Schrödinger (Schroedinger) Equation

Non-relativistic Spin-zero.

$$\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x} \quad , \quad \hat{x} = x \quad , \quad \hat{H} = \hbar i \frac{\partial}{\partial t}$$

$$\frac{\hat{p}^2}{2m}\Psi_{(x,t)} + V(\hat{x})\Psi = \hat{H}\Psi$$

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

Look for "stationary states" = states of definite energy = eigenstates of energy.

$$\hat{H}\Psi = E\Psi$$

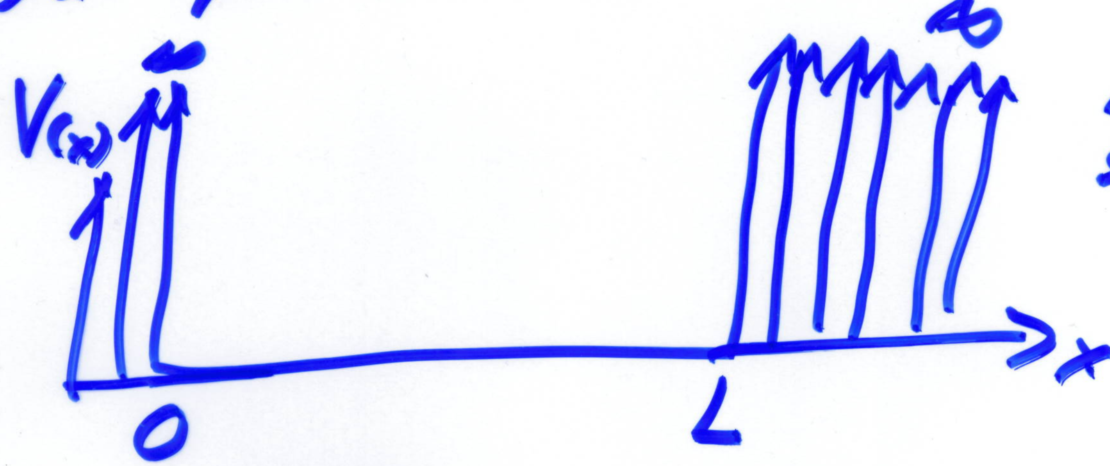
time dependence $e^{\frac{iEt}{\hbar}}$

$$\Psi(x,t) = e^{\frac{iEt}{\hbar}}\psi_{(x)}$$

Time-independent Schrödinger Eq.

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

Our problem: particle in a box



infinite square well

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

Try $\psi_{(x)} = A \sin(kx) + B\cos(kx)$

$$\frac{d}{dx}\psi_{(x)} = Ak\cos(kx) - Bk\sin(kx)$$

$$\frac{d^2}{dx^2}\psi_{(x)} = -Ak^2\sin(kx) - Bk^2\cos(kx)$$

$$= -k^2\psi_{(x)}$$

$$+\frac{\hbar^2}{2m}k^2\psi_{(x)} = E\psi_{(x)} \longrightarrow E = \frac{\hbar^2 k^2}{2m}$$

Boundary Conditions $\psi_{(0)} = 0 = \psi_{(L)}$

$$\psi_{(x)} = A \sin(kx) + B \cos(kx)$$

$$\psi_{(0)} = A \overset{0}{\sin(0)} + B \overset{1}{\cos(0)} = B = 0$$

$$\psi_{(x)} = A \sin(kx)$$

$$\psi_{(L)} = 0 = A \sin(kL)$$

$$A \neq 0 \Rightarrow \sin(kL) = 0$$

$$\Rightarrow kL = n\pi \qquad n = 1, 2, 3, \ldots$$

↑ Quantum number

$$k_n = \frac{n\pi}{L}$$

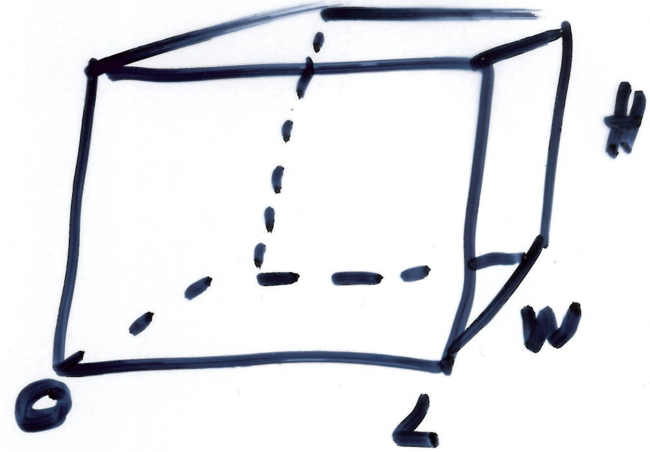
$$\psi_{(x)} = A \sin\left(\frac{n\pi x}{L}\right)$$

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

Normalize to get A : $\displaystyle\int_{x=0}^{L} \psi^*_{(x)} \psi_{(x)} \, dx = 1$

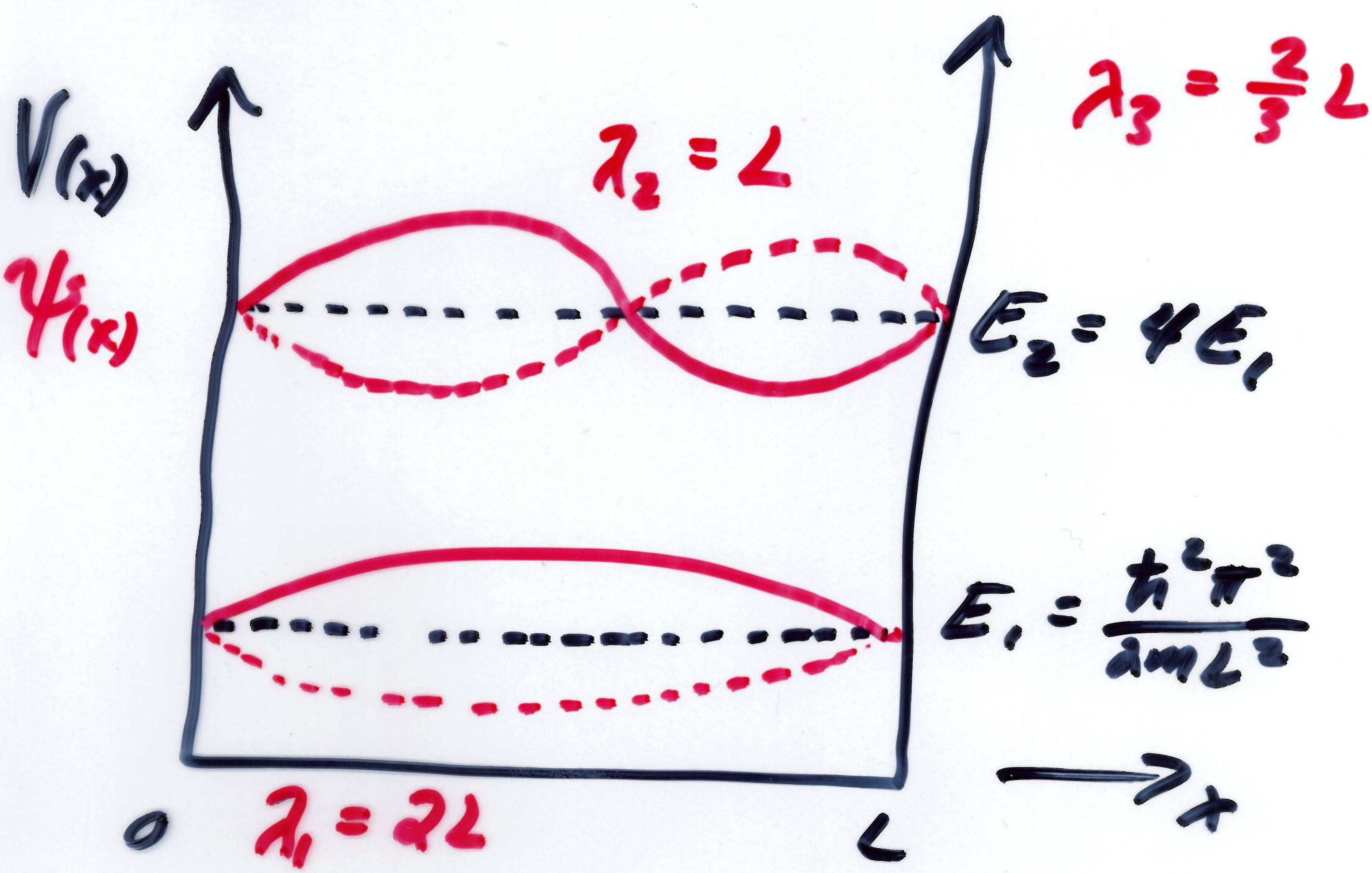
$$A = \sqrt{\frac{2}{L}}$$

3-dimensions



$$\psi_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{8}{LWH}}\,\sin\left(\frac{n_x \pi x}{L}\right)\sin\left(\frac{n_y \pi y}{W}\right)\cdot\sin\left(\frac{n_z \pi z}{H}\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2m}\left[\frac{n_x^2}{L^2}+\frac{n_y^2}{W^2}+\frac{n_z^2}{H^2}\right]$$



Pauli Exclusion Principle - one electron per quantum state (orbitals).

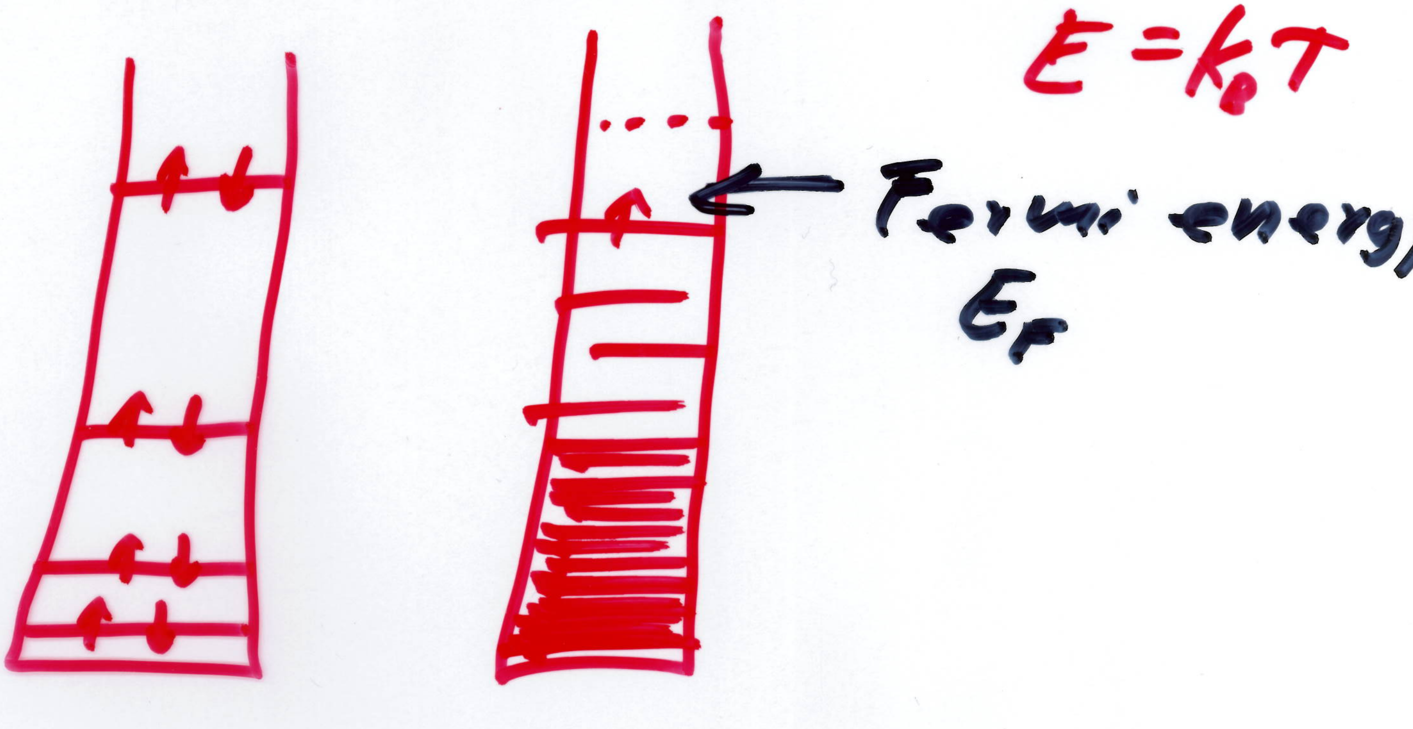
Quantum state labeled by two quantum numbers n and m_s where $m_s = \pm \frac{\hbar}{2}$ spin up / spin down

one dimension

Three dimensions

n_x, n_y, n_z, m_s

$E = k_B T$



k-space = Reciprocal Lattice

one k per $\frac{(2\pi)^3}{V}$

Density of states

spin states

$$D(k) \equiv \frac{dN}{dk} = \frac{2}{\frac{(2\pi)^3}{V}} = \frac{2V}{8\pi^3}$$

Total number of states is

N if each atom contributes one electron e.g. Na

$$N = D(k)\,\frac{4}{3}\pi k_F^3$$

$$= \frac{2V}{8\pi^3}\,\frac{4}{3}\pi k_F^3$$

k_F is the largest wavenumber

F for Fermi

$$\rightarrow k_F = \left[3\pi^2 \frac{N}{V}\right]^{1/3}$$

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left[3\pi^2 \frac{N}{V}\right]^{2/3}$$

e.g. Na one electron per atom

$$\frac{N}{V} = \frac{1}{V_{p\text{-cell}}} = \frac{2}{V_{\substack{\text{non-primitive}\\ \text{cube}}}} = \frac{2}{a_0^3}$$

$$E_F = \frac{\hbar^2}{2m_e}\left[3\pi^2 \frac{2}{a_0^3}\right]^{2/3} \sim 3.24\,\text{eV}$$

How are the states distributed with respect to energy

Density of states

$$D(E) \equiv \frac{dN}{dE} = ?$$

$$\underbrace{D(E)\,dE}_{} = D(k)\,dk\;4\pi k^2$$

# of states between energies E and $E + dE$.

$$D(E) = D(k)\frac{dk}{dE} = 4\pi k^2$$

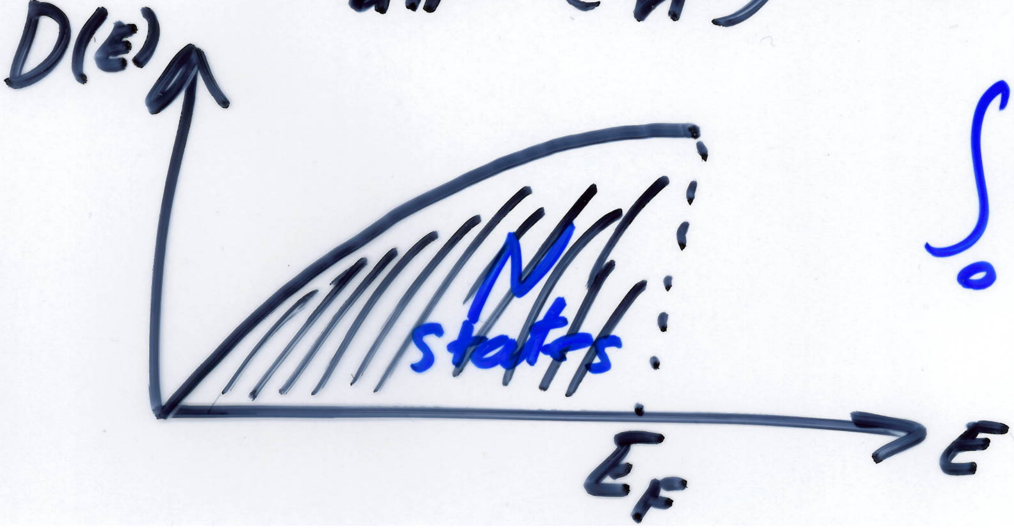
$$= \frac{2V}{8\pi^3}\,(?)$$

$$k^2 = \frac{2mE}{\hbar^2} \Rightarrow k = \sqrt{\frac{2m}{\hbar^2}}\,E^{1/2}$$

$$\frac{dk}{dE} = \sqrt{\frac{2m}{\hbar^2}}\,\frac{E^{-1/2}}{2}$$

$$D(E) = \frac{2V}{\hbar\, 8\pi^3}\sqrt{\frac{m}{2}}\,E^{-1/2}\,4\pi\,\frac{2mE}{\hbar^2}$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$



$$\int_0^{E_F} D(E)\,dE = N$$