PHY 481/581 Intro Nano-MSE:
Applying simple Quantum Mechanics to nanoscience problems, part II
Potential Barrier Penetration: Potential Step

We divide the system into two regions (I and II). In region I, the particle is free to move around as the potential energy $V = 0$. The Schrödinger equation can be simplified to

$$-\frac{\hbar^2}{8m\pi^2} \frac{d^2\psi_I}{dx^2} = E\psi_I$$

$$k^2 = \frac{8m\pi^2E}{\hbar^2}$$

Since the particle can travel in the forward as well as backward directions, we can express the wavefunction as

$$\psi_I(x) = Fe^{ikx} + Ge^{-ikx}$$

where the first term represents the incident wave while the second term represents the reflected wave. $F$ and $G$ are coefficients that can be determined using the boundary conditions.
For region II, the potential has a finite height of $V_o$ such that $V_o > E$, where $E$ is the energy of the particle. The Schrödinger equation can be expressed as

$$ -\frac{\hbar^2}{8m\pi^2} \frac{d^2\psi_{II}}{dx^2} = (E - V_o)\psi_{II} \quad (3.37) $$

We simply change sign to avoid going complex.

$$ \frac{d^2\psi_{II}}{dx^2} = \kappa^2 \psi_{II} \quad \kappa^2 = \frac{8m\pi^2(V_o - E)}{\hbar^2} $$

$$ \psi_{II}(x) = He^{-\kappa x} \quad (3.39) $$

To determine the coefficients $F$, $G$ and $H$ in Eqs. (3.36) and (3.39), $\psi(x)$ and $d\psi(x)/dx$ must be continuous at the boundary points $x = 0$. We have

$$ \psi_{I}(0) = \psi_{II}(0) \quad (3.40) $$

$$ \frac{d\psi_{I}}{dx} = \frac{d\psi_{II}}{dx} \quad (3.41) $$

and thus

$$ F + G = H \quad ik(F - G) = -\kappa H $$
For region I

\[ \psi_I(x) = F \left( e^{ikx} + \frac{ik + \kappa}{ik - \kappa} e^{-ikx} \right) \] (3.42)

For region II

\[ \psi_{II}(x) = F \frac{2ik}{ik - \kappa} e^{-\kappa x} \] (3.43)

Hence we can see that \( \psi(x) \) is non-zero inside the potential step and thus it is possible for a particle to penetrate into the potential barrier! This is not allowed in classical physics.

\( \psi_{II} \) is called the evanescent wave, it is rapidly (exponentially) decaying, also note that it has a real exponent, so it is not traveling (as the exponent cannot be converted into \( \cos \kappa x - i \sin \kappa x \) as we can for \( \psi_I \)), it cannot be detected in the barrier as it would not move into any detector, but has a non-zero probability density of being detected there

Also note that \( \psi_I \) is actually the sum of two traveling waves, one traveling to the right, (i.e. coming in) with \( \exp (ikx) \) and one traveling to the left with \( \exp (-ikx) \) being reflected, for a stream of particles, all particles are accounted for as many come in, as many get reflected, no particles disappears into the barrier
Potential Barrier and Quantum Tunneling

As mentioned in the previous section, there is a probability that the wavefunction can penetrate into the potential step. This situation becomes very interesting if the potential step is replaced by a potential barrier. If the potential barrier width $W$ is narrow, it is possible for a particle to penetrate through the potential barrier and appear on the other side! This phenomenon is known as quantum tunneling. Let us consider the potential barrier shown in Fig. 3.8. We divide the system into three region I, II and III as shown.
For regions I and III with $V = 0$, the Schrödinger equation is given by Eq. (3.34) hence we can write down the wavefunction as

$$\psi_I(x) = P e^{ikx} + Q e^{-ikx} \quad (3.44)$$

and

$$\psi_{III}(x) = S e^{ikx} \quad (3.45)$$

We have to account for the presence of the reflected wave in region I while there is no reflected wave in region III.

The intensities of the incident, reflected and transmitted probability current densities, $J$, are given by

$$J = v |P|^2, \quad J = v |Q|^2, \quad J = v |S|^2 \quad (3.46)$$

where $v = \frac{\hbar k}{m}$ represents the magnitude of the velocity of the particle. The reflection coefficient $R$ and the transmission coefficient $T$ add up to unity, no particle gets stuck in the barrier in other words, it is just that the amplitude of the transmitted wave will be smaller than the amplitude of the incoming wave, because there is also a reflected wave. (remember: amplitude corresponds to number of particles)
are respectively given by

\[ R = \frac{|Q|^2}{|P|^2} \]  \hspace{1cm} (3.47)

\[ T = \frac{|S|^2}{|P|^2} \]  \hspace{1cm} (3.48)

Similarly, for region II, the Schrödinger equation is given by Eq. (3.37). The wavefunction is therefore

\[ \psi_{II}(x) = Ue^{\kappa x} + Ve^{-\kappa x} \]  \hspace{1cm} (3.49)

To determine the coefficients in the wavefunctions, we make use of boundary conditions again.

\[ R = \left[ 1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(\kappa W)} \right]^{-1} \]  \hspace{1cm} (3.52)

\[ T = \left[ 1 + \frac{V_0^2 \sinh^2(\kappa W)}{4E(V_0 - E)} \right]^{-1} \]  \hspace{1cm} (3.53)

Note that \( \sinh(x) = \frac{e^x - e^{-x}}{2} \) and \( \cosh(x) = \frac{e^x + e^{-x}}{2} \).
If \( \kappa W \gg 1 \), then we can use the approximation \( \sinh(\kappa W) \sim \frac{1}{2} \exp(\kappa W) \), and the transmission coefficient becomes

\[
T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2\kappa W}
\]

(3.54)

The probability that the particle can tunnel through the barrier thus depends on the barrier width and the barrier potential height. This relation is an important result for quantum tunneling and the scanning tunneling microscope (see Chapter 8).

The pre-factor in front of the exponential is frequently set to unity as another approximation.

Note the difference \( (V_0 - E) \), the mass of the particle, the widths of the barrier, and h-bar are all in the exponent.

So if the mass is large, tunneling to some appreciable amount is not going to happen even if \( V_0 \) is very close to \( E \) and \( W \) is comparably small.
Analogy effect for classical waves

- If light passing through a glass prism reflects from an internal surface with an angle greater than the critical angle, total internal reflection occurs. However, the electromagnetic field is not exactly zero just outside the prism. If we bring another prism very close to the first one, experiments show that the electromagnetic wave (light) appears in the second prism. The situation is analogous to the tunneling described here. This effect was observed by Newton and can be demonstrated with two prisms and a laser. The intensity of the second light beam decreases exponentially as the distance between the two prisms increases.

- Light is totally internally reflected due to sudden change in refractive index from glass to air,
- for the critical angle of total internal reflection, this constitutes a barrier that cannot be penetrated, the mathematics of the classical (Helmholtz wave equation, however, requires an evanescent wave)

- Water waves tunnel as well, a situation analogous to total internal reflection has been set up in a water tank, a sudden increase in the water depth corresponds to a barrier where the water waves should speed up, reducing that barrier allows for the energy of the water wave to tunnel through the barrier and move away on the other side.
HYDROGEN-LIKE ATOMS: ORBITALS AND ATOMIC STRUCTURES

\[ V = - \frac{Ze^2}{4\pi\varepsilon_0 r} \]

\[- \frac{\hbar^2}{8m\pi^2} \left( \frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} \right) - \frac{Ze^2}{4\pi\varepsilon_0 r} \psi = E\psi \quad (3.56)\]

\[ x = r \sin(\theta)\cos(\phi) \]
\[ y = r \sin(\theta)\sin(\phi) \]
\[ z = r \cos(\theta) \]
\[ r = \sqrt{x^2 + y^2 + z^2} \]

1/r is the only variable of the potential (Z is just 1, 2 or 3), this is called a central force potential

\[ \psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \]

Figure 3.11. Relationship between spherical coordinates and cartesian coordinates.

In spherical coordinates, Eq. (3.56) takes the form

\[- \frac{\hbar^2}{8m\pi^2} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right) \psi \]

\[- \frac{Ze^2}{4\pi\varepsilon_0 r} \psi = E\psi \quad (3.62)\]
Same energy level formulae is obtained from Bohr’s model, also Bohr radius for the hydrogen atom, (which gives the most probable radial position of finding the electron when the atom is in the ground state, in a so called 1s orbital)

\[ E = -\frac{RhcZ^2}{n^2} \]  \hspace{1cm} (3.57)

where \( R \) is known as the Rydberg constant \( (= 1.0974 \times 10^7 \text{ m}^{-1}) \), and \( c \) corresponds to the speed of light. \( n \) is the principal quantum number and its value ranges from 1 to \( \infty \). A common form of the equation expressed in units of electron volts is given by

\[ E = -\frac{13.6Z^2}{n^2} \text{ (eV)} \]  \hspace{1cm} (3.58)

For \( Z = 1 \), hydrogen,

\[ E_n = E_0/n^2 \]

\( Z = 1, 2, 3 \), but there is only one electron going somehow around the respective nucleus, which contains 1, 2, or 3 protons

So it is numerically OK that special relativity is neglected, but conceptually we are missing the forth dimension of space time, i.e. a forth quantum number

Where \( \alpha \approx 1/137 \), fine structure constant, ratio of the speed of the electron in hydrogen in the first Bohr orbit to the speed of light
Spectral lines in the absence of a magnetic field (that would lift the degeneracies that are due to the very height symmetry of the potential energy function)

Energy levels of H, He$^+$ and Li$^{2+}$.

\[ E = -\frac{13.6eV \cdot Z^2}{n^2} \]

\[ E_{\text{photon}} = RhcZ^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \]
Degeneracy

- Analysis of the Schrödinger wave equation in three dimensions introduces three quantum numbers that quantize the energy.

- A quantum state is degenerate when there is more than one wave function for a given energy.

- Degeneracy results from particular properties of the potential energy function that describes the system. A breaking of the symmetry of the potential energy function removes the degeneracy or may create a different type of degeneracy.
Since it is a 3D problem, there needs to be 3 quantum numbers, $n$ is principal quantum number, $l$ is orbital (or angular momentum quantum number), $m_l$ is magnetic (or z-component angular momentum) quantum number, $n = 1$ to infinity, $l = 0$ to $n-1$, $m_l = -l$ to $l$ (including zero)

Quantization arises simply from the boundary conditions that wave functions have to approach zero at infinity!

The magnitude of the angular momentum, $L$ and the component of the angular momentum along the z-direction $L_z$ is given by:

$$L = \sqrt{l(l+1)} \frac{\hbar}{2\pi}$$

$$L_z = m_l \frac{\hbar}{2\pi}$$

So angular momentum is quantized in nature in a different manner than predicted by the Bohr’s model (as it neglects Heisenberg’s uncertainty relations).

By virtue of the uncertainty principle, there can only be certain orientations of the angular momentum vector, phenomenon is commonly referred to as space quantization.

Figure 4.8 Five allowed orientations of angular momentum $l = 2$, length of vector and z-projections in units of $\hbar$. Azimuthal angle is free to take any value.

$l = 2$, $m_l = -2, -1, 0, 1, 2$
\[ \psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \]

\( R(r) \) is known as the Radial Wavefunction

\( Y(\theta, \phi) \) Spherical Harmonic

**Angular momentum**^2 operator

\[ L^2Y = \frac{\hbar^2}{4\pi^2} l(l+1)Y \]  \hspace{1cm} (3.64)

Angular momentum along z direction operator

\[ L_z Y = m_l \frac{\hbar}{2\pi} Y \]

where the complete form for Eq. (3.64) can be written as

\[ -\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2 Y}{\partial \phi^2} \right] = -l(l+1) \frac{\hbar^2}{4\pi^2} Y \]  \hspace{1cm} (3.66)

On the other hand, the radial function satisfies the following equation:

\[ -\frac{\hbar^2}{8m\pi^2} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right) R(r) - \frac{Ze^2}{4\pi\varepsilon_0 r} R(r) = ER(r) \]  \hspace{1cm} (3.67)
\[ R(r) = R_{nl} \] so the products of the corresponding function for all three quantum numbers gives the full wave function
The maximum of finding the electron at a radial distance is the first Bohr radius for the $n = 1, l = 0$, the 1s state,

similarly for each quantum state with the highest angular momentum for each principle quantum number $n$, (e.g. 2,1; 3,2) the probability of finding the electron corresponds to Bohr’s semi-classical orbit predictions

$$r_n = a_0 n^2$$
Complex valued wave functions possess angular momentum, i.e. $\psi_{22\pm1}$, whereas $2p_x$, $2p_y$, $2p_z$ are all real, so do not possess angular momentum, $2p_x + i2p_y$ and $2p_x - i2p_y$ become complex valued.

### Table 4.1: One-electron wavefunctions in real form [9]

<table>
<thead>
<tr>
<th>Wavefunction designation</th>
<th>Wavefunction name, real form</th>
<th>Equation for real form of wavefunction*, where $\rho = Zr/a_o$ and $C_1 = Z^{3/2}/\sqrt{\pi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi_{100}$</td>
<td>1s</td>
<td>$C_1 e^{\rho}$</td>
</tr>
<tr>
<td>$\Psi_{200}$</td>
<td>2s</td>
<td>$C_2 (2-\rho) e^{-\rho/2}$</td>
</tr>
<tr>
<td>$\Psi_{21, \cos \phi}$</td>
<td>$2p_x$</td>
<td>$C_3 \rho \sin \theta \cos \phi e^{-\rho/2}$</td>
</tr>
<tr>
<td>$\Psi_{21, \sin \phi}$</td>
<td>$2p_y$</td>
<td>$C_4 \rho \sin \theta \sin \phi e^{-\rho/2}$</td>
</tr>
<tr>
<td>$\Psi_{210}$</td>
<td>$2p_z$</td>
<td>$C_5 \rho \cos \theta e^{-\rho/2}$</td>
</tr>
<tr>
<td>$\Psi_{300}$</td>
<td>3s</td>
<td>$C_6 \left((27-18\rho + 2\rho^2) e^{-\rho/3}\right)$</td>
</tr>
<tr>
<td>$\Psi_{31, \cos \phi}$</td>
<td>$3p_x$</td>
<td>$C_7 (6\rho - \rho^2) \sin \theta \cos \phi e^{-\rho/3}$</td>
</tr>
<tr>
<td>$\Psi_{31, \sin \phi}$</td>
<td>$3p_y$</td>
<td>$C_8 (6\rho - \rho^2) \sin \theta \sin \phi e^{-\rho/3}$</td>
</tr>
<tr>
<td>$\Psi_{310}$</td>
<td>$3p_z$</td>
<td>$C_9 (6\rho - \rho^2) \cos \theta e^{-\rho/3}$</td>
</tr>
<tr>
<td>$\Psi_{320}$</td>
<td>$3d_x^2$</td>
<td>$C_{10} \rho^2 (3\cos^2 \theta - 1) e^{-\rho/3}$</td>
</tr>
<tr>
<td>$\Psi_{32, \cos \phi}$</td>
<td>$3d_{xz}$</td>
<td>$C_{11} \rho^2 \sin \theta \cos \theta \cos \phi e^{-\rho/3}$</td>
</tr>
<tr>
<td>$\Psi_{32, \sin \phi}$</td>
<td>$3d_{yz}$</td>
<td>$C_{12} \rho^2 \sin \theta \cos \theta \sin \phi e^{-\rho/3}$</td>
</tr>
<tr>
<td>$\Psi_{32, \cos 2\phi}$</td>
<td>$3d_{x^2 - y^2}$</td>
<td>$C_{13} \rho^2 \sin^2 \theta \cos 2\phi e^{-\rho/3}$</td>
</tr>
<tr>
<td>$\Psi_{32, \sin 2\phi}$</td>
<td>$3d_{xy}$</td>
<td>$C_{14} \rho^2 \sin^2 \theta \sin 2\phi e^{-\rho/3}$</td>
</tr>
</tbody>
</table>

* $C_2 = C_1/4\sqrt{2}$, $C_3 = 2C_1/8\sqrt{3}$, $C_4 = C_3/2$, $C_5 = \sqrt{6}C_4$, $C_6 = C_5/2$. 

---

**Figure 4.7** $2p$ wavefunctions in schematic form. Left panel, complex forms carry angular momentum. Right panel, linear combinations have the same energy, now assume aspect of bonds.
Schrödinger’s time independent equation for a central force potential, is 3D, so we get three quantum numbers, it is an operator level statement that total energy is the sum of classical kinetic energy and potential energy and conserved, also it is a statement that the wave function is an eigenfunction of the Hamiltonian Operator and that the total energy is its eigenvalue

\[-\frac{\hbar^2}{8m\pi^2} \left(\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi\]  \hspace{1cm} (3.56)

Sketch of Stern-Gerlach experiment with (non-magnetic) Ag atoms, Hydrogen in the ground state, note the beam of atoms is split into two components by an inhomogeneous magnetic field, an inhomogeneous magnetic field separates atoms if they are carrying a magnetic moment, great surprise was that Ag and H in ground state need to have a magnetic moment although 1s\(^1\) for hydrogen (outermost 5s\(^1\) for Ag [Kr] 4d\(^{10}\) 5s1) does not magnetic quantum number \(m_l = 0\)

http://www.if.ufrgs.br/%7Ebetz/quantum/SGPeng.htm
Spin is something entirely quantum mechanical, it has no classical counterpart, it is an internal degree of freedom that has just two values, up or down about any possible axis, the electron is not spinning around its axis, if it were, it would need to spin significantly faster than the speed of light and also about any possible axis one can imagine.

From Dirac’s relativistic analysis

\[
S = \frac{\hbar}{2\pi} \sqrt{s(s+1)}
\]

\[
S_z = \frac{\hbar}{2\pi} m_s = \pm \frac{\hbar}{4\pi}
\]

Four dimensional space time requires 4 quantum numbers. We neglected special relativity because electron on first Bohr orbit was not very fast, while the numerical error was small, the conceptual blunder is large!

one spin up and one spin down electron fit in each orbital, Pauli’s exclusion principle

http://phet.colorado.edu/sims/stern-gerlach/stern-gerlach_en.html
Electronic structure can be explained approximately by the hydrogen orbital plus Pauli’s exclusion principle (each orbital has only space for one spin up and one spin down electron), plus Hund’s rule (often when orbitals can be occupied by single electrons with the same spin, this results in strong (ferro) magnetisms (at room temperature) in a few of the elements: Fe, Co, Ni, Gd, and Dy, \( \text{C}_{60} \) in a meta-stable high pressure-temperature hexagonal crystal phase might also be ferromagnetic due to structural defects since all electron spins are paired).

From Unsöld's theorem, about 1/3 of all atoms are nearly spherical symmetric.

There are many many many more molecules than atoms, beyond Bi all elements are unstable (radioactive), U is the heaviest element in nature.

The “living domain” of nature builds form complex molecules by lock and key mechanisms (rather than moving individual atoms into place with a STM), atomic orbitals of hydrogen can to some extend be used to model the shape of molecules, there sure will be modifications, e.g. hybridization, …
$r_n = a_0 n^2$

Shapes of many isolated atoms in ground state are nearly spherical.

Unsöld's theorem states that the square of the total electron wave function for a filled or half-filled sub-shell is spherically symmetric. Thus, atoms containing a half-filled or filled s orbital ($l = 0$), atoms of the second period with 3 or 6 p ($l = 1$) electrons are spherically shaped. Likewise, are atoms of the forth period in which there are 5 or 10 d ($l = 2$) electrons. Hence, spherical atoms are those of the 1st, 2nd, 7th, 12th, 15th and 18th columns of the periodic table. (also applicable to the lanthanides and actinides)

FIGURE 8-5 Sketches of $|\psi|^2$ for the hydrogen atom in three dimensions:
(a) the $n = 1$ state, (b) the $n = 2$ states, and (c) the $n = 3$ states. After R. Eisberg and R. Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles, Wiley (copyright © 1985).
both Bohr and Schrödinger model could be refined with the concept of reduced mass of the electron (the much heavier proton is not really stationary, both particles rotate about their common center of mass)

\[ \mu_e = \frac{m_{\text{electron}} \cdot M_{\text{proton}}}{m_{\text{electron}} + M_{\text{proton}}} \]

Since proton about 1836 times heavier \( \mu_e = 0.999456 \ m_{\text{electron}} \)

Rydberg constant (for infinite nuclear mass) needs to be multiplied with ratio reduced mass to rest mass of electron in order to predict position of spectral lines more precisely

\[ 13.6eV = R_\infty \cdot hc \]

With these concepts, **Positronium**, i.e. an electron and a positron going around each other before they annihilate each other and get converted into two gamma rays can be modeled by the Bohr/Schroedinger model, Bohr radius: 2 \( a_0 \), ground state/binging energy: 0.5 times 13.6 eV, these concepts around Positronium are important in certain characterizing techniques of crystalline materials, detecting certain defects by spectroscopic means

Also an (Mott-Wannier, loosely bound) **Exciton**, i.e. an electron loosely bound to a region of positive charge (hole) in a semiconductor can be modeled by the Bohr/Schroedinger model, depending on the effective mass of the electron and hole (which depend on the second derivative of the energy versus wave vector function – band structure) and the relative dielectric constants (since it is inside a semiconductor): Bohr radii are typically some 10 \( a_0 \), ground state/binging energies are typically: 0.1 times 13.6 eV, if the exciton is confined into a space below it’s Bohr radius, it acquires a set of different energy states, e.g. in self-assembled epi- or endotaxial quantum dots (in organic nano-crystals, there are tightly bound Frenkel excitons)
There are also epitaxial semiconductor quantum dots for low threshold lasers

Shell around the particles has larger band gap, i.e. it reduces leaking into the barrier, also surface reconstruction of the core material is avoided which would produce extra electronic states in the band gap and reduce the radioactive efficiency of the quantum dots.

**Figure 1.32.** The first few energy levels in the Rydberg series of a hydrogen atom (a), positronium (b), and a typical exciton (c).

**Figure 5.7** Fluorescence from CdSe quantum dots of different sizes. Change in wavelength of fluorescence as a function of size from CdSe quantum dots excited with UV light. Note how the wavelength is reduced (bluer emission) as the size of the quantum dot is reduced. Reproduced with permission from Prof. Bawendi, Department of Chemistry, MIT.

**Fig. 5.8** CdSe/ZnS core-shell quantum dot. Coating a CdSe quantum dot with ZnS prevents the surface reconstruction of the CdSe surface that leads to the creation of additional electronic states in the bandgap. These promote the relaxation of the excited electrons via non-radiative transitions and decrease the quantum yield of the dot.
Another important result of relativistic quantum mechanics (that revealed the existence of the particle property spin) for more than one particle: there are actually three types of identical particles in the universe, two of them possess the feature of being genuinely indistinguishable from each other by virtue of the uncertainty principle, these are the two identical “quantum particles”, fermions and bosons.

Fermions are the constituents of matter, have half integer spin, electrons, protons, neutrons / bosons are the field particles (and some composites of fermions) with integer spin, e.g. photons, alpha particles

Different statistics apply in each case, below are the probability of finding a certain type of particle as a function of its energy, (kT being thermal energy, A a factor that serves similar “normalization purposes” but differs from energy distribution function to energy distribution function)

<table>
<thead>
<tr>
<th></th>
<th>( f(E) )</th>
<th>Identities but distinguishable particles, e.g. Molecular speed distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell-Boltzmann</td>
<td>( \frac{1}{Ae^{E/kT}} )</td>
<td>\</td>
</tr>
<tr>
<td>(classical)</td>
<td></td>
<td>\</td>
</tr>
<tr>
<td>Bose-Einstein</td>
<td>( \frac{1}{Ae^{E/kT} - 1} )</td>
<td>Identical indistinguishable particles with integer spin (bosons), e.g. Thermal radiation, specific heat</td>
</tr>
<tr>
<td>(quantum)</td>
<td></td>
<td>\</td>
</tr>
<tr>
<td>Fermi-Dirac</td>
<td>( \frac{1}{Ae^{E/kT} + 1} )</td>
<td>Identical indistinguishable particles with half-integer spin (fermions), e.g. Electrons in a metal, conduction in semiconductor</td>
</tr>
<tr>
<td>(quantum)</td>
<td></td>
<td>\</td>
</tr>
</tbody>
</table>

For thermal equilibrium of system of particles
Even without spin being integer or half integer multiple, is the characteristic of indistinguishability that makes quantum statistics different from classical statistics.

The possible configurations for two distinguishable (particles A and B) in either of two energy states:

<table>
<thead>
<tr>
<th>State 1</th>
<th>State 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>AB</td>
<td></td>
</tr>
</tbody>
</table>

The probability of each is one-fourth (0.25). **But if the two particles are indistinguishable (X instead of A and B):**

Since two particles can occupy the same state here, we are talking about Bosons (and not Fermions)

<table>
<thead>
<tr>
<th>State 1</th>
<th>State 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>XX</td>
</tr>
</tbody>
</table>

The probability of each is one-third (~0.33).
At large temperatures or energies, all three energy state probability distributions converge,

but at very high T, Maxwell-Boltzmann breaks down anyway because it is non relativistic!
Fermi energy is only weakly dependent on temperature, so that dependency is often neglected.

\[ f_{FD}(E) = \frac{1}{e^{(E-E_F)/(k_B T)} + 1} \]

Fermi Energy: at T = 0, all levels below \( E_F \) are filled, all levels above it are empty.

\[ n(E) \, dE = g(E) \, f(E) \, dE \]

will be number of electrons as a function of energy,

at T > 0, only “a few” electrons will be able to acquire some extra energy from the thermal environment to be able to move around freely and transport electricity or heat from one place to another.
A gas of classical particles would have to be heated to $T_{\text{Fermi}}$ in order to have an average kinetic energy per particle that is equal to the Fermi Energy.
n(E) is number of electrons per unit volume with energy between E and E + dE

this is the product of the density of state function (here for a bulk material, which is large in all three dimensions) and f(E) for the Fermi-Dirac energy state occupation distribution function

Only those electrons in the narrow shaded rectangle of width $k_B T$ can be thermally excited, their fraction $f$ is approximately the ratio of that small area to the total area under the curve

$$f \approx \frac{3T}{2T_F}$$

total energy gained per mol is

$$U \approx \frac{3RT^2}{2T_F}$$

Electronic heat capacity

$$C_{\text{electron\_in\_crystal}} = \frac{dU}{dT} \approx 3R \frac{T}{T_F}$$

with typical values for Fermi Temperature and 300 K, electronic heat capacity is only about 1 % of the classically expected heat capacity for a Maxwell-Boltzmann gas !!
Under what physical conditions can Maxwell-Boltzmann statistics be employed?

Whenever the wave-particle duality can be ignored, e.g. when average distance between particles, \(d\), is large compared to quantum uncertainty in particle position, \(\Delta x\)

\[ \Delta x \ll d \]

For such a particle moving in one direction, average kinetic energy \(p_{x-\text{average}}^2 / 2m = k_B T / 2\) from equipartition theorem

\[ \Delta p_x \Delta x \geq \frac{\hbar}{2} \quad \Delta x \geq \frac{\hbar}{2 \sqrt{mk_B T}} \quad d = \left(\frac{V}{N}\right)^{\frac{1}{3}} \frac{\hbar}{2 \sqrt{mk_B T}} \ll \left(\frac{V}{N}\right)^{\frac{1}{3}} \]

Let’s do two estimations, 1. hydrogen gas at standard temperature and pressure (STP)

\[
\frac{N}{V} \frac{\hbar^3}{8 \cdot 3^{\frac{1}{3}} \sqrt{mk_B T}} \ll 1
\]

273 K, 1 atmosphere, 1 mol \(H_2\) gas 6.02 \(1^{23}\) molecules occupies 22.4 liter, \(k_B T = 3.77 \times 10^{-21} \) J

\[ = 8.83 \times 10^{-8} \ll 1, \text{ so all is fine for ideal gas law, steam engines, Carnot cycle, … (modification real gas laws)} \]

Let’s do two estimations, 2. electrons in silver at 300 K?

\[ n = \left(\frac{N}{V}\right) = 5.86 \times 10^{28} \text{ free electrons m}^{-3}, \] (about 2000 times denser than hydrogen gas at STP), electron much lighter than \(H_2\)

\[ = 3.71 \text{ not much smaller than 1 !! so anything to do with electrons in the solid state is to be treated with quantum statistics !} \]
Free electron gas (Drude theory) in a metal,

there are positively charged ions (the former atoms of the metal) that have donated their outer electron (or electrons depending on the chemical valance) to the collective “sea of electrons”, some of the electrons are free to move in the crystal lattice, if it were not for deviations from the perfect lattice, i.e. point defects or lattice vibrations, they would not be scattered, however they do obey Fermi-Dirac statistics since they are Fermions, neglecting this property and assuming the validity of classical physics (Maxwell-Boltzmann statistics instead) leads at best to fortuitous results

“similar” models for thermal and electrical conductivity for metals, on basis of free electron gas, treated with Maxwell-Boltzmann statistics – i.e. as if it were an ideal gas

Lorenz numbers, a fortuitous result, don’t be fooled, the physics (Maxwell-Boltzmann statistics) behind it is not applicable as we estimated earlier

But Fermi-Dirac statistics gets us the right physics

Drude, J.J. Thomson, Lorenz assumed wrongly that the free electron gas would behave classically
Table 12.5  Thermal Conductivity, $K$, and Electrical Conductivity, $\sigma$, of Selected Substances at Room Temperature

<table>
<thead>
<tr>
<th>Substance</th>
<th>$K$ in $W \cdot m^{-1}K^{-1}$</th>
<th>$\sigma$ in $(\Omega \cdot m)^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>427</td>
<td>$62 \times 10^6$</td>
</tr>
<tr>
<td>Copper</td>
<td>390</td>
<td>$59 \times 10^6$</td>
</tr>
<tr>
<td>Gold</td>
<td>314</td>
<td>$41 \times 10^6$</td>
</tr>
<tr>
<td>Aluminum</td>
<td>210</td>
<td>$35 \times 10^6$</td>
</tr>
<tr>
<td>Iron</td>
<td>63</td>
<td>$10 \times 10^6$</td>
</tr>
<tr>
<td>Steel</td>
<td>50</td>
<td>$1.4 \times 10^6$</td>
</tr>
<tr>
<td>Nichrome</td>
<td>14</td>
<td>$0.9 \times 10^6$</td>
</tr>
<tr>
<td>Quartz</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>7.0</td>
<td>$&lt; 10^{-4}$</td>
</tr>
</tbody>
</table>

Metals have high conductivities for both electricity and heat. To explain both the high conductivities and the trend in this table we need to have a model for both thermal and electrical conductivity, that model should be able to explain empirical observations, i.e. Ohm's law, thermal conductivity, Wiedemann-Franz law,
### Table 12.7  Experimental Lorentz Numbers $K/\sigma T$ in Units of $10^{-8} \ W \cdot \Omega / K^2$*

<table>
<thead>
<tr>
<th>Metal</th>
<th>273 K</th>
<th>300 K</th>
<th>373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>2.31</td>
<td>2.3</td>
<td>2.37</td>
</tr>
<tr>
<td>Au</td>
<td>2.35</td>
<td>2.55</td>
<td>2.40</td>
</tr>
<tr>
<td>Cd</td>
<td>2.42</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>2.23</td>
<td>2.2</td>
<td>2.33</td>
</tr>
<tr>
<td>Ir</td>
<td>2.49</td>
<td></td>
<td>2.49</td>
</tr>
<tr>
<td>Mo</td>
<td>2.61</td>
<td></td>
<td>2.79</td>
</tr>
<tr>
<td>Pb</td>
<td>2.47</td>
<td>2.56</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>2.51</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>2.52</td>
<td>2.49</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>3.04</td>
<td>3.20</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>2.31</td>
<td>2.33</td>
<td></td>
</tr>
</tbody>
</table>

Wiedemann and Franz Law, 1853, ratio $K/\sigma T = \text{Lorenz number} = \text{constant} \approx 2.4 \times 10^{-8} \ W \ \Omega \ K^{-2}$

independent of the metal considered!! So both phenomena should be based on similar physical idea!!

Classical from Drude (early 1900s) theory of free electron gas that behaves classically

$$\frac{K}{\sigma T} = \frac{3k_B^2}{2e^2} \approx 1.12 \times 10^{-8} W \Omega K^{-2}$$

Too small by factor 2, seems not too bad???
To explain the high conductivities and the trend we need to have a model for both thermal and electrical conductivity, that model should be able to explain Ohm's law, empirical for many metals and insulators, ohmic solids. Conductivity $\sigma$, resistivity $\rho$, is its reciprocal value.

$$J = \sigma \ E$$ current density is proportional to applied electric field

$$R = \frac{U}{I}$$ for a wire $R = \frac{\rho \ 1}{A}$

$\rho$: specific resistivity

$\sigma$: electrical conductivity $\Omega^{-1} \ m^{-1}$, reciprocal value of electrical resistivity

$E$: electric field $V/m$

$$\sigma = \rho^{-1}$$

A constant that does depend on the material and temperature but not the applied electric field and represents the connection between current and voltage.
Gas of classical charged particles, electrons, moves through immobile heavy ions arranged in a lattice, \( v_{\text{rms}} \) from equipartition theorem (which is of course derived from Boltzmann statistics).

\[
\frac{1}{2} m_e \overline{v^2} = \frac{3}{2} k_B T
\]

\[
v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3 k_B T}{m_e}}
\]

Between collisions, there is a mean free path length: \( L = v_{\text{rms}} \tau \)

and a mean free time \( \tau \) (tau)

Figure 12.11 (a) Random successive displacements of an electron in a metal without an applied electric field.
If there is an electric field $E$, there is also a drift speed $v_d$ ($10^8$ times smaller than $v_{rms}$) but proportional to $E$, equal for all electrons.

$$v_d = \frac{eE\tau}{m_e}$$

Figure 12.11 (b) A combination of random displacements and displacements produced by an external electric field. The net effect of the electric field is to add together multiple displacements of length $v_d \tau$ opposite the field direction. For purposes of illustration, this figure greatly exaggerates the size of $v_d$ compared with $v_{rms}$. 

6
n is density of electrons per volume

\[ J = \frac{neAv_d dt}{Adt} = nev_d \]

Substituting for \( v_d \)

\[ J = \frac{ne^2 \tau}{m_e} E \]

So the correct form of Ohm’s law is predicted by the Drude model !!

\[ J = \sigma E \]
\[ \sigma = \frac{n e^2 \tau}{m_e} \]

With mean free time \( \tau = \frac{L}{v_{\text{rms}}} \)

\[ \sigma = \frac{n e^2 L}{m_e v_{\text{rms}}} \]

With \( v_{\text{rms}} \) according to Maxwell-Boltzmann statistics

\[ \sigma = \frac{n e^2 L}{\sqrt{3k_B T m_e}} \]

Proof of the pudding: \( L \) should be on the order of magnitude of the inter-atomic distances, e.g. for Cu 0.26 nm

\[ \sigma = \frac{8.49 \cdot 10^{22} \text{cm}^{-3} (6.02 \cdot 10^{-19} \text{C})^2 \cdot 0.26 \text{nm}}{\sqrt{3 \cdot 1.381 \cdot 10^{-23} \text{JK}^{-1} \cdot 300 \text{K} \cdot 9.109 \cdot 10^{-31} \text{kg}}} \]

\[ \sigma_{\text{Cu, 300 K}} = 5.3 \cdot 10^6 \, \text{m}^{-1} \text{m}^{-1} \text{compared with experimental value 59} \cdot 10^6 \, \text{m}^{-1} \text{m}^{-1} \text{, something must be wrong with the classical } L \text{ and } v_{\text{rms}}. \]
Result of Drude theory one order of magnitude too small, so $L$ must be much larger, this is because the electrons are not classical particles, but wavicals, don’t scatter like particles, in addition, the $v_{\text{rms}}$ from Boltzmann-Maxwell is one order of magnitude smaller than the $v_{\text{fermi}}$ following from Fermi-Dirac statistics.

### Table 12.6  Electrical Conductivity of Metals at 300 K

<table>
<thead>
<tr>
<th>Substance</th>
<th>Measured $\sigma$ in $(\Omega \cdot m)^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>$59 \times 10^6$</td>
</tr>
<tr>
<td>Aluminum</td>
<td>$35 \times 10^6$</td>
</tr>
<tr>
<td>Sodium</td>
<td>$22 \times 10^6$</td>
</tr>
<tr>
<td>Iron</td>
<td>$10 \times 10^6$</td>
</tr>
<tr>
<td>Mercury</td>
<td>$1.0 \times 10^6$</td>
</tr>
</tbody>
</table>
\[ \sigma^{-1} = \frac{\sqrt{3k_B T m_e}}{ne^2 L} = \rho \]

So \( \rho \sim T^{0.5} \) theory for all temperatures, but \( \rho \sim T \) for experiment reasonably high \( T \), so Drude’s theory must be wrong!

Figure 12.13 The resistivity of pure copper as a function of temperature.
Phenomenological similarity conduction of electricity and conduction of heat, so free electron gas should also be the key to understanding thermal conductivity.

\[ J = -\sigma \frac{\Delta V}{\Delta x} \]

Ohm’s law with Voltage gradient,

\[ \frac{\Delta Q}{A \Delta t} = -K \frac{\Delta T}{\Delta x} \]

thermal energy conducted through area A in time interval \( \Delta t \) is proportional to temperature gradient

\[ K = \frac{1}{3} C_v v_{rms} L \]

Using Maxwell-Boltzmann statistics, equipartition theorem, formulae of \( C_v \) for ideal gas = \( \frac{3}{2} k_B n \)

\[ K = \frac{k_B n v_{rms} L}{2} \]

Classical expression for K
\[ v_{rms} = \sqrt{\frac{-2}{v}} = \sqrt{\frac{3k_B T}{m_e}} \]

For 300 K and Cu

\[ v_{rms} = \sqrt{\frac{3 \cdot 1.381 \cdot 10^{-23} \text{JK}^{-1} 300K}{9.109 \cdot 10^{-31} \text{kg}}} \approx 10^5 \text{ m/s} \]

\[ K = \frac{k_B n v_{rms} L}{2} \]

\[ K = \frac{1.381 \cdot 10^{-23} \text{JK}^{-1} \cdot 8.48 \cdot 10^{22} \text{cm}^{-3} \cdot 1.1681 \cdot 10^5 \text{ms}^{-1} \cdot 0.26 \text{nm}}{2} \]

\[ K = \frac{1.381 \cdot 10^{-23} \text{JK}^{-1} \cdot 8.48 \cdot 10^{28} \text{m}^{-3} \cdot 1.1681 \cdot 10^5 \text{ms}^{-1} \cdot 0.26 \cdot 10^{-9} \text{m}}{2} \]

\[ K = 17.78 \frac{W_s}{Kms} \]

Experimental value for Cu at (300 K) = 390 Wm\(^{-1}\)K\(^{-1}\), again one order of magnitude too small, actually roughly 20 times too small
$$\sigma = \frac{ne^2L}{m_e\nu_{rms}}$$

This was also one order of magnitude too small,

$$\frac{K}{\sigma} = \frac{k_B n \nu_{rms} L m_e \nu_{rms}}{2ne^2L} = \frac{k_B m_e \nu^{2}_{rms}}{2e^2}$$

With Maxwell-Boltzmann

$$\nu_{rms} = \sqrt{\frac{2}{\nu}} = \sqrt{\frac{3k_B T}{m_e}}$$

Lorenz number classical $$\frac{K}{\sigma}$$

Wrong only by a factor of about 2,
Such an agreement is called fortuitous

$$\frac{K}{\sigma T} = \frac{3k_B^2}{2e^2} \approx 1.12 \cdot 10^{-8} W \Omega K^{-2}$$
Table 12.7  Experimental Lorentz Numbers $K/\sigma T$ in Units of $10^{-8}$ W · Ω/K²*

<table>
<thead>
<tr>
<th>Metal</th>
<th>273 K</th>
<th>373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>2.31</td>
<td>2.37</td>
</tr>
<tr>
<td>Au</td>
<td>2.35</td>
<td>2.40</td>
</tr>
<tr>
<td>Cd</td>
<td>2.42</td>
<td>2.43</td>
</tr>
<tr>
<td>Cu</td>
<td>2.23</td>
<td>2.33</td>
</tr>
<tr>
<td>Ir</td>
<td>2.49</td>
<td>2.49</td>
</tr>
<tr>
<td>Mo</td>
<td>2.61</td>
<td>2.79</td>
</tr>
<tr>
<td>Pb</td>
<td>2.47</td>
<td>2.56</td>
</tr>
<tr>
<td>Pt</td>
<td>2.51</td>
<td>2.60</td>
</tr>
<tr>
<td>Sn</td>
<td>2.52</td>
<td>2.49</td>
</tr>
<tr>
<td>W</td>
<td>3.04</td>
<td>3.20</td>
</tr>
<tr>
<td>Zn</td>
<td>2.31</td>
<td>2.33</td>
</tr>
</tbody>
</table>
replace $L_{\text{for}_a\text{_particle}}$ with $L_{\text{for}_a\text{_wavial}}$ and $v_{\text{rms}}$ with $v_{\text{fermi}},$

\[ \sigma_{\text{classical}} = \frac{ne^2 L_{\text{for}_a\text{_particle}}}{m_e v_{\text{rms}}} \quad \rightarrow \quad \sigma_{\text{quantum}} = \frac{ne^2 L_{\text{for}_a\text{_wavical}}}{m_e v_{\text{fermi}}} \]

\[ L_{\text{for}_a\text{_wavical}} = \frac{m_e v_{\text{fermi}} \sigma_{\text{quantum}}}{ne^2} \]

\[ v_{\text{rms}} = \sqrt{\frac{3k_B T}{m_e}} \quad \rightarrow \quad v_{\text{fermi}} = \sqrt{\frac{2E_F}{m_e}} \]

For Cu (at 300 K), $E_F = 7.05$ eV, Fermi energies have only small temperature dependency, frequently neglected.
$$v_{\text{fermi}} = \sqrt{\frac{2E_F}{m_e}}$$

$$v_{\text{fermi, copper, 300K}} = \sqrt{\frac{2 \times 7.05 \times 1.602 \times 10^{-9} J}{9.109 \times 10^{-31} kg}} = 1.57 \times 10^6 ms^{-1}$$

One order of magnitude larger than classical $v_{\text{rms}}$

For ideal gas

$$L_{\text{for a wavical}} = \frac{m_e v_{\text{fermi}} \sigma_{\text{quantum}}}{ne^2}$$

$$L_{\text{for a wavical, copper}} = \frac{9.109 \times 10^{-31} kg \cdot 1.57 \times 10^6 ms^{-1} \cdot 5.9 \times 10^7 \Omega^{-1} m^{-1}}{8.49 \times 10^{-28} m^{-3} (1.602 \times 10^{-19} C)^2}$$

$$L_{\text{for a wavical, copper}} = 39 nm$$

Two orders of magnitude larger than classical result for particle}

Actually the wavical would not scatter if it were not for irregularities in the crystal lattice
We used spacing of ions: 0.26 nm

\[ \sigma_{\text{classical}} = \frac{ne^2 L_{\text{for particle}}}{m_e v_{\text{rms}}} \approx 0.1 \text{ of observed value} \]

So here something two orders of two magnitude too small (L) gets divided by something one order of magnitude too small (v_{rms}), i.e. the result for electrical conductivity must be one order of magnitude too small, which is observed!!

But L_{for particle} is quite reasonable, so replace V_{rms} with V_{fermi} and the conductivity gets one order of magnitude larger, which is close to the experimental observation, so that one keeps the Drude theory of electrical conductivity as a classical approximation for room temperature.
in effect, neither the high \( v_{\text{rms}} \) of \( 10^5 \) m/s of the electrons derived from the equipartion theorem or the 10 times higher Fermi speed do not contribute directly to conducting a current since each electrons goes in any directions with an equal likelihood and this speeds averages out to zero charge transport in the absence of \( E \).

**Figure 12.11** (a) Random successive displacements of an electron in a metal without an applied electric field. (b) A combination of random displacements and displacements produced by an external electric field. The net effect of the electric field is to add together multiple displacements of length \( v_d \tau \) opposite the field direction. For purposes of illustration, this figure greatly exaggerates the size of \( v_d \) compared with \( v_{\text{rms}} \).

\[
\tau = \frac{L}{\nu}
\]
\[ K_{\text{classical}} = \frac{k_B n v_{\text{rms}} L_{\text{classical}}}{2} \]

\( V_{\text{rms}} \) was too small by one order of magnitude, \( L_{\text{classical}} \) was too small by two orders of magnitude, the classical calculations should give a result 3 orders of magnitude smaller than the observation (which is of course well described by a quantum statistical treatment)

so there must be something fundamentally wrong with our ideas on how to calculate \( K \), **any idea ???**
Wait a minute, $K$ has something to do with the heat capacity that we derived from the equipartion theorem.

\[ K_{\text{classical}} = \frac{1}{3} C_{V \text{ for ideal gas}} v_{\text{rms}} L_{\text{for particle}} \]

Must be too large by two orders of magnitude.

We had the result earlier that the contribution of the electron gas is only about one hundredth of what one would expect from an ideal gas, $C_{V \text{ for ideal gas}}$ is actually two orders or magnitude larger than for a real electron gas, so that are two orders of magnitude in excess, with the product of $v_{\text{rms}}$ and $L_{\text{for particle}}$ three orders of magnitude too small, we should calculate classically thermal conductivities that are one order of magnitude too small, which is observed !!!
\[
\frac{K}{\sigma} = \frac{k_B n v_{\text{rms}} L m_e v_{\text{mrs}}}{2 n e^2 L} = \frac{k_B m_e v_{\text{mrs}}^2}{2 e^2}
\]

\[
\frac{K}{\sigma T} = \frac{3 k_B^2}{2 e^2} \approx 1.12 \cdot 10^{-8} W \Omega K^{-2}
\]

Fortunately \( L \) cancelled, but \( v_{\text{rms}} \) gets squared, we are indeed very very very very fortuitous to get the right order of magnitude for the Lorenz number from a classical treatment (one order of magnitude too small squared is about two orders of magnitude too small, but this is “compensated” by assuming that the heat capacity of the free electron gas can be treated classically which in turn results in a value that is by itself two order of magnitude too large—two “missing” orders of magnitude times two “excessive orders of magnitudes levels about out.
\[ K_{\text{fermi}} = \frac{\pi^2}{3} \left( \frac{k_B^2 T}{m_e v_{\text{fermi}}} \right) n L_{\text{for \_ a \_ wavical}} \]

\[ \sigma_{\text{quantum}} = \frac{ne^2 L_{\text{for \_ a \_ wavical}}}{m_e v_{\text{fermi}}} \]

That gives for the Lorenz number in a quantum treatment

\[ \frac{K}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} = 2.45 \cdot 10^{-8} \text{W} \Omega K^{-2} \]
Back to the problem of the temperature dependency of resistivity

Drude’s theory predicted a dependency on square root of $T$, but at reasonably high temperatures, the dependency seems to be linear.

This is due to Debye’s phonons (lattice vibrations), which are bosons and need to be treated by Bose-Einstein statistics, electrons scatter on phonons, so the more phonons, the more scattering.

Number of phonons proportional to Bose-Einstein distribution function

\[ n_{\text{phonons}} \propto \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \]

Which becomes for reasonably large $T$

\[ n_{\text{phonons}} \propto \frac{k_B T}{\hbar \omega} \]
At low temperatures, there are hardly any phonons, scattering of electrons is due to impurity atoms and lattice defects, if it were not for them, there would not be any resistance to the flow of electricity at zero temperature.

Matthiessen’s rule, the resistivity of a metal can be written as

\[ \sigma = \sigma_{\text{lattice defects}} + \sigma_{\text{lattice vibrations}} \]