Ch. 8: Electron Levels In Periodic Potential

What are the consequences of a periodic potential on the form of the wave functions, irrespective of the exact form of the potential and irrespective of whether the material is a conductor or an insulator? $U$ is the effective one-electron potential.

$$U(\vec{r} + \vec{R}) = U(\vec{r})$$

**Bloch’s Theorem:** The eigenstates of the one-electron Hamiltonian, with a periodic potential in a Bravais lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice.

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

Or, equivalently

$$\psi_{nk}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{nk}(\vec{r})$$

**1st Proof Of Bloch’s Theorem**

Define translation operator $T_{\vec{R}}$:

$$T_{\vec{R}} f(\vec{r}) = f(\vec{r} + \vec{R})$$

Hamiltonian is periodic,

$$T_{\vec{R}} H(\vec{r}) \psi(\vec{r}) = H(\vec{r} + \vec{R}) \psi(\vec{r} + \vec{R})$$

$$T_{\vec{R}} H = HT_{\vec{R}}$$

But, also

$$T_{\vec{R}} T_{\vec{R}'} = T_{\vec{R}'} T_{\vec{R}} = T_{\vec{R} + \vec{R}'}$$

Since $H$ and all $T_{\vec{R}}$’s commute with one another, eigenstate of $H$ can be chosen to be eigenstate of all $T_{\vec{R}}$’s.

$$H \psi = \epsilon \psi$$

$$T_{\vec{R}} \psi(\vec{r}) = c(\vec{R}) \psi(\vec{r})$$

a number
**1st Proof Of Bloch’s Theorem**

\[ H \psi = \epsilon \psi \quad T_R \psi(\vec{r}) = c(\vec{R}) \psi(\vec{r}) \]

\[ c(\vec{R} + \vec{R}') = c(\vec{R})c(\vec{R}') \]

Let \[ c(\vec{a}_i) = e^{2\pi i x_i} \]

primitive vector

\[ \vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \]

\[ c(\vec{R}) = e^{2\pi i n_1 x_1} e^{2\pi i n_2 x_2} e^{2\pi i n_3 x_3} \]

\[ c(\vec{R}) = e^{i \vec{k} \cdot \vec{R}} \]

\[ \vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3 \]

**Born – von Karman Boundary Condition**

\[ \psi(\vec{r} + N_i \vec{a}_i) = \psi(\vec{r}) \quad i = 1, 2, 3 \quad \text{PBC} \]

\[ \psi_{n_k}(\vec{r} + N_i \vec{a}_i) = e^{i \vec{k} \cdot \vec{a}_i} \psi_{n_k}(\vec{r}) \quad i = 1, 2, 3 \]

\[ \vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3 \]

\[ e^{2\pi i N_i x_i} = 1 \]

\[ x_i = m_i / N_i \quad m_i \text{ integer} \]

\[ \Delta \vec{k} = \frac{\vec{b}_1}{N_1} \left( \frac{\vec{b}_2}{N_2} \times \frac{\vec{b}_3}{N_3} \right) = \frac{1}{N} \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) \]

\[ \Delta \vec{k} = \frac{(2\pi)^3}{N V_{\text{cell}}} \]

same as free electron gas!
2nd Proof of Bloch’s Theorem (Plane Wave Expansion)

Working within the Born-von Karman periodic boundary condition, we expand both the one-electron wave function and the effective potential in plane waves:

\[ \psi(\mathbf{r}) = \sum_k c_k e^{i \mathbf{k} \cdot \mathbf{r}} \quad U(\mathbf{r}) = \sum_k U_k e^{i \mathbf{k} \cdot \mathbf{r}} \]

\( k \)'s are all the wave vectors allowed by the PBC, but \( K \)'s are only reciprocal lattice vectors because the potential is periodic.

Plugging into Schrödinger’s eq. to look for eigen states:

\[ H \psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi = \varepsilon \psi \]

\[ \sum_k \left\{ \frac{\hbar^2 k^2}{2m} c_k e^{i \mathbf{k} \cdot \mathbf{r}} + \sum_k U_k c_k e^{i (\mathbf{k} + \mathbf{L}) \cdot \mathbf{r}} \right\} = \varepsilon \sum_k c_k e^{i \mathbf{k} \cdot \mathbf{r}} \]

Since \( k \)'s form a complete orthogonal set, coefficient for a specific plane wave on LHS must equal coefficient for the same \( k \) on the RHS.

Plane Wave Expansion (cont.)

\[ \left( \frac{\hbar^2 k^2}{2m} - \varepsilon \right) c_k + \sum_k U_k c_{k-K} = 0 \]

The \( C \) coefficient for plane wave with a specific \( k \) is coupled to the coefficients for all wave vectors \( k' \) related to \( k \) by \( k' = k + \mathbf{K} \), where \( K \) is a reciprocal lattice vector and \( U_k \) is non-zero.

For a specific \( \varepsilon \), this equation has non-trivial solutions only for a few \( k \)'s (or for none).

Plane waves not differing by a reciprocal lattice vector are unrelated. Or, if a plane wave is to couple, it can only couple to other plane waves with wave vectors differing by \( K \) from its own. Grab all plane waves with wave vectors related to \( k \) and form a subset (Hilbert space) that is independent of other subsets. Now a plane wave can only couple to waves within its own subset. To distinguish subsets we can identify them by the one wave vector, \( q \), in each subset that belongs to the first Brillouin zone.

What does it mean physically?

1. If \( U_k \) vanishes for large \( K \)'s, say, \( K > G \) ?
2. If \( U_k \) vanishes for a series of \( K \)'s (e.g. \( nG \), where \( n \) is an odd integer)?
Plane Wave Expansion (cont.)

\[
\left( \frac{\hbar^2 k^2}{2m} - \varepsilon \right) c_k + \sum_k U_{k,\hat{k}-k} c_{\hat{k}} = 0
\]

There is an infinite number of plane waves in each subset (because the number of reciprocal lattice points is infinite). However, the number of subsets is finite (number of allowed \( q \) = number of unit cells in the Born von Karman box). Within each subset, the above matrix can be diagonalized to yield an infinite number of discrete eigenvalues \( \varepsilon_n(q) \), \( n=0, 1, 2, \ldots \). Each eigenstate is composed of a (sub)set of plane waves from one subset, with their proper \( C \) coefficients, which satisfies the Schrödinger equation

\[
H\psi_{n\vec{q}} = \varepsilon_n \psi_{n\vec{q}} \quad \psi_{n\vec{q}}(\vec{r}) = \sum_{\hat{k}} c_{n,\vec{q}+\hat{k}} e^{i(\vec{q}+\hat{k}) \cdot \vec{r}}
\]

Eigenstates with same \( q \) but different \( n \) can be made to be orthogonal to each other. Perturbation theory tells us that for an incremental change in \( q \), (i.e. neighboring subsets) there must be allowed eigenvalues that are incremental changed from each other. These states can be viewed as forming bands and \( n \) is then the band index.

What can we say about the \( C \)'s, if the periodic potential is weak?

Plane Wave Expansion (cont.)

\[
\psi(\vec{r}) = \sum_{\vec{k}} c_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}
\]

Looking at the Schrödinger equation and requesting that \( \Psi \) be an eigenstate with eigenvalue \( \varepsilon \), we see that only a very small number of subsets could have \( \varepsilon \) as one of their eigenvalues. A specific \( \Psi \) can be expanded in plane waves from these few independent subsets with a specific, allowed, eigenvalue.

\[
\psi(n\vec{q})(\vec{r}) = \sum_{\hat{k}} c_{n,\vec{q}+\hat{k}} e^{i(\vec{q}+\hat{k}) \cdot \vec{r}}
\]

We have as many choices as there are terms in the sum to define eigenstates. Certainly, any eigenfunction can be chosen to have only contribution(s) from one \( q \).


**2nd Proof of Bloch’s Theorem**

\[
\psi_{n\bar{q}}(\vec{r}) = \sum_{\bar{K}} c_{n,\bar{q}+\bar{K}} e^{i(\bar{q}+\bar{K})\vec{r}}
\]

any eigen function of a periodic lattice

\[
\psi_{n\bar{q}}(\vec{r}) = e^{i\bar{q} \vec{r}} \sum_{\bar{K}} c_{n,\bar{q}+\bar{K}} e^{i\bar{K} \vec{r}}
\]

all terms periodic with lattice

\[
\psi_{nk}(\vec{r}) = e^{i\vec{k} \vec{r}} u_{nk}(\vec{r})
\]

\[
u_{nk}(\vec{r}) = u_{nk}(\vec{r} + \vec{R})
\]

**Velocity of Bloch Electrons**

\[
\left(-\frac{\hbar^2}{2m} \tilde{\nabla}^2 + U(\vec{r})\right)\psi_{nk}(\vec{r}) = \varepsilon_{nk} \psi_{nk}(\vec{r})
\]

\[
H_{\vec{k}+\vec{q}} u_{\vec{k}}(\vec{r}) = \left(\frac{\hbar^2}{2m} (-i\tilde{\nabla} + \tilde{\vec{k}})^2 + U(\vec{r})\right) u_{\vec{k}}(\vec{r}) = \varepsilon_{\vec{k}} u_{\vec{k}}(\vec{r})
\]

\[
u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})
\]

But, we also know that

\[
\varepsilon_{\vec{k}+\vec{q}}(\vec{k} + \vec{q}) = \varepsilon_{\vec{k}}(\vec{k}) + \sum_{\vec{k},\vec{k}'} \frac{\hbar^2}{m^2} (-i\tilde{\nabla} + \vec{k}) u_{\vec{k}'} + \ldots
\]

\[
\varepsilon_{\vec{k}+\vec{q}}(\vec{k} + \vec{q}) = \varepsilon_{\vec{k}}(\vec{k}) + \vec{q} \cdot \tilde{\nabla}_{\vec{k}} \varepsilon_{\vec{k}} + \frac{1}{2} \sum_{i,j} \frac{\partial^2 \varepsilon_{\vec{k}}}{\partial \tilde{\vec{k}}_i \partial \tilde{\vec{k}}_j} q_i q_j + \ldots
\]

\[
\frac{\partial \varepsilon_{\vec{k}}}{\hbar \partial \vec{k}} = \int d\tilde{\vec{r}} \psi_{nk}^* (\tilde{\vec{r}}) \frac{1}{m} (-i\hbar \tilde{\nabla}) \psi_{nk} (\tilde{\vec{r}}) = \tilde{\vec{v}}_{nk}
\]
About Bloch’s Theorem

1. Allowed wave vector $k$ follow same PBC as free electrons, but $k$ is no longer momentum/$h$ bar.

2. $k$ can always be confined to the first Brillouin zone.

3. Band index $n$

$$u_k(r) = u_{k + \mathcal{K}}(r)$$

$$H_k u_k(r) = \left( \frac{\hbar^2}{2m} \left(-i \nabla + \mathcal{K} \right)^2 + U(r) \right) u_k(r) = \varepsilon_k u_k(r)$$

4. Repeated zone representation

$$\psi_{n,k}(r) = \psi_{n,k + \mathcal{K}}(r)$$

$$\varepsilon_{n,k} = \varepsilon_{n,k + \mathcal{K}}$$

5. Velocity of electron

6. Filled bands, empty bands, partially filled bands and Fermi surface.

Density of Levels

One is often interested in summing quantities from occupied individual electronic levels. In the limit of large crystals, the summation can be replaced by an integral.

If the interested quantity only depends on $k$ through energy, then the integral can be carried out

$$q = \frac{O}{V} = \int d\varepsilon g(\varepsilon) Q(\varepsilon)$$

$$g(\varepsilon) = \sum_n g_n(\varepsilon) = \sum_n \int \frac{d\mathcal{K}}{4\pi} \delta(\varepsilon - \varepsilon_n(\mathcal{K}))$$

Consider equi-energy surfaces in reciprocal space. For small enough energy difference, we get

$$g_n(\varepsilon) d\varepsilon = \int_{S_k(\varepsilon)} \frac{dS}{4\pi^3} \delta(\mathcal{K})$$

$$d\varepsilon = |\nabla \varepsilon_n(\mathcal{K})| \, d\mathcal{K}$$

$$g_n(\varepsilon) = \int_{S_k(\varepsilon)} \frac{dS}{4\pi^3} \frac{1}{|\nabla \varepsilon_n(\mathcal{K})|}$$
van Hove Singularities

van Hove singularities in 3D: $g_{\text{nn}}$ is finite. However, slope diverges.

Ch. 9: Electrons In Weak Periodic Potential

Assuming weak periodic potential in some metals, a reasonable starting point for eigenstates of conduction electrons is plane waves.

Why do we even expect the periodic potential experienced by some conduction (outer-shell) electrons to be weak in some metals?

1. Outer shell electrons are forbidden from coming close to the ion cores.
2. Outside the cores, potential is effectively screened by mobile electrons.

Bloch’s theorem

$$\psi_k(\vec{r}) = \sum_{\vec{k}} c_{\vec{k}-\vec{k}} e^{i(\vec{k}-\vec{k}) \cdot \vec{r}}$$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r})\right) \psi_k(\vec{r}) = \epsilon \psi_k(\vec{r})$$

$$\left(\frac{\hbar^2 (\vec{k} - \vec{K})^2}{2m} - \epsilon\right) c_{\vec{k}-\vec{K}} + \sum_{\vec{k}} U_{\vec{k} \cdot \vec{K}} c_{\vec{k} \cdot \vec{K}} = 0$$

Weak Potential: $U_{\vec{k}}'s \sim U << \text{typical } \epsilon$
Extreme Case: Free Electrons

In the case of ultimately weak potential (free electron gas),

\[ \psi_q \propto e^{i\mathbf{q} \cdot \mathbf{r}} \]

\[ E_q = \frac{\hbar^2 q^2}{2m} \]

\[ E_0 = \frac{\hbar^2}{2m} q_0 \]

\[ E_0^0 = E_0^0 \]

\[ \psi_0 = \sum_{j=1}^{n_0} a_j e^{i \mathbf{K}_j \cdot \mathbf{r}} \]

'\(a\)'s are independent and arbitrary

For free electrons or nearly free electrons, energy is related to the plane wave vector in an obvious way. Inconvenient to use band index. Convenient to use extend zone scheme, i.e. full wave vector.

Nearly Free Electrons: Non-degenerate

\[ \sum_{k} e^{i\mathbf{k} \cdot \mathbf{r}} \left\{ E_0^0 c_k + \sum_{K} U_{kK} c_{k+K} \right\} = E \sum_{k} e^{i\mathbf{k} \cdot \mathbf{r}} c_k \]

First, non-degenerate cases, by which we mean

\[ |E_{k-K}^0 - E_{k-K'}^0| \gg U \quad \text{for all } \mathbf{k}' \neq \mathbf{k} \]

Concentrate on eigenstate "derived" from \(k-K_1\) plane wave

Expect energies and wave functions to be only slightly modified from FEG case.

To find \(c_{k,K}\) we rewrite the topmost eq.

\[ (E - E_{k,K}^0) c_{k,K} = U_{k,K} c_{k+K,K} + \sum_{k'} U_{k',K} c_{k',K} \]

summing over all \(K\) \((U_0 = 0)\)

factor of \(U/\epsilon\) smaller than \(c_{k,K}\)

eigenvalue "derived" from \(k-K_1\), not \(k-K\)
Non-Degenerate NFE

$$c_{\vec{k}'-\vec{K}} = \frac{U_{\vec{k}_1'-\vec{k}'_1} c_{\vec{k}_1'-\vec{K}_1}}{\varepsilon - \varepsilon_0^{0}_{\vec{k}'-\vec{K}}} + \sum_{\vec{k}' = \vec{K}_1} U_{\vec{k}'-\vec{K}_1} c_{\vec{k}'-\vec{K}}$$

$$O(U^2)$$

$$(\varepsilon^{0}_{\vec{k}'-\vec{K}_1} - \varepsilon) c_{\vec{k}'-\vec{K}_1} + \sum_{\vec{k}} U_{\vec{k}'-\vec{K}_1} c_{\vec{k}'-\vec{K}_1} = 0$$

To order of $U^2$, $\varepsilon = \varepsilon^{0}_{\vec{k}'-\vec{K}_1} + \frac{1}{c_{\vec{k}'-\vec{K}_1}} \sum_{\vec{k}} U_{\vec{k}'-\vec{K}_1} U_{\vec{K}'-\vec{K}_1} c_{\vec{k}'-\vec{K}_1} + \ldots$

$$\varepsilon = \varepsilon^{0}_{\vec{k}'-\vec{K}_1} + \sum_{\vec{k}} \frac{|U_{\vec{k}'-\vec{K}_1}|^2}{\varepsilon^{0}_{\vec{k}'-\vec{K}_1} - \varepsilon^{0}_{\vec{k}'-\vec{K}}} + O(U^3)$$

Shift in energy is to order of $U^2$. Repelled by other energy levels.

Perturbation Theory

Equivalently, we could have used perturbation theory and would have gotten the answer quicker

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 \quad H_1 = U(\vec{r})$$

$$\psi_0 \propto e^{i(\vec{k}\cdot\vec{r})}$$

$$\varepsilon = \varepsilon^0 + <\vec{k}' - \vec{K}_1|U|\vec{k}' - \vec{K}_1> + \sum_{\vec{k}_1} \frac{|<\vec{k}' - \vec{K}_1|U|\vec{k}' - \vec{K}>|^2}{\varepsilon^{0}_{\vec{k}'-\vec{K}_1} - \varepsilon^{0}_{\vec{k}'-\vec{K}}} + \ldots$$

$$|\vec{k}' - \vec{K}_1>_{new} = |\vec{k}' - \vec{K}_1> + \sum_{\vec{k}_1} \frac{U_{\vec{k}_1'-\vec{k}'_1}}{\varepsilon^{0}_{\vec{k}_1'-\vec{K}_1} - \varepsilon^{0}_{\vec{k}'-\vec{K}}} |\vec{k}' - \vec{K}> + \ldots$$

$$= c^{0}_{\vec{k}'-\vec{K}_1} / c^{0}_{\vec{k}'-\vec{K}}$$
Nearly Free Electrons: m-Fold Near-Degeneracy

Near degeneracy means:

\[ |\epsilon_{k-K}^0 - \epsilon_{k-K_i}^0| \leq U, \quad i, j = 1, \ldots, m \]

\[ |\epsilon_{k-K}^0 - \epsilon_{k-K_i}^0| \gg U, \quad i = 1, \ldots, m \quad \tilde{K} \neq \tilde{K}_1, \ldots, \tilde{K}_m \]

In non-degenerate case the c’s for the plane wave component to the state derived from k-K_i is

\[ c_{k-K} = \frac{U_{\tilde{K}_i-K} c_{\tilde{K}_i-K}}{\epsilon - \epsilon_{k-K}^0} + \sum_{k \neq k_i} \frac{U_{\tilde{K}_i-K} c_{\tilde{K}_i-K'}}{\epsilon - \epsilon_{k-K}^0} \]

In case of near-degeneracy, c’s are not necessarily small. Eigen states are not (necessarily) dominated by one plane wave component, even for very weak potential.

Degenerate NFE

from plane wave expansion

\[ \left( \epsilon_{k-K}^0 - \epsilon \right) c_{k-K} + \sum_{K} U_{K-K'} c_{K-K'} = 0 \]

distinguish two groups

\[ \left( \epsilon - \epsilon_{k-K}^0 \right) c_{k-K} = \sum_{j=1}^{m} U_{K_j-K} c_{k-K_j} + \sum_{\tilde{K} \neq \tilde{K}_1, \ldots, \tilde{K}_m} U_{\tilde{K}-k} c_{\tilde{K}-k}, \quad i = 1, \ldots, m \]

\[ c_{k-K} = \frac{1}{\epsilon - \epsilon_{k-K}^0} \left( \sum_{j=1}^{m} U_{K_j-K} c_{k-K_j} + \sum_{\tilde{K} \neq \tilde{K}_1, \ldots, \tilde{K}_m} U_{\tilde{K}-k} c_{\tilde{K}-k} \right), \quad \tilde{K} \neq \tilde{K}_1, \ldots, \tilde{K}_m \]

\[ c_{k-K} = \frac{1}{\epsilon - \epsilon_{k-K}^0} \sum_{j=1}^{m} U_{K_j-K} c_{k-K_j} + O(U^2), \quad \tilde{K} \neq \tilde{K}_1, \ldots, \tilde{K}_m \]
Degenerate NFE

\[ (e - e^0_{k+K_1, k-K_1}) c_{k, K_1} = \sum_{j=1}^{m} U_{k', K_1} c_{k', K_1} + \sum_{j=1}^{m} \left( \sum_{k''=K_1}^{K_1} \frac{U_{K''-K, K''-K}}{e - e^0_{K''-K}} \right) + O(U^3), \quad i = 1, \ldots, m \]

\[ (e - e^0_{k-K_j}) c_{k-K_j} = \sum_{j=1}^{m} U_{k_j-K_j} c_{k_j-K_j} + O(U^2), \quad i = 1, \ldots, m \]

To first order in $U$, only need to consider the nearly degenerate states.

Eigenvalue evolves with wave vector. When degeneracy occurs for certain $k-K_i$, it occurs for a small volume around that point in the $k$-space.

Splitting Near Single Bragg Plane

Only two vectors $K_1$ and $K_2$ lead to near-degeneracy (within $U$) of the $k-K$ level near a single Bragg plane. Namely, not 3- or more-fold degenerate.

Choose $U$ such that $U = \epsilon = 0$.

\[ \vec{K} = \vec{K}_2 - \vec{K}_1 \quad \vec{q} = \vec{K} - \vec{K}_1 \]

\[ |\epsilon^0_{k-K} - \epsilon^0_{q-K} | < U \quad |\epsilon^0_{q-K} - \epsilon^0_{q-k} | >> U \quad \text{for} \quad \vec{K}' \neq \vec{K}, \vec{0} \]

\[ (e - \epsilon^0_{q-K}) c_{q-K} = U_{q-K} c_{q-K} \]

\[ (e - \epsilon^0_{q-K}) c_{q-K} = U_{q-K} c_{q-K} \]

Why are degenerate FE states always on some Bragg planes?
Single Bragg Plane

For non-trivial solutions to be found,

\[
\begin{vmatrix}
\varepsilon - \varepsilon_q^0 - U_K & -U_K \\
-\bar{U}_K & \varepsilon - \varepsilon_{\bar{q}-\bar{K}}^0
\end{vmatrix} = 0
\]

\[
\varepsilon^2 - \varepsilon \left( \varepsilon_q^0 + \varepsilon_{\bar{q}-\bar{K}}^0 \right) + \varepsilon_q^0 \varepsilon_{\bar{q}-\bar{K}}^0 - |U_K|^2 = 0
\]

\[
\varepsilon = \frac{1}{2} \left( \varepsilon_q^0 + \varepsilon_{\bar{q}-\bar{K}}^0 \right) \pm \sqrt{\left( \frac{\varepsilon_q^0 - \varepsilon_{\bar{q}-\bar{K}}^0}{2} \right)^2 + |U_K|^2}
\]

For \( \varepsilon \) lying in the Bragg plane

\[
\varepsilon = \varepsilon_q^0 \pm |U_K|
\]

Additional Comments: Single Bragg Plane

\[
\varepsilon = \frac{1}{2} \left( \varepsilon_q^0 + \varepsilon_{\bar{q}-\bar{K}}^0 \right) \pm \sqrt{\left( \frac{\varepsilon_q^0 - \varepsilon_{\bar{q}-\bar{K}}^0}{2} \right)^2 + |U_K|^2}
\]

\[
\frac{\partial \varepsilon}{\partial \varepsilon} = \frac{\hbar^2}{m} \left( \bar{q} - \frac{1}{2} \bar{K} \right)
\]

Gradient lies in the Bragg plane.
Constant energy surface perp. to plane.

stationary state (standing wave)

\[
(\varepsilon - \varepsilon_q^0)c_q = U_K c_{\bar{q}-\bar{K}}
\]

higher band

\[
c_q = \pm \text{sgn}(U_K) c_{\bar{q}-\bar{K}}
\]

Assume \( U_K \) to be real (potential has inversion symmetry)

lower band
Nature of States

\[ c_q = \pm \text{sgn}(U_{\vec{k}}) \ c_{\vec{k}} \]

\[ \psi^{(+)} = e^{i \vec{q} \cdot \vec{r}} + e^{i (\vec{q} + \vec{K}) \cdot \vec{r}} = e^{i (\vec{q} + \vec{K}/2) \cdot \vec{r}} \cos(\frac{1}{2} \vec{K} \cdot \vec{r}) / 2 \]

\[ \psi^{(-)} = e^{i \vec{q} \cdot \vec{r}} - e^{i (\vec{q} + \vec{K}) \cdot \vec{r}} = e^{i (\vec{q} + \vec{K}/2) \cdot \vec{r}} i \sin(\frac{1}{2} \vec{K} \cdot \vec{r}) / 2 \]

Direction of propagation?

\[ U_{\vec{k}} > 0 \]

\[ \left\{ \begin{aligned}
\psi(\vec{r})^2 &\propto (\cos + \vec{K} \cdot \vec{r})^2 & \epsilon = \epsilon_0 + |U_{\vec{k}}| \\
\psi(\vec{r})^2 &\propto (\sin + \vec{K} \cdot \vec{r})^2 & \epsilon = \epsilon_0 - |U_{\vec{k}}| 
\end{aligned} \right. \]

Ion cores at a/2.

\[ U_{\vec{k}} < 0 \]

\[ \left\{ \begin{aligned}
\psi(\vec{r})^2 &\propto (\sin + \vec{K} \cdot \vec{r})^2 & \epsilon = \epsilon_0 + |U_{\vec{k}}| \\
\psi(\vec{r})^2 &\propto (\cos + \vec{K} \cdot \vec{r})^2 & \epsilon = \epsilon_0 - |U_{\vec{k}}| 
\end{aligned} \right. \]

s-like

Energy Bands In 1D

In one dimension, no degeneracy higher than 2-fold is possible.

Extended Zone Scheme
Reduced Zone Scheme
Repeated Zone Scheme
3D Examples

There are as many k-states in a Brillouin zone as there are cells in the Born von Karman box. Two electrons (spin up and down) to each k-state. At 1 electron per unit cell, the lowest band should be exactly half-filled or, in some extreme cases, about half-filled.

Brillouin Zones And Fermi Surfaces

(1) Draw the free electron Fermi surface
(2) Deform it slightly near Bragg plane
(3) Translate the portion within n-th Brillouin zone through all reciprocal lattice vectors. This constructs a repeated zone Fermi surface.

FEG energy bands. Note degeneracy.
Energy gaps at Bragg planes.
Shape of N-th Brillouin Zones

Figure 9.8
Surfaces of the first, second, and third Brillouin zones for (a) body-centered cubic and (b) face-centered cubic crystals. (Only the exterior surfaces are shown.) It follows from the definition on page 165 that the interior surface of the nth zone is identical to the exterior surface of the (n−1)th zone. Evidently the surfaces bounding the zones become increasingly complex as the zone number increases. In practice it is often simplest to construct free electron Fermi surfaces by procedures such as those described in Problem 4) that avoid making use of the explicit form of the Brillouin zones. (After R. Lück, doctoral dissertation, Technische Hochschule, Stuttgart, 1965.)

Free Electron Fermi Surface

Figure 9.9
The free electron Fermi sphere for a face-centered cubic metal of valence 4. The first zone lies entirely within the interior of the sphere, and the sphere does not extend beyond the fourth zone. Thus the only zone surfaces (intersected by the surface of the sphere are the (octahedral) surfaces of the second and third zones (cf. Figure 8.9). The second-zone Fermi surface consists of those parts of the surface of the sphere lying entirely within the polyhedron bounding the second zone (i.e., all of the sphere except the parts extending beyond the polyhedron in 8). When translated through reciprocal lattice vectors into the first zone, the parts of the second-zone surface give the simply connected figure shown in (b). (It is known as a "finite surface"; the sides it encloses have higher energies than those outside.) The fourth-zone Fermi surface consists of those parts of the surface of the sphere lying outside of the second zone (i.e., the parts extending beyond the polyhedron in 8). When translated through reciprocal lattice vectors into the first zone, these parts of the sphere give the multiply connected structure shown in (d). The fourth-zone Fermi surface consists of the remaining parts of the surface of the sphere that lie outside the third zone (as shown in 8)). When translated through reciprocal lattice vectors into the first zone these parts of the surface give the multiply connected structure shown in (e). Figures (b) and (c) show only the intersection of the third and fourth zone Fermi surfaces with the surface of the free zone. (From R. Lück, op. cit.)

valence 4
FCC Valence 2 and 3

Lattices with Basis (Identical Atoms)

U(\vec{r}) = \sum_{\vec{R}} \sum_{j} \phi(\vec{r} - \vec{R} - \vec{d}_j)

U_k = \frac{1}{V_{\text{cell}}} \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} \sum_{\vec{R},j} \phi(\vec{r} - \vec{R} - \vec{d}_j) = \frac{1}{V_{\text{space}}} \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} \sum_{j} \phi(\vec{r} - \vec{d}_j)

U_k = \frac{1}{V} \phi(\vec{K}) S_k^* \quad \phi(\vec{K}) = \int d\vec{r} e^{-i\vec{K}\cdot\vec{r}} \phi(\vec{r})

Geometrical Structure Factor

S_k = \sum e^{-i\vec{k}\cdot\vec{d}_j}

No splitting on Bragg planes with vanishing structure factors, e.g. basal planes of hcp metal. Convenient to use "Jones zones": zero-gap planes ignored.
Other Contributions To Degeneracy Removal

\[ H_0 = -\frac{\hbar^2}{2m} \nabla^2 \]

\[ H_1 = U(\vec{r}) \]

\[ H_2 = \xi \vec{L} \cdot \vec{S} \quad \text{Spin-orbit coupling} \]

Spin-orbit coupling is important for heavy elements and for degeneracy not removed by weak periodic potential.

Homework Chapter 8 - 10

Chapter 8: Problems 1
Chapter 9: Problems 1, 3
Chapter 10: Problem 1

Due 3/16/2012