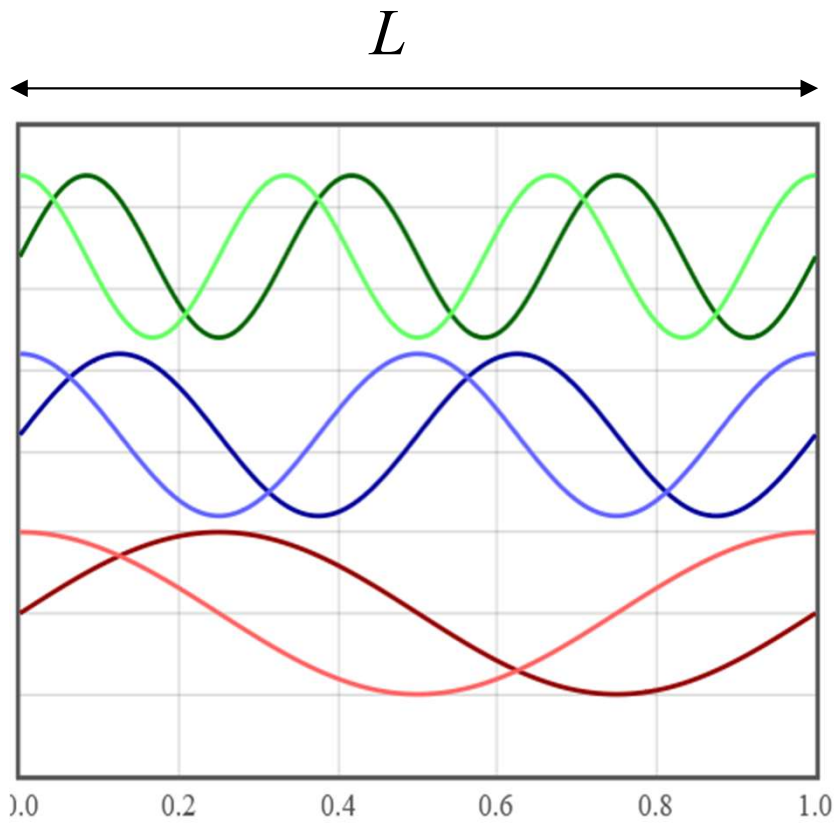
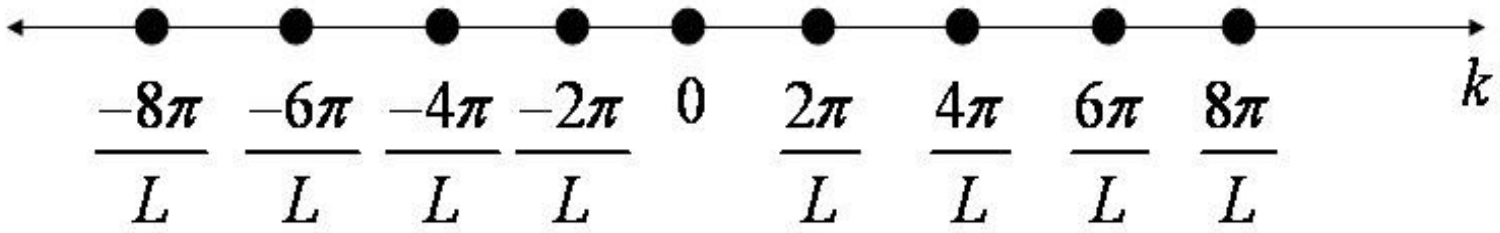
Electrons

Periodic boundary conditions

$$\psi_k = \frac{e^{i(kx-\omega t)}}{\sqrt{L}}$$



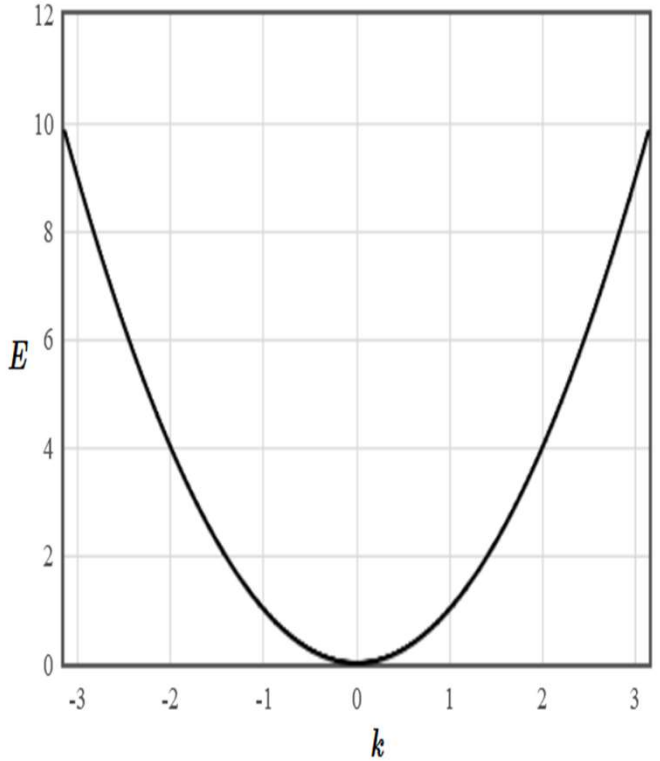


Free particles in 1-d

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} \qquad V = 0$$

Eigen function solutions: $\psi_k = \dfrac{e^{i(kx-\omega t)}}{\sqrt{L}}$

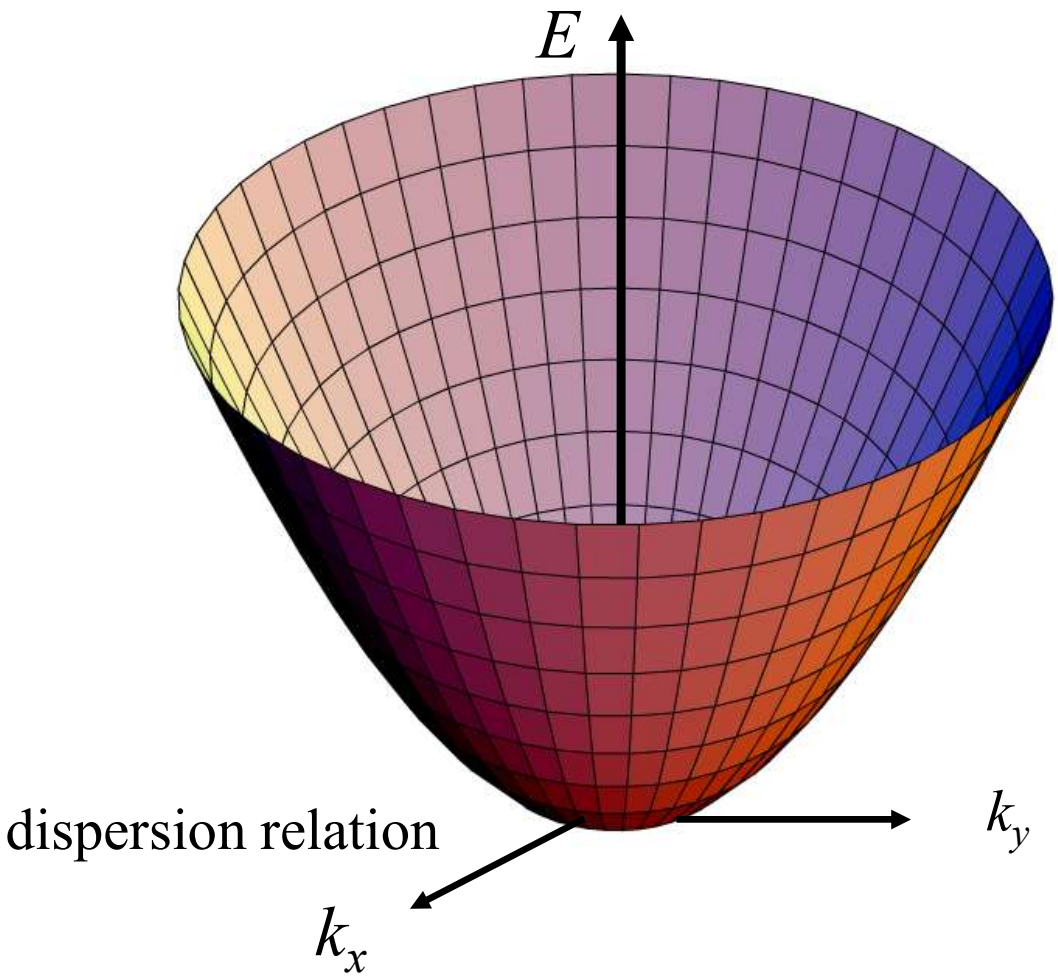
Dispersion relation: $E = \hbar\omega = \dfrac{\hbar^2 k^2}{2m} = \dfrac{1}{2}mv^2$



free electrons (simple model for a metal)

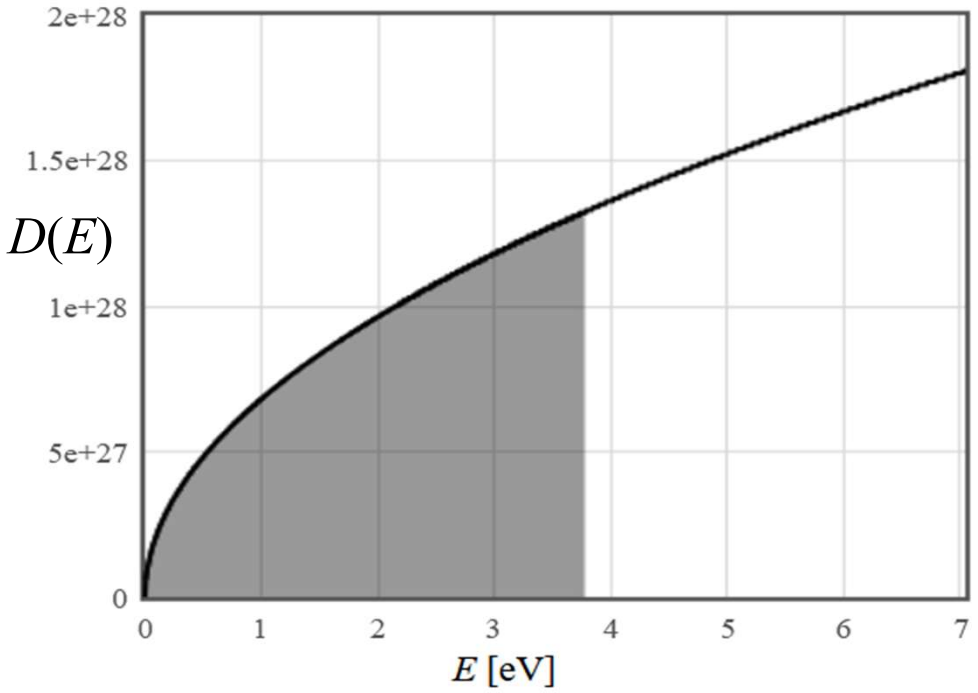
$$\vec{p} = \hbar\vec{k}$$

$$E(\vec{k}) = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$



dispersion relation

3-d density of states



$$D(E) = \begin{cases} 0 & \text{for} \quad E < 0 \\ \dfrac{(2m)^{3/2}}{2\pi^2\hbar^3}\sqrt{E} & \text{for} \quad E > 0 \end{cases}$$

Internal energy density

$$u = \int_{-\infty}^{\infty} ED(E)f(E)dE$$

$$D(E) = \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E} \quad \mathrm{J}^{-1}\,\mathrm{m}^{-3}$$

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

Sommerfeld expansion

$$\frac{d}{dE}K(E)f(E) = \frac{dK(E)}{dE}f(E) + K(E)\frac{df(E)}{dE}$$

Integrate by parts

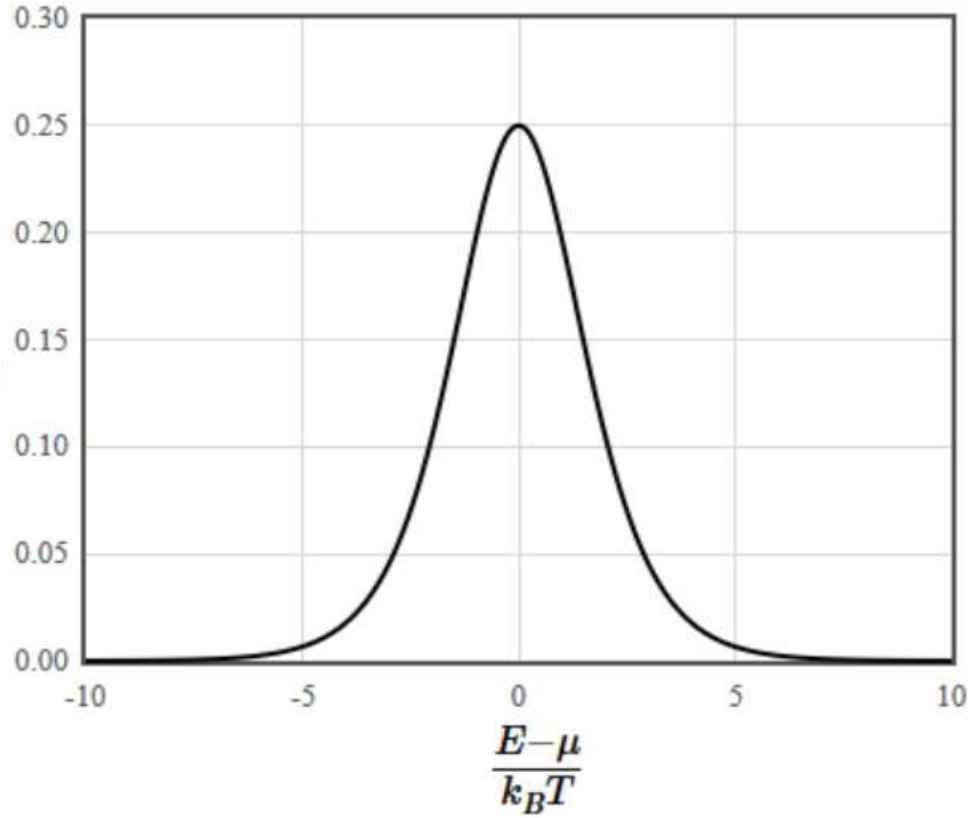
$$\int_{-\infty}^{\infty} H(E)f(E)\,dE = K(\infty)f(\infty) - K(-\infty)f(-\infty) - \int_{-\infty}^{\infty} K(E)\frac{df}{dE}dE$$

$$K(E) = \int_{-\infty}^{E} H(E')\,dE'$$

Sommerfeld expansion

$$\int_{-\infty}^{\infty} H(E) f(E)\, dE = -\int_{-\infty}^{\infty} K(E) \frac{df}{dE} dE,$$

$$-\frac{df(E)}{dE} = \frac{\exp\left(\frac{E-\mu}{k_B T}\right)}{k_B T \left(\exp\left(\frac{E-\mu}{k_B T}\right)+1\right)^2}$$



Sommerfeld expansion

Chemical potential μ Implicitly defined by $n = \int_{-\infty}^{\infty} D(E) f(E) dE$	$\mu \approx E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(E_F)}{D(E_F)}$ [J]
Internal energy $u = \int_{-\infty}^{\infty} E D(E) f(E)\, dE$	$u \approx \int_{-\infty}^{E_F} E D(E) dE + \frac{\pi^2 D(E_F)}{6}(k_B T)^2$ [J m^{-3}]
Specific heat $c_v = \left(\frac{du}{dT}\right)_{V=\text{const}}$	$c_v \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T$ [J m^{-3} K^{-1}]
Entropy $s = \int \frac{c_v}{T} dT$	$s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T$ [J m^{-3} K^{-1}]
Helmholtz free energy $f = u - Ts$	$f \approx \int_{-\infty}^{E_F} E D(E) dE - \frac{\pi^2 D(E_F)}{6}(k_B T)^2$ [J m^{-3}]

$u \approx \frac{3}{5} n E_F + \frac{\pi^2}{4} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\,m^{-3}}$
$c_v \approx \frac{\pi^2}{2} \frac{n}{E_F} k_B^2 T \quad \mathrm{J\,K^{-1}\,m^{-3}}$
$s \approx \frac{\pi^2}{2} \frac{n}{E_F} k_B^2 T \quad \mathrm{J\,K^{-1}\,m^{-3}}$
$f \approx \frac{3}{5} n E_F - \frac{\pi^2}{4} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\,m^{-3}}$
$P \approx \frac{2}{5} n E_F + \frac{\pi^2}{6} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{N\,m^{-2}}$
$B \approx \frac{2}{3} n E_F + \frac{\pi^2}{18} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{N\,m^{-2}}$
$h \approx n E_F + \frac{5\pi^2}{12} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\,m^{-3}}$
$g \approx n E_F - \frac{\pi^2}{12} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\,m^{-3}}$

All properties depend on n and m

$$D(E_F) = \frac{3}{2} \frac{n}{E_F} \quad \mathrm{J^{-1}\,m^{-3}}$$

$$D'(E_F) = \frac{3}{4} \frac{n}{E_F^2} \quad \mathrm{J^{-2}\,m^{-3}}$$

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad \mathrm{J}$$

Fit data to n and m

Sommerfeld expansion

Free electrons:

$$D(E_F) = \frac{3}{2}\frac{n}{E_F} \qquad \mathrm{J}^{-1}\,\mathrm{m}^{-3}$$

$$D'(E_F) = \frac{3}{4}\frac{n}{E_F^2} \qquad \mathrm{J}^{-2}\,\mathrm{m}^{-3}$$

	$D(E_F)$ J^{-1} m^{-3}	$D'(E_F)$ J^{-2} m^{-3}
Al	1.3×10^{47}	-5.8×10^{65}
Cu	3.24×10^{47}	-1.2×10^{65}
Cr	5.2×10^{47}	9.4×10^{65}
Li	1.5×10^{47}	7.0×10^{65}
Na	8.4×10^{46}	2.2×10^{65}
V	9.9×10^{47}	-8.9×10^{65}

For the exam

- Electrons move like waves, but exchange energy and momentum like particles. When they act like particles their energy is $E = \hbar\omega$ and their momentum is $\vec{p} = \hbar\vec{k}$.
- The wave-like nature of an electron is described by a wave function ψ. The wave function is a solution to the Schrödinger equation and the probability of finding the electron at a position is $\psi^*\psi$.
- The valence electrons of metals become unbound from their atomic nuclei due to electron screening. These electrons act like noninteracting fermions moving in a constant potential $V = 0$. This is the free electron approximation.
- The wave function for free electrons is,

$$\psi(\vec{r}) = \frac{1}{\sqrt{L^3}} e^{i\vec{k}\cdot\vec{r}},$$

  and the energy of free electrons is,

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

  L is the size of the crystal and $\vec{k}$ is restricted to those values that satisfy the periodic boundary conditions.
- The electrons fill the energy levels according to the Pauli exclusion principle, starting with the lowest energy level at $\vec{k} = 0$. Two electrons can occupy every $\vec{k}$ state due to spin.
- In a typical metal, there are some many energy levels that an electron density of states $D(E)$ is defined which states how many energy levels there are at each energy per m³. This density of states is 0 for $E < 0$ and is proportional to $1/\sqrt{E}$ in one dimension, is constant in two dimensions, and is proportional to $\sqrt{E}$ in three dimensions.

For the exam

- The probability that an electron state is occupied is given by the Fermi function,

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

  where μ is the chemical potential and is determined by the condition,

$$n = \int_{-\infty}^{\infty} \frac{D(E)}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1} dE.$$

  where n is the valence electron density.
- At room temperature, the chemical potential is almost the same as the chemical potential at $T = 0$ and it is typically weakly temperature dependent.
- The internal energy density u is the energy E times the number of electron states at that energy $D(E)$ times the probability that a state at that energy is occupied $f(E)$, summed over all energies,

$$u = \int_{-\infty}^{\infty} E D(E) f(E) dE \approx \frac{3}{5} n E_F + \frac{\pi^2}{4} \frac{n}{E_F} (k_B T)^2 \quad \mathrm{J\ m^{-3}}.$$

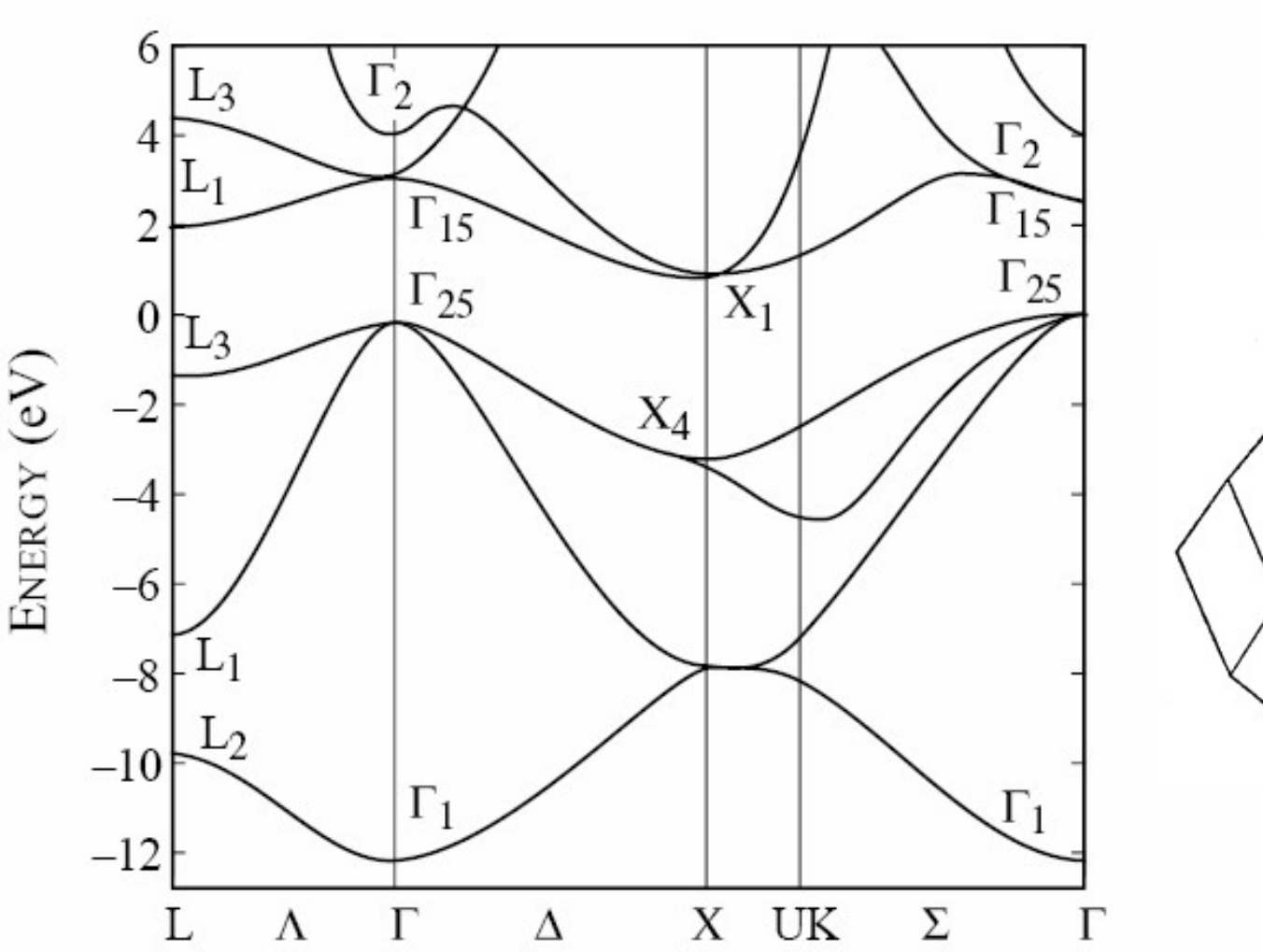
  Here, the last approximate expression was derived using the Sommerfeld expansion.
- Once the internal energy is known, other thermodynamic properties such as the chemical potential, internal energy, Helmholtz free energy, specific heat, entropy, pressure, and bulk modulus can be calculated.
- Measured thermodynamic properties such as the specific heat and the bulk modulus are fit to the free electron expressions using the electron density n and the electron effective mass m as parameters.

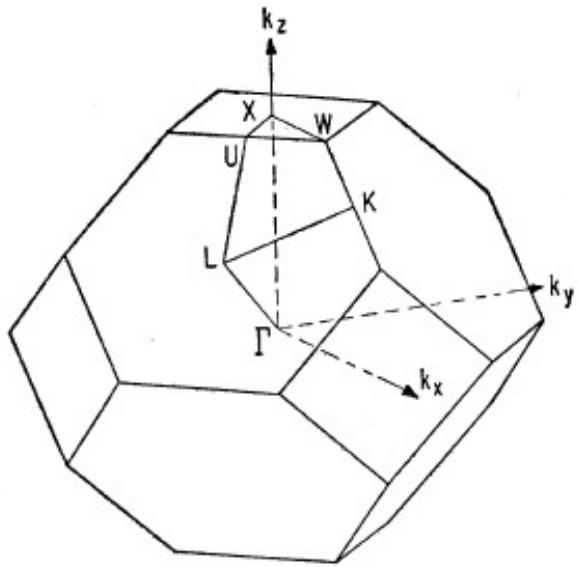
For the exam

- To separate the electron contribution from the phonon contribution to the specific heat, the low temperature measurement is fit to $c_v = \gamma T + AT^3$ where γT is the electron contribution and AT^3 is the phonon contribution.

Electron Band Theory

Calculate the dispersion relation for electrons in a crystal



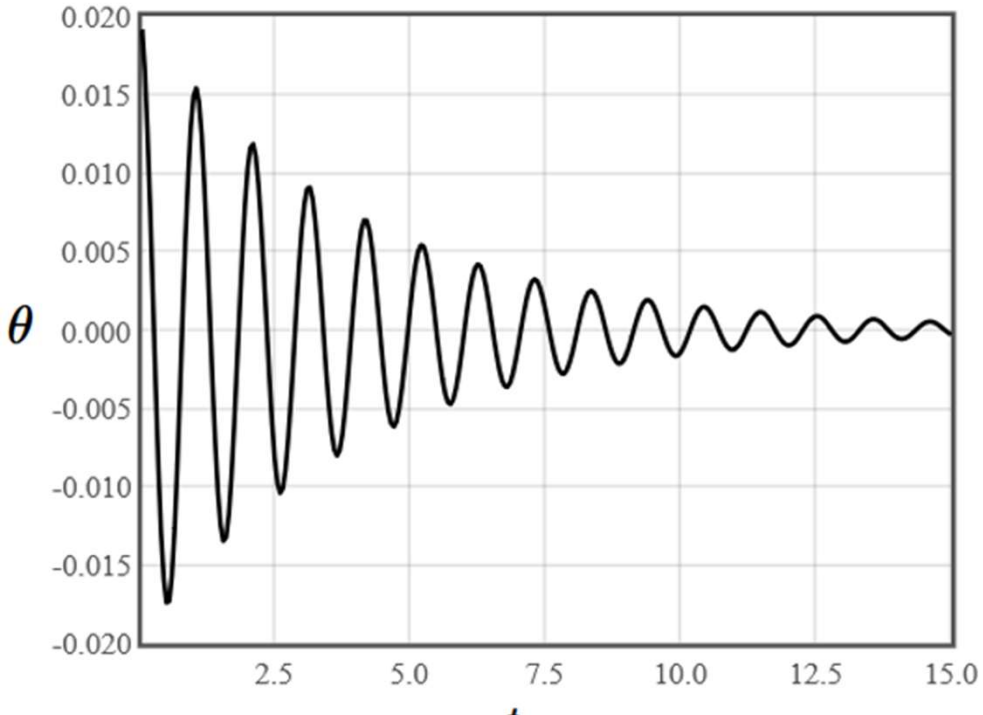


silicon

Swing

Solving for the wavefunctions of electrons in a crystal falls into the same category of differential equations as the problem of a child on a swing. (Second order linear differential equations with periodic coefficients).

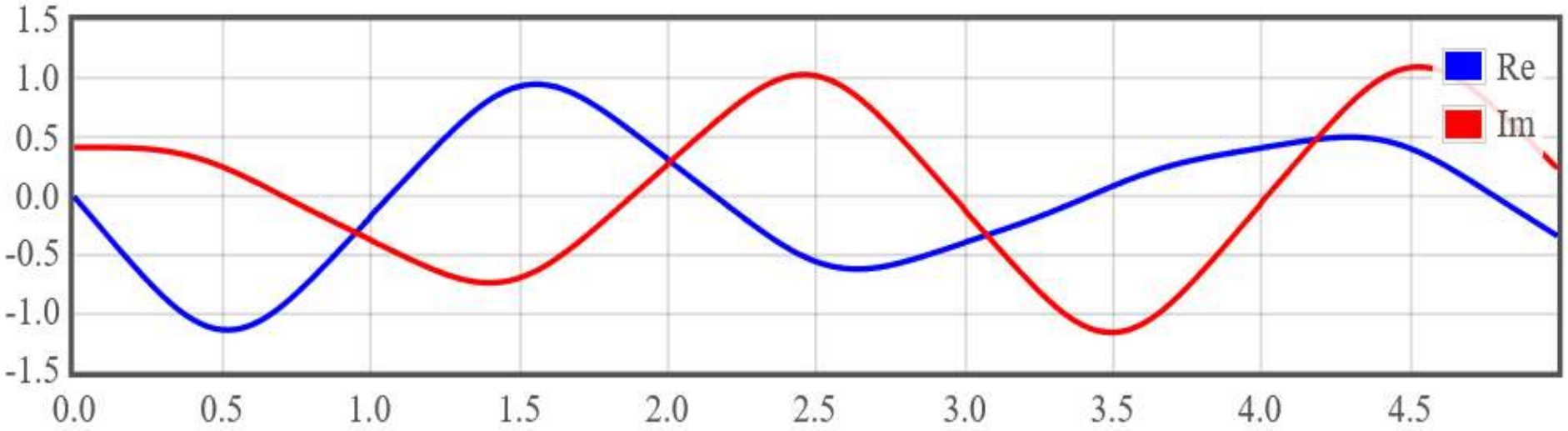
$$m\frac{d^2\theta}{dt^2} + b\frac{d\theta}{dt} + \frac{mg}{l}\theta = 0.$$



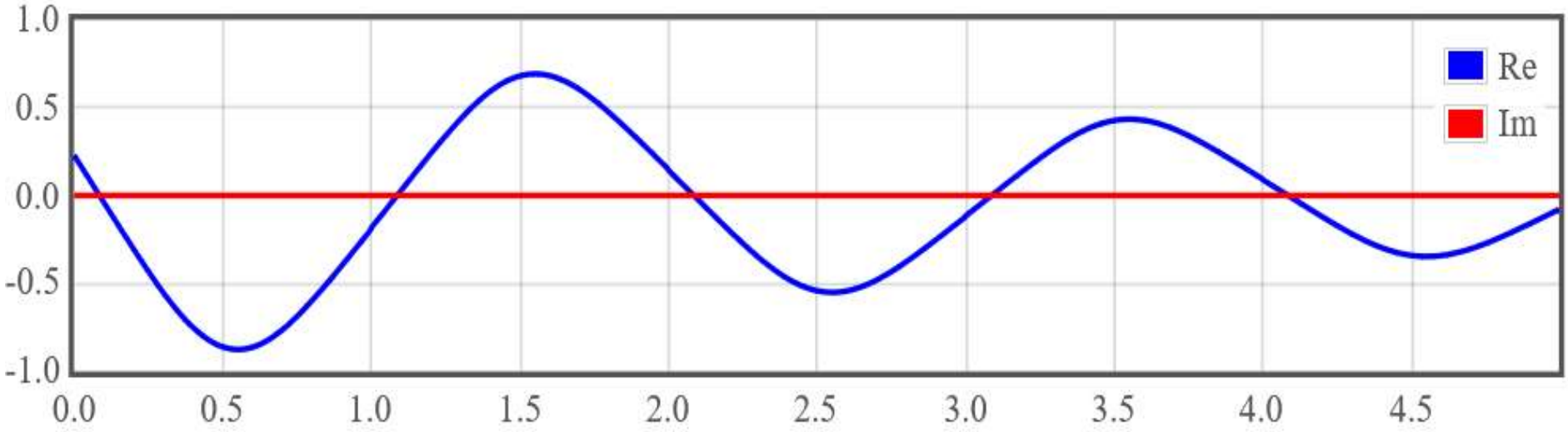
https://lampz.tugraz.at/~hadley/ss1/book/bands/swing.php

Electrons wavefunctions

There are solutions in a band



or in a band gap.



Bloch Theorem

Bloch form $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$

$u_{\vec{k}}(\vec{r})$ is a periodic function.

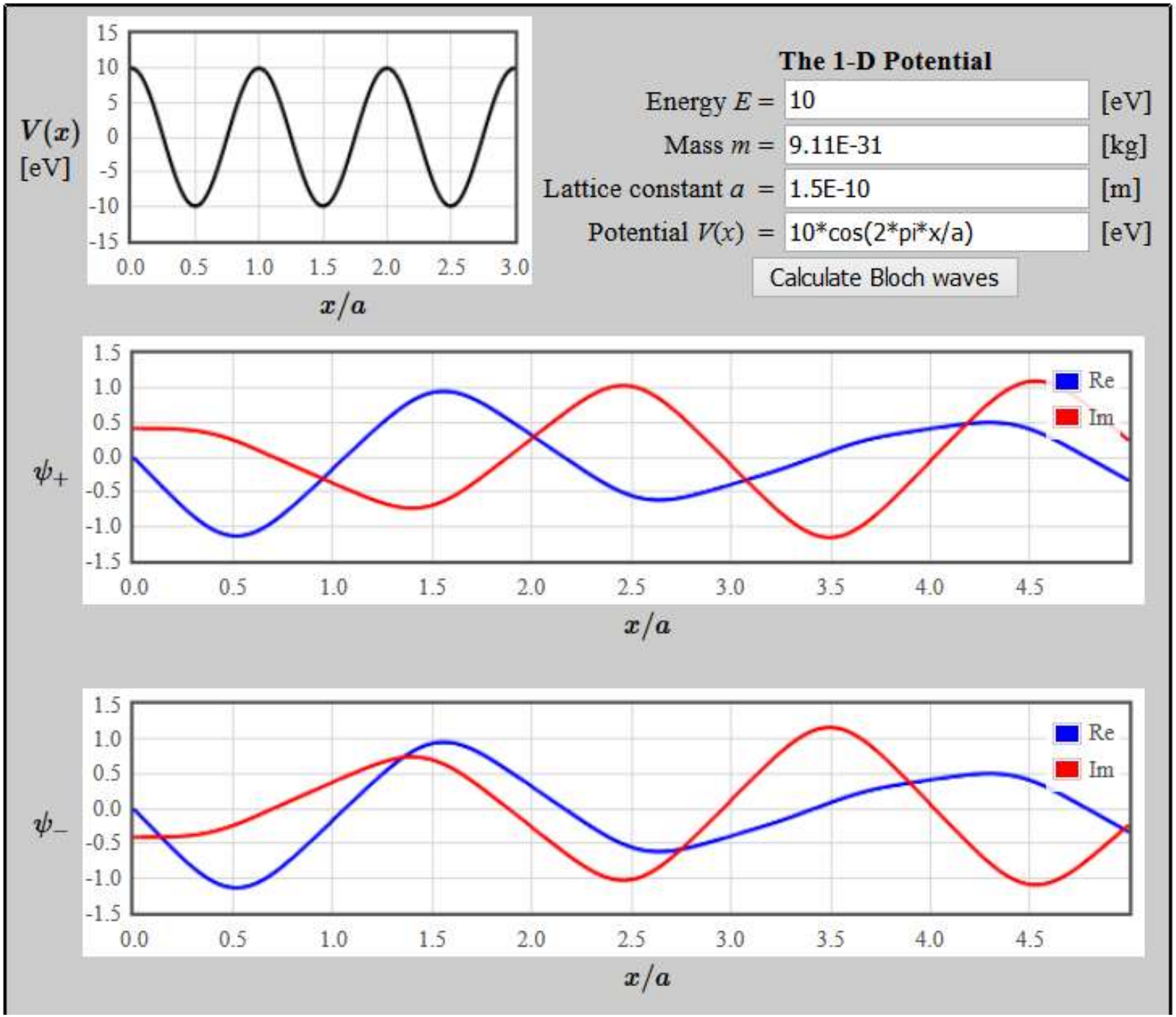
$\vec{k}$ is a wavevector in the first Brillouin zone.

Eigenfunction solutions of the Schrödinger equation have Bloch form.

$$\mathbf{T}\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot(\vec{r}+\vec{T})} u_{\vec{k}}(\vec{r}+\vec{T}) = e^{i\vec{k}\cdot\vec{T}} e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{T}} \psi_{\vec{k}}(\vec{r})$$

Bloch waves in 1-D

$$\psi = e^{ikx} u_k(x)$$



Band structure in 1-D