Chapter 3 Electrons in Periodic Potentials

3.1 Bloch Theorem

1. Translational symmetry

The effective 1-e Schrödinger equ. in a crystal reads

$$\hat{H}\Psi(\mathbf{r}) \equiv \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

where $V(\{\alpha \mid \mathbf{R}_l\}\mathbf{r}) = V(\mathbf{r})$, $\{\alpha \mid \mathbf{R}_l\} \in G$ (space group).

Translational invariance: $V(\{E|\mathbf{R}_l\}\mathbf{r}) = V(\mathbf{R}_l + \mathbf{r}) = V(\mathbf{r})$.

(1) $\hat{H}(\mathbf{R}_l + \mathbf{r}) = \hat{H}(\mathbf{r})$ is also translational invariant.

(2) Translational operator $T_{\mathbf{R}_l}f(\mathbf{r}) = f(\mathbf{R}_l + \mathbf{r})$ commutes with $\hat{H}(\mathbf{r})$.

2. Bloch theorem

Thus, a complete set of simultaneous eigenfunctions $\{\Psi_n(\mathbf{r})\}$ for $\hat{H}$ and $T_{\mathbf{R}l}$ exist, i.e., $\hat{H}\,\Psi_n(\mathbf{r}) = E_n\Psi_n(\mathbf{r})$ and $T_{\mathbf{R}l}\,\Psi_n(\mathbf{r}) = \lambda^{(l)}\Psi_n(\mathbf{r})$, where $|\lambda^{(l)}|^2 = 1$ and can be written as $exp(i\alpha(l))$.
Hence, we can write $T_{\mathbf{R}l}\Psi_n(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}l}\Psi_n(\mathbf{r})$.

Bloch theorem: The solutions of $\hat{H}\,\Psi_n(\mathbf{r}) = E_n\Psi_n(\mathbf{r})$ are also eigenfunctions of $T_{\mathbf{R}l}$ with eigenvalues $exp[i\mathbf{k}\cdot\mathbf{R}_l]$. Alternatively, the eigenfunction of $\hat{H}$ can be written as
$\Psi_n(\mathbf{k},\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_n(\mathbf{k},\mathbf{r})$, $u_n(\mathbf{k},\mathbf{R}_l+\mathbf{r}) = u_n(\mathbf{r})$ (cell periodic).

3. Bloch function and crystal momentum

In a crystal, the $\hat{H}$ eigenfunctions
$$\Psi_n(\mathbf{k},\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\, u_n(\mathbf{k},\mathbf{r}),\ u_n(\mathbf{k},\mathbf{R}_l+\mathbf{r}) = u_n(\mathbf{r})\ \text{(cell periodic)}$$
are called Bloch functions, describing the crystal electrons.

The **k** has the meaning of momentum $\hbar\mathbf{k}$, although introduced as a parameter to determines the eigenvalues of $T_{\mathbf{R}l}$.
If $u_n(\mathbf{k},\mathbf{r}) = C,\ \Psi_n(\mathbf{k},\mathbf{r}) = Ce^{i\mathbf{k}\cdot\mathbf{r}}$, i.e., in the free electron limit, $\hbar\mathbf{k}$ is identical to the momentum of the free electron.

(a) A Bloch electron is represented by a plane wave modulated by the periodicity of lattice.

(b) The charge density of a Bloch electron is periodic with the periods of the lattice.
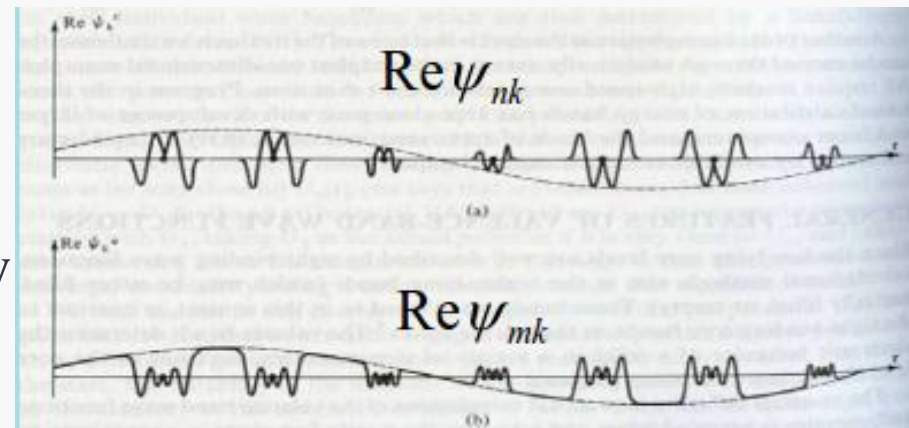
3.2 Band Structure

1. Translational symmetry in **k**-space and energy bands

Since $\mathbf{G}_m \cdot \mathbf{R}_l = 2\pi N$, $T_{\mathbf{R}l}\Psi(\mathbf{k}+\mathbf{G}_m,\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{R}_l}\Psi(\mathbf{k}+\mathbf{G}_m,\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}_l}\Psi(\mathbf{k}+\mathbf{G}_m,\mathbf{r})$

Thus, all **k**, $\mathbf{k}' = \mathbf{k}+\mathbf{G}_m$ are equivalent, i.e., $\Psi(\mathbf{k}+\mathbf{G}_m,\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}_l}\Psi(\mathbf{k},\mathbf{r})$.

In classifying the Bloch wave functions, the **k** values from one Brillouin zone are sufficient. Also, $E_n(\mathbf{k}) = E_n(\mathbf{k}+\mathbf{G}_n)$ can be limited to the first Brillouin zone.

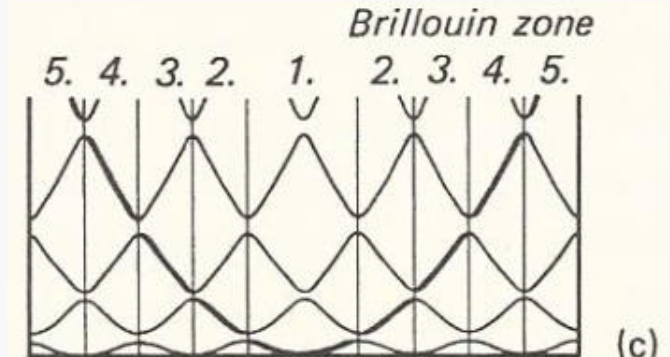For a given n, function $E_n(\mathbf{k})$ is a *continuous* and *differentiable* (apart from degenerate points) function of **k**, called an energy band. All the bands together $[E_n(\mathbf{k})]$ is referred to as the band structure.
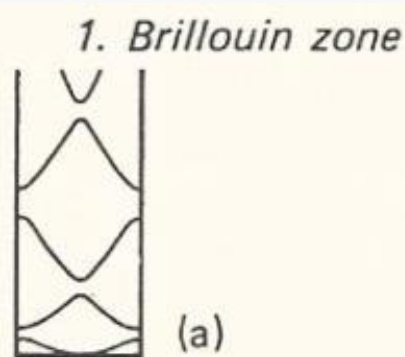
(a) Reduced zone scheme
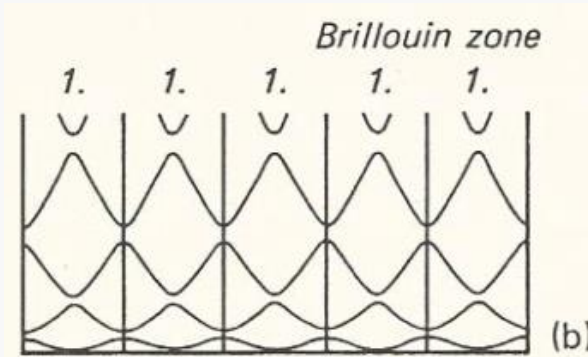
(b) Repeated zone scheme

(c) Extended zone scheme

2. Rotational symmetries and irreducible Brillouin zone wedge

(1) Point group symmetry properties

In addition to the translational symmetry, i.e., $E_n(\mathbf{k}+\mathbf{G}_m) = E_n(\mathbf{k})$, $E_n(\mathbf{k})$ also possess point symmetries.

If $\alpha \in \{\alpha|O\}$ (point group), we can define $\Phi(\mathbf{r}) = \Psi_n(\mathbf{k}, \alpha\mathbf{r}) = A_\alpha^{-1} \Psi_n(\mathbf{k},\mathbf{r})$. $\Phi(\mathbf{r})$ is another eigenfunction of $\hat{H}$ with the same $E_n(\mathbf{k})$.
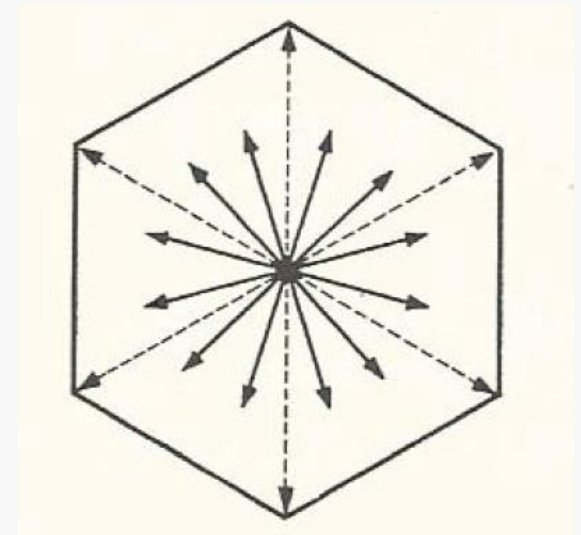
What $\mathbf{k}$ vector labels $\Phi(\mathbf{r})$?

$$\Psi_n(\mathbf{k}, \alpha(\mathbf{r}+\mathbf{R}_l)) = e^{i\mathbf{k}\cdot\alpha\mathbf{R}_l} \Psi_n(\mathbf{k}, \alpha\mathbf{r}) \quad \text{(Bloch theorem)}$$

$$= e^{i\alpha^{-1}\mathbf{k}\cdot\mathbf{R}_l} \Psi_n(\mathbf{k}, \alpha\mathbf{r}) \quad (\alpha\mathbf{A}\cdot\alpha\mathbf{B}=\mathbf{A}\cdot\mathbf{B}).$$

Thus, $\Phi(\mathbf{r}+\mathbf{R}_l) = e^{i\alpha^{-1}\mathbf{k}\cdot\mathbf{R}_l} \Phi(\mathbf{r})$, i.e., $\Phi(\mathbf{r}) = \Psi_n(\alpha^{-1}\mathbf{k}, \mathbf{r})$.

$\Phi(\mathbf{r})$ is labeled by the vector $\alpha^{-1}\mathbf{k}$, *and*

$\Psi_n(\alpha^{-1}\mathbf{k}, \mathbf{r}) = \Psi_n(\mathbf{k}, \alpha\mathbf{r})$, and $E_n(\alpha^{-1}\mathbf{k}) = E_n(\mathbf{k})$.

Stars of two k-vectors in 2D hexagonal BZ.

(2) Irreducible Brillouin zone wedge.

The band structure of a crystal has the symmetry properties:
$E_n(\alpha \mathbf{k}) = E_n(\mathbf{k})$ $(\alpha \in \{\alpha | O\})$, and $E_n(\mathbf{k}) = E_n(-\mathbf{k})$ (Kramers theorem).
Thus, it is sufficient to know $E_n(\mathbf{k})$ over only part of the Brillouin zone which is called the irreducible Brillouin zone.
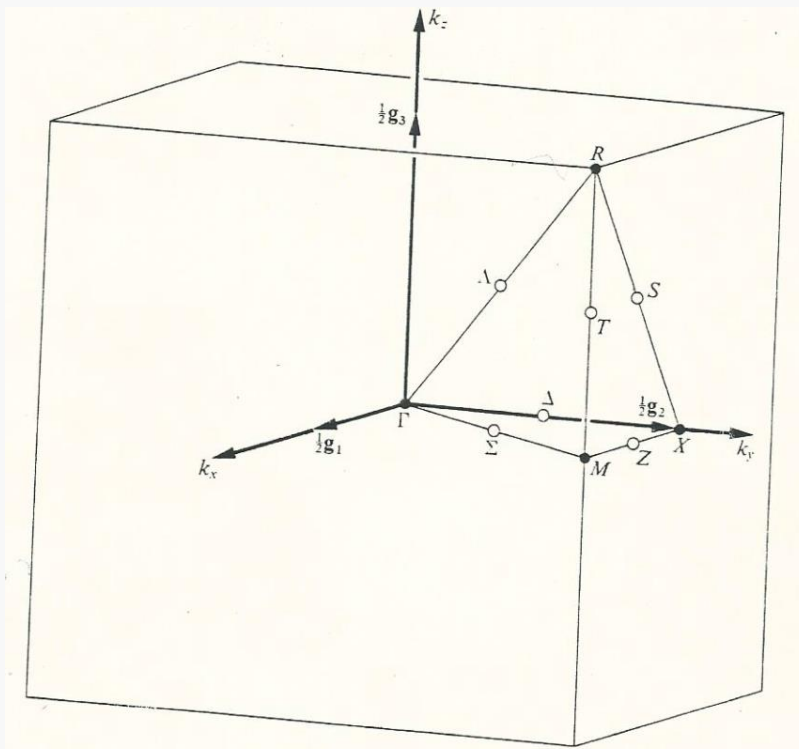

FIG. 3.13. The Brillouin zone for Γ_c. $\Gamma = (000)$; $X = (0\frac{1}{2}0)$; $M = (\frac{1}{2}\frac{1}{2}0)$; $R = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$.
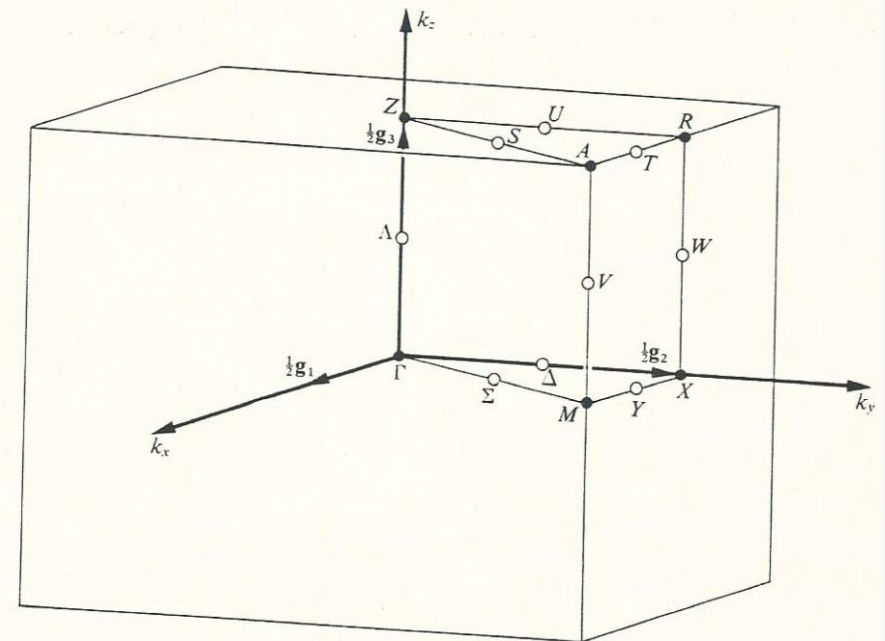
FIG. 3.9. The Brillouin zone for Γ_q. $\Gamma = (000)$; $M = (\frac{1}{2}\frac{1}{2}0)$; $Z = (00\frac{1}{2})$; $A = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$; $R = (0\frac{1}{2}\frac{1}{2})$; $X = (0\frac{1}{2}0$
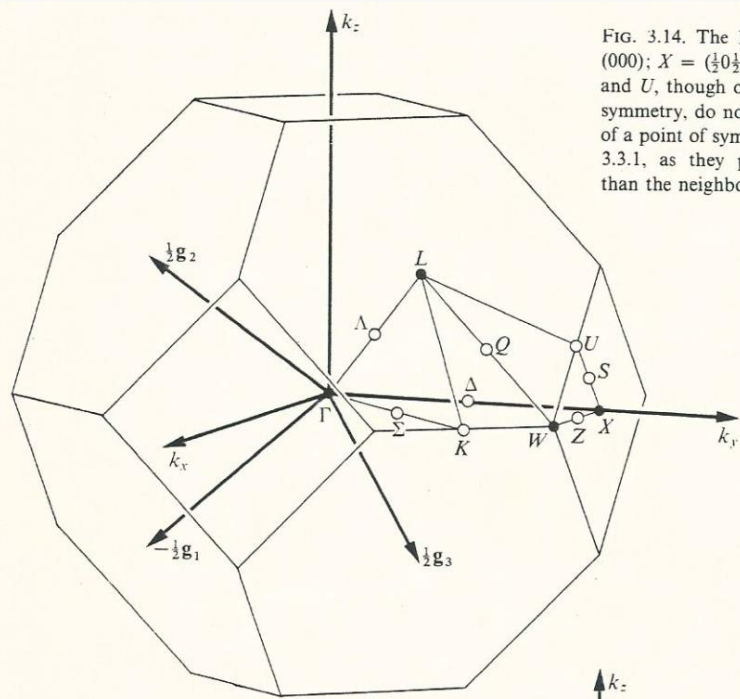
FIG. 3.14. The Brillouin zone for Γ_c^f. $\Gamma = (000)$; $X = (\frac{1}{2}0\frac{1}{2})$; $L = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$; $W = (\frac{1}{2}\frac{1}{4}\frac{3}{4})$. K and U, though often referred to as points of symmetry, do not come within the definition of a point of symmetry as given in Definition 3.3.1, as they possess no more symmetry than the neighbouring lines Σ and S, respectively.
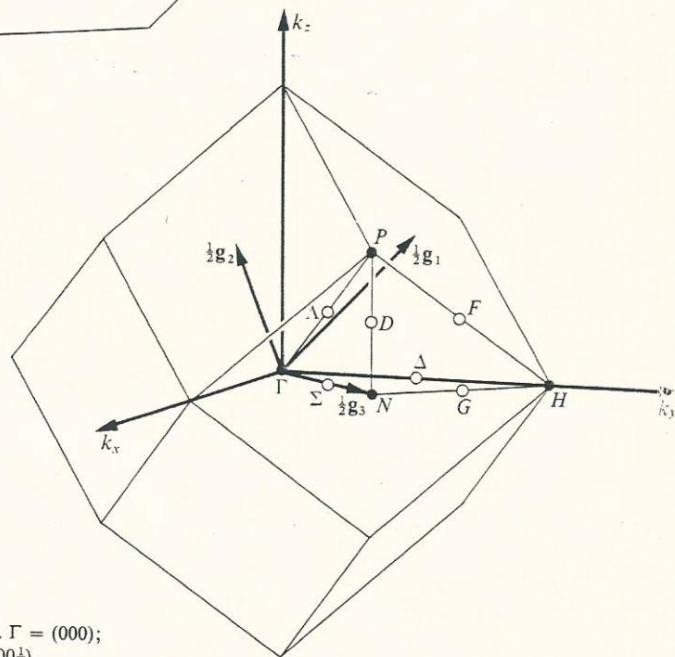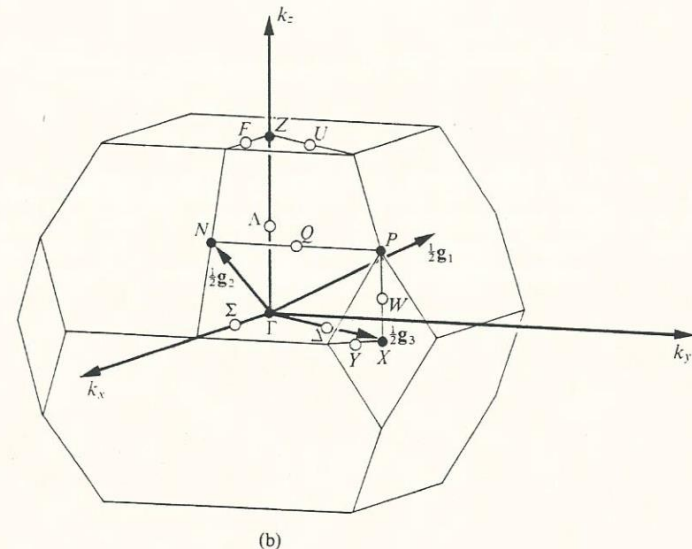
(b)

FIG. 3.10. The Brillouin zone for Γ_q^v. (a) $a > c$, $\Gamma = (000)$; $N = (0\frac{1}{2}0)$; $X = (00\frac{1}{2})$; $Z = (\frac{\bar{1}}{2}\frac{1}{2}\frac{1}{2})$; $P = (\frac{1}{4}\frac{1}{4}\frac{1}{4})$; (b) $c > a$, $\Gamma = (000)$; $N = (0\frac{1}{2}0)$; $X = (00\frac{1}{2})$; $Z = (\frac{1}{2}\frac{1}{2}\frac{\bar{1}}{2})$; $P = (\frac{1}{4}\frac{1}{4}\frac{1}{4})$.

FIG. 3.15. The Brillouin zone for Γ_c^v. $\Gamma = (000)$; $H = (\frac{1}{2}\frac{\bar{1}}{2}\frac{1}{2})$; $P = (\frac{1}{4}\frac{1}{4}\frac{1}{4})$; $N = (00\frac{1}{2})$.
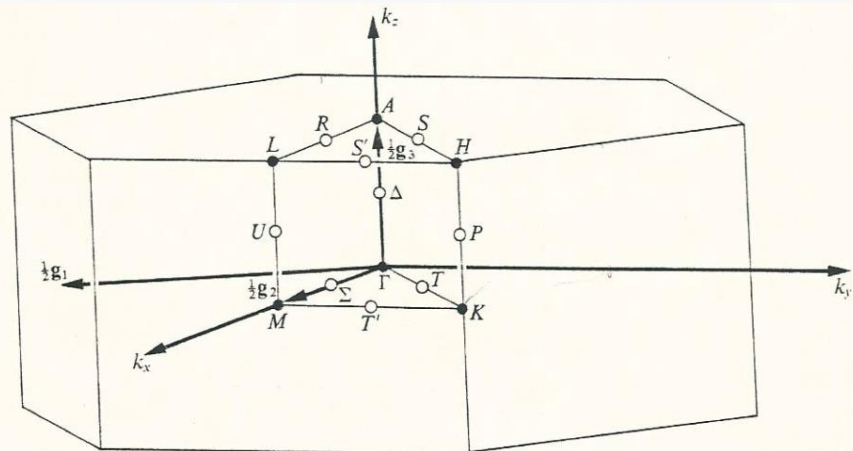
FIG. 3.12. The Brillouin zone for Γ_h. $\Gamma = (000)$; $M = (0\frac{1}{2}0)$; $A = (00\frac{1}{2})$; $L = (0\frac{1}{2}\frac{1}{2})$; $K = (\frac{\bar{1}}{3}\frac{2}{3}0)$; $H = (\frac{\bar{1}}{3}\frac{2}{3}\frac{1}{2})$.

3. Density of states

(1) Density of states in **k**-space

Born-von Karman (periodic) boundary conditions

$$\Psi(\mathbf{k}, \mathbf{r} + N_i \mathbf{a}_i) = \Psi(\mathbf{k}, \mathbf{r}) \ (i = 1, 2, 3 \text{ and } N_i \text{ are large integers})$$

$$\Psi(\mathbf{k}, \mathbf{r} + N_i \mathbf{a}_i) = e^{i\mathbf{k} \cdot N_i \mathbf{a}_i} \Psi(\mathbf{k}, \mathbf{r}) = \Psi(\mathbf{k}, \mathbf{r})$$

$$N_i \mathbf{k} \cdot \mathbf{a}_i = 2\pi N_i x_i = 2\pi m_i, \ m_i \text{ are integers } (\mathbf{k} = x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3)$$

$$x_i = m_i / N_i, m_i = 0, \pm 1, \pm 2, \cdots, N_i.$$

Allowed Bloch wavevectors are $\mathbf{k} = \sum_{i=1}^{3} (m_i / N_i) \mathbf{b}_i$.

Thus, there are $N = N_1 N_2 N_3$ allowed vectors **k** (i.e., states) in the BZ. The states per unit volume in **k**-space is

$$1 / [(2\pi / N_1 a_1)(2\pi / N_2 a_2)(2\pi / N_3 a_3)] = V / (2\pi)^3.$$

(2) Density of states in E-space $[D_n(E)]$

Definition: $D_n(E)dE$ = total number of allowed **k** in the nth band from E to $E+dE$.

Tetrahedron method

$$E(\mathbf{k}+\delta\mathbf{k}) = E(\mathbf{k})+\delta E(\mathbf{k}) = E(\mathbf{k})+|\nabla E(\mathbf{k})|\,\delta k(\mathbf{k})$$

$$\delta k(\mathbf{k}) = dE/|\nabla E(\mathbf{k})|$$

$$D(E)dE = \frac{gV}{(2\pi)^3}\int_{E<E(\mathbf{k})<E+dE} d^3k = \frac{gV}{(2\pi)^3}\int_{E<E(\mathbf{k})<E+dE} dS_{E(k)}\,\delta k(\mathbf{k})$$

$$D(E) = \frac{gV}{(2\pi)^3}\int_{E<E(\mathbf{k})<E+dE} \frac{dS_{E(k)}}{|\nabla E(\mathbf{k})|}/\delta k(\mathbf{k}).$$

An irreducible BZ wedge can always be divided into a large number of tetrahedra. In each tetrahedron, the energy is assumed to varies linearly, and thus the integral of a function can be expressed in terms of the energies and functions at the **k**-points at the 4 corners.

$$E_2 \; \vec{k}_2$$
$$\vec{k}_1 \; E_1 \qquad E_3 \; \vec{k}_3$$
$$E_4 \; \vec{k}_4$$
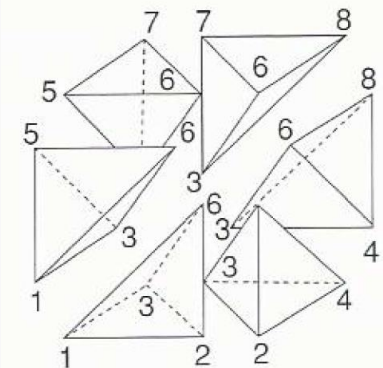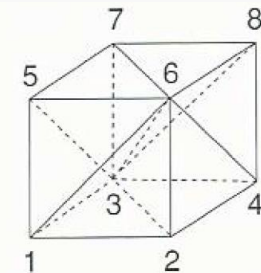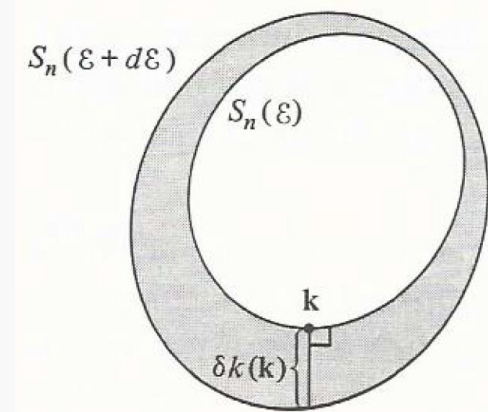
$$E_4 \leq E_3 \leq E_2 \leq E_1$$

$$E_n(\vec{k}) = E_n(\vec{k}_l) + \nabla_{\vec{k}} E_n(\vec{k}) \Big|_{\vec{k}=\vec{k}_l} \cdot (\vec{k} - \vec{k}_l)$$

energy varies linearly

$$E(\vec{k}) = E(\vec{k}_4) + \vec{b} \cdot (\vec{k} - \vec{k}_4)$$

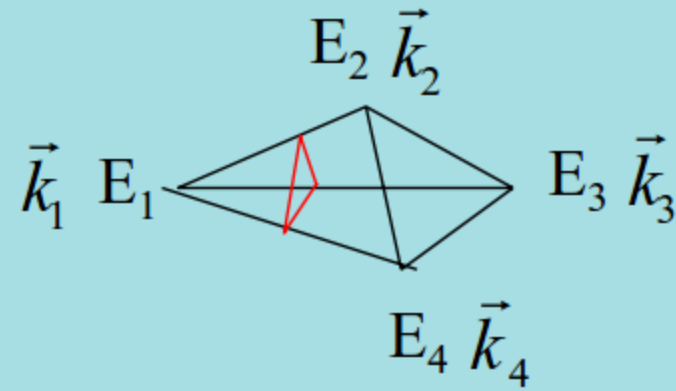$$\vec{b} = \sum_{i=1}^{3} \left[E(\vec{k}_i) - E(\vec{k}_4) \right] \cdot \vec{r}_i$$

where

$$\vec{r}_1 = \frac{\vec{k'}_2 \times \vec{k'}_3}{V} \; ; \vec{r}_2 = \frac{\vec{k'}_3 \times \vec{k'}_1}{V} \; ; \vec{r}_3 = \frac{\vec{k'}_1 \times \vec{k'}_2}{V}$$

$$\vec{r}_i \times \vec{k}_j = \delta_{ij} ; \vec{k}_j' = \vec{k}_j - \vec{k}_4, \; j = 1,2,3$$

$$V = \vec{k'}_1 \times \vec{k'}_2 \times \vec{k'}_3$$

$$D_{nl}(E) = \frac{2\Omega}{(2\pi)^3} \frac{dS(E)}{|\vec{b}|} \quad \text{,where } \vec{b} = \vec{\nabla}_k E(\vec{k}) = \vec{b}$$
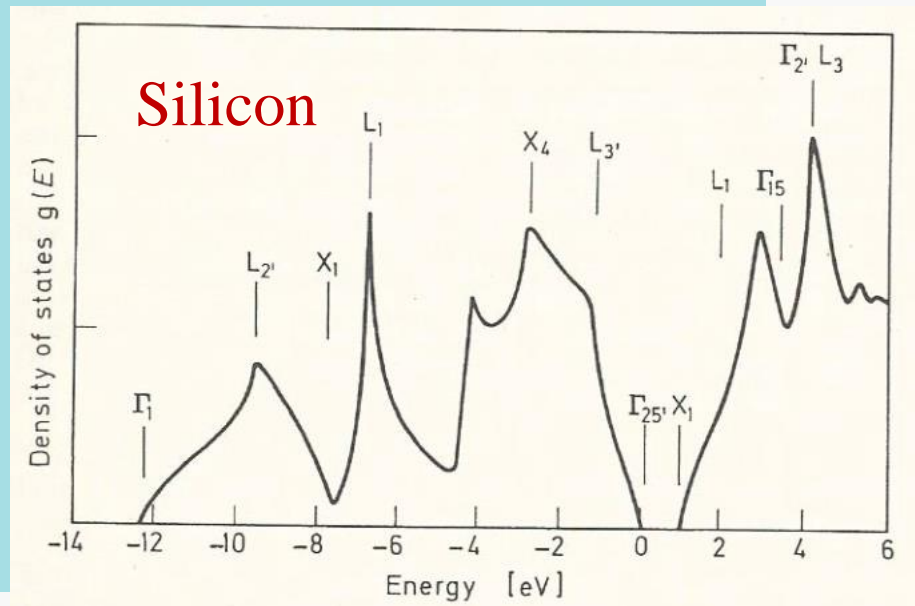
$$dS = \begin{cases} f_0 & E_4 \leq E \leq E_3 \\ f_0 - f_1 & E_3 \leq E \leq E_4 \\ f_3 & E_2 \leq E \leq E_1 \\ 0 & E \leq E_4 \text{ or } E_1 \leq E \end{cases}$$

$$\frac{f_0}{|\vec{b}|} = \frac{V}{2} \frac{(E - E_4)^2}{(E_3 - E_4)(E_2 - E_4)(E_1 - E_4)}$$

$$\frac{f_1}{|\vec{b}|} = \frac{V}{2} \frac{(E - E_3)^2}{(E_3 - E_4)(E_2 - E_3)(E_1 - E_3)}$$

$$\frac{f_3}{|\vec{b}|} = \frac{V}{2} \frac{(E - E_1)^2}{(E_1 - E_4)(E_1 - E_3)(E_1 - E_2)}$$
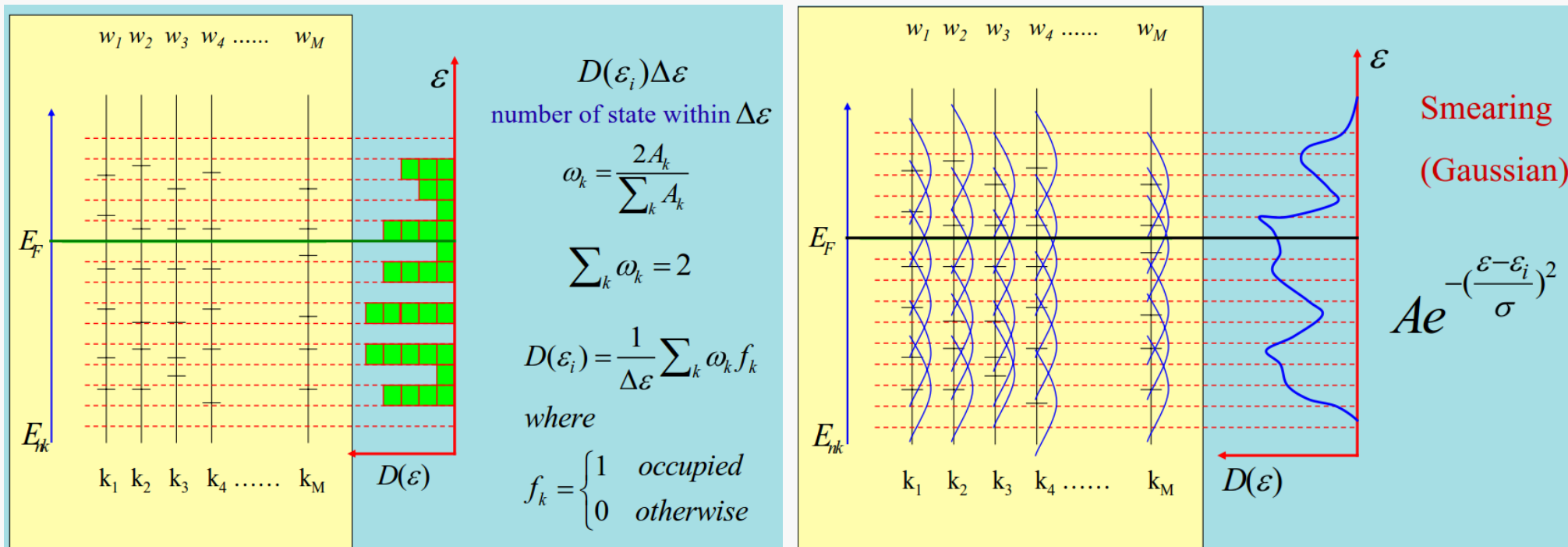

$E_2\ \vec{k}_2$

$\vec{k}_1\ E_1$ $E_3\ \vec{k}_3$

$E_4\ \vec{k}_4$

Silicon

Gaussian smearing method

$$D(E) = \frac{g}{(2\pi)^3} \int d^3k\, \delta(E - E(\mathbf{k})).$$

The Dirac $\delta(x)$ delta function is approximated by a Gaussian function

$$\delta(x) \approx \frac{1}{\sqrt{2\pi}\Gamma} e^{-x^2/(2\Gamma^2)}.$$

$$D(E) = \frac{g}{V}\sum_{\mathbf{k}} \delta(E - E(\mathbf{k})) = \frac{g}{\sqrt{2\pi}V\Gamma}\sum_{\mathbf{k}} e^{-(E-E(\mathbf{k})^2/2\Gamma^2}, \text{ noting } \frac{V}{(2\pi)^3}\int d^3k = \sum_{\mathbf{k}}.$$

$w_1\ w_2\ w_3\ w_4\ ......\quad w_M$

$\mathcal{E}$

E_F

E_{nk}

$k_1\ k_2\ k_3\ k_4\ ......\ k_M \qquad D(\varepsilon)$

$D(\varepsilon_i)\Delta\varepsilon$

number of state within $\Delta\varepsilon$

$$\omega_k = \frac{2A_k}{\sum_k A_k}$$

$$\sum_k \omega_k = 2$$

$$D(\varepsilon_i) = \frac{1}{\Delta\varepsilon}\sum_k \omega_k f_k$$

where

$$f_k = \begin{cases} 1 & occupied \\ 0 & otherwise \end{cases}$$

$w_1\ w_2\ w_3\ w_4\ ......\quad w_M$

$\mathcal{E}$

E_F

E_{nk}

$k_1\ k_2\ k_3\ k_4\ ......\ k_M \qquad D(\varepsilon)$

Smearing

(Gaussian)

$$Ae^{-\left(\frac{\varepsilon-\varepsilon_i}{\sigma}\right)^2}$$

4. Momentum, group velocity and effective mass of Bloch electrons

Comparison of free electrons and crystal (Bloch) electrons

|	free electron	Bloch electron
Wave function	$e^{i\mathbf{k}\cdot\mathbf{r}}$	$e^{i\mathbf{k}\cdot\mathbf{r}}\,u(\mathbf{k},\mathbf{r})$
Band structure	$(\hbar k)^2/2m$	$E_n(\mathbf{k})$
Momentum	$\hbar\mathbf{k}$	$(m/\hbar)\nabla E_n(\mathbf{k})$
Velocity	$\hbar\mathbf{k}/m$	$(1/\hbar)\nabla E_n(\mathbf{k})$
Effective mass	$(1/m)\delta_{ij}$	$(1/\hbar^2)[\partial^2 E_n(\mathbf{k})\,/\partial k_i \partial k_j]$
Density of states	$(g/2\pi^2)(m/\hbar^2)E^{3/2}$	$[g/(2\pi)^3]\int_{En(\mathbf{k})=E} ds/|\nabla E_n(\mathbf{k})|$

g = spin degeneracy.

3.3 Nearly free Bloch electrons

1. Free electron band structure

This is the natural way to introduce the energy bands for metals. Consider the extended BZ scheme.

(a) One energy paraboloid at every $\mathbf{G}_m$ point. (b) The paraboloids intersect where Bragg reflections [$k^2 = (\mathbf{k} - \mathbf{G}_m)^2$] occur. (c) At each paraboloid intersection, $E_n(\mathbf{k})$ for free electrons is degenerate. (d) The degeneracies can be removed by some perturbations, e.g., lattice potential $V(\mathbf{r})$.
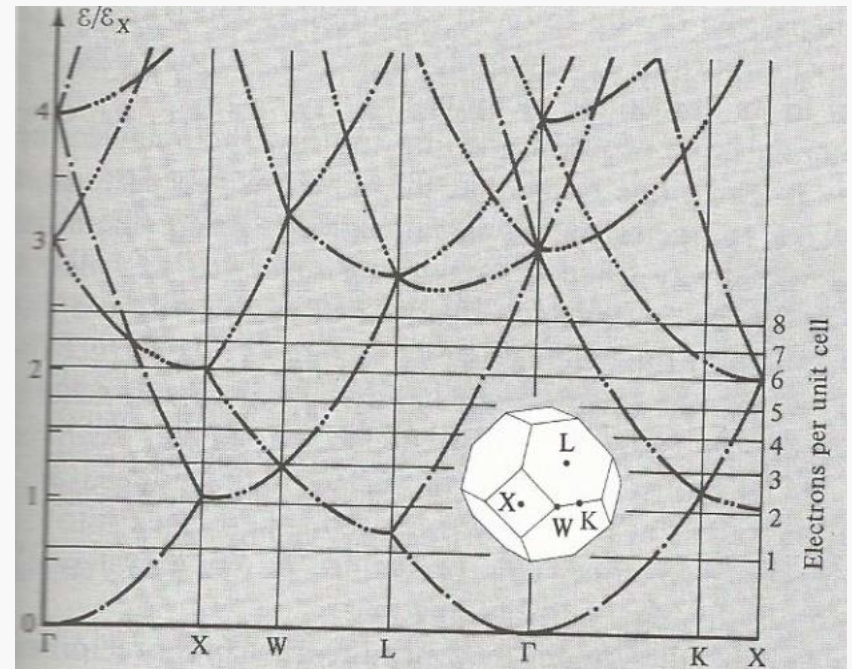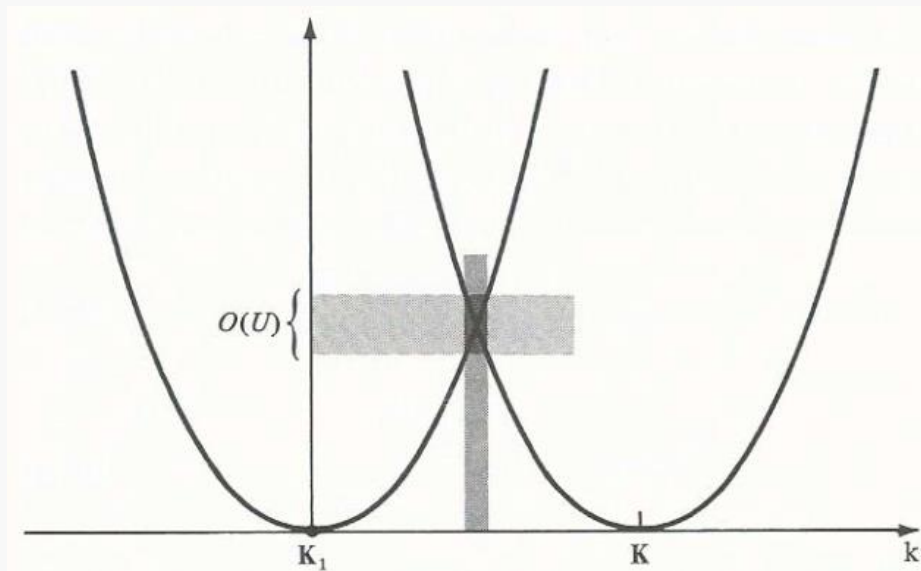
2. Effects of Bragg reflections (weak lattice potential)

$$V(\mathbf{r}) = \sum_m {}' V(\mathbf{G}_m) e^{-i\mathbf{G}_m \cdot \mathbf{r}}, \text{ since } [V(\mathbf{R}_l + \mathbf{r}) = V(\mathbf{r})]$$

$$\Psi_n(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_n(\mathbf{k}, \mathbf{r}), \quad u_n(\mathbf{k}, \mathbf{r}) = \sum_m C_n(\mathbf{G}_m) e^{-i\mathbf{G}_m \cdot \mathbf{r}}, \quad [u_n(\mathbf{R}_l + \mathbf{r}) = u_n(\mathbf{r})]$$

$$\Psi_n(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k} \cdot \mathbf{r}} \sum_m C_n(\mathbf{G}_m) e^{-i\mathbf{G}_m \cdot \mathbf{r}}$$

Note that the $m = 0$ term represents the unperturbed plane wave.

$$\frac{1}{\sqrt{\Omega}} \sum_m \left[\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{G}_m)^2 - E_n(\mathbf{k}) + \sum_l {}' V(\mathbf{G}_l) e^{-i\mathbf{G}_l \cdot \mathbf{r}} \right] C_n(\mathbf{G}_m) e^{-i\mathbf{G}_m \cdot \mathbf{r}} = 0,$$

$$\left[\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{G}_m)^2 - E_n(\mathbf{k}) \right] C_n(\mathbf{G}_m) + \sum_{m'} {}' V(\mathbf{G}_m - \mathbf{G}_{m'}) C_n(\mathbf{G}_m) = 0.$$

Weak lattice potential approximation:

a) $E_n(\mathbf{k}) \approx \dfrac{\hbar^2 k^2}{2m}$, $C_n(0) \approx 1$, $|C_n(\mathbf{G}_m)| \ll 1$. Thus,

$$\left[\frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{G}_m)^2 - \frac{\hbar^2 k^2}{2m}\right] C_n(\mathbf{G}_m) + V(\mathbf{G}_m)C_n(0) = 0, \quad C_n(\mathbf{G}_m) = \frac{2mV(\mathbf{G}_m)}{\hbar^2\left[(\mathbf{k}-\mathbf{G}_m)^2 - k^2\right]}.$$

Thus, $k^2 - (\mathbf{k} - \mathbf{G}_m)^2 \neq 0$, $C_n(\mathbf{G}_m)$ is small since $V(\mathbf{G}_m)$ is small.

b) Near $k^2 = (\mathbf{k} - \mathbf{G}_m)^2$ (BZ boundaries), $C_n(\mathbf{G}_m)$ become large. Consider only two levels case, $C_n(0)$ & $C_n(\mathbf{G}_m = K)$,

$$E_0(\mathbf{k}) = \frac{\hbar^2}{2m}k^2, \quad E_0(\mathbf{k}-\mathbf{K}) = \frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{K})^2,$$

$$\left[E_0(\mathbf{k}) - E_n(\mathbf{k})\right]C_n(0) + V(-\mathbf{K})C_n(\mathbf{K}) = 0, \quad (m=0),$$

$$\left[E_0(\mathbf{k}-\mathbf{K}) - E_n(\mathbf{k})\right]C_n(\mathbf{K}) + V(\mathbf{K})C_n(0) = 0.$$

$$\begin{bmatrix} E_0(\mathbf{k}) - E_n(\mathbf{k}) & V^*(\mathbf{K}) \\ V(\mathbf{K}) & E_0(\mathbf{k}-\mathbf{K}) - E_n(\mathbf{k}) \end{bmatrix} \begin{bmatrix} C_n(0) \\ C_n(\mathbf{K}) \end{bmatrix} = 0, \quad [V(-\mathbf{K}) = V^*(\mathbf{K})].$$

A standard eigenvalue problem.

$$\begin{vmatrix} E_0(\mathbf{k}) - E_n(\mathbf{k}) & V^*(\mathbf{K}) \\ V(\mathbf{K}) & E_0(\mathbf{k} - \mathbf{K}) - E_n(\mathbf{k}) \end{vmatrix} = 0,$$
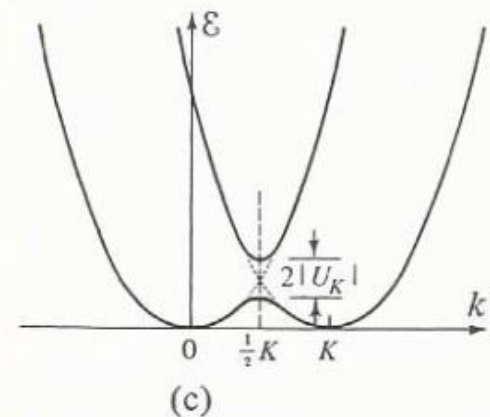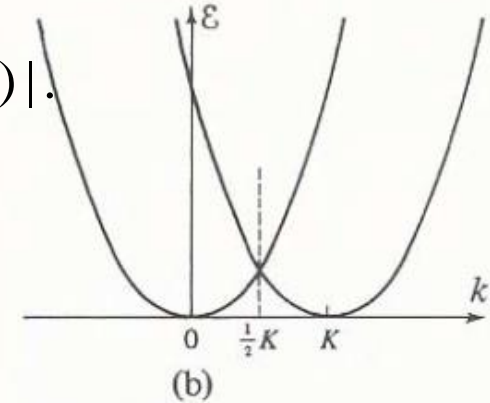
$$E_n(\mathbf{k})^2 - \left[E_0(\mathbf{k}) + E_0(\mathbf{k} - \mathbf{K}) \right] E_n(\mathbf{k}) + \left[E_0(\mathbf{k}) + E_0(\mathbf{k} - \mathbf{K}) - |V(\mathbf{K})|^2 \right] = 0,$$
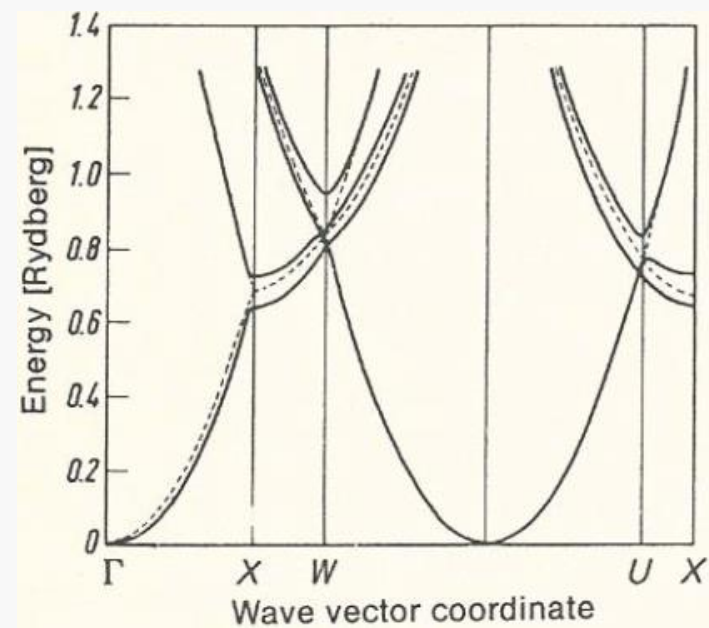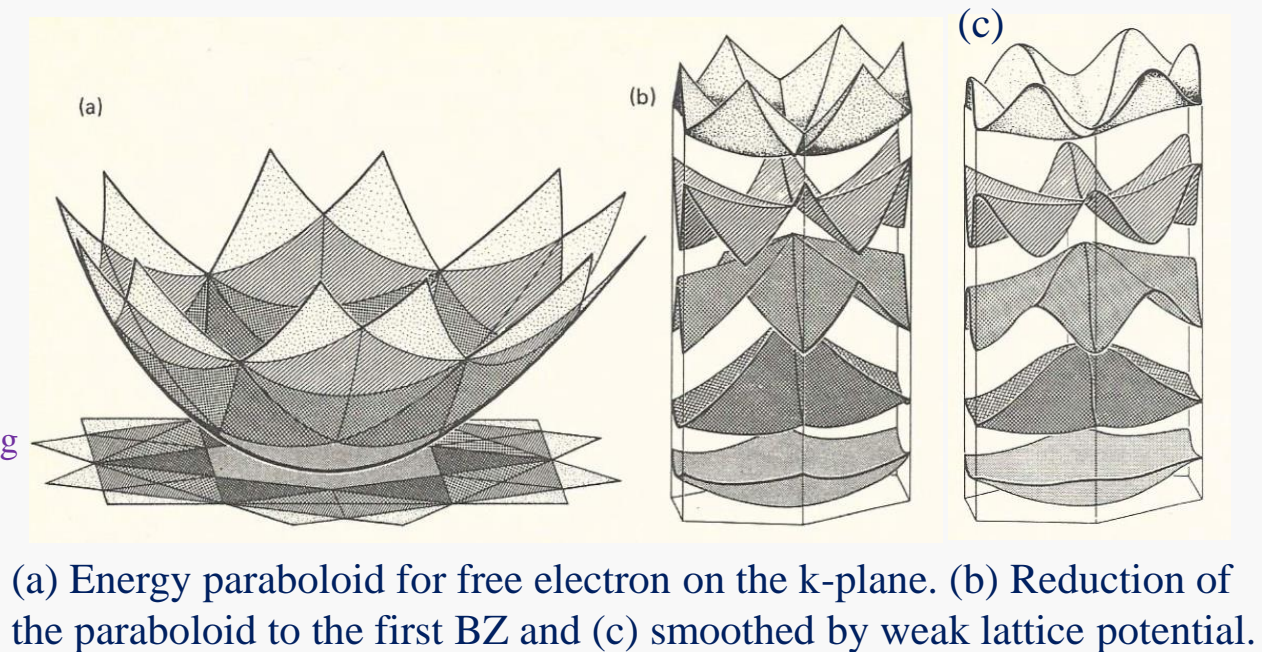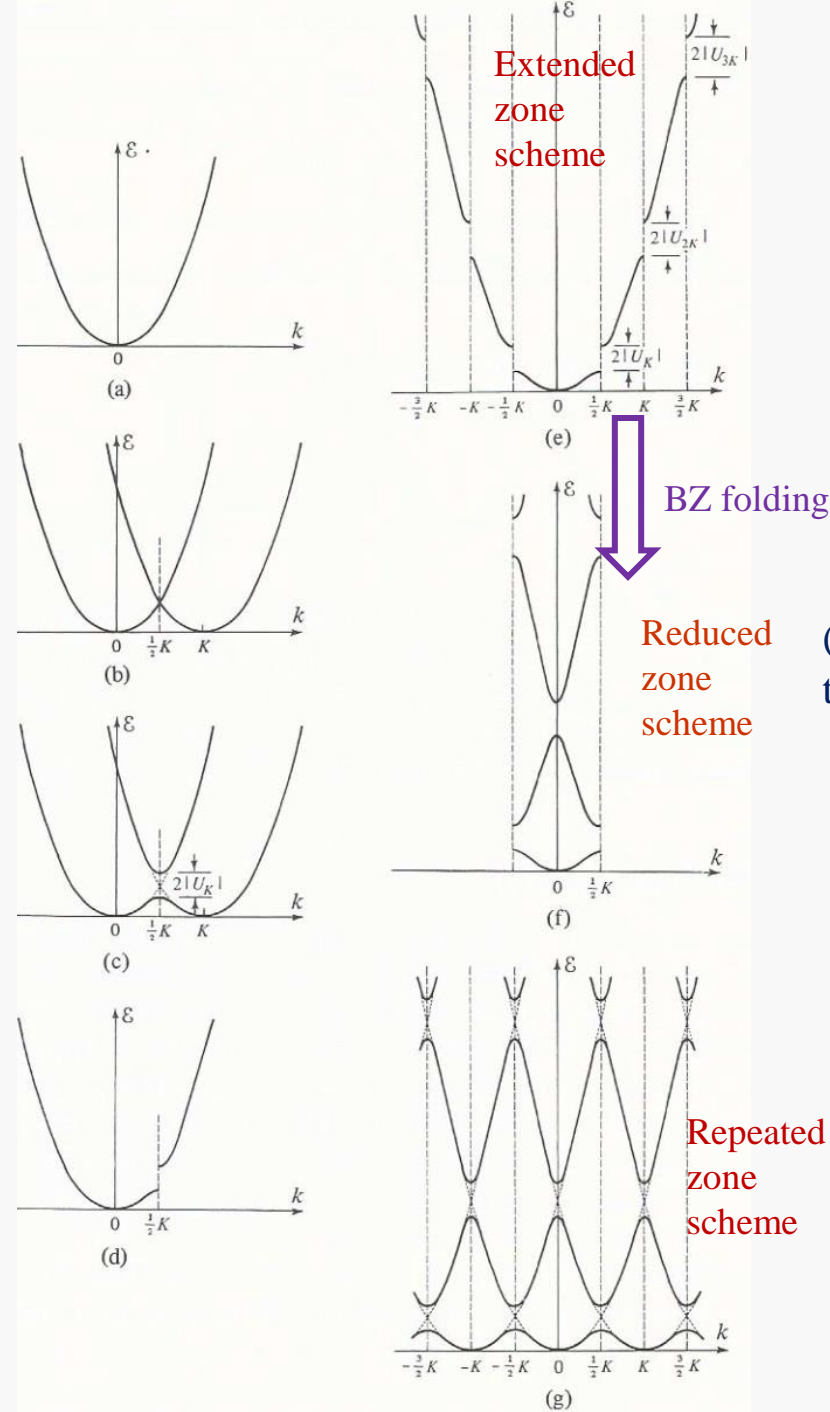
$$E_n(\mathbf{k}) = \frac{1}{2} \left[E_0(\mathbf{k}) + E_0(\mathbf{k} - \mathbf{K}) \right] \pm \left[\frac{1}{4} \left[E_0(\mathbf{k}) + E_0(\mathbf{k} - \mathbf{K}) \right]^2 + |V(\mathbf{K})|^2 \right]^{1/2}.$$

3. Formation of energy gaps (band gaps)

If $k^2 = (\mathbf{k} - \mathbf{K})^2$, $E_0(\mathbf{k}) = E_0(\mathbf{k} - \mathbf{K}) = \dfrac{\hbar^2 k^2}{2m}$, $E_n(\mathbf{k}) = \dfrac{\hbar^2 k^2}{2m} \pm |V(\mathbf{K})|$.

Hence, on the BZ surface, the degeneracy of the free electron bands is lifted if $|V(\mathbf{K})| \neq 0$, i.e., energy bands may be separated by energy gaps in which no electronic states exist. This is one of the important results of band theory and has a fundamental role in the band theory of the physical properties of solids.

BZ folding

Reduced zone scheme

Repeated zone scheme

(c)

(a) Energy paraboloid for free electron on the k-plane. (b) Reduction of the paraboloid to the first BZ and (c) smoothed by weak lattice potential.

Band structure of aluminium

# 3.4 Tightly bound crystal electrons

1. Atomic picture of the formation of energy bands

Formation of a band structure from discrete levels of isolated atoms by bringing the atoms together into a crystal.

(a) In simple metals such as sodium, s- and p-levels lead to s- and p-bands which overlap in the crystal.
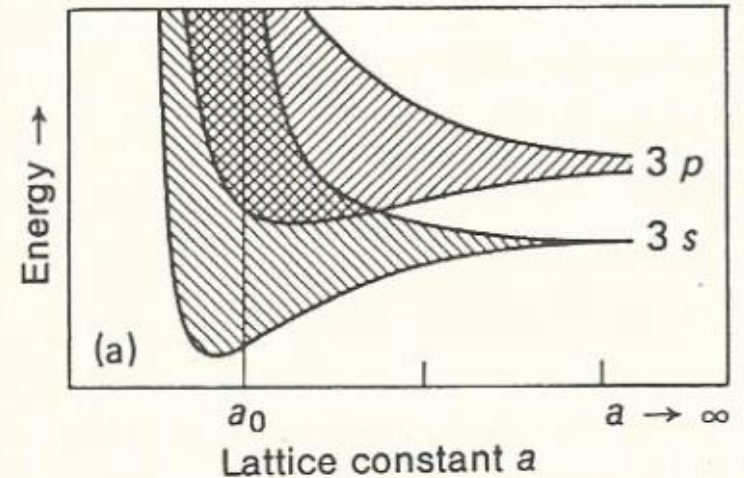
(b) In covalent materials such as diamond, as the atoms approach, there is a rearrangement of the s- and p-levels to hybrid sp^3-states. Two sp^3-bands are formed, separated by an energy gap.
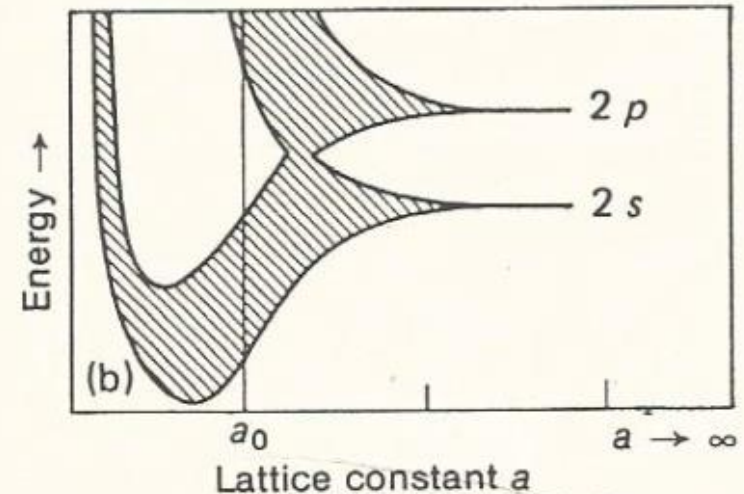
2. Wannier functions

Bloch functions are periodic in $\mathbf{k}$-space, i.e., $\Psi_n(\mathbf{k}) = \Psi_n(\mathbf{k} + \mathbf{G}_m)$.

Thus, $\Psi_m(\mathbf{k}, \mathbf{r}) = \dfrac{1}{\sqrt{N}} \displaystyle\sum_{n=1}^{N} W_m(\mathbf{R}_n, \mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{R}n}$.
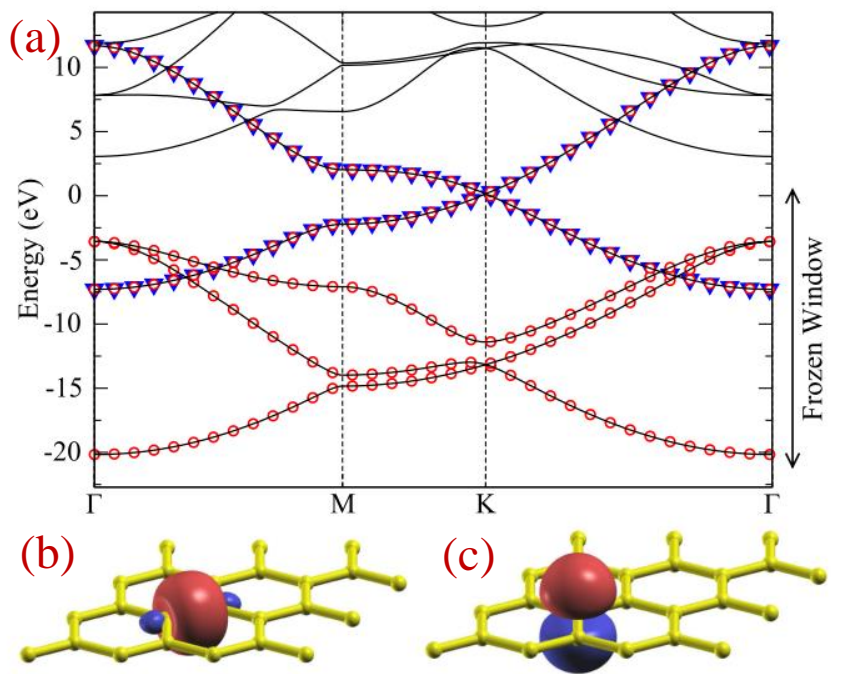
The functions $W_m(\mathbf{R}_n, \mathbf{r})$ in the expansion are called Wannier functions.

$$W_m(\mathbf{R}_n, \mathbf{r}) = \dfrac{1}{\sqrt{N}} \sum_{\mathbf{k}\in BZ} \Psi_m(\mathbf{k}, \mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{R}n} = \dfrac{1}{\sqrt{N}} \sum_{\mathbf{k}\in BZ} u_m(\mathbf{k}, \mathbf{r}) e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}n)}.$$

(a) Every Wannier function is centred at the WS cell center since $W_m(\mathbf{R}_n, \mathbf{r})$ depends only on $(\mathbf{r}\text{-}\mathbf{R}_n)$ due to the periodicity of $u_m(\mathbf{k}, \mathbf{r})$.
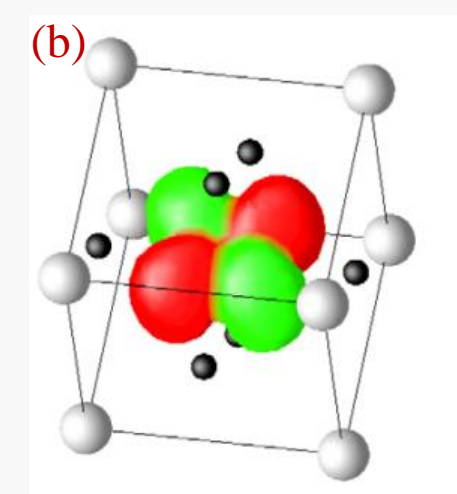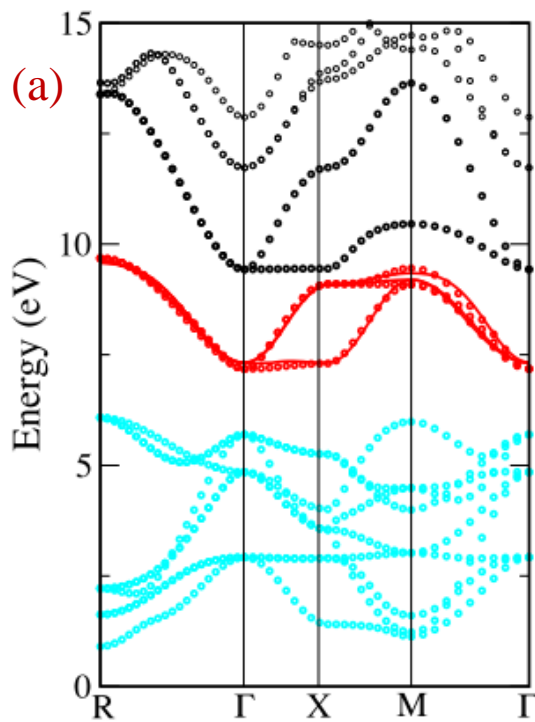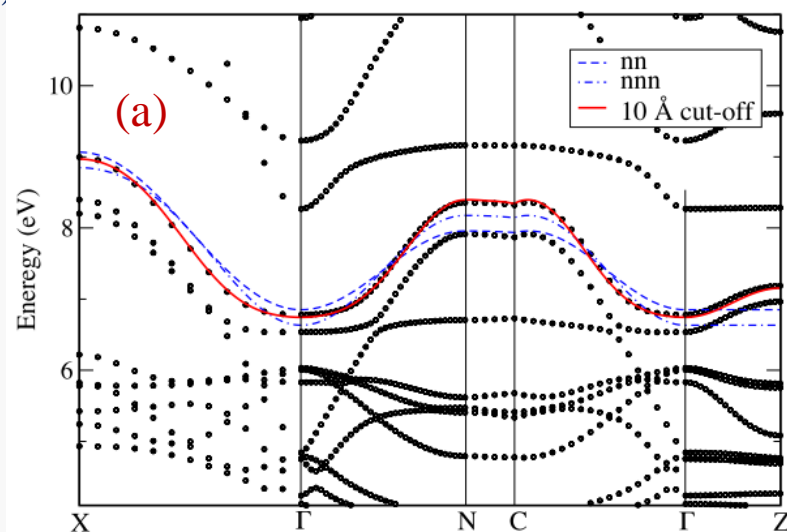
(b) Wannier functions for all W_m and $\mathbf{R}_n$ form an orthogonal set, like Bloch functions $\Psi_n(\mathbf{k}, \mathbf{r})$ for all n.

$$\int W_m^*(\mathbf{r} - \mathbf{R}_n) W_{m'}(\mathbf{r} - \mathbf{R}_{n'}) d\tau = \dfrac{1}{\sqrt{N}} \sum_{\mathbf{k},\mathbf{k}'} e^{i(\mathbf{k}\cdot\mathbf{R}n - \mathbf{k}'\cdot\mathbf{R}n')} \int \Psi_m^*(\mathbf{k}, \mathbf{r}) \Psi_{m'}(\mathbf{k}', \mathbf{r}) d\tau$$

$$= \dfrac{1}{\sqrt{N}} \left[\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}n - \mathbf{R}n')} \right] \delta_{mm'} = \delta_{mm'} \delta_{nn'}.$$
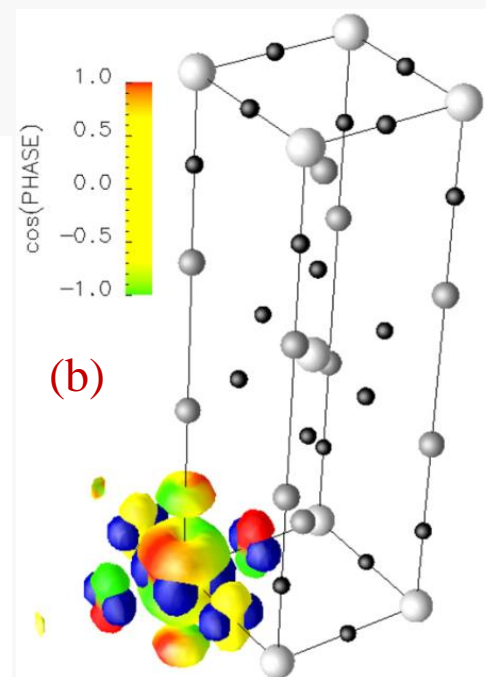
(a) Band structure and (b-c) isosurface contours of maximally localized Wannier functions (MLWF) in graphite. (b) σ (sp^2)–type MLWF and (c) π (p_z)-type MLWF.

(a) Band structure and (b) V d_{xy} Wannier orbital of $SrVO_3$.

(a) Band structure and (b) Ir $J = 1/2$ Wannier orbital $w_+,[0,0,0](\mathbf{r})$ in Sr_2IrO_4.

3. Linear combination of atomic orbitals

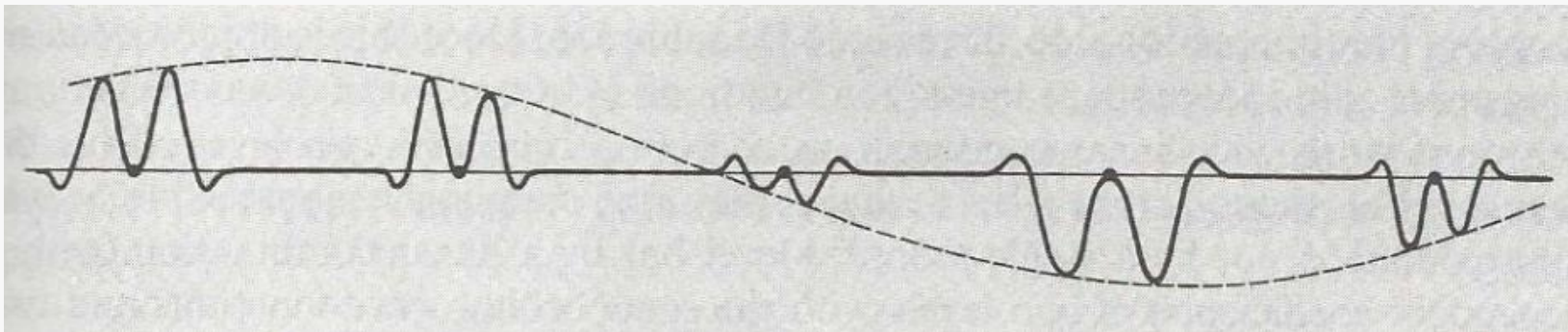Consider one atom per unit cell with one orbital (e.g., s-orbital).
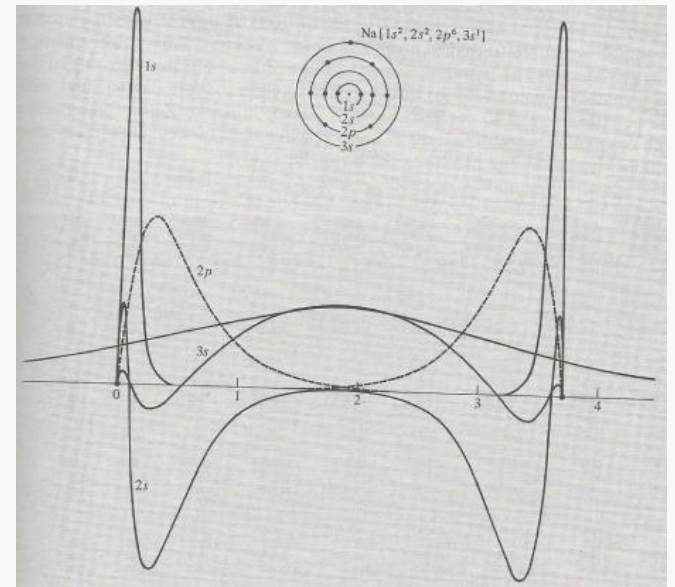
Let $\Phi^{\text{at}}(\mathbf{r}\text{-}\mathbf{R}_n)$ be the solution of Schrödinger equ. for the free atom,

$$[-\frac{\hbar^2}{2m}\nabla^2 + V^{\text{at}}(\mathbf{r}-\mathbf{R}_n)]\Phi_m^{\text{at}}(\mathbf{r}-\mathbf{R}_n) = \varepsilon_m^{\text{at}}\Phi_m^{\text{at}}(\mathbf{r}-\mathbf{R}_n).$$

For large atom separations, one can use $\Phi^{\text{at}}(\mathbf{r})$ for the Wannier functions,

$$\Psi_m(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{n=1}^{N}\Phi_m^{\text{at}}(\mathbf{r}-\mathbf{R}_n)e^{i\mathbf{k}\cdot\mathbf{R}_n}.$$

This is known as the Bloch sum or linear combination of atomic orbitals (LCAO).

Tight-binding method:

Thus, $\dfrac{1}{\sqrt{N}}\displaystyle\sum_{n=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}n}\left[V(\mathbf{r})-V^{at}(r-\mathbf{R}_n)+\varepsilon_m^{at}-E_m(\mathbf{k})\right]\Phi_m^{at}(\mathbf{k},\mathbf{r}-\mathbf{R}_n)=0,$

$\left[E_m(\mathbf{k})-\varepsilon_m^{at}\right]\displaystyle\sum_{n=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}n}\int\Phi_m^{at*}(\mathbf{r})\Phi_m^{at}(\mathbf{r}-\mathbf{R}_n)d\tau$

$\quad\quad\quad = \displaystyle\sum_{n=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}n}\int\Phi_m^{at*}(\mathbf{r})\left[V(\mathbf{r})-V^{at}(\mathbf{r}-\mathbf{R}_n)\right]\Phi_m^{at}(\mathbf{r}-\mathbf{R}_n)d\tau.$

Assuming in the wave functions of neighboring atoms overlap weakly, the $|\mathbf{R}n/=0$ term dominates on the LHS, and on the RHS, for the $|\mathbf{R}n/\neq 0$ terms, only the contributions from the nearest neighbors are relevant. Thus,
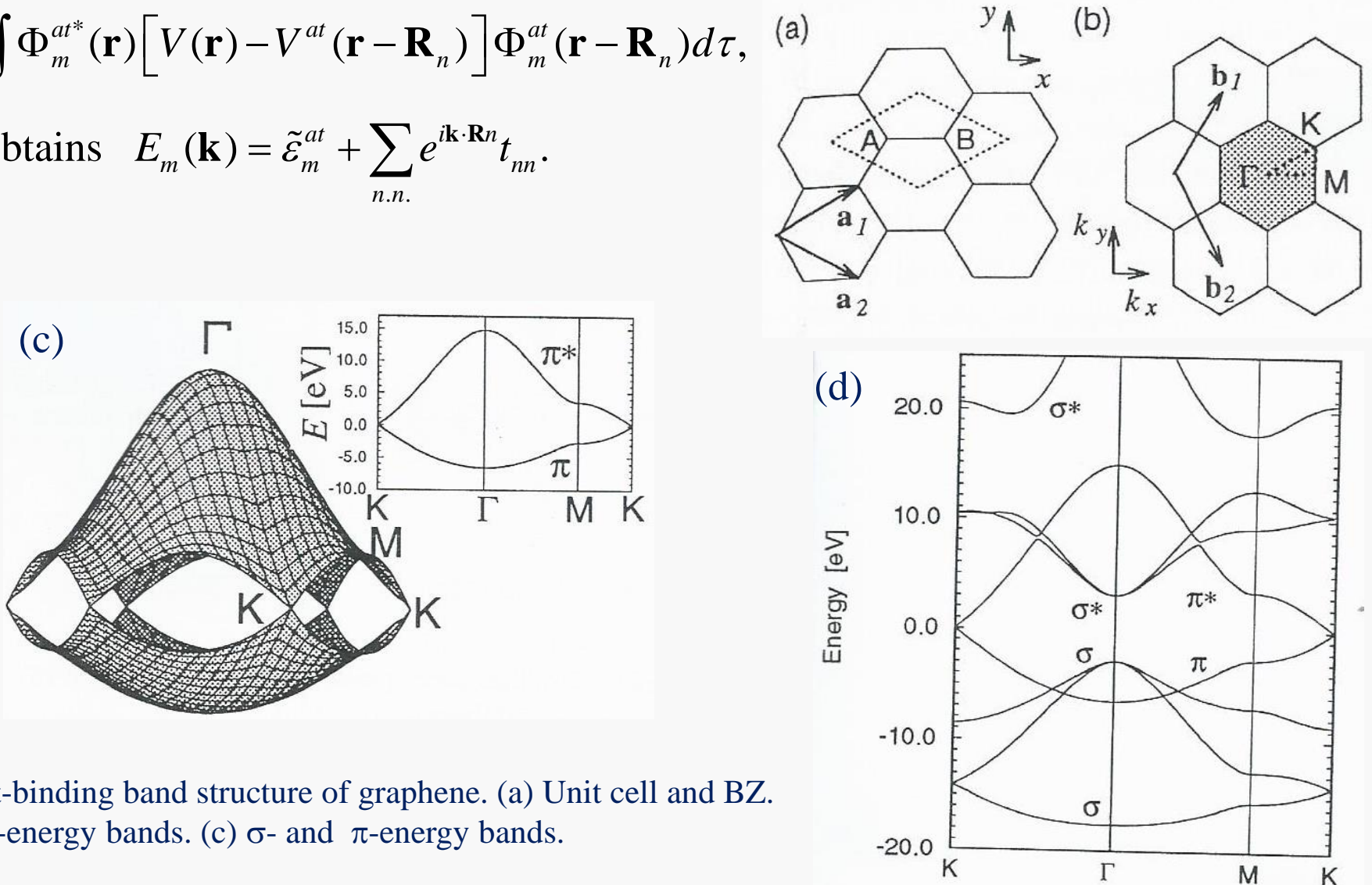
$E_m(\mathbf{k})=\varepsilon_m^{at}+\displaystyle\int\Phi_m^{at*}(\mathbf{r})\left[V(\mathbf{r})-V^{at}(\mathbf{r})\right]\Phi_m^{at}(\mathbf{r})d\tau$

$\quad\quad +\displaystyle\sum_{n.n.} e^{i\mathbf{k}\cdot\mathbf{R}n}\int\Phi_m^{at*}(\mathbf{r})\left[V(\mathbf{r})-V^{at}(\mathbf{r}-\mathbf{R}_n)\right]\Phi_m^{at}(\mathbf{r}-\mathbf{R}_n)d\tau.$

Rewrite $[\varepsilon_m^{at} + \int \Phi_m^{at*}(\mathbf{r})\left[V(\mathbf{r})-V^{at}(\mathbf{r})\right]\Phi_m^{at}(\mathbf{r})d\tau]$ as $\tilde{\varepsilon}_m^{at}$ (onsite energy)

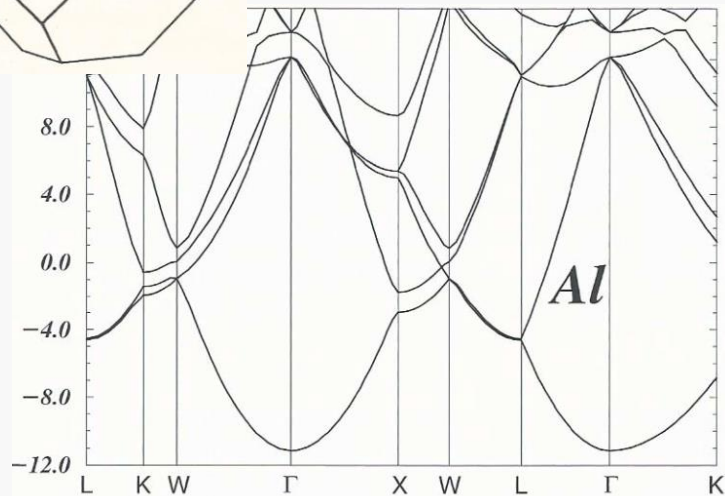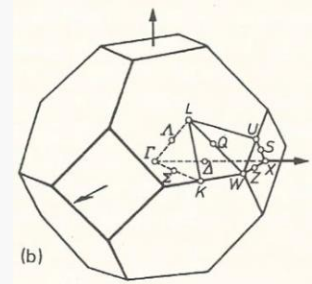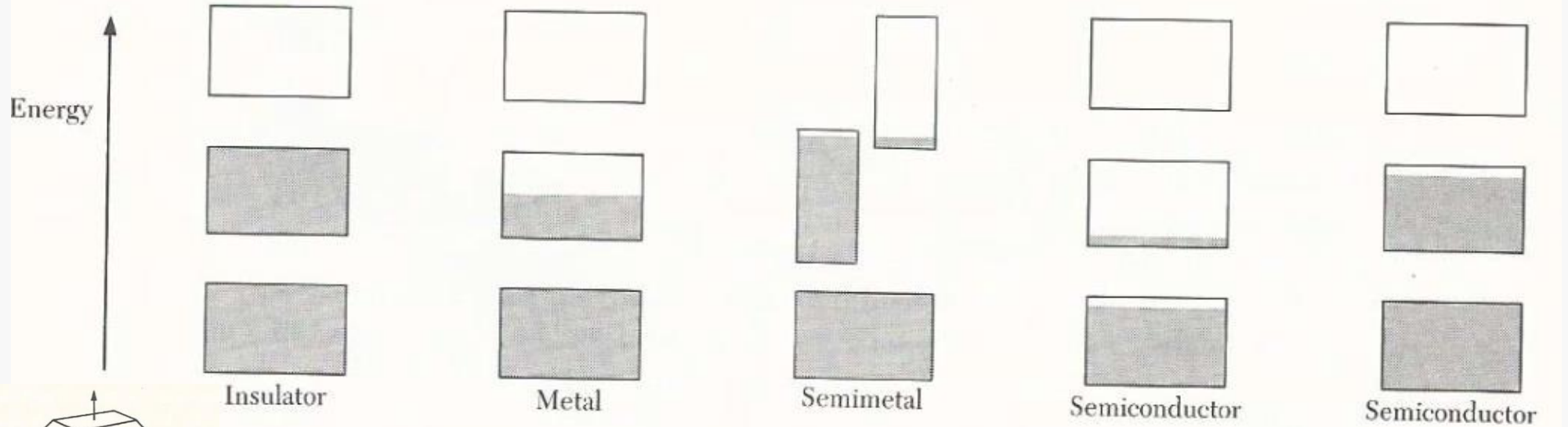and treat the transfer integral (hopping energy) as a parameter

$$t_{nn} = \int \Phi_m^{at*}(\mathbf{r})\left[V(\mathbf{r})-V^{at}(\mathbf{r}-\mathbf{R}_n)\right]\Phi_m^{at}(\mathbf{r}-\mathbf{R}_n)d\tau,$$

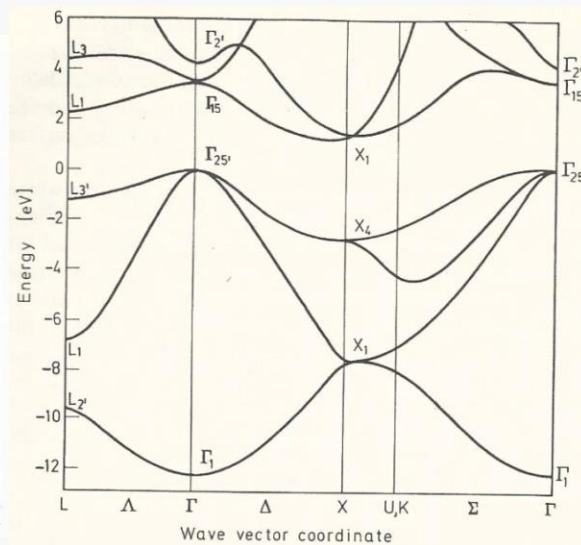one obtains $\quad E_m(\mathbf{k}) = \tilde{\varepsilon}_m^{at} + \sum_{n.n.} e^{i\mathbf{k}\cdot\mathbf{R}n}t_{nn}.$

(a)

(b)

(c)

(d)

Tight-binding band structure of graphene. (a) Unit cell and BZ.
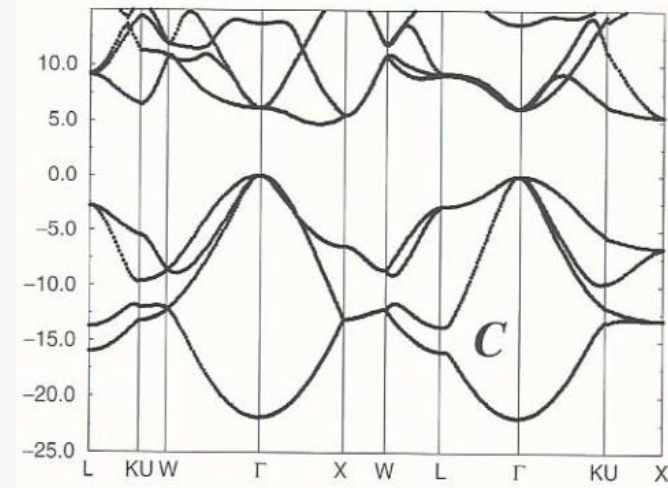(b) π-energy bands. (c) σ- and π-energy bands.

4. Reading the band structure

Energy

Insulator   Metal   Semimetal   Semiconductor   Semiconductor

(b)

8.0

4.0

0.0

−4.0

−8.0

−12.0

L   K W   Γ   X W   L   Γ   K

Al

Band structure of aluminium

6

4

2

0

−2

−4

−6

−8

−10

−12

Energy [eV]

L_3

L_1

$L_{3'}$

L_1

$L_{2'}$

Γ_1

$\Gamma_{2'}$

Γ_{15}

$\Gamma_{25'}$

X_1

X_4

X_1

$\Gamma_{2'}$

Γ_{15}

$\Gamma_{25'}$

Γ_1

L   Λ   Γ   Δ   X   U,K   Σ   Γ

Wave vector coordinate

Band structure of silicon

10.0

5.0

0.0

−5.0

−10.0

−15.0

−20.0

−25.0

L   KU W   Γ   X W   L   Γ   KU   X

C

Band structure of diamond