Electrons in Metal

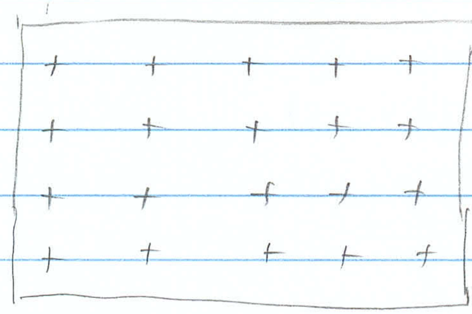
Copper atom ($Z = 29$)

electronic structure: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
$= [Ar] 4s^1 3d^{10}$

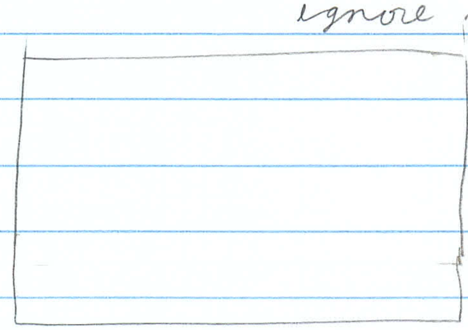
Copper ion: Cu^+

electronic structure: $[Ar] 3d^{10}$

Copper metal: lattice of Cu^+ ions
with spacing 3.6 Å
gas of electrons, one per ion



Simplest useful model: electrons in a box
ignore periodic potential
ignore repulsion between electrons



Cubic box of length L

number of electrons: $N = \left(\frac{L}{3.6\,\text{Å}}\right)^3$

Hamiltonian for N electrons

$$H = \sum_{i=1}^{N} \left[\frac{1}{2m} \vec{p}_i^{\,2} + V(\vec{r}_i) \right]$$

potential $V(\vec{r})$ restricts electrons to $0 < x < L$

$0 < y < L$

$0 < z < L$

$$V(\vec{r}) = 0 \quad \text{inside cube}$$
$$= \infty \quad \text{outside cube}$$

electrons are identical spin-$\frac{1}{2}$ fermions

single-electron Hamiltonian

$$H_1 = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V(x,y,z)$$

orbitals: $|n_x, n_y, n_z, m_s\rangle$ $\quad n_x, n_y, n_z = 1, 2, 3, \ldots$

$m_s = \pm\frac{1}{2}$

energies: $\epsilon_{n_x,n_y,n_z} = \left(n_x^2 + n_y^2 + n_z^2\right)\frac{\pi^2\hbar^2}{2mL^2}$

ground state for N electrons:

1 electron in each of N lowest orbitals

lowest orbital: $3\frac{\pi^2\hbar^2}{2mL^2}$

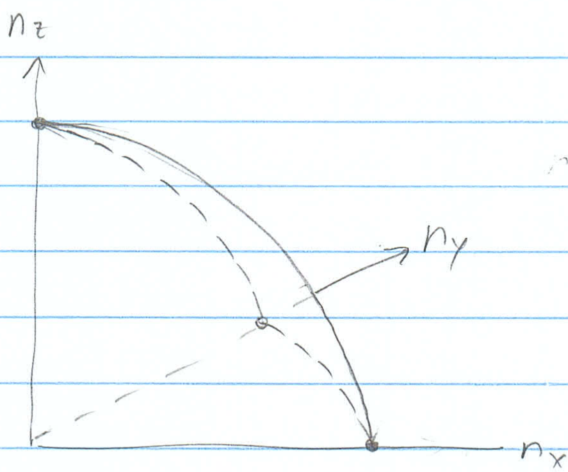
highest occupied orbital: ϵ_F "Fermi energy"

occupied orbitals: $|n_x, n_y, n_z, m_s\rangle$

with $(n_x^2 + n_y^2 + n_z^2)\frac{\pi^2\hbar^2}{2mL^2} < \epsilon_F$

$\sqrt{n_x^2+n_y^2+n_z^2} < \frac{\sqrt{2m\epsilon_F}\,L}{\pi\hbar}$

$\frac{1}{8}$ of sphere of radius $\frac{\sqrt{2m\epsilon_F}\,L}{\pi\hbar}$
in n_x, n_y, n_z space



number of points (n_x, n_y, n_z)
with integer coordinates
inside radius $\frac{\sqrt{2m\epsilon_F}\,L}{\pi\hbar}$

$\approx$ volume of $\frac{1}{8}$ sphere

$$= \frac{1}{8}\left[\frac{4}{3}\pi\left(\frac{\sqrt{2m\epsilon_F}}{\pi\hbar}L\right)^3\right]$$

$$= \frac{\pi}{6}\frac{(2m\epsilon_F)^{3/2}}{\pi^3\hbar^3}L^3$$

number of electrons = number of occupied orbital

$$N = 2\,\frac{\pi}{6}\frac{(2m\epsilon_F)^{3/2}}{\pi^3\hbar^3}L^3$$

2 spin states for each n_x, n_y, n_z

solve for Fermi energy

$$\frac{N}{L^3} = \frac{1}{3\pi^2}\frac{(2m\epsilon_F)^{3/2}}{\hbar^3}$$

$$\epsilon_F = (3\pi^2)^{2/3}\frac{\hbar^2}{2m}\left(\frac{N}{L^3}\right)^{2/3}$$

insert $\frac{L^3}{N} = (3.6\times10^{-10}\,m)^3$ for Cu

predicted Fermi energy: $\epsilon_F = 7.2\,eV$

measured value: $\epsilon_F = 7.0\,eV$

much greater than kT at room temperature: $kT \approx 0.0026\,eV$