# Outline of the Course (Computational Solid State Physics)

➢ **Fundamentals of basic solid state physics will be covered**

➢ **Modern Electronic structure calculations in solid state physics**

➢ **Practical methods of Band theory, Phonon dispersion, optical properties, response functions, semi-classical transport etc.**

➢ **Open-source Codes will be used from https://www.quantum-espresso.org/**

➢ **Coding is not required but basic knowledge of coding will be usefull. Basic knowledge Linux commands and editor like "vi".**

➢ **SSP Books: 1) Kittel 2) Ashcroft & Mermin**

➢ **Books: 1) Electronic structure by R. M. Martin 2) Atomic and electronic structure of solids by E. Kaxiras 3) Online tutorials**

➢ **You should be able to run code 1) directly on your laptop 2) or connect to IITH workstations**
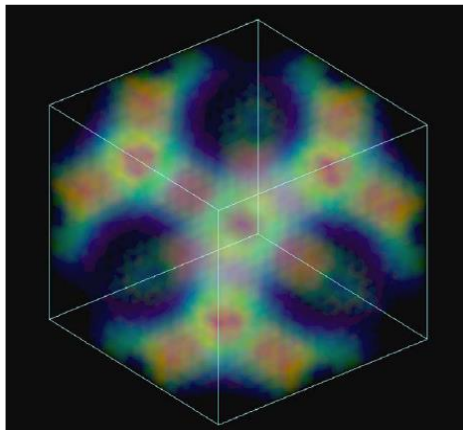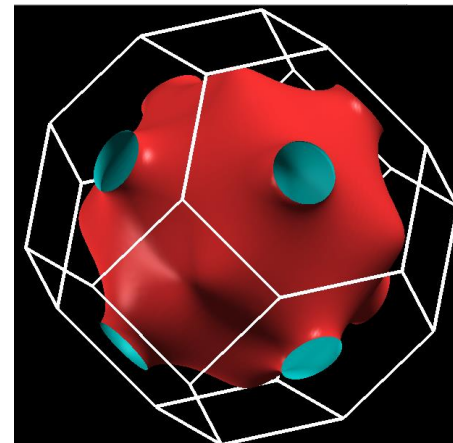
Simple examples of Electronic Structure calculations
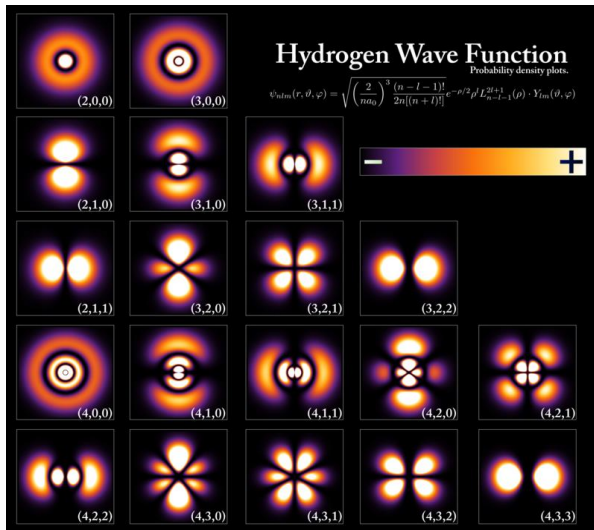
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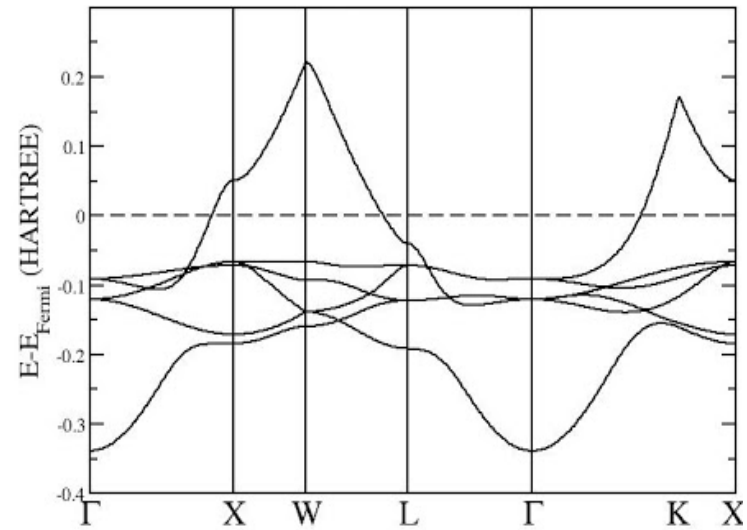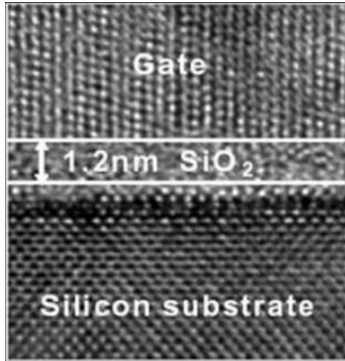

Band structure of Copper

Charge distribution in Silicon
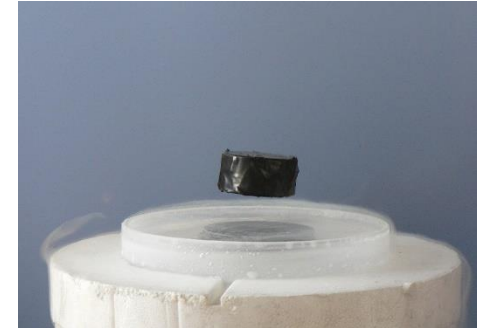

Fermi surface of Copper

Condensed matter and Solid State Systems as Quantum Fluids

Transistor

Diamond

Superconductor

➢ **A condensed matter system is 'Interacting system of quantum particles' of electrons, ions, quasiparticles, collective excitations etc.**

➢ **Emergence of new phenomena is defining feature of condensed matter systems (Ex: Band picture, Superconductivity, Superfluidity, New macroscopic quantum states, Topological order etc.)**

$$\Psi(r_1, r_2, r_3, \ldots \ldots \ldots, r_N)$$ Many-particle wavefunction $N = 1 - 10^{23}$

$$H\Psi(r_1, r_2, r_3 \ldots \ldots \ldots, r_N) = E\Psi(r_1, r_2, r_3 \ldots \ldots, r_N)$$ Many-particle Schrodinger Equation

Many-particle Quantum theory + Statistical Mechanics + Symmetry

Physics of Condensed matter and Solid State Systems

- A condensed matter system (CMS) is 'Interacting system of quantum particles' of electrons, ions, quasiparticles, collective excitations etc. (Quantum Fluids)

- Particles in Condensed matter and Solid State systems are fundamentally correlated and not independent

- Particle interactions arise due to Pauli exclusion principle, coulomb interaction etc.

- Condensed matter and Solid State system can be divided in two categories: 1) Weakly correlated systems 2) Strongly correlated systems

- Weakly correlated system: If the interacting particle system can be treated as independent particle system in some effective potential (Mean field theory)

- Strongly correlated system: If all the particles behave as a collective (Superfluid etc.)

- The degree of interaction or correlation among particles is determined by quantum exchange-correlation energies.

- Often the system can be studied depending on what we wish to study. In such cases a system can be modelled using simple effective model Hamiltonian

Properties of matter: Ground and Excited state properties

➢ **The properties of matter fall into two categories: 1) Electronic ground state 2) Electronic excited states**

- Ground state: cohesive energy, equilibrium crystal structure, phase transitions between structures, elastic constants, charge density, magnetic order, static dielectric and magnetic susceptibilities, nuclear vibrations and motion (in the adiabatic approximation), and many other properties.
- Excited states: low-energy excitations in metals involved in specific heat, Pauli spin susceptibility, transport, etc; higher energy excitations that determine insulating gaps in insulators, optical properties, spectra for adding or removing electrons, and many other properties.

Equation of interacting electrons and nuclei system (1/4)

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{U},$$ **Coupled elec.-nuclei Hamiltonian**

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},$$

$$\hat{H}\Psi_s(\{\mathbf{r}, \mathbf{R}\}) = E_s \Psi_s(\{\mathbf{r}, \mathbf{R}\}),$$ **Schrodinger Equa. of electron-nuclei system**

$$\{r\} \equiv (r_1, r_2, \ldots \ldots \ldots r_N) \equiv \text{All electron coordinates}$$

$$\{R\} \equiv (R_1, R_2, \ldots \ldots \ldots R_N) \equiv \text{All nuclei coordinates}$$

➢ **Coupled Electron-Nuclei equation can be decoupled and thus separated into electrons only and Nuclei only equations (Born-Oppenheimer approximation)**

➢ **Ions are ~2000-500000 times heavier than electrons and thus electrons adjust in new ground state almost instantly if we perturb nuclei**

➢ **Thus Electrons only Hamiltonian is obtained by ignoring the Nuclei kinetic energy (or it can be treated as perturbation to solve phonon problems)**

Basic Equations of interacting many-electrons system (2/4)

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},$$

Interacting electron Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}} + E_{II}. \qquad \hat{T} = \sum_i -\frac{1}{2}\nabla_i^2, \qquad \hat{V}_{\text{ext}} = \sum_{i,I} V_I(|\mathbf{r}_i - \mathbf{R}_I|), \qquad \hat{V}_{\text{int}} = \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

Schrodinger Equa. of interacting electrons system

$$i\hbar \frac{d\Psi(\{\mathbf{r}_i\};t)}{dt} = \hat{H}\,\Psi(\{\mathbf{r}_i\};t), \qquad \hat{H}|\Psi_m\rangle = E|\Psi\rangle. \qquad \Psi(\{\mathbf{r}_i\};t) \equiv \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; t),$$

➢ **Only electronic coordinates appear (Born-Oppenheimer approximation)**

➢ **Electrons interactions with nuclei appears as "external interaction". There can be other external fields as well**

➢ **Thus coupled electrons-nuclei system is now electrons only system in external field.**

Particle density of system

$$n(\mathbf{r}) = \frac{\langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle}{\langle\Psi|\Psi\rangle} = N\frac{\int d^3r_2\cdots d^3r_N\sum_{\sigma_1}|\Psi(\mathbf{r},\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)|^2}{\int d^3r_1 d^3r_2\cdots d^3r_N|\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)|^2}, \qquad \cdot\hat{n}(\mathbf{r}) = \sum_{i=1,N}\delta(\mathbf{r}-\mathbf{r}_i),$$

Total Energy of system

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \equiv \langle\hat{H}\rangle = \langle\hat{T}\rangle + \langle\hat{V}_{\text{int}}\rangle + \int d^3r\, V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{II},$$

$$E = \langle\hat{T}\rangle + (\langle\hat{V}_{\text{int}}\rangle - E_{\text{Hartree}}) + E^{CC},$$

$$E^{CC} = E_{\text{Hartree}} + \int d^3r\, V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{II},$$

Expression looks like Classical coulomb energy of many-electron system including interaction with nuclei

$$E_{\text{Hartree}} = \frac{1}{2}\int d^3r d^3r'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}.$$

Expression looks like Classical coulomb energy of many-electrons (also known as Hartree energy)

➢ **Energy of many-electron system = Total classical energy + Quantum corrections**

➢ **Quantum corrections to energy = Exchange energy + Correlation energy**

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3 r \, V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{II},$$

$$E = \langle \hat{T} \rangle + (\langle \hat{V}_{\text{int}} \rangle - E_{\text{Hartree}}) + E^{\text{CC}},$$

K.E	Exchange+ Correlation energy	Classical Coulomb

$$E^{\text{CC}} = E_{\text{Hartree}} + \int d^3 r \, V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{II},$$

$$E_{\text{Hartree}} = \frac{1}{2} \int d^3 r d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

➢ **Note that Hartree energy expression looks like classical coulomb interaction energy. However it is not exact classical coulomb energy since density is calculated using quantum mechanics**

➢ **We use the term classical since the expression looks like classical expression though charge density is calculated using quantum mechanics**

How to solve many-electrons Schrodinger Equations (1/2)

Schrodinger Equa. of interacting electrons system

$$\Psi(\{\mathbf{r}_i\}; t) \equiv \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; t),$$

$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}_l^2}{2M_l} + \frac{1}{2} \sum_{l \neq l'} \frac{q_l q_{l'}}{|\hat{R}_l - \hat{R}_{l'}|}. \qquad \hat{H}|\Psi_m\rangle = E|\Psi\rangle.$$

➢ Full equation is almost impossible to solve for large systems (N=10^23)

➢ Full solution may not be required and even desired

➢ Physics can be understood using simple effective model Hamiltonians

➢ Many useful approximations may be made depending on the given system

➢ For many practical problems, the many-particle equations can be approximated as series of independent single-particle equations

Approximations to solve many-electrons Schrodinger Equations (2/2)

$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}_l^2}{2M_l} + \frac{1}{2} \sum_{l \neq l'} \frac{q_l q_{l'}}{|\hat{R}_l - \hat{R}_{l'}|}$$

Nuclei treated as classical potentials. Many electrons combined with nuclei in closed shells to form ions.

All electronic degrees of freedom eliminated, turned to effective potential for ions. Phonon dynamics.

Ions treated as static potential. **Born-Oppenheimer approximation.**

Ions treated classically. Studies of cohesive energy, molecular dynamics.

Coulomb interaction incorporated self-consistently into lattice potential. **Single electron approximation**, partially justified by Fermi liquid theory

Ionic potential eliminated, interacting electrons move in uniform positive potential. **Jellium**, starting point for field theoretic work.

Ions arranged in a lattice, forming periodic potential for single electrons. Starting point for first-principles' calculations. Weak ionic potentials justified by **pseudopotentials.**

Ionic potential eliminated. **Free Fermi gas**, surprisingly effective with alkali metals.

Free Electron Gas Model (1/25)

- ➢ **The electrons are assumed to be independent without any interaction. However, electrons are treated as free quantum fermion particle obeying 'Pauli exclusion principle**

- ➢ **Many properties of metal can be understood using Free electron gas model**

- ➢ **Free electron gas model works due to weakening of e-e interactions due to Pauli exclusion principle (Landau's Fermi liquid theory).**

- ➢ **Free electron gas Model fails for many system as discussed later (See detailed notes in Ashcroft and Mermin)**

- ➢ **Notes in following slides are from book "Ashcroft and Mermin".**

GROUND-STATE PROPERTIES OF THE ELECTRON GAS

We must calculate the ground-state properties of N electrons confined to a volume V. Because the electrons do not interact with one another (independent electron approximation) we can find the ground state of the N electron system by first finding the energy levels of a single electron in the volume V, and then filling these levels up in a manner consistent with the Pauli exclusion principle, which permits at most one electron to occupy any single electron level.[6]

A single electron can be described by a wave function $\psi(\mathbf{r})$ and the specification of which of two possible orientations its spin possesses. If the electron has no interactions, the one electron wave function associated with a level of energy ε satisfies the time-independent Schrödinger equation[7]:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}). \qquad (2.4)$$

We shall represent the confinement of the electron (by the attraction of the ions) to the volume V by a boundary condition on Eq. (2.4). The choice of boundary condition, whenever one is dealing with problems that are not explicitly concerned with effects of the metallic surface, is to a considerable degree at one's disposal and can be determined by mathematical convenience, for if the metal is sufficiently large we should expect its *bulk* properties to be unaffected by the detailed configuration of its surface.[8] In this spirit we first select the shape of the metal to suit our analytic convenience. The time-honored choice is a cube[9] of side $L = V^{1/3}$.

Next we must append a boundary condition to the Schrödinger equation (2.4), reflecting the fact that the electron is confined to this cube. We also make this choice in the belief that it will not affect calculated bulk properties. One possibility is to require the wave function $\psi(\mathbf{r})$ to vanish whenever $\mathbf{r}$ is on the surface of the cube. This, however, is often unsatisfactory, for it leads to standing-wave solutions of (2.4), while the transport of charge and energy by the electrons is far more conveniently discussed in terms of running waves. A more satisfactory choice is to emphasize the inconsequence of the surface by disposing of it altogether. We can do this by imagining each face of the cube to be joined to the face opposite it, so that an electron coming to the surface is not reflected back in, but leaves the metal, simultaneously reentering at a corresponding point on the opposite surface. Thus, if our metal were one-dimensional, we would simply replace the line from 0 to L to which the electrons were confined, by a circle of circumference L. In three dimensions the geometrical embodiment of the boundary condition, in which the three pairs of opposite faces on the cube are joined, becomes topologically impossible to construct in three-dimensional space. Nevertheless, the analytic form of the boundary condition is easily generalized. In one dimension the circular model of a metal results in the boundary condition $\psi(x + L) = \psi(x)$, and the generalization to a three-dimensional cube is evidently

$$
\begin{aligned}
\psi(x, y, z + L) &= \psi(x, y, z), \\
\psi(x, y + L, z) &= \psi(x, y, z), \\
\psi(x + L, y, z) &= \psi(x, y, z).
\end{aligned}
\tag{2.5}
$$

Equation (2.5) is known as the Born-von Karman (or periodic) boundary condition. We shall encounter it often (sometimes in a slightly generalized[9] form).

We now solve (2.4) subject to the boundary condition (2.5). One can verify by differentiation that a solution, neglecting the boundary condition, is

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2.6}$$

with energy

$$\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}. \tag{2.7}$$

where **k** is any position independent vector. We have picked the normalization constant in (2.6) so that the probability of finding the electron *somewhere* in the whole volume V is unity:

$$1 = \int d\mathbf{r} \, |\psi(\mathbf{r})|^2. \tag{2.8}$$

To see the significance of the vector **k**, note that the level $\psi_k(\mathbf{r})$ is an eigenstate of the momentum operator,

$$\mathbf{p} = \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} = \frac{\hbar}{i} \nabla, \quad \left(p_x = \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad \text{etc.} \right), \tag{2.9}$$

with eigenvalue $\mathbf{p} = \hbar \mathbf{k}$, for

$$\frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar \mathbf{k} \, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{2.10}$$

In view of this the energy (2.7) can be written in the familiar classical form,

$$\varepsilon = \frac{p^2}{2m} = \tfrac{1}{2}mv^2. \tag{2.13}$$

We can also interpret **k** as a wave vector. The plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ is constant in any plane perpendicular to **k** (since such planes are defined by the equation $\mathbf{k}\cdot\mathbf{r} = $ constant) and it is periodic along lines parallel to **k**, with wavelength

$$\lambda = \frac{2\pi}{k}, \tag{2.14}$$

known as the de Broglie wavelength.

We now invoke the boundary condition (2.5). This permits only certain discrete values of **k**, since (2.5) will be satisfied by the general wave function (2.6) only if

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1. \tag{2.15}$$

Since $e^z = 1$ only if $z = 2\pi in$, where n is an integer,[10] the components of the wave vector **k** must be of the form:

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}. \qquad n_x, n_y, n_z \text{ integers.} \tag{2.16}$$

Thus in a three-dimensional space with Cartesian axes k_x, k_y, and k_z (known as k-space) the allowed wave vectors are those whose coordinates along the three axes are given by integral multiples of $2\pi/L$. This is illustrated (in two dimensions) in Figure 2.2.

Generally the only practical use one makes of the quantization condition (2.16) is this: One often needs to know how many allowed values of **k** are contained in a region of k-space that is enormous on the scale of $2\pi/L$, and that therefore contains a vast number of allowed points. If the region is very large,[11] then to an excellent approximation the number of allowed points is just the volume of k-space contained within the region, divided by the volume of k-space per point in the network of

allowed values of **k**. That latter volume (see Figure 2.2) is just $(2\pi/L)^3$. We therefore conclude that a region of k-space of volume Ω will contain

$$\frac{\Omega}{(2\pi/L)^3} = \frac{\Omega V}{8\pi^3} \qquad (2.17)$$

allowed values of **k**, or, equivalently, that the number of allowed k-values per unit volume of k-space (also known as the k-space density of levels) is just

$$\frac{V}{8\pi^3}. \qquad (2.18)$$

In practice we shall deal with k-space regions so large ($\sim 10^{22}$ points) and so regular (typically spheres) that to all intents and purposes (2.17) and (2.18) can be regarded as exact. We shall begin to apply these important counting formulas shortly.
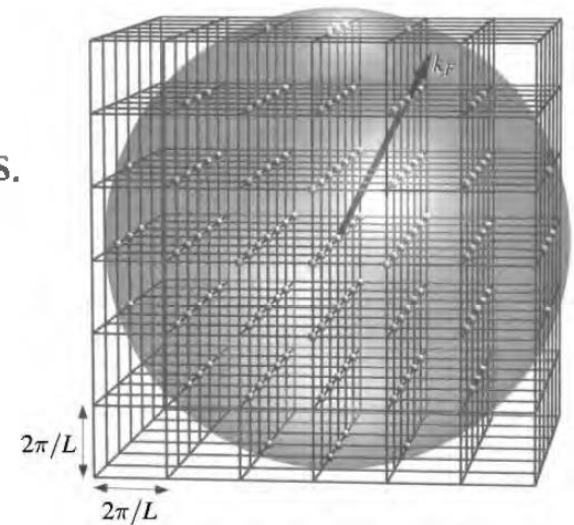
Figure 2.2
Points in a two-dimensional k-space of the form $k_x = 2\pi n_x / L$. $k_y = 2\pi n_y / L$. Note that the area per point is just $(2\pi / L)^2$. In d dimensions the volume per point is $(2\pi / L)^d$.
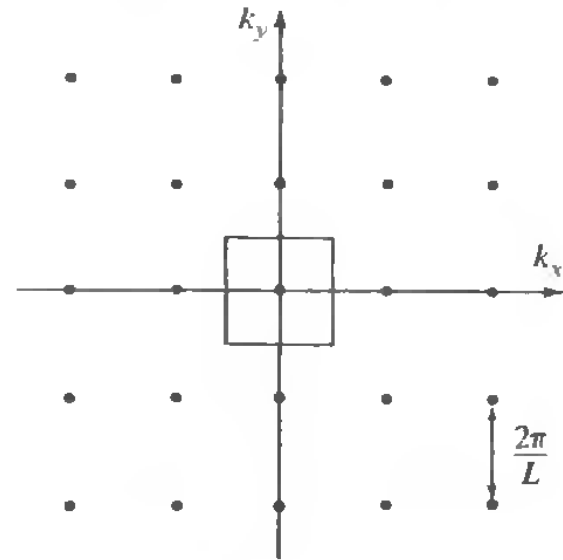
$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}. \qquad n_x, n_y, n_z \text{ integers.}$$

Because we assume the electrons are noninteracting we can build up the N-electron ground state by placing electrons into the allowed one-electron levels we have just found. The Pauli exclusion principle plays a vital role in this construction (as it does in building up the states of many electron atoms): we may place at most one electron in each single electron level. The one-electron levels are specified by the wave vectors $\mathbf{k}$ and by the projection of the electron's spin along an arbitrary axis, which can take either of the two values $h/2$ or $-h/2$. Therefore associated with each allowed wave vector $\mathbf{k}$ are *two* electronic levels, one for each direction of the electron's spin.

Thus in building up the N-electron ground state we begin by placing two electrons in the one-electron level $\mathbf{k} = 0$, which has the lowest possible one-electron energy $\varepsilon = 0$. We then continue to add electrons, successively filling the one-electron levels of lowest energy that are not already occupied. Since the energy of a one-electron level is directly proportional to the square of its wave vector (see (2.7)), when N is enormous the occupied region will be indistinguishable from a sphere.[12] The radius of this sphere is called k_F (F for Fermi), and its volume Ω is $4\pi k_F^3/3$. According to (2.17) the number of allowed values of $\mathbf{k}$ within the sphere is

$$\left(\frac{4\pi k_F^3}{3}\right)\left(\frac{V}{8\pi^3}\right) = \frac{k_F^3}{6\pi^2}\, V. \tag{2.19}$$

Since each allowed k-value leads to two one-electron levels (one for each spin value), in order to accommodate N electrons we must have

$$N = 2 \cdot \frac{k_F{}^3}{6\pi^2} V = \frac{k_F{}^3}{3\pi^2} V. \qquad (2.20)$$

Thus if we have N electrons in a volume V (i.e., an electronic density $n = N/V$), then the ground state of the N-electron system is formed by occupying all single-particle levels with k less than k_F, and leaving all those with k greater than k_F unoccupied, where k_F is given by the condition:

$$n = \frac{k_F{}^3}{3\pi^2}. \qquad (2.21)$$

The surface of the Fermi sphere, which separates the occupied from the unoccupied levels is called the *Fermi surface*. (We shall see, starting with Chapter 8, that the Fermi surface is one of the fundamental constructions in the modern theory of metals; in general it is not spherical.)

The momentum $\hbar k_F = p_F$ of the occupied one-electron levels of highest energy is known as the *Fermi momentum*; their energy, $\mathcal{E}_F = \hbar^2 k_F{}^2/2m$ is the *Fermi energy*; and their velocity, $v_F = p_F/m$, is the *Fermi velocity*. The Fermi velocity plays a role in the theory of metals comparable to the thermal velocity, $v = (3k_B T/m)^{1/2}$, in a classical gas.

All these quantities can be evaluated in terms of the conduction electron density, via Eq. (2.21). For estimating them numerically it is often more convenient to express them in terms of the dimensionless parameter r_s/a_0 (see page 4), which varies from about 2 to 6 in the metallic elements. Taken together, Eqs. (1.2) and (2.21) give

$$k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{1.92}{r_s}, \qquad (2.22)$$

or

$$k_F = \frac{3.63}{r_s/a_0} \text{Å}^{-1}. \qquad (2.23)$$

Since the Fermi wave vector is of the order of inverse angstroms, the de Broglie wavelength of the most energetic electrons is of the order of angstroms.

The Fermi velocity is

$$v_F = \left(\frac{\hbar}{m}\right) k_F = \frac{4.20}{r_s/a_0} \times 10^8 \text{ cm/sec.} \qquad (2.24)$$

This is a substantial velocity (about 1 percent of the velocity of light). From the viewpoint of classical statistical mechanics this is quite a surprising result, for we are describing the ground state ($T = 0$), and all particles in a classical gas have zero velocity at $T = 0$. Even at room temperature the thermal (i.e., average) velocity for a classical particle with the electronic mass is only of order 10^7 cm/sec.

The Fermi energy is conveniently written in the form (since $a_0 = \hbar^2/me^2$)

$$\mathcal{E}_F = \frac{\hbar^2 k_F{}^2}{2m} = \left(\frac{e^2}{2a_0}\right)(k_F a_0)^2. \tag{2.25}$$

Here $e^2/2a_0$, known as the rydberg (Ry), is the ground-state binding energy of the hydrogen atom, 13.6 electron volts.[13] The rydberg is as convenient a unit of atomic energies as the Bohr radius is of atomic distances. Since $k_F a_0$ is of the order of unity, Eq. (2.25) demonstrates that the Fermi energy has the magnitude of a typical atomic binding energy. Using (2.23) and $a_0 = 0.529 \times 10^{-8}$ cm, we find the explicit numerical form:

$$\mathcal{E}_F = \frac{50.1 \text{ eV}}{(r_s/a_0)^2}, \tag{2.26}$$

indicating a range of Fermi energies for the densities of metallic elements between 1.5 and 15 electron volts.

FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS[a]

ELEMENT	r_s/a_0	$\mathcal{E}_F$	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	1.12×10^8 cm^{-1}	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40

To calculate the ground-state energy of N electrons in a volume V we must add up the energies of all the one-electron levels inside the Fermi sphere[14]:

$$E = 2 \sum_{k < k_F} \frac{\hbar^2}{2m} k^2. \tag{2.27}$$

Quite generally, in summing any smooth function $F(\mathbf{k})$ over all allowed values of $\mathbf{k}$, one may proceed as follows:

Because the volume of k-space per allowed $\mathbf{k}$ value is $\Delta\mathbf{k} = 8\pi^3/V$ (see Eq. (2.18)) it is convenient to write

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{V}{8\pi^3} \sum_{\mathbf{k}} F(\mathbf{k}) \, \Delta\mathbf{k}, \tag{2.28}$$

for in the limit as $\Delta\mathbf{k} \to 0$ (i.e., $V \to \infty$) the sum $\Sigma F(\mathbf{k}) \, \Delta\mathbf{k}$ approaches the integral $\int d\mathbf{k} \, F(\mathbf{k})$, provided only that $F(\mathbf{k})$ does not vary appreciably[15] over distances in k-space of order $2\pi/L$. We may therefore rearrange (2.28) and write

$$\lim_{V \to \infty} \frac{1}{V} \sum_{\mathbf{k}} F(\mathbf{k}) = \int \frac{d\mathbf{k}}{8\pi^3} F(\mathbf{k}). \tag{2.29}$$

In applying (2.29) to finite, but macroscopically large, systems one always assumes that $(1/V) \, \Sigma F(\mathbf{k})$ differs negligibly from its infinite volume limit (for example, one assumes that the electronic energy per unit volume in a 1-cm cube of copper is the same as in a 2-cm cube).

Using (2.29) to evaluate (2.27), we find that the energy density of the electron gas is:

$$\frac{E}{V} = \frac{1}{4\pi^3} \int_{k<k_F} d\mathbf{k} \, \frac{\hbar^2 k^2}{2m} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}. \tag{2.30}$$

To find the energy per electron, E/N, in the ground state, we must divide this by $N/V = k_F^3/3\pi^2$, which gives

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} \mathcal{E}_F. \tag{2.31}$$

We can also write this result as

$$\frac{E}{N} = \frac{3}{5} k_B T_F \tag{2.32}$$

where T_F, the *Fermi temperature*, is

$$\boxed{T_F = \frac{\mathcal{E}_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4 \text{ K}.} \tag{2.33}$$

Note, in contrast to this, that the energy per electron in a classical ideal gas, $\frac{3}{2}k_B T$, vanishes at $T = 0$ and achieves a value as large as (2.32) only at $T = \frac{2}{5}T_F \approx 10^4$ K.

Given the ground-state energy E, one can calculate the pressure exerted by the electron gas from the relation $P = -(\partial E/\partial V)_N$. Since $E = \frac{3}{5}N\mathcal{E}_F$ and $\mathcal{E}_F$ is proportional to $k_F{}^2$, which depends on V only through a factor $n^{2/3} = (N/V)^{2/3}$, it follows that[16]

$$P = \frac{2}{3}\frac{E}{V}. \tag{2.34}$$

One can also calculate the compressibility, K, or bulk modulus, $B = 1/K$, defined by:

$$B = \frac{1}{K} = -V\frac{\partial P}{\partial V}. \tag{2.35}$$

Since E is proportional to $V^{-2/3}$, Eq. (2.34) shows that P varies as $V^{-5/3}$, and therefore

$$B = \frac{5}{3}P = \frac{10}{9}\frac{E}{V} = \frac{2}{3}n\mathcal{E}_F \tag{2.36}$$

or

$$B = \left(\frac{6.13}{r_s/a_0}\right)^5 \times 10^{10} \text{ dynes/cm}^2. \tag{2.37}$$

BULK MODULI IN 10^{10} DYNES/CM^2 FOR SOME TYPICAL METALS[a]

METAL	FREE ELECTRON B	MEASURED B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76.0

[a] The free electron value is that for a free electron gas at the observed density of the metal, as calculated from Eq. (2.37).

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: THE FERMI-DIRAC DISTRIBUTION

When the temperature is not zero it is necessary to examine the excited states of the N-electron system as well as its ground state, for according to the basic principles of statistical mechanics, if an N-particle system is in thermal equilibrium at temperature T, then its properties should be calculated by averaging over all N-particle stationary states, assigning to each state of energy E a weight $P_N(E)$ proportional to e^{-E/k_BT}:

$$P_N(E) = \frac{e^{-E/k_BT}}{\Sigma e^{-E_\alpha^N/k_BT}}. \qquad (2.38)$$

(Here E_α^N is the energy of the αth stationary state of the N-electron system, the sum being over all such states.)

Because of the exclusion principle, to construct an N-electron state one must fill N different one-electron levels. Thus each N-electron stationary state can be specified by listing which of the N one-electron levels are filled in that state. A very useful quantity to know is f_i^N, the probability of there being an electron in the particular one-electron level i, when the N-electron system is in thermal equilibrium.[17] This probability is simply the sum of the independent probabilities of finding the N-electron system in any one of those N-electron states in which the ith level is occupied:

$$f_i^N = \sum P_N(E_\alpha{}^N) \qquad \text{(summation over all } N\text{-electron states } \alpha \text{ in which there is an electron in the one-electron level } i\text{).} \qquad (2.41)$$

$$f_i^N = \frac{1}{e^{(\varepsilon_i - \mu)/k_B T} + 1}.$$

$$N = \sum_i f_i = \sum_i \frac{1}{e^{(\varepsilon_i - \mu)/k_B T} + 1},$$

THERMAL PROPERTIES OF THE FREE ELECTRON GAS: APPLICATIONS OF THE FERMI-DIRAC DISTRIBUTION

In a gas of free and independent electrons the one-electron levels are specified by the wave vector $\mathbf{k}$ and spin quantum number s, with energies that are independent of s (in the absence of a magnetic field) and given by Eq. (2.7); i.e.,

$$\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}. \qquad (2.50)$$

We first verify that the distribution function (2.49) is consistent with the ground-state $(T = 0)$ properties derived above. In the ground state those and only those levels are occupied with $\mathcal{E}(\mathbf{k}) \leqslant \mathcal{E}_F$, so the ground-state distribution function must be

$$
\begin{aligned}
f_{\mathbf{k}s} &= 1, \quad \mathcal{E}(\mathbf{k}) < \mathcal{E}_F; \\
&= 0, \quad \mathcal{E}(\mathbf{k}) > \mathcal{E}_F.
\end{aligned}
\qquad (2.51)
$$

On the other hand, as $T \to 0$, the limiting form of the Fermi-Dirac distribution (2.48) is

$$
\begin{aligned}
\lim_{T \to 0} f_{\mathbf{k}s} &= 1, \quad \mathcal{E}(\mathbf{k}) < \mu; \\
&= 0, \quad \mathcal{E}(\mathbf{k}) > \mu.
\end{aligned}
\qquad (2.52)
$$

For these to be consistent it is necessary that

$$\lim_{T \to 0} \mu = \mathcal{E}_F. \qquad (2.53)$$

We shall see shortly that for metals the chemical potential remains equal to the Fermi energy to a high degree of precision, all the way up to room temperature. As a result, people frequently fail to make any distinction between the two when dealing with metals. This, however, can be dangerously misleading. In precise calculations it is essential to keep track of the extent to which μ, the chemical potential, differs from its zero temperature value. ε_F.

The most important single application of Fermi-Dirac statistics is the calculation of the electronic contribution to the constant-volume specific heat of a metal,

$$c_v = \frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial u}{\partial T}\right)_V, \qquad u = \frac{U}{V}. \tag{2.54}$$

In the independent electron approximation the internal energy U is just the sum over one-electron levels of $\varepsilon(\mathbf{k})$ times the mean number of electrons in the level[22]:

$$U = 2\sum_{\mathbf{k}} \varepsilon(\mathbf{k})f(\varepsilon(\mathbf{k})). \tag{2.55}$$

We have introduced the *Fermi function* $f(\varepsilon)$ to emphasize that $f_{\mathbf{k}}$ depends on $\mathbf{k}$ only through the electronic energy $\varepsilon(\mathbf{k})$:

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}. \tag{2.56}$$

If we divide both sides of (2.55) by the volume V, then (2.29) permits us to write the energy density $u = U/V$ as

$$u = \int \frac{d\mathbf{k}}{4\pi^3} \, \mathcal{E}(\mathbf{k}) f(\mathcal{E}(\mathbf{k})). \tag{2.57}$$

If we also divide both sides of (2.49) by V, then we can supplement (2.57) by an equation for the electronic density $n = N/V$, and use it to eliminate the chemical potential:

$$n = \int \frac{d\mathbf{k}}{4\pi^3} \, f(\mathcal{E}(\mathbf{k})). \tag{2.58}$$

In evaluating integrals like (2.57) and (2.58) of the form

$$\int \frac{d\mathbf{k}}{4\pi^3} \, F(\mathcal{E}(\mathbf{k})), \tag{2.59}$$

one often exploits the fact that the integrand depends on $\mathbf{k}$ only through the electronic energy $\mathcal{E} = \hbar^2 k^2/2m$, by evaluating the integral in spherical coordinates and changing variables from k to $\mathcal{E}$:

$$\int \frac{d\mathbf{k}}{4\pi^3} \, F(\mathcal{E}(\mathbf{k})) = \int_0^\infty \frac{k^2 \, dk}{\pi^2} \, F(\mathcal{E}(\mathbf{k})) = \int_{-\infty}^\infty d\mathcal{E}\, g(\mathcal{E}) F(\mathcal{E}). \tag{2.60}$$

Here

$$g(\mathcal{E}) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\mathcal{E}}{\hbar^2}}, \quad \mathcal{E} > 0;$$

$$= 0, \qquad\qquad\qquad \mathcal{E} < 0. \tag{2.61}$$

Since the integral (2.59) is an evaluation of $(1/V) \sum_{ks} F(\mathcal{E}(\mathbf{k}))$, the form in (2.60) shows that

$$g(\mathcal{E}) \, d\mathcal{E} = \left(\frac{1}{V}\right) \times [\text{the number of one-electron levels in the energy range from } \mathcal{E} \text{ to } \mathcal{E} + d\mathcal{E}]. \tag{2.62}$$

For this reason $g(\mathcal{E})$ is known as the density of levels per unit volume (or often simply as the density of levels). A dimensionally more transparent way of writing g is

$$g(\mathcal{E}) = \frac{3}{2} \frac{n}{\mathcal{E}_F} \left(\frac{\mathcal{E}}{\mathcal{E}_F}\right)^{1/2}, \quad \mathcal{E} > 0;$$
$$= 0, \qquad\qquad \mathcal{E} < 0, \tag{2.63}$$

where $\mathcal{E}_F$ and k_F are *defined* by the zero-temperature equations (2.21) and (2.25). A quantity of particular numerical importance is the density of levels at the Fermi energy, which (2.61) and (2.63) give in either of the two equivalent forms:

$$g(\mathcal{E}_F) = \frac{mk_F}{\hbar^2 \pi^2} \tag{2.64}$$

or

$$g(\mathcal{E}_F) = \frac{3}{2} \frac{n}{\mathcal{E}_F}. \tag{2.65}$$

Using this notation, we rewrite (2.57) and (2.58) as:

$$u = \int_{-\infty}^{\infty} d\mathcal{E}\, g(\mathcal{E})\mathcal{E}f(\mathcal{E}) \qquad (2.66)$$

and

$$n = \int_{-\infty}^{\infty} d\mathcal{E}\, g(\mathcal{E})f(\mathcal{E}). \qquad (2.67)$$

We do this both for notational simplicity *and* because in this form the free electron approximation enters only through the particular evaluation (2.61) or (2.63) of the density of levels g. We can define a density of levels, via (2.62), in terms of which (2.66) and (2.67) remain valid for any set of noninteracting (that is, independent) electrons.[23] Thus we shall later be able to apply results deduced from (2.66) and (2.67) to considerably more sophisticated models of independent electrons in metals.
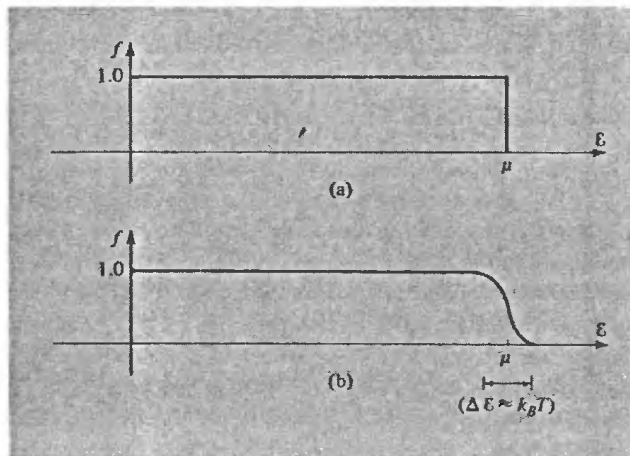

Figure 2.3

The Fermi function, $f(\mathcal{E}) = 1/[e^{\beta(\mathcal{E}-\mu)} + 1]$ versus $\mathcal{E}$ for given μ, at (a) $T = 0$ and (b) $T \approx 0.01\mu$ (of order room temperature, at typical metallic densities). The two curves differ only in a region of order $k_B T$ about μ.

$$\int_{-\infty}^{\infty} H(\mathcal{E}) f(\mathcal{E})\, d\mathcal{E}$$

$$= \int_{-\infty}^{\mu} H(\mathcal{E})\, d\mathcal{E} + \frac{\pi^2}{6} (k_B T)^2 H'(\mu) + \frac{7\pi^4}{360} (k_B T)^4 H'''(\mu) + O\left(\frac{k_B T}{\mu}\right)^6.$$

$$\mu = \mathcal{E}_F\left[1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\mathcal{E}_F}\right)^2\right], \qquad c_v = \left(\frac{\partial u}{\partial T}\right)_n = \frac{\pi^2}{3} k_B^2 T g(\mathcal{E}_F) \qquad c_v = \frac{\pi^2}{2}\left(\frac{k_B T}{\mathcal{E}_F}\right) n k_B.$$

$$\frac{c_v}{T} = \gamma + A T^2.$$

SOME ROUGH EXPERIMENTAL VALUES FOR THE COEFFICIENT OF THE LINEAR TERM IN T OF THE MOLAR SPECIFIC HEATS OF METALS, AND THE VALUES GIVEN BY SIMPLE FREE ELECTRON THEORY

ELEMENT	FREE ELECTRON γ	MEASURED γ	RATIO[a]
	(in 10^{-4} cal-mole^{-1}-K^{-2})		(m^*/m)
Li	1.8	4.2	2.3
Na	2.6	3.5	1.3
K	4.0	4.7	1.2
Rb	4.6	5.8	1.3
Cs	5.3	7.7	1.5
Cu	1.2	1.6	1.3
Ag	1.5	1.6	1.1

DIFFICULTIES WITH THE FREE ELECTRON MODEL

1. **Inadequacies in the Free Electron Transport Coefficients**

    (a) *The Hall Coefficient*   Free electron theory predicts a Hall coefficient which at metallic densities of electrons has the constant value $R_H = -1/nec$, independent of the temperature, the relaxation time, or the strength of the magnetic field. Although observed Hall coefficients have this order of magnitude, generally speaking they depend on both the magnetic field strength and the temperature (and presumably on the relaxation time, which is rather harder to control experimentally). Often this dependence is quite dramatic. In aluminum, for example, R_H (see Figure 1.4) never gets within a factor of three of the free electron value, depends strongly on the strength of the field, and at high fields does not even have the sign predicted by free electron theory. Such cases are not atypical. Only the Hall coefficients of the alkali metals come even close to behaving in accordance with the predictions of free electron theory.

    (b) *The Magnetoresistance*   Free electron theory predicts that the resistance of a wire perpendicular to a uniform magnetic field should not depend on the strength of the field. In almost all cases it does. In some cases (notably the noble metals, copper, silver, and gold) it can be made to increase apparently without limit as the field increases. In most metals the behavior of the resistance in a field depends quite drastically on the manner in which the metallic specimen is prepared and, for suitable specimens, on the orientation of the specimen with respect to the field.

(c) **The Thermoelectric Field**   The sign of the thermoelectric field, like the sign of the Hall constant, is not always what free electron theory predicts it should be. Only the order of magnitude is right.

(d) **The Wiedemann-Franz Law**   That great triumph of free electron theory, the Wiedemann-Franz law, is obeyed beautifully at high (room) temperatures and also quite probably at very low (a few degrees K) temperatures. At intermediate temperatures it fails, and $\kappa/\sigma T$ depends on the temperature.

(e) **Temperature Dependence of the DC Electrical Conductivity**   Nothing in free electron theory can account for the temperature dependence of the DC conductivity (revealed, for example, in Table 1.2). It has to be mechanically inserted into the theory as an *ad hoc* temperature dependence in the relaxation time τ.

(f) **Directional Dependence of the DC Electrical Conductivity**   In some (but by no means all) metals the DC conductivity depends on the orientation of the specimen (if suitably prepared) with respect to the field. In such specimens the current **j** need not even be parallel to the field.

(g) **AC Conductivity**   There is a far more subtle frequency dependence to the optical properties of metals than the simple free electron dielectric constant can hope to produce. Even sodium, in other respects a fairly good free electron metal, appears to fail this test in the detailed frequency dependence of its reflectivity. In other metals the situation is far worse. We cannot begin to explain the colors of copper and gold in terms of reflectivities calculated from the free electron dielectric constant.