## Midterm Exam (30 points)

- Possible date:
  October 26 10:00am-1:00pm
- Location: TBA
- **Ground rules:**
  Open book, open notes
  Do all problems in **Part I**, do 5 out of 10 problems in **Part II**



## Supplementary material link

http://www.physics.uwo.ca/~lgonchar/courses/p9812/additional

Username: P9812
Password: ~vector~

Lecture 1
1_all.pdf 2_all.pdf 3_all.pdf

Lecture 2
5.pdf

Lecture 3
11.pdf 13.pdf

Lecture 4
6.pdf 7.pdf



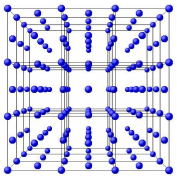
## Lecture 4

### 4. The Single-Electron Model

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2}\sum_{i\neq i'} \frac{q_i q_{i'}}{\left|\hat{R}_i - \hat{R}_{i'}\right|}$$

… or Free Electron Fermi Gas

Free electrons subject to the Pauli principle



In 1D: $H\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \varepsilon_n \psi_n$

References:
1. Marder, Chapters 6
2. Kittel, Chapter 6, pp.144-156
3. Ashcroft and Mermin, Chapter 8
4. Ziman, Chapter 3, pp.77-91
5. Kaxiras, Chapter 3
6. Phillips, Chapter 1
7. Ibach, Chapter 6

## Approximations

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2}\sum_{i\neq i'} \frac{q_i q_{i'}}{|\hat{R}_i - \hat{R}_{i'}|}$$

**Born-Oppenheimer approximation**: nuclei treated as classical potentials; many electrons combined with nuclei in closed shells to form ions; ions treated as static potential

All electronic degrees of freedom eliminated; effective potentials for ions.

**Single electron approximation:** Coulomb interaction incorporated into lattice potential

**Jellium:** interacting electrons move in uniform positive potential

Ions arranged in a lattice, forming periodic potential for single electrons. Weak ionic potentials justified by **pseudopotentials**

**Free Fermi gas:** Ionic potential eliminated, *surprisingly effective for alkali metals*



## Metals

- For an isolated atom the valence electrons are in the potential well due to the nucleus and core electrons
- As the atoms approach each other to build a crystal, the overlap of the atomic potentials causes the valence electrons to be in an effective potential that is lower than in the isolated atoms
- For metals can consider a "smooth" potential well W
- **Drude's Model** (1900): an application of the kinetic theory of electron gas in a solid; uses average energy and Maxwell-Bolzmann distribution of the electron velocities
- **Sommerfeld theory**: quantum mechanics approach to find energy and velocities; uses Pauli exclusion principle to fill up the quantized states

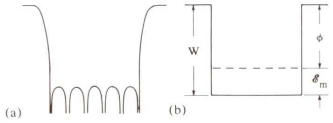



**Fig. 9-1** (a) The potential in a crystal. (b) A model of this potential in which the electrons are in a "box" of depth W.



## Important Terms

- Free electron gas
- Occupation number
- Fermi energy
- Fermi surface
- Density of states
- Fermi-Dirac Statistics and Temperature Effects
- Sommerfeld expansion
- Heat Capacity of the Electron Gas and Sommerfeld parameter

## Basic Hamiltonian

Single-electron model:

$$H\Psi = \sum_{i=1}^{N}\left(\frac{-\hbar^2\nabla_i^2}{2m} + U(\vec{r}_i)\right)\Psi(\vec{r}_1...\vec{r}_N) = \mathcal{E}\Psi(\vec{r}_1...\vec{r}_N)$$

*N* conduction electrons, interacting with external potential U but does not interacting with the other conduction electrons

Find eigenfunctions $\psi_i(\vec{r}_i)$ for single electrons obeying:

$$\left(\frac{-\hbar^2\nabla^2}{2m} + U(\vec{r})\right)\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

$\Rightarrow$ eigenfunctions describing many particles are products of one-particle functions

**Free electron gas:** (no external potential U)

$$\boxed{\frac{-\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2\Psi(\vec{r}_1...\vec{r}_N) = \mathcal{E}\Psi(\vec{r}_1...\vec{r}_N)}$$



## Energy Levels in 1D

In 1D: $H\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \varepsilon_n\psi_n$

The boundary conditions are imposed by the infinite potential energy barriers:

$$\psi_n(0) = 0; \psi_n(L) = 0$$

They are satisfied by sinelike wavefunction:

$$\psi_n = A\sin\left(\frac{2\pi}{\lambda_n}x\right);\ \frac{1}{2}n\lambda_n = L$$

$$\frac{d\psi_n}{dx} = A\left(\frac{n\pi}{L}\right)\cos\left(\frac{n\pi}{L}x\right);\ \frac{d^2\psi_n}{dx^2} = -A\left(\frac{n\pi}{L}\right)^2\sin\left(\frac{n\pi}{L}x\right)$$

The energy is given by: $\varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$

Accommodate *N* electrons, recall Pauli exclusion principle (*n*, $m_S$=±1/2*)*

The **Fermi energy $\varepsilon_F$** is defined as the energy of the topmost filled level in the ground state of the N electron system:

$$\boxed{\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{n_F\pi}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{N\pi}{L}\right)^2}$$

8

## Free Electron Gas in 3D

In 3D: $-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_k(\vec{r}) = \varepsilon_k\psi_k(\vec{r})$

Apply periodic boundary conditions (period L):

$$\psi(x,y,z) = \psi(x+L,y,z);\ \psi(x,y,z) = \psi(x,y+L,z);\ \psi(x,y,z) = \psi(x,y,z+L)$$

Wavefunctions satisfying Schrödinger equation and boundary conditions are:

$$\psi_{\vec{k}}(\vec{r}) = \exp(i\vec{k}\cdot\vec{r}),$$

where the components of the wavevector $\vec{k}$ are: $k_x = 0;\pm\frac{2\pi}{L};\pm\frac{4\pi}{L};...$

We can confirm that the values of $k_x$ satisfy periodic boundary condition:

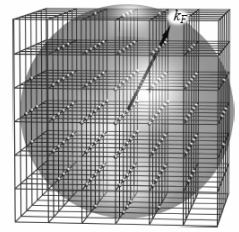
$$\exp(ik_x(x+L)) = \exp(i\cdot n\frac{2\pi}{L}(x+L)) = \exp(i\cdot n\frac{2\pi}{L}x)\exp(i\cdot n\frac{2\pi}{L}L) = \exp(i\cdot k_x x)$$

The eigenvalue corresponding to the wavefunction is:

$$\boxed{\varepsilon_{\vec{k}} = \frac{\hbar^2}{2m}\vec{k}^2 = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)}$$

9

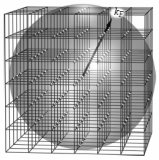
## *k* – or reciprocal space




$\vec{k}$ states described by equation above occupy a cubic lattice in $\vec{k}$ or reciprocal space, with neighbouri ng points separated by distances of $\frac{2\pi}{\mathrm{L}}$,

*k* space volume per state is $\left(\frac{2\pi}{L}\right)^3$, or $V = L^3 \Rightarrow \frac{(2\pi)^3}{V}$

## Occupation number




The ground state of *N* electrons is build from…

…by putting two electrons into the lowest state |*k*|=0;

next into all states with $\left|\vec{k}\right| = \frac{2\pi}{L}$, and so on

**Occupation number** $f_k$ of a state indexed by $\vec{k}$

is 1 if this one-electron state is part of the ground state, and 0 otherwise

In the ground state of a system of *N* free electrons the occupied orbitals are points inside a sphere in k-space

- the energy at the surface of the sphere is the Fermi energy: $\varepsilon_F = \frac{\hbar^2}{2m} k_F{}^2$

The total number of orbitals in the sphere of volume $\frac{4\pi k_F^3}{3}$ is $\frac{4\pi k_F^3}{3}\frac{L^3}{(2\pi)^3} \times 2 = N$



## Fermi Energy

The total number of orbitals in the sphere is $N = \frac{4\pi k_F^3}{3}\frac{L^3}{(2\pi)^3} \times 2 = \frac{V}{3\pi^2} k_F^3$

Radius $k_F$ can be defined as (only N dependent):

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

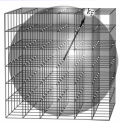
**Fermi energy is related to the electron concentration N/V!!!**

$$\varepsilon_F = \frac{\hbar^2}{2m} k_F{}^2 = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$N = \frac{V}{3\pi^2} k_F^3 = \frac{V}{3\pi^2} e_F^{3/2} \frac{(2m)^{3/2}}{\hbar^3}$$

## Definition of Density of states, D

$$\sum_{\vec{k}} F_{\vec{k}}, \qquad \sum_{\vec{k}} \left(\frac{2\pi}{L}\right)^3 F_{\vec{k}} = \int F_{\vec{k}} d\vec{k} \Rightarrow \frac{V}{(2\pi)^3}\int F_{\vec{k}} d\vec{k}$$



Density of electronic states or density of levels

$$D_{\vec{k}} = 2\frac{1}{(2\pi)^3}$$

Defined so that $\sum_{\vec{k}} F_{\vec{k}} = V\int D_{\vec{k}} F_{\vec{k}} d\vec{k}$

Several separate functions D are all referred to as density of states

$\Rightarrow$ distinguish by their argument

*Energy density of states D(E)*



## Energy Density of States

The number of orbitals per unit energy range, $D(E)$ – density states

$$\sum_{k\sigma} F(E_{\vec{k}}) = V\int D(E)F(E)dE$$

To find $D(E)$, note that $N = \frac{V}{3\pi^2}k_F^3 = \frac{V}{3\pi^2}e_F^{3/2}\frac{(2m)^{3/2}}{\hbar^3}$

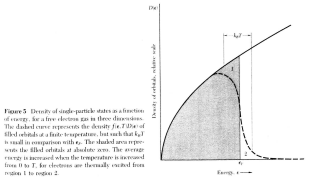
$$D(E) = \frac{dN}{dE} = \frac{d}{dE}\left(\frac{V}{3\pi^2}E^{3/2}\frac{(2m)^{3/2}}{\hbar^3}\right) = \frac{V}{3\pi^2}\left(\frac{(2m)^{3/2}}{\hbar^3}\right)\frac{3}{2}E^{1/2} = \frac{V}{2\pi^2}\left(\frac{(2m)^{3/2}}{\hbar^3}\right)E^{1/2}$$

Note dimensionality effect:

- for **3D**: $D(E) \propto$
- for **2D**: $D(E) \propto$
- for **1D**: $D(E) \propto$



## Experimental confirmation



see Kittel

**Soft X-ray emission spectra**:

If Al metal is bombarded by electrons with enough energy to knock a 2p-electron from the Al core then X-rays are emitted

Al $1s^2 2s^2 2p^6 3s^2 3p^1$

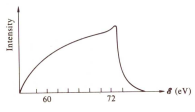



Fig. 9-6 The intensity of x-ray emission for aluminum.

## Fermi-Dirac Statistics and Temperature Effects

**Recall**: in the Drude theory we used a single average energy, av. velocity, *etc*

Need a proper ***statistical*** approach to characterize thermal occupancy of the allowed quantum states. Particles with a spin of ½ obeys **Fermi-Dirac** statistics

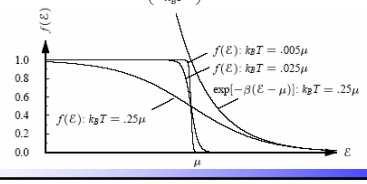
For an ideal electron gas in thermal equilibrium with a heat bath at a temperature T, the probability that an allowed state, with energy E, will be occupied is

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$$

*f(E)* **Fermi function** or the occupation probability

**At low T** ($\rightarrow$ 0 K)

Note: when $E = E_F$, $f(E) = 1/2$

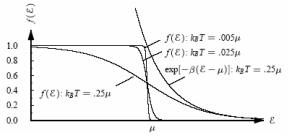





## Temperature Effects

**At higher T**: the kinetic energy of the electron gas increases as the temperature is increased: some energy levels are occupied which were vacant at absolute zero

$$f(E) = \frac{1}{\exp\left(\frac{E - \mu}{k_B T}\right) + 1}$$




when $E$-$\mu >> k_B T$;

the exponent term is dominant'

$\Rightarrow$ the Boltzmann distribution

$$f(E) \cong \exp^{\frac{\mu - E}{k_B T}}$$

**Fermi temperature:** $T_F = \frac{E_F}{k_B}$



## Elements as free electron gases

| Element | $Z$ | $n$ ($10^{22}$ cm$^{-3}$) | $k_F$ ($10^8$ cm$^{-1}$) | $\mathcal{E}_F$ (eV) | $T_F$ ($10^4$ K) | $v_F$ ($10^8$ cm s$^{-1}$) | $r_s/a_0$ |
|---|---|---|---|---|---|---|---|
| Li | 1 | 4.60 | 1.11 | 4.68 | 5.43 | 1.28 | 3.27 |
| Ag | 1 | 5.86 | 1.20 | 5.50 | 6.38 | 1.39 | 3.02 |
| Be | 2 | 24.72 | 1.94 | 14.36 | 16.67 | 2.25 | 1.87 |
| Al | 3 | 18.07 | 1.75 | 11.66 | 13.53 | 2.02 | 2.07 |
| Sn | 4 | 14.83 | 1.64 | 10.22 | 11.86 | 1.89 | 2.22 |
| Sb | 5 | 16.54 | 1.70 | 10.99 | 12.75 | 1.97 | 2.14 |
| Mn | 4 | 32.61 | 2.13 | 17.28 | 20.05 | 2.46 | 1.70 |
| Fe | 2 | 16.90 | 1.71 | 11.15 | 12.94 | 1.98 | 2.12 |
| Co | 2 | 18.18 | 1.75 | 11.70 | 13.58 | 2.03 | 2.07 |
| Ni | 2 | 18.26 | 1.76 | 11.74 | 13.62 | 2.03 | 2.07 |

## Results for Free Electrons

$$D(E) = \frac{V}{2\pi^2}\left(\frac{(2m)^{3/2}}{\hbar^3}\right)E^{1/2} = 6.812\times10^{21}\sqrt{\frac{E}{eV}}eV^{-1}cm^{-3}$$

**The Fermi wave vector** $k_f$ is related to the density of electrons ($n=N/V$) by

$$k_F = \left(3\pi^2 n\right)^{1/3} = 3.09[n\cdot \text{Å}^3]^{1/3}\,\text{Å}^{-1}$$

**Radius parameter**, $r_s$

$$\frac{V}{N} = \frac{4\pi}{3}r_s^3 \Rightarrow r_s = \left[\frac{3V}{4\pi N}\right]^{1/3}$$

**Fermi energy**, $E_F$ or Fermi level

$$\varepsilon_F = \frac{\hbar^2}{2m}k_F{}^2 = 36.46[n\cdot \text{Å}^3]^{2/3}eV$$

**Fermi surface**, electrons with energy $E_F$

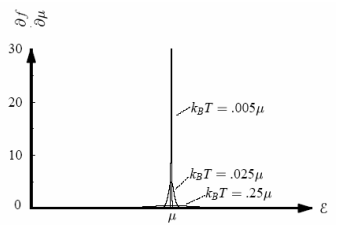
Can be treated as the total number of conduction electrons divided by the Fermi energy



## Sommerfeld Expansion

Paradox that density of states too small solved by

$$c_v \propto TD(\varepsilon_F)$$




Derivatives of Fermi function for various $k_BT$

$f$ is only nonzero over an energy range around the Fermi energy

## Sommerfeld Expansion

$$\langle H\rangle = \int_{-\infty}^{\infty} H(E)f(E)dE$$

$$\langle H\rangle = \int_{-\infty}^{\mu} H(E)dE + \sum_{n=1}^{\infty}\ldots$$

$$\langle H\rangle = \int_{-\infty}^{\mu} H(E)dE + \frac{\pi^2}{6}[k_BT]^2 H'(\mu) + \frac{7\pi^4}{360}[k_BT]^4 H'''(\mu) + \ldots$$

for quantum-mechanical thermal averages at low T

## Heat Capacity of the Electron Gas

**Classical statistical mechanics**:
free particle heat capacity 3/2 $k_B$ (for system of N atoms – 3/2 N$k_B$) ⇒ experimental value 0.01 ×3/2 N $k_B$

When sample is heated, only those electrons in orbitals within an energy range $k_BT$ of the Fermi level are excited thermally ⇒ only a fraction of the order $T/T_F$ can be excited thermally at temperature T

$$U \approx \left(\frac{NT}{T_F}\right) k_B T$$

At low temperature ($k_BT$<<$E_F$) we can derive a quantitative expression for the electronic heat capacity

$$\Delta U = \int_0^{\infty} ED(E) f(E) dE - \int_0^{E_F} ED(E) dE$$



## Specific Heat

For non-interacting electrons at low T

$$c_V = \frac{1}{V}\frac{\partial E}{\partial T}\Big|_{NV}$$

$$\frac{E}{V} =$$

$$\frac{\partial \mu}{\partial T}\Big|_{NV} = -\frac{\frac{\partial N}{\partial T}\Big|_{\mu V}}{\frac{\partial N}{\partial \mu}\Big|_{TV}}$$

$$N = V\int dE'$$

$$\frac{\partial \mu}{\partial T}\Big|_{NV} =$$



## Specialize to Free Fermi Gas

$$\mu = E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(E_F)}{D(E_F)}$$

As predicted, $c_V \propto D(E_F)\, T$
Linear coefficient, **Sommerfeld parameter** $\gamma = \frac{c_V}{T}$

## Experimental Heat Capacity of Metals

At T below both the Debye temperature and the Fermi temperature, the heat capacity has **electron** and **phonon** contributions:

$$C = \gamma T + A T^3,$$

where $\gamma$ (Sommerfeld parameter) and A are constants characteristic of the material

$$C/T = \gamma + A T^2$$

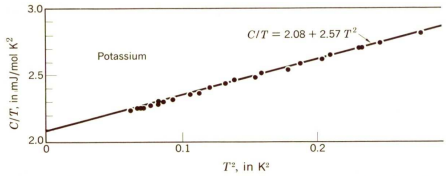



**Figure 6** Experimental heat capacity values for potassium, plotted as $C/T$ versus $T^2$. The solid points were determined with an adiabatic demagnetization cryostat. [After W. H. Lien and N. E. Phillips, Phys. Rev. **133**, A1370 (1964).]



## Comparison of free-electron estimate of Sommerfeld parameter with experiment

| Metal | Z | $\gamma$ (mJ mole$^{-1}$ K$^{-2}$) Expt. | Eq. (6.78) | Metal | Z | $\gamma$ (mJ mole$^{-1}$ K$^{-2}$) Expt. | Eq. (6.78) |
|---|---|---|---|---|---|---|---|
| Li | 1 | 1.65 | 0.74 | Al | 3 | 1.35 | 0.91 |
| Na | 1 | 1.38 | 1.09 | Ga | 3 | 0.60 | 1.02 |
| K | 1 | 2.08 | 1.67 | In | 3 | 1.66 | 1.23 |
| Rb | 1 | 2.63 | 1.90 | Sn | 4 | 1.78 | 1.41 |
| Cs | 1 | 3.97 | 2.22 | Pb | 4 | 2.99 | 1.50 |
| Cu | 1 | 0.69 | 0.50 | Sb | 5 | 0.12 | 1.61 |
| Ag | 1 | 0.64 | 0.64 | Bi | 5 | 0.008 | 1.79 |
| Au | 1 | 0.69 | 0.64 | Mn | 2 | 12.8 | 1.10 |
| Be | 2 | 0.17 | 0.5 | Fe | 2 | 4.90 | 1.06 |
| Mg | 2 | 1.6 | 0.99 | $UPt_3$ | | 450 | |
| Ca | 2 | 2.73 | 1.51 | $UBe_{13}$ | | 1100 | |
| Sr | 2 | 3.64 | 1.79 | | | | |
| Ba | 2 | 2.7 | 1.92 | | | | |

Heavy fermions

Marder, Table 6.2



## Connection with metal conductivity

**Read at home:**

- **DC Conductivity (Ohm's law)**
- **Wiedemann-Franz Law**

  The thermal conductivity $\kappa$ is the constant of proportionality between flux of thermal energy, Q, (energy/area time) and the temperature gradient (temperature/distance), where the energy flows in the opposite direction of the temperature gradient

  $Q = -\kappa \nabla T$, where $\kappa = L V_m \frac{N}{V} \frac{C_v}{3}$
- **Frequency Dependent Conductivity**

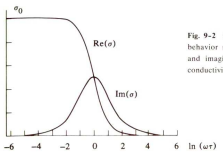



Fig. 9-2 Classical relaxation behavior shown by the real and imaginary parts of the conductivity.