PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 20:

Review: Chapters 1-6 in GGGPP

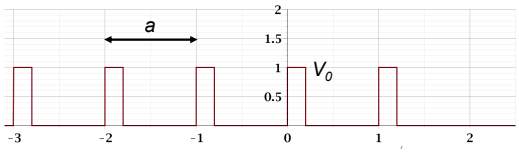
1. Bloch theorem
2. Kronig-Penny model
3. Group theory

3	Mon, 8/31/2015	Chap. 1.4	Tight binding models	#3
4	Wed, 9/02/2015	Chap. 1.6, 2.1	Crystal structures	#4
5	Fri, 9/04/2015	Chap. 2	Group theory	#5
6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015	Chap. 2.4-2.7	Densities of states	#8
10	Wed, 9/16/2015	Chap. 3	Free electron model	#9
11	Fri, 9/18/2015	Chap. 4	One electron approximations to the many electron problem	#10
12	Mon, 9/21/2015	Chap. 4	One electron approximations to the many electron problem	#11
13	Wed, 9/23/2015	Chap. 4	Density functional theory	#12
14	Fri, 9/25/2015	Chap. 5	Implementation of density functional theory	#13
15	Mon, 9/28/2015	Chap. 5	Implementation of density functional theory	#14
16	Wed, 9/30/2015	Chap. 5	First principles pseudopotential methods	#15
17	Fri, 10/02/2015	Chap. 6	Example electronic structures	#16
18	Mon, 10/05/2015	Chap. 6	Ionic and covalent crystals	#17
19	Wed, 10/07/2015	Chap. 6	More examples of electronic structures	#18
20	Fri, 10/09/2015	Chap. 1-6	Review	Start exam
	Mon, 10/12/2015		No class	Take-home exam
	Wed, 10/14/2015		No class	Exam due before 10/19/2015
	Fri, 10/16/2015		Fall break -- no class	
23	Mon, 10/19/2015			

Bloch theorem for solution $\Psi_{\mathbf{k}}(\mathbf{r})$ to the Schroedinger equation for an electron in a periodic solid in terms of translation vector $\mathbf{T}$:

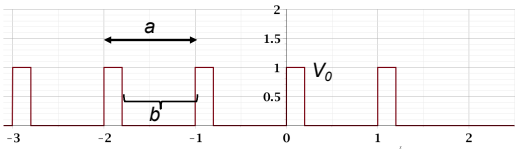
$\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\Psi_{\mathbf{k}}(\mathbf{r})$

Consider an electron moving in a one-dimensional model potential (Kronig and Penney, *Proc. Roy. Soc. (London)* **130,** 499 (1931)



Schroedinger equation for electron:

$$\left(-\frac{\hbar^2\nabla^2}{2m}+V(x)\right)\Psi(x)=E\Psi(x)$$

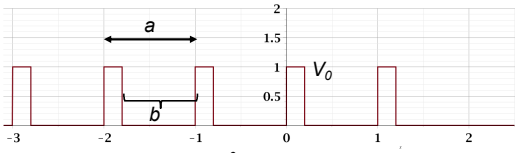


Matching conditions reduce to:

$$\cos(ka) = F(E)\cos\left(\alpha b - \Delta(E)\right)$$

$$F(E) \equiv \left(1 + \frac{V_0^2}{4E\left(E - V_0\right)}\sinh^2\left(\beta(a-b)\right)\right)^{1/2}$$

$$\tan\Delta(E) = \frac{V_0 - 2E}{2\sqrt{E\left(V_0 - E\right)}}\tanh\left(\beta(a-b)\right)$$



Details for $V_0 = \frac{\hbar^2}{2m}\frac{(2\pi)^2 49}{16b^2}$; $b = \frac{16}{17}a$

Let $f \equiv \frac{E}{V_0}$

$$\cos(ka) = \left(1 + \frac{\sinh^2\left(0.687\sqrt{1-f}\right)}{4f\left(1-f\right)}\right)^{1/2}\cos\left(11.7\sqrt{f} - \Delta(f)\right)$$

$$\tan\Delta(f) = \frac{1-2f}{2\sqrt{f\left(1-f\right)}}\tanh\left(0.687\sqrt{1-f}\right)$$

$$\cos(ka) = \left(1 + \frac{\sinh^2\left(0.687\sqrt{1-f}\right)}{4f\left(1-f\right)}\right)^{1/2}\cos\left(11.7\sqrt{f} - \Delta(f)\right)$$

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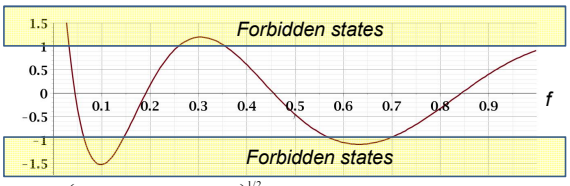
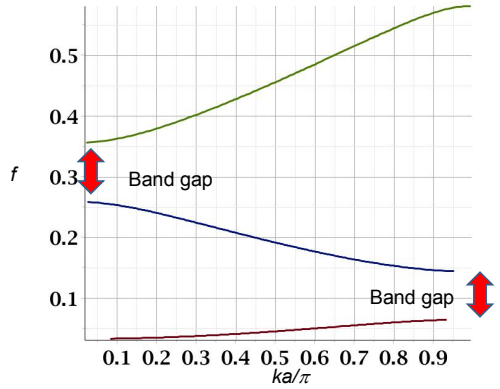
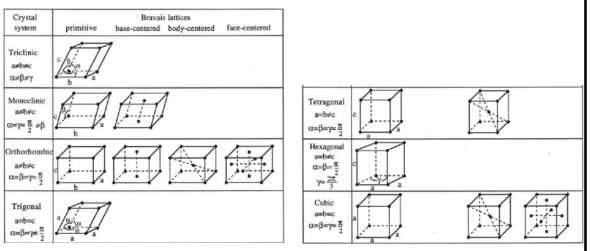


$$X(f) = \left(1 + \frac{\sinh^2\left(0.687\sqrt{1-f}\right)}{4f\left(1-f\right)}\right)^{1/2}\cos\left(11.7\sqrt{f} - \Delta(f)\right)$$



Classification of lattice types –
14 Bravais lattices
230 space groups



Short digression on abstract group theory
What is group theory ?

A group is a collection of "elements" – $A, B, C, \ldots$ and a "multiplication" process. The abstract multiplication $(\cdot)$ pairs two group elements, and associates the "result" with a third element. (For example $(A \cdot B = C)$.) The elements and the multiplication process must have the following properties.

1. The collection of elements is closed under multiplication. That is, if elements A and B are in the group and $A \cdot B = C$, element C must be in the group.
2. One of the members of the group is a "unit element" (E). That is, for any element A of the group, $A \cdot E = E \cdot A = A$.
3. For each element A of the group, there is another element A^{-1} which is its "inverse". That is $A \cdot A^{-1} = A^{-1} \cdot A = E$.
4. The multiplication process is "associative". That is for sequential mulplication of group elements A, B, and C, $(A \cdot B) \cdot C = A \cdot (B \cdot C)$.

Group theory – some comments

- The elements of the group may be abstract; in general, we will use them to describe symmetry properties of our system

Representations of a group

A representation of a group is a set of matrices (one for each group element) -- $\Gamma(A),\Gamma(B)...$ that satisfies the multiplication table of the group. The dimension of the matrices is called the dimension of the representation.

The great orthogonality theorem

Notation: $h \equiv$ order of the group

$R \equiv$ element of the group

$\Gamma^i(R)_{\alpha\beta} \equiv$ ith representation of R

$_{\alpha\beta}$ denote matrix indices

$l_i \equiv$ dimension of the representation

$$\sum_R \left(\Gamma^i(R)_{\mu\nu}\right)^* \Gamma^j(R)_{\alpha\beta} = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}\delta_{\nu\beta}$$

Analysis shows: $\sum_i l_i^2 = h$

Note: only irreducible representations are used.

Simplified analysis in terms of the "characters" of the representations

$$\chi^j(R) \equiv \sum_{\mu=1}^{l_j} \Gamma^j(R)_{\mu\mu}$$

Character orthogonality theorem

$$\sum_R \left(\chi^i(R)\right)^* \chi^j(R) = h\delta_{ij}$$

Note that all members of a class have the same character for any given representation *i*.

Reciprocal lattice

$\mathbf{t}_i \cdot \mathbf{g}_j = 2\pi\delta_{ij}$

real lattice reciprocal lattice

Unit vectors of the reciprocal lattice

$$\mathbf{g}_1 = \frac{2\pi}{\Omega}\mathbf{t}_2 \times \mathbf{t}_3, \quad \mathbf{g}_2 = \frac{2\pi}{\Omega}\mathbf{t}_3 \times \mathbf{t}_1, \quad \mathbf{g}_3 = \frac{2\pi}{\Omega}\mathbf{t}_1 \times \mathbf{t}_2, \quad \text{and} \quad \Omega = \mathbf{t}_1 \cdot (\mathbf{t}_2 \times \mathbf{t}_3),$$

General reciprocal lattice vector

$$\mathbf{g}_m = m_1\mathbf{g}_1 + m_2\mathbf{g}_2 + m_3\mathbf{g}_3$$

Reciprocal lattice

$\mathbf{t}_i \cdot \mathbf{g}_j = 2\pi\delta_{ij}$

real lattice reciprocal lattice

Unit vectors of the reciprocal lattice

$$\mathbf{g}_1 = \frac{2\pi}{\Omega}\mathbf{t}_2 \times \mathbf{t}_3, \quad \mathbf{g}_2 = \frac{2\pi}{\Omega}\mathbf{t}_3 \times \mathbf{t}_1, \quad \mathbf{g}_3 = \frac{2\pi}{\Omega}\mathbf{t}_1 \times \mathbf{t}_2, \quad \text{and} \quad \Omega = \mathbf{t}_1 \cdot (\mathbf{t}_2 \times \mathbf{t}_3),$$

General reciprocal lattice vector

$$\mathbf{g}_m = m_1\mathbf{g}_1 + m_2\mathbf{g}_2 + m_3\mathbf{g}_3$$

Quantum Theory of materials

Exact Schrödinger equation:

$$\mathcal{H}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = E_{\alpha\nu}\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Electronic coordinates

Atomic coordinates

where

$$\mathcal{H}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) + \mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Born-Oppenheimer approximation

Born & Huang, **Dynamical Theory of Crystal Lattices**, Oxford (1954)

Approximate factorization:

$$\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = X^{\text{Nuclei}}_{\alpha\nu}(\{\mathbf{R}^a\})\Upsilon^{\text{Electrons}}_{\alpha}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Quantum Theory of materials -- continued

Electronic Schrödinger equation:

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = U_\alpha(\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{a,i}\frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Nuclear Hamiltonian: (Often treated classically)

$$\mathcal{H}^{\text{Nuclei}}\left(\{\mathbf{R}^a\}\right)X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\}) = W_{\alpha\nu}X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Nuclei}}\left(\{\mathbf{R}^a\}\right) = \sum_a \frac{\mathbf{P}^{a2}}{2M^a} + U_\alpha(\{\mathbf{R}^a\})$$

Effective nuclear interaction provided by electrons

First consider electronic Hamiltonian

Electronic Schrödinger equation:

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = U_\alpha(\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{a,i}\frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Replace by "jellium"

Independent electron contributions

Jellium model of metals

- Nuclear potential represented by a uniform background of positive charge with charge density $n_0 = Z/V$ (V representing volume per atom)
- Electrons represented as independent free electrons occupying free-electron states $E(k) = \frac{\hbar^2 k^2}{2m}$ for $0 \le k \le k_F$

Figure from GGGPP

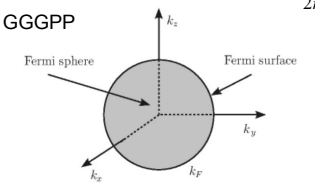
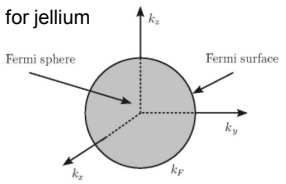


Figure 3.2 Schematic representation in the **k**-space of the Fermi sphere of occupied states and of the Fermi surface of the free-electron gas. At $T = 0$ each state of wavevector **k**, with $k < k_F$, is occupied by two electrons of either spin.

Calculation of the Fermi level for jellium



$$N = \sum_{\mathbf{k}}^{k<k_F} 2 = 2\frac{V}{(2\pi)^3}\frac{4}{3}\pi k_F^3 = \frac{V}{3\pi^2}k_F^3 \quad \Longrightarrow \quad k_F^3 = 3\pi^2 n,$$

Density of states analysis of free electron gas

$$D(E) = 2\frac{V}{(2\pi)^3}\int \delta\left(E - \frac{\hbar^2 k^2}{2m}\right) d\mathbf{k} = \frac{V}{4\pi^3}\int_0^\infty 4\pi k^2 \delta\left(E - \frac{\hbar^2 k^2}{2m}\right) dk.$$

The change of variable $\hbar^2 k^2/2m = x$ gives

$$D(E) = \frac{V}{2\pi^2}\int_0^\infty \left(\frac{2m}{\hbar^2}\right)^{3/2} x^{1/2}\,\delta(E-x)\,dx = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}, \quad E > 0. \tag{3.8a}$$

$$D(E) = \frac{3}{2}\frac{N}{E_F}\left(\frac{E}{E_F}\right)^{1/2},$$

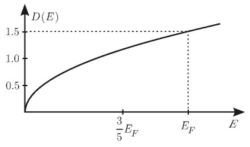


Figure 3.3 Density-of-states, in units of N/E_F, for a free-electron gas; the average electron energy (3/5) E_F is also indicated.

Practical modeling schemes – based on density functional theory

Kohn-Sham formulation of density functional theory
Results of self-consistent calculations

Variationally determined --

Ground state energy $E_v[n]$

Electron density $n(\mathbf{r})$

Some remaining issues

- Theory for $E_{exc}[n]$ still underdevelopment
- This formalism does not access excited states
- Strongly correlated electron systems are not well approximated

Practical solution of Kohn-Sham equations in solids