Conductivity – Periodic arrays of ions

Bill Celmaster

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Section 1

Crystals

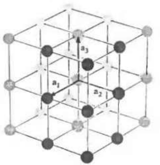
Improving on the free electron approximation

- Drude and Sommerfeld models use **free electron approximation**
  Neglect the ionic field on e^-
- There are significant prediction-modifications if we include that field
- Assume (for now) that ions form a perfect static crystal structure
  - Ashcroft and Mermin chapters 4,5, 7 classify all such crystals
  - I will focus on SCC (simple cubic) configs
- (For now) look at predictions only dependent on crystal structure
  - Most other details of the ion-e^- potential won't matter

Bravais lattice and primitive vectors

- A *Bravais lattice* consists of points $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$
    - n_i are integers
    - $\mathbf{a}_i$ are three independent vectors called *primitive vectors*
    - $\mathbf{R}$ is a *Bravais vector*
    - $\mathbf{a}_i$ *span* or *generate* the lattice
- Example: Simple cubic (SC) lattice

$$\mathbf{a}_1 = (1, 0, 0), \mathbf{a}_2 = (0, 1, 0), \mathbf{a}_3 = (0, 0, 1)$$



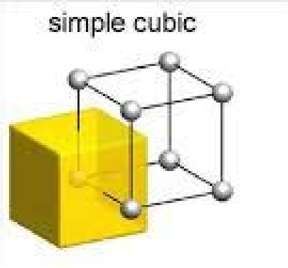
Simple cubic Bravais lattice

- The *coordination number* is # of nearest-neighbors of any point.
    - On an SCC, the coordination number is 6.

Cells

Cells are spacial regions. Space can be filled by non-overlapping regions that are translations of cells by a subset of Bravais vectors.

- *primitive (unit) cell*: One lattice point per cell
- *(conventional) unit cell*: Cell has same symmetry as lattice
- *Wigner-Seitz cell*: Primitive cell with same symmetry as lattice
  The Wigner-Seitz cell about a lattice point is the region of space that is closer to that point than to any other lattice point

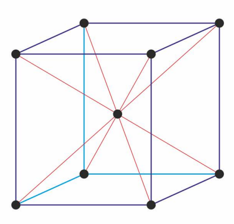


Simple cubic Wigner Seitz cell

Crystal structures a.k.a lattices with bases

Crystal: Each copy of primitive cell has identical collection of ions

- Crystal structure locations are given by the *lattice basis* $\mathbf{c}^j$
  - Ions are located at $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 + \mathbf{c}^j$
  - In general, there could be different species of ions at different j
- Examples starting with the SC Bravais lattice (n_1, n_2, n_3)
  - Monatomic SC crystal: $\mathbf{c}^1 = 0$.
  - Body-centered cubic crystal: $\mathbf{c}^1 = 0, \mathbf{c}^2 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$



Body-centered crystal structure

Example Bravais lattices

(a) Bravais lattice (b) Wigner Seitz cell

Body-centered cubic

(a) Bravais lattice (b) Wigner Seitz cell

Face-centered cubic

Reciprocal lattice

The reciprocal lattice is the set of **K'** with $e^{i\mathbf{K'}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K'}\cdot\mathbf{r}}$ for all **r** and for every Bravais vector **R**.[1]

- $e^{i\mathbf{K'}\cdot\mathbf{R}} = 1$
- $e^{i\mathbf{K'}\cdot\mathbf{r}}$ are plane waves with periodicity of the (direct) Bravais lattice
- It can be proven that the reciprocal lattice is a Bravais lattice with generators $\mathbf{b}_i$ (Ashcroft and Mermin Chptr 5)
- Also, the reciprocal of the reciprocal lattice is the direct lattice.
- Example 1 Reciprocal lattice of SC is SC.
- Example 2 Reciprocal lattice of BCC is FCC (and vice versa)
- If v is the volume of a primitive cell of the direct lattice, then $\frac{(2\pi)^3}{v}$ is the volume of a primitive cell of the reciprocal lattice.
- Wigner Seitz cell of reciprocal lattice is called the *first Brillouin zone*

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[1] I use the notation **K'** rather than **K** in Ascroft and Mirman, because for the special 1D case, K is reserved for $\frac{2\pi}{a}$.

Section 2

Electron Levels in a Periodic Potential

The periodic potential

See Ashcroft and Mermin Chapter 8.

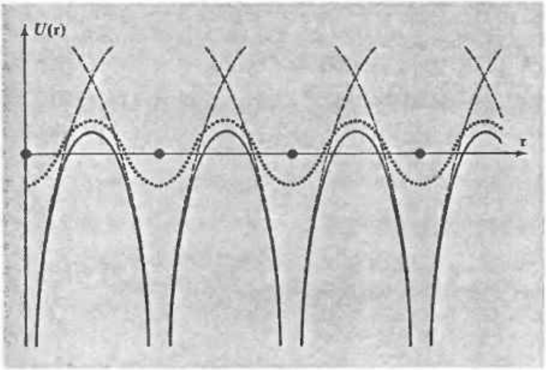


Figure 8.1
A typical crystalline periodic potential, plotted along a line of ions and along a line midway between a plane of ions. (Closed circles are the equilibrium ion sites; the solid curves give the potential along the line of ions; the dotted curves give the potential along a line between planes of ions; the dashed curves give the potential of single isolated ions.)

We will examine single-electron Hamiltonians with the form

$$H_P\psi = \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + U(\mathbf{r})\right)\psi$$

where $U(\mathbf{r})$ is the periodic potential of an ionic crystal.

Of particular interest are the eigensolutions $H_P\psi = E\psi$.

Subsection 1

Bloch's theorem

Statement of Bloch's theorem

Bloch's theorem is proven (2 ways) in Ashcroft and Mermin.

Bloch's theorem states that all eigenfunctions of H_P have the form

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

where $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ for all Bravais vectors $\mathbf{R}$

- Note that $u_{n\mathbf{k}}$ has the periodicity of the Bravais lattice
- The index n is called the *band index*
  - As it turns out, for each allowed $\mathbf{k}$ there are many solutions.
- Bloch's theorem is equivalent to this: The eigenstates of H_P can be chosen so that associated with each ψ is a wave vector $\mathbf{k}$ such that

  $$\psi(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$$

  for every Bravais vector $\mathbf{R}$.

Born-Von Karman (BVK) boundary conditions

- A free e^- in unbounded volume has a continuum of energy levels
- In nature, and for math simplicity, put e^- in finite volume.
  - Set periodic boundary conditions (for math simplicity) on sites
  - There can be multiple electrons per site
  - Obtain discrete levels
- Crystal symmetry bdry conditions – Born-Von Karman (BVK)
  - Pick N_1, N_2, N_3 so $N = N_1 N_2 N_3$ is total number of sites
  - Require $\psi(\mathbf{r} + N_i \mathbf{a}_i) = \psi(\mathbf{r})$ for $i = 1, 3$; primitive vectors $\mathbf{a}_i$.
  - With Block's theorem, this forces $\mathbf{k} = \sum_{i=1}^{3} \frac{m_i}{N_i} \mathbf{b}_i$ for ints m_i
  - There are N allowed wavelengths per primitive reciprocal cell.
- It can be shown that $\boldsymbol{\Delta}\mathbf{k} = \frac{(2\pi)^3}{V}$ is the volume of $\mathbf{k}$-space per allowed value of $\mathbf{k}$.
- Same as for free electron.

Some remarks on periodicity and band structure

- We can restrict $\mathbf{k}$ to the first Brillouin zone. Proof follows:
  - We want to show that if $\psi_{n\mathbf{k}}$ is an eigenfunction, then it equals an eigenfunction $\psi_{n'\mathbf{k}'}$ where $\mathbf{k}'$ is in the first Brillouin zone.
  - If $\mathbf{k}$ isn't in the first Brillouin zone, pick $\mathbf{K'}$ so $k + \mathbf{K'}$ is.
  - $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}n}(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{K'})\cdot\mathbf{r}} \left(e^{-i\mathbf{K'}\cdot\mathbf{r}} u_{\mathbf{k}n}(\mathbf{r})\right)$
  - Let $v_n(\mathbf{r}) \equiv e^{-i\mathbf{K'}\cdot\mathbf{r}} u_{\mathbf{k}n}(\mathbf{r})$
  - Since $e^{i\mathbf{K'}\cdot R} = 1$ and since $u_{\mathbf{k}n}$ is periodic, then

$$v_n(\mathbf{r}+\mathbf{R}) = e^{-i\mathbf{K'}\cdot(\mathbf{r}+\mathbf{R})} u_{\mathbf{k}n}(\mathbf{r}+\mathbf{R}) = e^{-i\mathbf{K'}\cdot\mathbf{r}} u_{\mathbf{k}n}(\mathbf{r}) = v_n(\mathbf{r})$$

  - Therefore we've shown that $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{K'})\cdot\mathbf{r}} v_n(\mathbf{r})$.
  - By assumption $\psi_{n\mathbf{k}}$ is an eigenfunction.
  - It is expressed as $e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$ times a periodic function.
  - Set $\mathbf{k}' = \mathbf{k}+\mathbf{K'}$
  - So we can express this eigenfunction as $\psi_{n'\mathbf{k}'}$. **QED**
- Since the index "n" is an arbitrary designation of distinct eigenvalues, we can, using notation from the above proof, relabel n' to n when $\mathbf{k}$ is in the first Brillouin zone. Then $\psi_{n\mathbf{k}} = \psi_{n(\mathbf{k}+\mathbf{K'})}$.
- From Schrodinger's equation, $\psi_{n\mathbf{k}}$ is continuous in $\mathbf{k}$ so by periodicity, the eigenvalues are bounded in $\mathbf{k}$ hence "energy bands".

The 1D Schrodinger theory in a periodic potential

- The 1D single-electron Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)$$

- The energy levels are values of E for eigensolutions

$$H\psi = E\psi$$

- Version of Bloch's theorem.
  - When U is periodic with period "a", there is a k so that

$$\psi_{nk}(x) = e^{ikx}u_{nk}(x)$$

  where $u_{nk}(x+a) = u_{nk}(x)$ and $|k| < K/2$, where $K = 2\pi/a$.
  - We'll call this a **canonical form**

Note that there are many canonical forms differing from one another by permutations of the n index, or the k index of u_{nk}. Any of these could be used for the band-structure analysis that we do later.

U=0

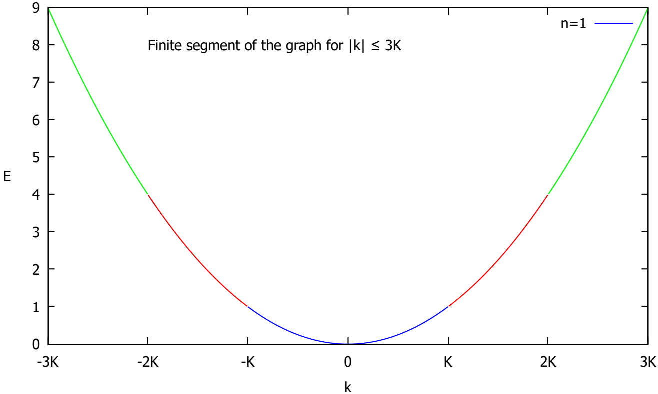
Note that when $U = 0$, it is periodic for any value of a.

- Eigensolutions are $\psi_k = \frac{1}{\sqrt{2\pi}} e^{ikx}$ for all values of k.

$$\begin{aligned} H\psi_k &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(\frac{1}{\sqrt{2\pi}} e^{ikx}\right) \\ &= \frac{\hbar^2 k^2}{2m}\left(\frac{1}{\sqrt{2\pi}} e^{ikx}\right) = E_k\psi_k \end{aligned} \tag{1}$$

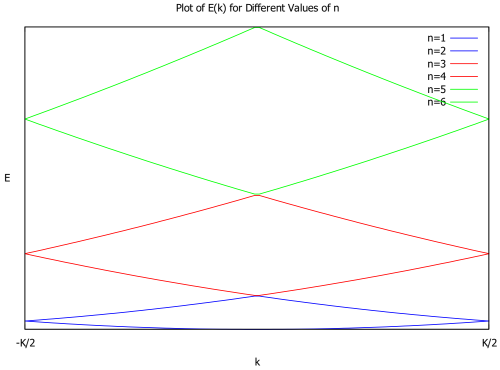
- So the energy eigenvalues are $E_k = \frac{\hbar^2 k^2}{2m}$.

Standard form



Standard form: $\psi_k = \frac{1}{\sqrt{2\pi}} e^{ikx}$

Canonical form



$$\psi_{nk}(x) = e^{ikx} u_{nk}(x) \text{ where } (2\pi)^{\frac{1}{2}}\, u_{nk}(x) = e^{i\left(\operatorname{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)x}$$

u_{nk} is periodic.

First Brillouin zone

$$u_{nk}(x+R) = e^{i\left(\operatorname{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)(x+R)} = e^{i\left(\operatorname{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)x} e^{i\left(\operatorname{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)R}$$

$$= e^{i\left(\operatorname{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)x} \times 1 = u_{nk}(x)$$

In the equations above, note the floor function $\left[\,*\,\right]$.

Homework exercise

Show that the canonical form leads to the above graph. Hints:

- First consider $n = 1$, and derive ψ_{1k}.
- Then apply the Hamiltonian operator to ψ_{1k} and show that $H\psi_{1k} = \frac{\hbar^2 k^2}{2m}\psi_{1k}$.
- Since this is of the form $H\psi_{1k} = E\psi_{1k}$ say what the energy is as a function of k.
- Compare to the standard form when $|k| < \frac{K}{2}$ – the lower half of the blue section
- Now set $n = 2$ and derive ψ_{2k}.
- Apply the Hamiltonian operator and, as before, derive the energy as a function of k.
- Compare the upper blue graph (in the canonical form) to the standard form – but when $\frac{K}{2} < |k| < K$.
- Pick some other random n (less than 5) to see how the rest of the graph works.

Subsection 2

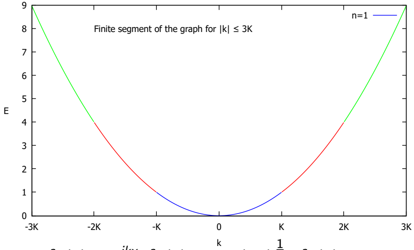
Ionic potential $U \approx 0$

Setup

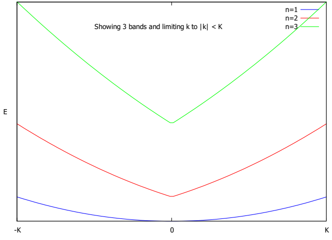
This follows Ashcroft and Mermin Chapter 9.
Start with a 1D system with $U = 0$. Each electron is free.

- Eigenfunctions are $\psi_k(x) = \frac{1}{(2\pi)^{\frac{1}{2}}} e^{ikx}$
- For each k, the energy is $\frac{\hbar^2 k^2}{2m}$.
- Let K' be a vector of the reciprocal lattice.

Bloch decompositions I



$$\psi^a_{1k}(x) = e^{ikx} u^a_{1k}(x) \text{ where } (2\pi)^{\frac{1}{2}} u^a_{1k}(x) = 1$$

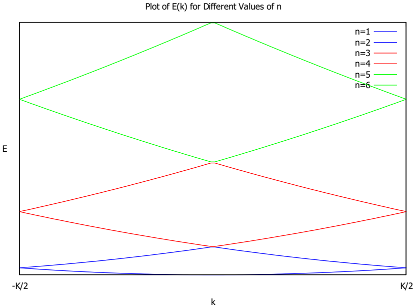


$$\psi^b_{nk}(x) = e^{ikx} u^b_{nk}(x) \text{ where } (2\pi)^{\frac{1}{2}} u^b_{nk}(x) = e^{i(\mathrm{sgn}(k)(n-1)Kx)}$$

u^b_{nk} is periodic.

$$u^b_{nk}(x+R) = e^{i(\mathrm{sgn}(k)(n-1)K)(x+R)} = e^{i(\mathrm{sgn}(k)(n-1)K)x} e^{i(\mathrm{sgn}(k)(n-1)K)R} = e^{i(\mathrm{sgn}(k)(n-1)K)x} \times 1 = u^b_{nk}(x)$$

Bloch decompositions II



$$\psi^c_{nk}(x) = e^{ikx} u^c_{nk}(x) \text{ where } (2\pi)^{\frac{1}{2}}\; u^c_{nk}(x) = e^{i\left(\mathrm{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)x}$$

u^c_{nk} is periodic.

First Brillouin zone

$$u^c_{nk}(x+R) = e^{i\left(\mathrm{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)(x+R)} = e^{i\left(\mathrm{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)x} e^{i\left(\mathrm{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)R}$$

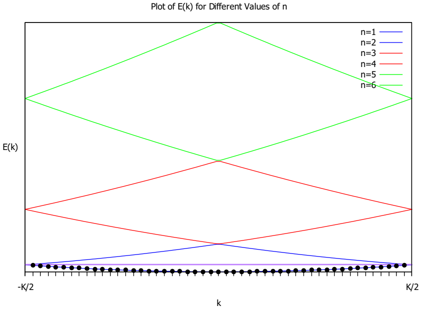
$$= e^{i\left(\mathrm{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)x} \times 1 = u^c_{nk}(x)$$

In the equations above, note the floor function $\left[\, * \,\right]$.

Fermi surface

The Fermi surface is the surface of smallest energy E_F such that all low-temperature electrons have an energy less than E_F.

- Let N be the number of primitive cells (or sites)
- So number of BVK wavelengths per band $= N$
- Each wavelength has two spins so there are $2N$ states per band.
- Assume 50 sites, with one electron per site $\implies$ 50 electrons.
- 100 states per band; at $T = 0$, first band is half-filled.



50 electrons in their ground state, half-populating first level up to a Fermi energy shown as a horizontal purple line

U small but nonzero

- Since U is small, use a perturbation expansion from free case.
- 1D case from Ashcroft and Mirman

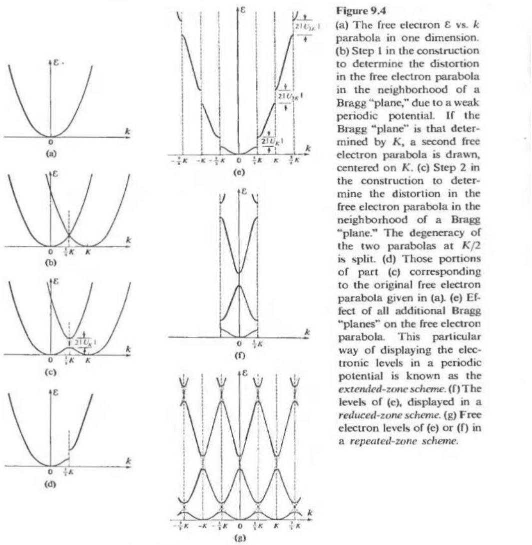


Figure 9.4

(a) The free electron ℰ vs. k parabola in one dimension. (b) Step 1 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane," due to a weak periodic potential. If the Bragg "plane" is that determined by K, a second free electron parabola is drawn, centered on K. (c) Step 2 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane." The degeneracy of the two parabolas at $K/2$ is split. (d) Those portions of part (c) corresponding to the original free electron parabola given in (a). (e) Effect of all additional Bragg "planes" on the free electron parabola. This particular way of displaying the electronic levels in a periodic potential is known as the *extended-zone scheme*. (f) The levels of (e), displayed in a *reduced-zone scheme*. (g) Free electron levels of (e) or (f) in a *repeated-zone scheme*.

Subsection 3

Tight binding

Neutral atom energy levels

Instead of angstrom-separated atoms with almost-free electrons, imagine cm-spaced neutral atoms.

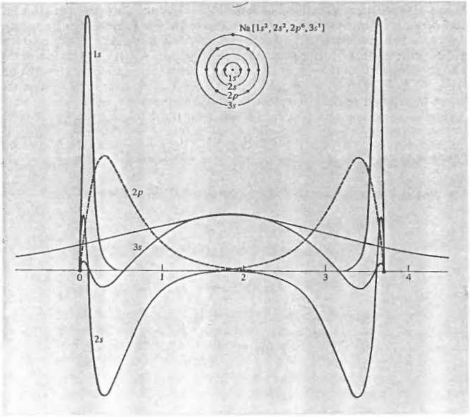


Figure 10.1

Calculated electron wave functions for the levels of atomic sodium, plotted about two nuclei separated by the nearest-neighbor distance in metallic sodium, 3.7 Å. The solid curves are $r\psi(r)$ for the $1s$, $2s$, and 3s levels. The dashed curve is r times the radial wave function for the $2p$ levels. Note how the $3s$ curves overlap extensively, the $2s$ and $2p$ curves overlap only a little, and the $1s$ curves have essentially no overlap. The curves are taken from calculations by D. R. Hartree and W. Hartree, *Proc. Roy. Soc.* **A193**, 299 (1948). The scale on the r-axis is in angstroms.

Band structure follows atomic energy levels

- Recall $H = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})$.
    - U is periodic
- Let $H_{at} = -\frac{\hbar^2}{2m}\nabla^2 + U_{at}(\mathbf{r})$
    - U_{at} is the single-atom potential centered at $r = 0$.
- Start by solving $H_{at}\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r})$.
    - $\psi_n(\mathbf{r})$ are centered around $\mathbf{r} = 0$.
- Now write H as $H_{at} + \Delta U$.
- Since U is periodic, ΔU is only small between sites.
- If you do perturbation theory around $\mathbf{r} = 0$, you make small modifications of ψ_n and E_n.
- Approximately, $\psi_n(\mathbf{r}+\mathbf{R})$ is an eigensolution with eigenvalue E_n.
- Bloch form (see Ashcroft and Mirman Chapter 10)

$$\psi_n(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\psi_n(\mathbf{r}\text{-}\mathbf{R})$$

    - For each of the N BVK crystal-momenta $\mathbf{k}$.