MSE 423 Fall 2025 – Week 9

Bloch by Bloch

Last week

- Homonuclear diatomic levels
- Empirical tight binding/Hückel model
- Energy levels and molecular orbitals of benzene
- Symmetry operations, group theory
- Symmetry to classify solutions (e.g. in benzene)
- Solutions and spectra in rings
- Translational symmetry, Bravais lattices
- A crystal as a Bravais lattice + basis

Bravais Lattices

- Infinite array of points with an arrangement and orientation that appears exactly the same regardless of the point from which the array is viewed.

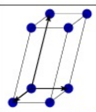
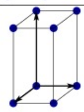
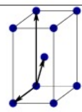
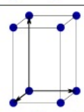
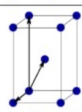
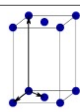
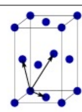
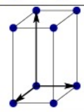
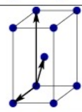
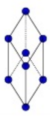
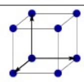
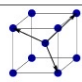
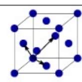
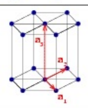
$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \quad \text{l,m and n integers}$$

$$\vec{a}_1, \vec{a}_2 \text{ and } \vec{a}_3 \text{ primitive lattice vectors}$$

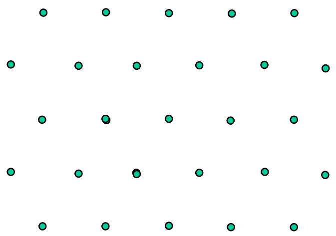
- 14 Bravais lattices exist in 3 dimensions (1848)
- M. L. Frankenheimer in 1842 thought they were 15. So, so naïve…

4 Lattice types

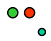
7 Crystal classes

14 Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

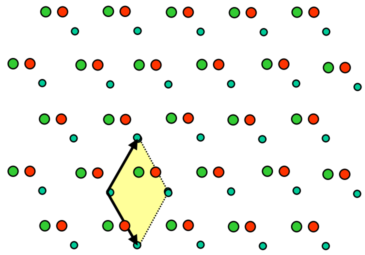
Crystal Structure = Lattice + Basis



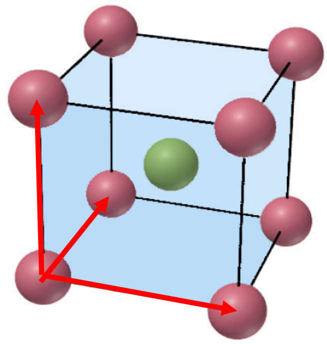
Lattice



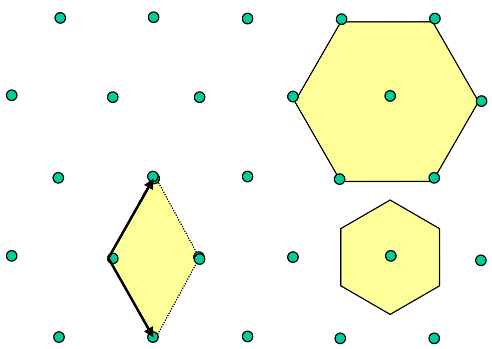
Basis

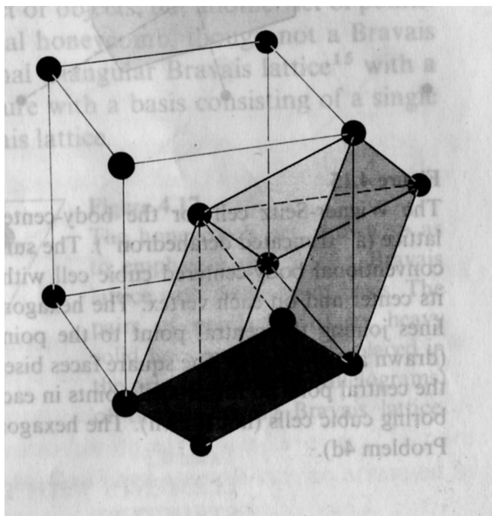


Crystal Structure = Lattice + basis

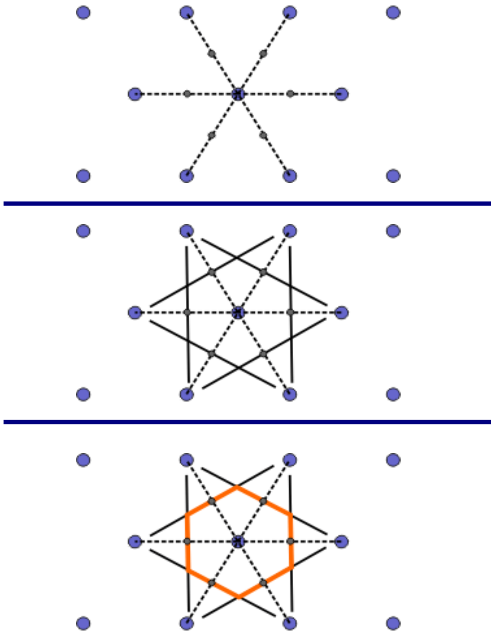


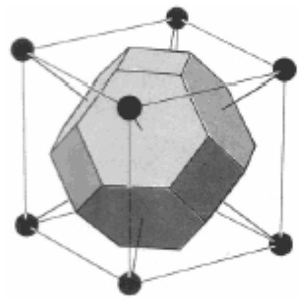
Primitive unit cell and conventional unit cell

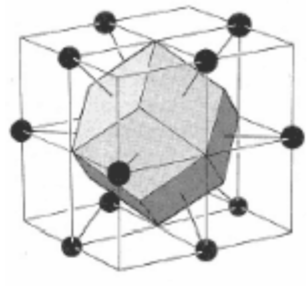




Wigner-Seitz cell

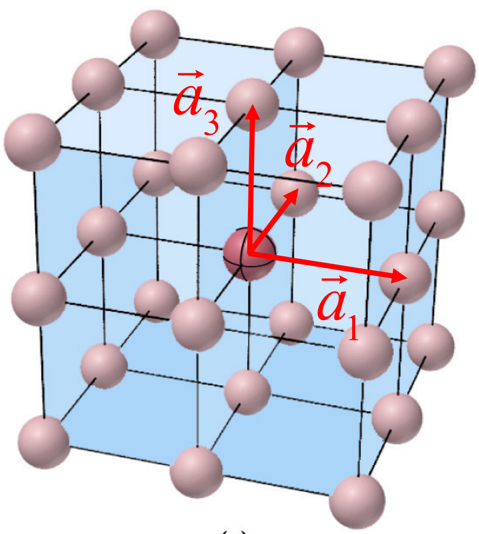






Reciprocal lattice (I)

- Let's start with a Bravais lattice, defined in terms of its primitive lattice vectors…



$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

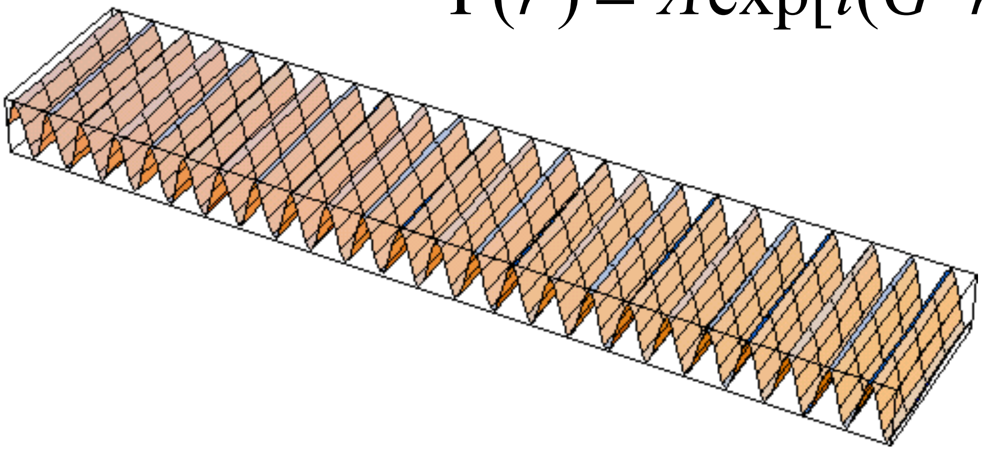
l, m, n integer numbers

$$\vec{R} = (l, m, n)$$

Reciprocal lattice (II)

- …and then let's take a plane wave

$$\Psi(\vec{r}) = A\exp[i(\vec{G}\cdot\vec{r})]$$



Reciprocal lattice (III)

- What are the wavevectors for which our plane wave has the same amplitude at all lattice points ?

$$\exp[i(\vec{G}\cdot\vec{r})] = \exp[i(\vec{G}\cdot(\vec{r}+\vec{R}))]$$
$$\exp[i(\vec{G}\cdot\vec{R})] = 1$$
$$\exp[i(\vec{G}\cdot(l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3))] = 1$$

$\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ define the primitive unit cell

Reciprocal lattice (IV)

$\vec{G}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$ n integer is satisfied by

$\vec{G} = h\vec{b}_1 + i\vec{b}_2 + j\vec{b}_3$ with h,i,j integers,

provided $\vec{b}_1 = 2\pi \frac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot\left(\vec{a}_2\times\vec{a}_3\right)}$ $\vec{b}_2 = 2\pi \frac{\vec{a}_3\times\vec{a}_1}{\vec{a}_1\cdot\left(\vec{a}_2\times\vec{a}_3\right)}$ $\vec{b}_3 = 2\pi \frac{\vec{a}_1\times\vec{a}_2}{\vec{a}_1\cdot\left(\vec{a}_2\times\vec{a}_3\right)}$

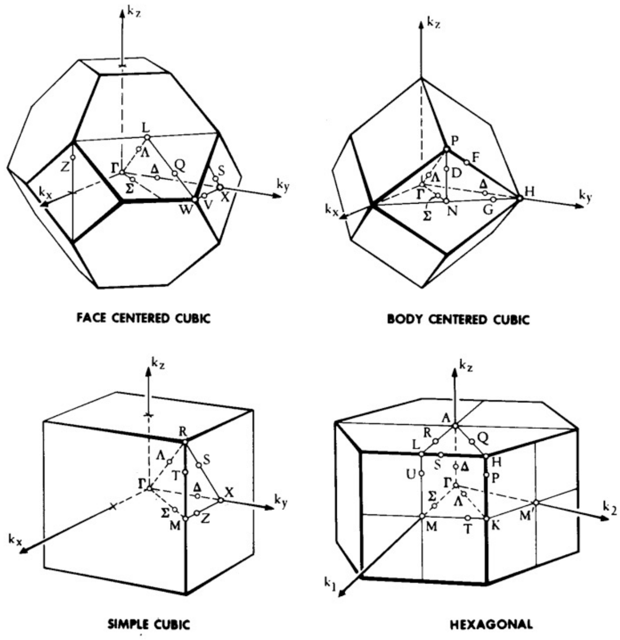
$\vec{G} = \left(h,i,j\right)$ are the reciprocal-lattice vectors

Examples of reciprocal lattices

Direct lattice	Reciprocal lattice
Simple cubic	Simple cubic
FCC	BCC
BCC	FCC
Orthorhombic	Orthorhombic

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot\left(\vec{a}_2\times\vec{a}_3\right)}$$

Brillouin zones



Brillouin zones are the Wigner-Seitz unit cells of the reciprocal lattice

https://www.materialscloud.org/work/tools/seekpath

Hamiltonian in a periodic potential

Periodic potential

Bloch Theorem

The one-particle effective Hamiltonian $\hat{H}$ in a periodic lattice commutes with the lattice-translation operator $\hat{T}_{\mathrm{R}}$, allowing us to choose the common eigenstates according to the prescriptions of Bloch theorem:

$$[\,\hat{H}\,,\,\hat{T}_{\mathrm{R}}\,] = 0 \quad \Rightarrow \quad \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\,e^{i\mathbf{k}\cdot\mathbf{r}}$$

- n, k are the quantum numbers (band index and crystal momentum), u is periodic
- From two requirements: a translation can't change the charge density, and two translations must be equivalent to one that is the sum of the two

Bloch Theorem

Bloch Theorem

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

Bloch Theorem

Bloch Theorem (in two equiv forms)

$$\Psi_{\vec{k}}\left(\vec{r}+\vec{R}\right)=\exp\left(i\vec{k}\cdot\vec{R}\right)\Psi_{\vec{k}}\left(\vec{r}\right)$$

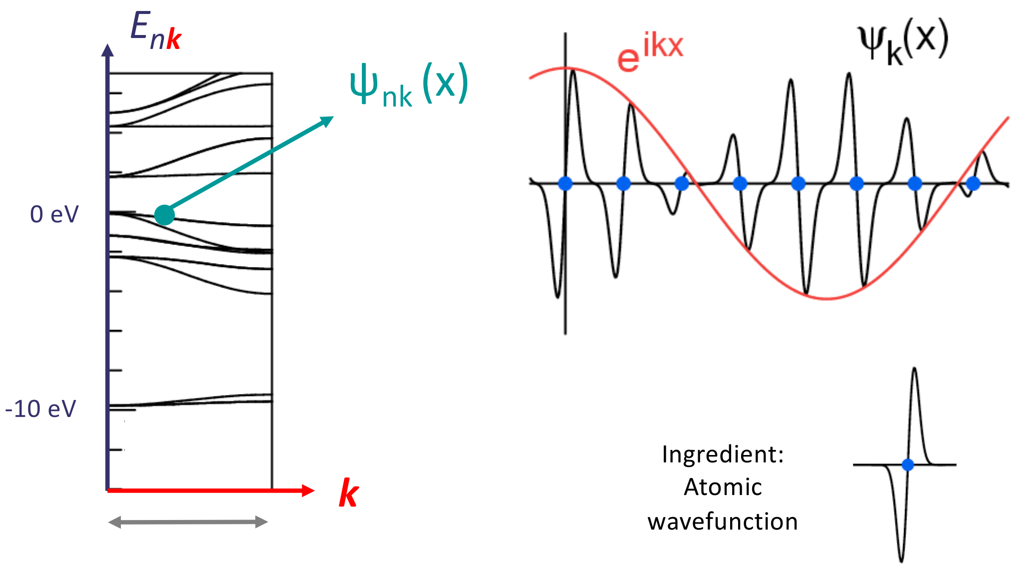
Bloch Theorem (in two equiv forms)

$$\Psi_{\vec{k}}\left(\vec{r}+\vec{R}\right)=\exp\left(i\vec{k}\cdot\vec{R}\right)\Psi_{\vec{k}}\left(\vec{r}\right)$$

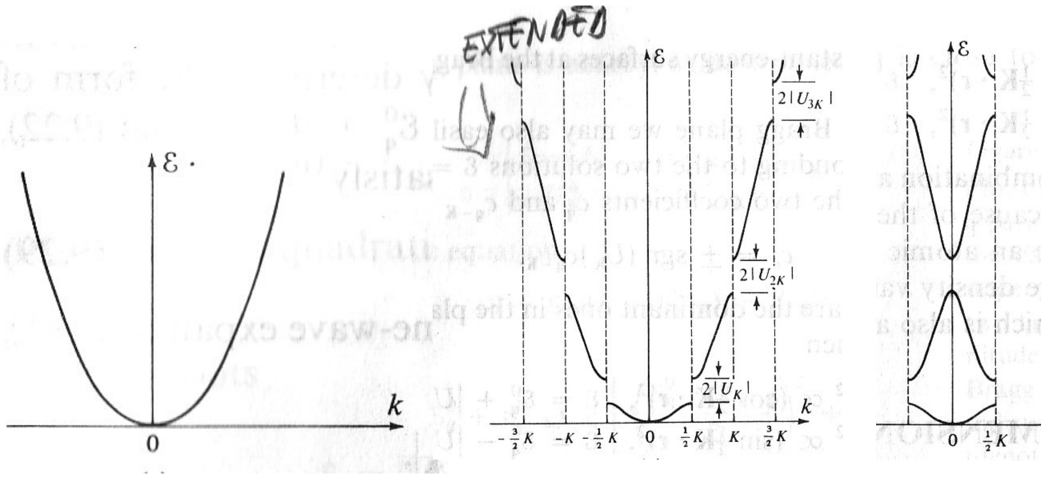
$$\Psi_{\vec{k}}\left(\vec{r}\right)=\exp\left(i\vec{k}\cdot\vec{r}\right)u_{\vec{k}}\left(\vec{r}\right)$$

Bloch Theorem

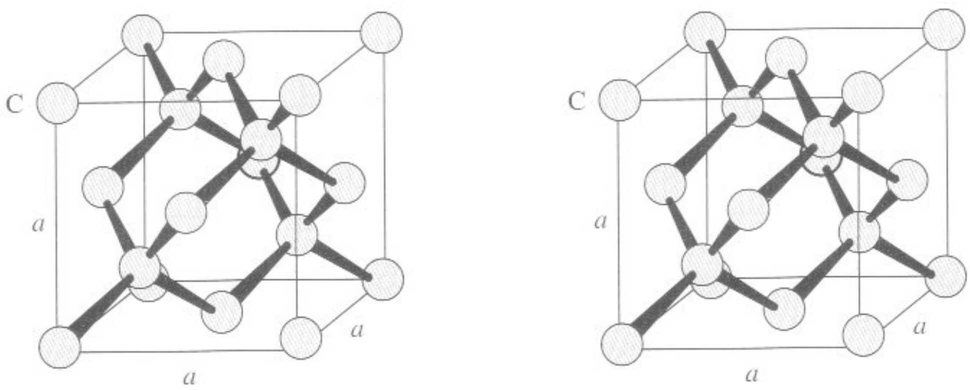
Bloch wavefunction



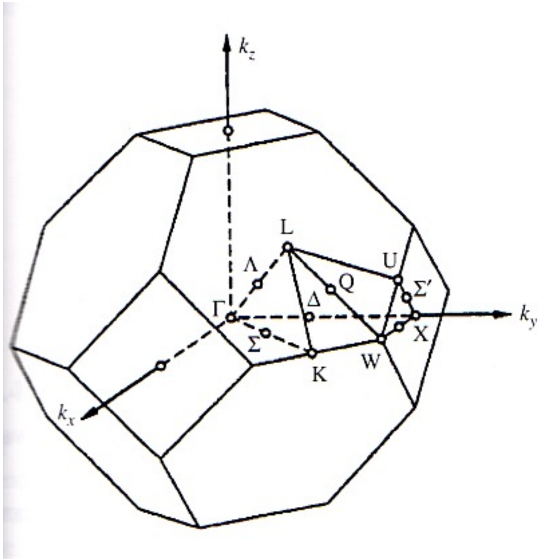
From extended to primitive



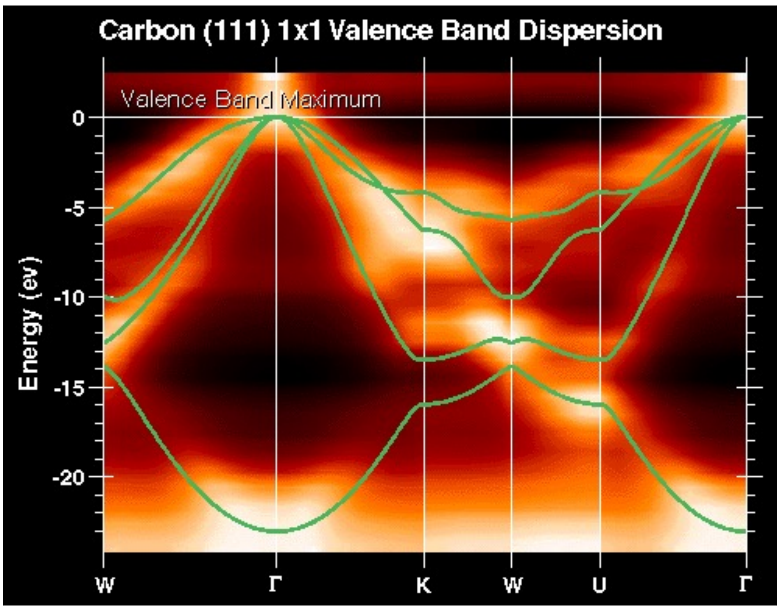
Diamond and Zincblend



Brillouin Zone (fcc)

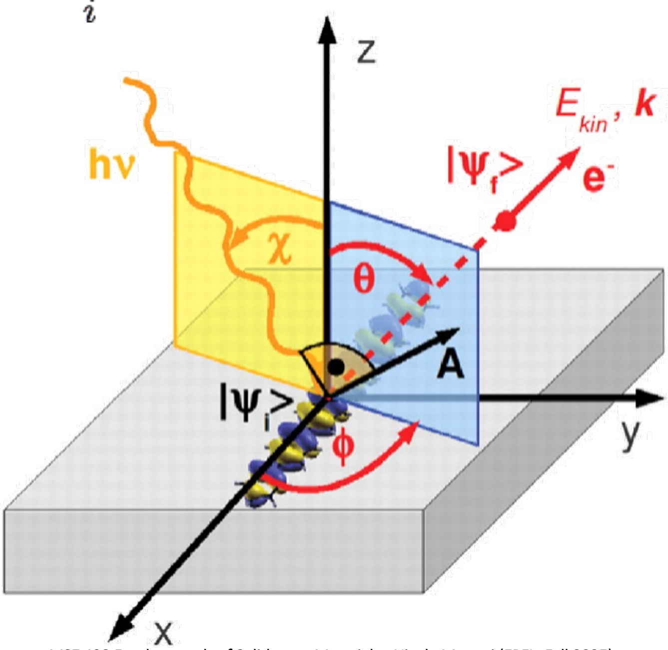


Band Structure of Diamond

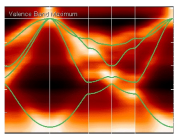


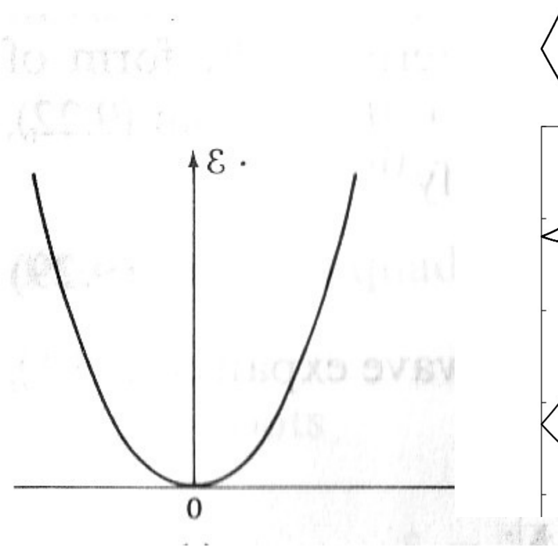
ARPES: Angle resolved photoemission spectroscopy

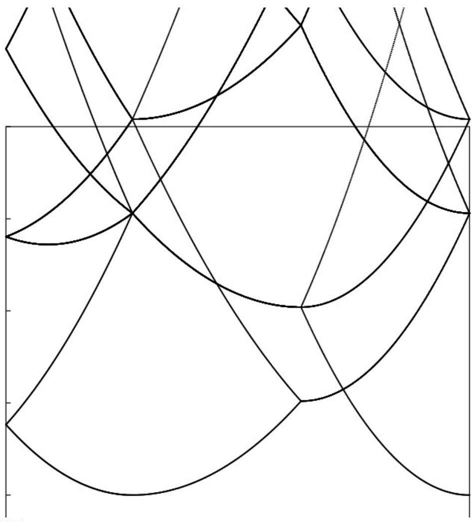
$$I(\omega) = \sum_i |\langle \varphi_f | \hat{H}_{\text{int}} | \varphi_i \rangle|^2 \delta(\epsilon_f - \epsilon_i - \hbar\omega)$$



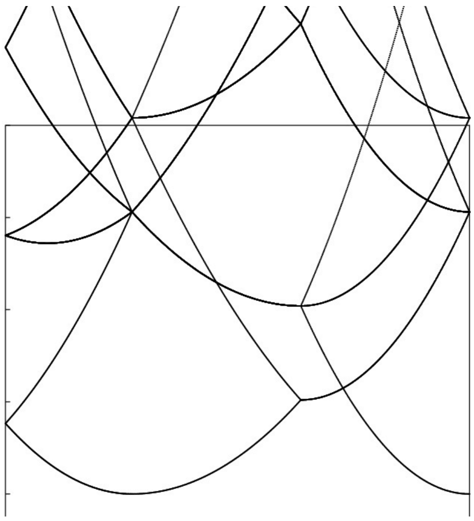
Why does it look like this?

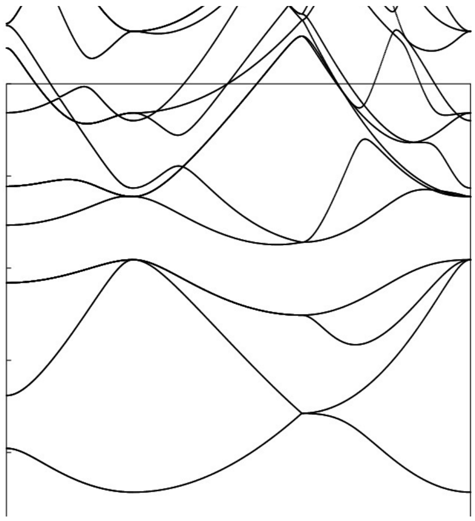






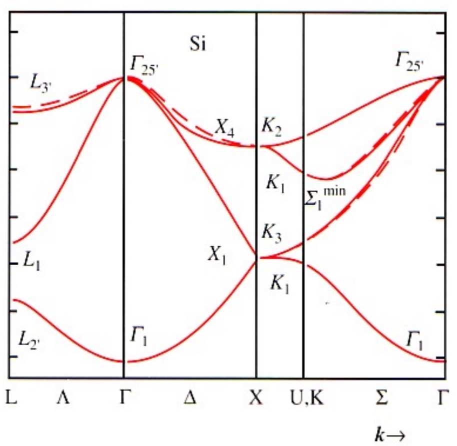
Band Structures: Free Electron Gas, Silicon

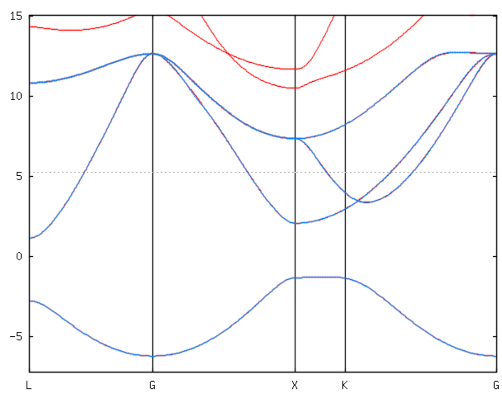




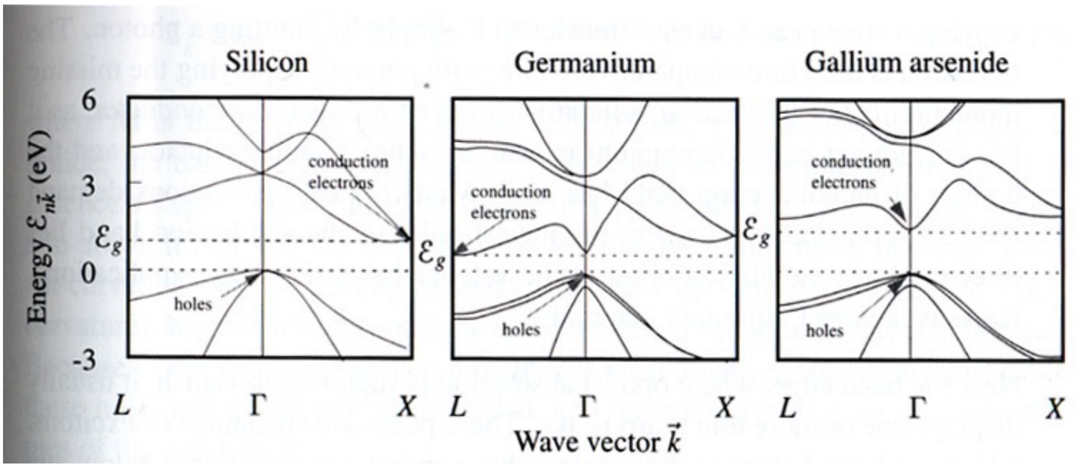
Silicon

Lead





Band structure of Si, Ge, GaAs



Conduction band minima (in 3d)

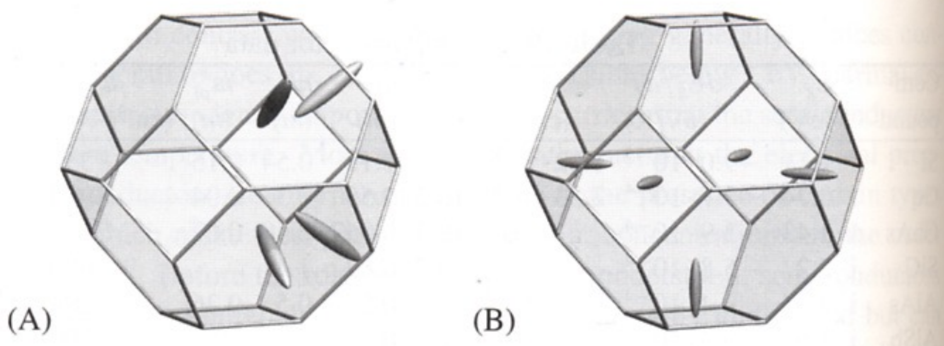


Figure 19.9. (A) The conduction band minima in germanium lie along (111) and straddle the zone boundary, producing four inequivalent pockets of electrons with a highly anisotropic effective mass. (B) In silicon, the conduction band minima lie 8/10 of the way toward (100), producing six pockets of electrons, but only three with distinct symmetries.