Solids

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Introduction

Solid State

- some loosely bound, outermost valence electrons from each atom detached
- not subject to Coulomb field of a specific nucleus
  - subject to potential of entire crystal lattice

Primitive Models

1. electron gas theory of Sommerfeld
   - ignores all forces except confining boundaries
   - treats wandering electrons as free particles in a box (∞ cube well)

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1. electron gas theory of Sommerfeld
   - ignores all forces except confining boundaries
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2. Bloch's theory
   - periodic potential representing electrical attraction of regularly spaced nucleii
   - ignores electron-electron repulsion

The Free Electron Gas

Schrödinger Equation

- rectangular solid with dimensions ℓ_x, ℓ_y, ℓ_z

$$V(x,y,z) = \begin{cases} 0, & \text{if } 0 < x < \ell_x,\ 0 < y < \ell_y, \text{ and } 0 < z < \ell_z \\ \infty, & \text{otherwise} \end{cases}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

$$\psi(x,y,z) = X(x)\,Y(y)Z(z)$$

Schrödinger Equation (cont.)

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}, k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}, k_z \equiv \frac{\sqrt{2mE_z}}{\hbar},$$

General solutions

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x);\;\; Y(y) = \ldots;\;\; Z(z) = \ldots$$

Schrödinger Equation (cont.)

Boundary conditions require

$$X(0) = Y(0) = Z(0) = 0$$

so

$$B_x = B_y = B_z = 0$$

and

$$X(\ell_x) = Y(\ell_y) = Z(\ell_z)$$

meaning

$$k_x\ell_x = n_x\pi; \quad k_y\ell_y = n_y\pi; \quad k_z\ell_z = n_z\pi$$

Schrödinger Equation (cont.)

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin\left(\frac{n_x \pi}{\ell_x} x\right) \sin\left(\frac{n_y \pi}{\ell_y} y\right) \sin\left(\frac{n_z \pi}{\ell_z} z\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{\ell_x^2} + \frac{n_y^2}{\ell_y^2} + \frac{n_z^2}{\ell_z^2}\right) = \frac{\hbar^2 k^2}{2m}$$

$$k = \|\mathbf{k}\|$$

$$\mathbf{k} = (k_x, k_y, k_z)$$

k-space

- 3D space with axes k_x, k_y, and k_z
- planes drawn at $k_x = (\pi/\ell_x), (2\pi/\ell_x), \ldots$, $k_y = \ldots$, $k_z = \ldots$
- each intersection represents a distinct (one-particle) stationary state
- each block occupies a volume in (k-space) of

$$k_x k_y k_z = \frac{\pi^3}{\ell_x \ell_y \ell_z} = \frac{\pi^3}{V_{\text{object}}}$$

- each block contains two electrons (↑↓)

k-space

- all free electrons fill 1 octant of sphere in k-space, centered at origin
  - sphere has radius k_F

$$V_{\text{octant}} = \frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right) = \frac{Nq}{2}\left(\frac{\pi^3}{V_{\text{object}}}\right)$$

$$k_F = (3\rho\pi^2)^{1/3}$$

$$\rho \equiv \frac{Nq}{V_{\text{object}}}$$

Fermi surface

- boundary separating occupied and unoccupied states in k-space
- corresponding energy is Fermi energy, E_F

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3}$$

Total Energy

- a shell of thickness dk has volume

$$\frac{1}{8}(4\pi k^2)\mathrm{d}k$$

- number of electron states in shell

$$\frac{2[(1/2)\pi k^2 \mathrm{d}k]}{\pi^3/V} = \frac{V}{\pi^2}k^2\mathrm{d}k$$

- each carries energy $\hbar^2 k^2/2m$, so energy of shell is

$$\mathrm{d}E = \frac{\hbar^2 k^2}{2m}\frac{V}{\pi^2}k^2\mathrm{d}k$$

Total Energy (cont.)

$$
\begin{aligned}
E_{\text{tot}} &= \int_0^{k_F} \mathrm{d}E = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_f} k^4 \mathrm{d}k \\
&= \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2 (3\pi^2 N q)^{5/3}}{10\pi^2 m} V^{-2/3}
\end{aligned}
$$

- total energy is inversely proportional to total volume

Degeneracy pressure

- if the box expands by $\mathrm{d}\,V$, the total energy decreases

$$\mathrm{d}E_{\mathrm{tot}} = -\frac{2}{3}\frac{\hbar^2(3\pi^2 Nq)^{5/3}}{10\pi^2 m}\,V^{-5/3}\mathrm{d}\,V = -\frac{2}{3}E_{\mathrm{tot}}\frac{\mathrm{d}\,V}{V}$$

- shows up as work done on outside ($\mathrm{d}\,W = P\mathrm{d}\,V$) by quantum pressure P

$$P = \frac{2}{3}\frac{E_{\mathrm{tot}}}{V} = \frac{2}{3}\frac{\hbar^2 k_F^5}{10\pi^2 m} = \frac{(3\pi^2)^{2/3}\hbar^2}{5m}\rho^{5/3}$$

- stabilizing internal pressure, independent of e-e & thermal repulsion

Band Structure

Introduction

- we improve on the free electron model by including forces exerted by nucleii
  - regularly spaced
  - positively charged
  - stationary

Dirac Comb

- model the potential by a 1D Dirac comb
  - evenly spaced delta function spikes
- periodic in x at intervals of a

$$V(x+a) = V(x)$$

Bloch's Theorem

the solutions to the Schrödinger equation

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

can be taken to satisfy the condition

$$\psi(x+a) = e^{\imath K a}\psi(x)$$

for some constant K (independent of x but not necessarily E)

Displacement Operator

$$Df(x) = f(x+a)$$

- for a periodic potential, D commutes with the Hamiltonian

$$[D, H] = 0$$

- free to choose eigenfunctions of H that are eigenfunctions of D

$$D\psi = \lambda\psi \implies \psi(x+a) = \lambda\psi(x)$$

Wave Function

- considering the loop model, $0 < x < a$ yields the wave function:

$$\psi(x) = A\sin(kx) + B\cos(kx), \quad (0 < x < a)$$

- Bloch's theorem allows us to write for final cell:

$$\psi(x) = e^{-\imath Ka}[A\sin k(x+a) + B\cos k(x+a)], \quad (-a < x < 0)$$

Wave Function (cont.)

- from boundary conditions:

$$B = e^{-\imath Ka}[A\sin(ka) + B\cos(ka)],$$

  whose derivative is discontinuous proportional to magnitude of δ fn
- solving for $A\sin(ka)$ gives

$$A\sin(ka) = \left[e^{\imath Ka} - \cos(ka)\right]B$$

Wave Function (cont.)

- derivative of the wave function is given by

$$\Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = -\frac{2m\alpha}{\hbar^2}\psi(0)$$

- plugging into B given by boundary conditions:

$$kA - e^{-\imath Ka}k[A\cos(ka) - B\sin(ka)] = \frac{2m\alpha}{\hbar^2}B$$

Wave Function (cont.)

- plugging into $A\sin(ka)$ gives

$$\left[e^{\imath Ka}-\cos(ka)\right]\left[1-e^{-\imath Ka}\cos(ka)\right]+e^{-\imath Ka}\sin^2(ka)=\frac{2m\alpha}{\hbar k}\sin(ka)$$

- simplifies to

$$\cos(Ka)=\cos(ka)+\frac{m\alpha}{\hbar^2 k}\sin(ka)$$

Discrete Energy States

$$\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)$$

- allows us to find the possible values of k and allowed energies
- we define this dimensionless notation:

$$z \equiv ka, \quad \beta \equiv \frac{m\alpha a}{\hbar^2}$$

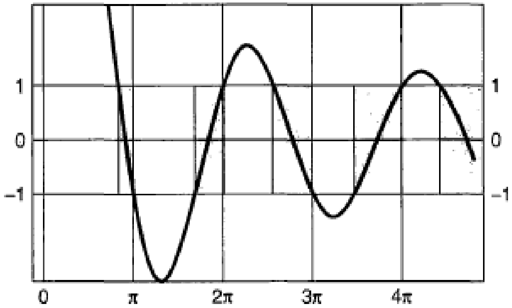
- and rewrite the top as

$$f(z) \equiv \cos(z) + \beta\frac{\sin(z)}{z}$$

- β is the “strength” of the delta function

Forbidden Energies

- plot $f(z)$ using $\beta = 10$

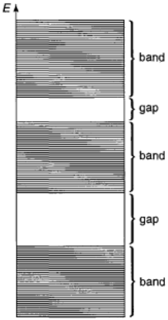


Forbidden Energy Considerations

- $f(z)$ exists outside the range $(-1, +1)$
- unsolvable in these regions
  - $\cos(Ka)$ is confined between $(-1, +1)$
- gives rise to forbidden energy regions
  - energy gaps
- gaps are separated by allowed regions
  - bands
- practically any energy allowed within given band $(Ka = 2\pi n/N)$

Energy Bands

- draw N horizontal lines on previous graph at values of $\cos(2\pi n/N)$
- intersection points represent energy levels within each band



Multielectron Systems

- we have only considered one electron in the potential
- in reality there are Nq electrons
- Pauli exclusion principle dictates at most 2 electrons may occupy one state
- with N states, we have the following possibilities
    - $q = 1 \implies$ first band half filled
    - $q = 2 \implies$ first band completely filled
    - $q = 3 \implies$ second band half filled
    - etc.

System Classifications

- entirely filled band requires relatively large energy to excite electron
  - electrical **insulators**
- partly filled band requires very small energy to excite electron
  - electrical **conductors**

Doped Insulators

- we dope an insulator with some atoms of a different q
- two cases arise:
  1. $q_2 > q_1 \implies$ obtain extra electrons in next higher band
  2. $q_2 < q_1 \implies$ create holes in previously filled band
- in both cases, small electric currents may flow
  - **semiconductors**

Thank You