot corresponding electron densities

$$|\psi_n(x)|^2 = A^2\sin^2\left(\frac{n\pi}{L_x}x\right), \quad n = 1, 2, 3, \ldots$$

➡ The distribution of SINGLE particle



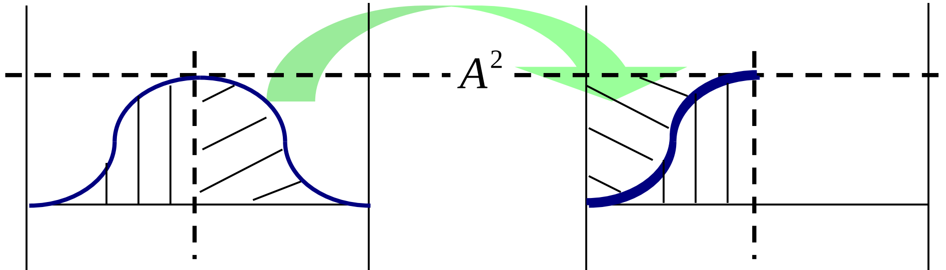
ONE particle => density is normalized to ONE

Case 2:
Electron in infinite well
E << U

(Step 6) Normalization (determine the constant A)

Method 1) Use symmetry property of sinusoidal function

$$|\psi_n(x)|^2 = A^2 \sin^2\left(\frac{n\pi}{L_x}x\right)$$



$$(\text{Area}) = 1 = \frac{L_x}{2} \times A^2$$

$$\therefore A = \sqrt{\frac{2}{L_x}}$$

Method 2) Integrate $|\psi_n(x)|^2$ over $0 \sim L_x$

$$1 = \int_0^{L_x} |\psi_n(x)|^2 dx = \int_0^{L_x} A^2 \sin^2\left(\frac{n\pi}{L_x}x\right) dx = A^2 \int_0^{L_x} \frac{1-\cos\left(\frac{2n\pi x}{L_x}\right)}{2} dx = A^2 \frac{L_x}{2}$$

$$\therefore \psi_n(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n\pi}{L_x}x\right), \quad n = 1,2,3,\ldots \quad 0 < x < L_x$$

1-D Particle in a Box - The Solution

Case 2:
Electron in infinite well
E << U

(Step 7) Plug the wave function back into the Schrödinger equation

$$\therefore \psi_n(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n\pi}{L_x} x\right), \quad n = 1, 2, 3, \ldots \quad 0 < x < L_x$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

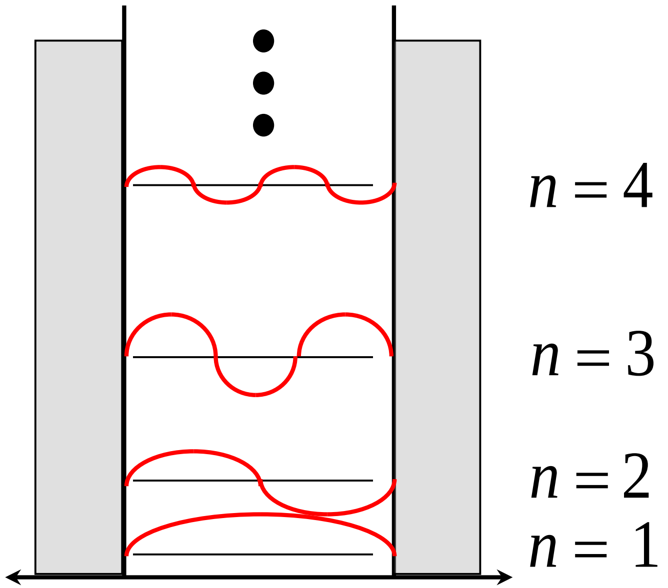
$$\frac{\hbar^2}{2m}\frac{n^2\pi^2}{L_x^2} = E_n$$

$$\psi_n(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n\pi}{L_x} x\right)$$

$$E_n = \frac{\hbar^2\pi^2}{2mL_x^2} n^2$$

$$n = 1, 2, 3, \ldots, \quad 0 < x < L_x$$

Discrete Energy Levels!



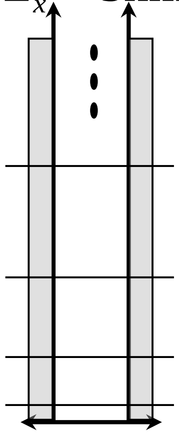
1-D Particle in a Box - Quantum vs. Macroscopic

- Quantum world → Macroscopic world
- Effect of system size

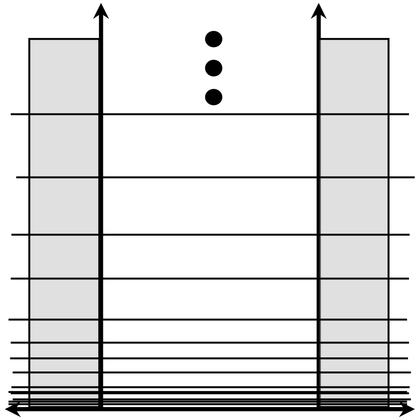
Case 2:
Electron in infinite well
E << U

$$E_n = \frac{\hbar^2 \pi^2}{2mL_x^2} n^2$$

$L_x = 5\text{nm}$



$L_x = 50\text{nm}$



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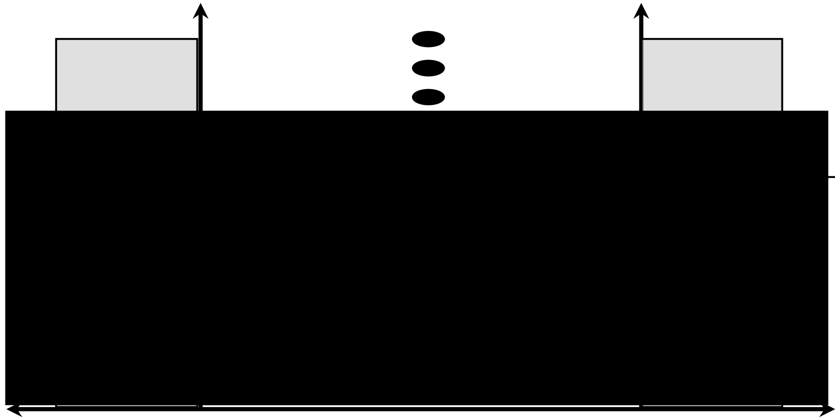

- Energy level spacing becomes smaller as physical dimension increases.
- In macroscopic world, where the energy spacing is too small to resolve, we see continuum of energy values.
- Therefore, this electronic quantum phenomenon is only observed in nanoscale environment.
- 1980s ~ 2000 - A whole research field struggles to make systems small enough to uncover quantum effects reliably

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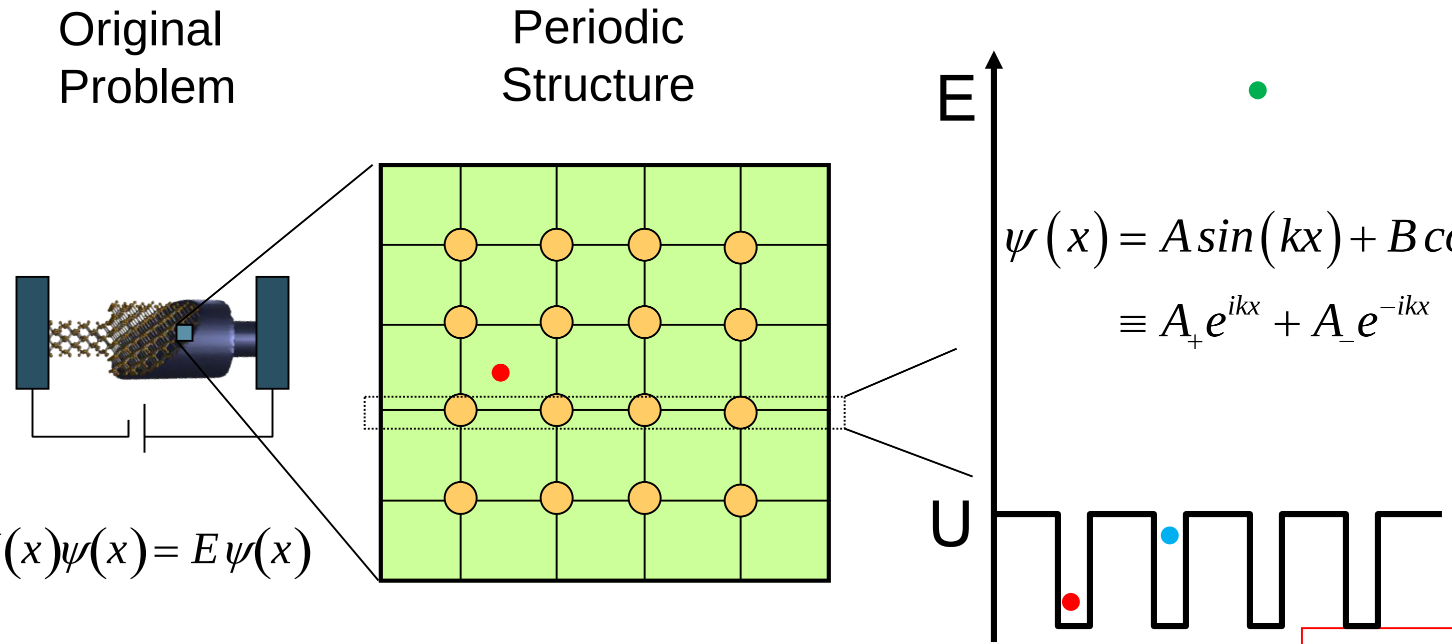

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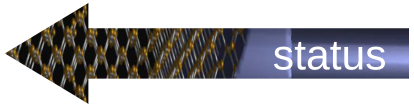

$$E_n=\frac{\hbar^2\pi^2}{2mL_x^2}n^2$$

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- Section 5.2 - Electrons in a finite potential well

$$\therefore\ \psi_n(x)=\sqrt{\frac{2}{L_x}}\sin\left(\frac{n\pi}{L_x}x\right),\quad n=1,2,3,\ldots,\quad 0<x<L_x$$

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Section 5
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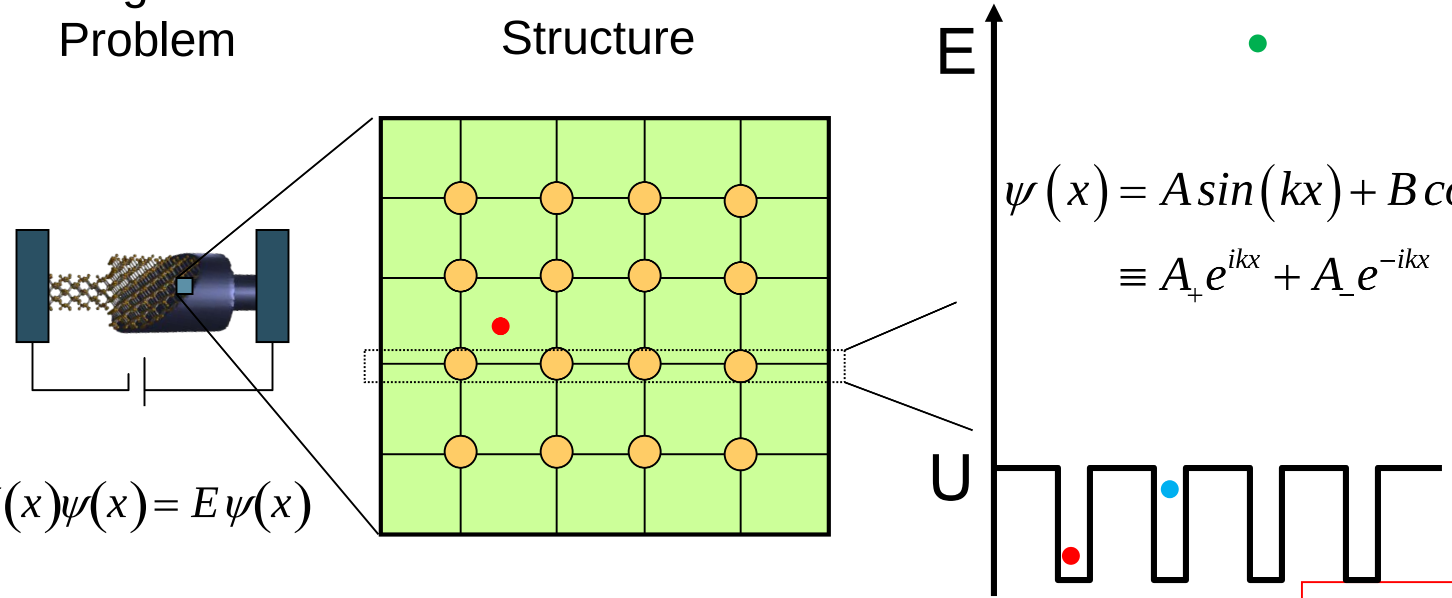
Original Problem

Periodic Structure



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