



# Chapter 3: Lattice and band structure

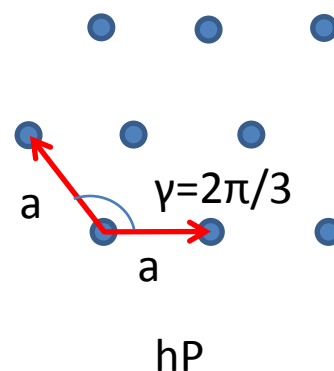
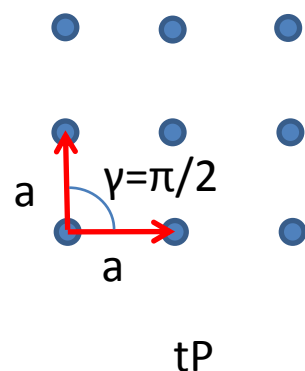
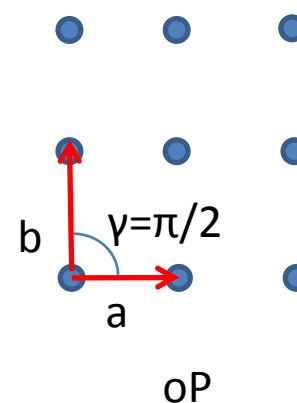
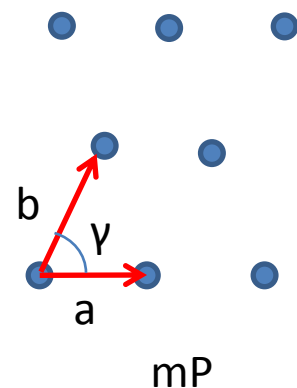
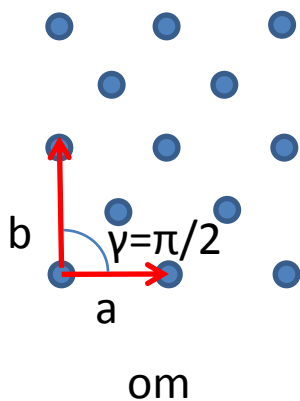
1. Crystal structure
2. Brillouin zone
3. Band gap
4. Bloch theorem
5. Applications

# Lattice

Crystal : regular arrangement of the atoms/molecules

Crystal = lattice + basis

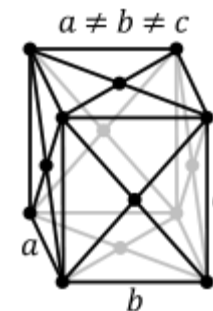
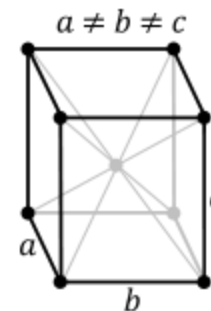
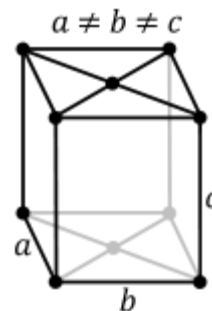
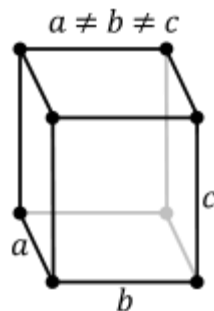
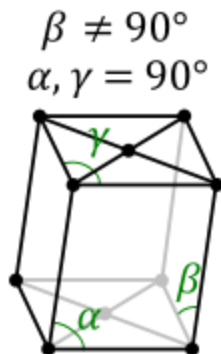
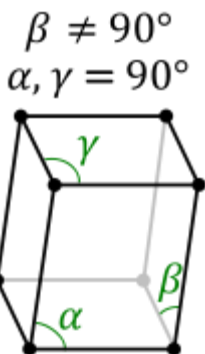
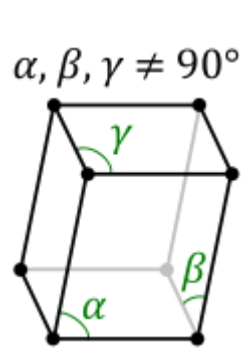
4 2D crystal systems :  
5 2D Bravais lattice



# Lattice

7 3D primitive unit cells :

14 2D Bravais lattice



Triclinic (aP)

Monoclinic (mP)

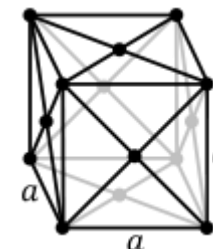
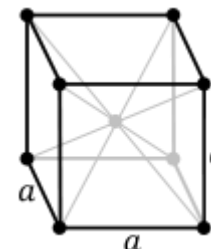
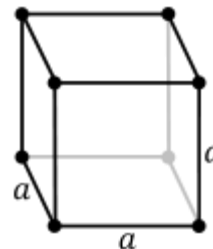
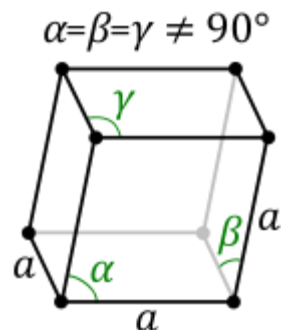
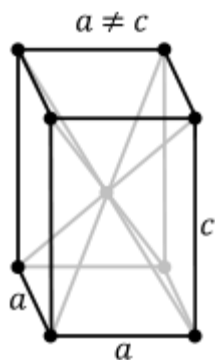
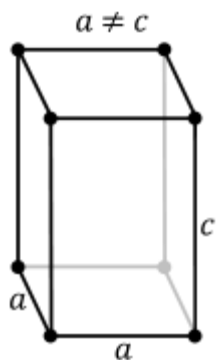
Monoclinic (mC)

Orthorhombic (oP)

(oC)

(oI)

(oF)



Tetragonal (tP)

Tetragonal (tI)

Rhombohedral (R)

Hexagonal (h)

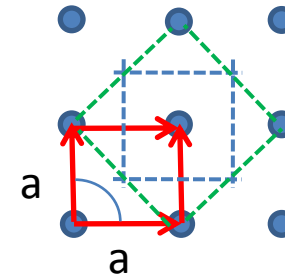
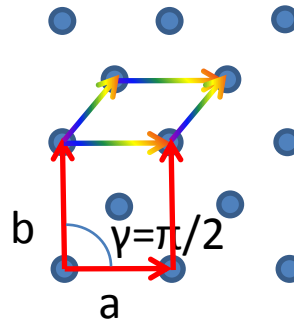
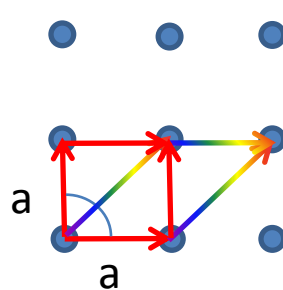
Cubic (cP)

Cubic (cI)

Cubic (cF)

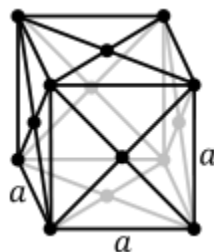
# Unit Cell

1. Conventional unit cell
  2. Primitive unit cell
  3. Wigner-Seitz cell
- ← Display true symmetry
- } Smallest unit cell, contains one lattice point

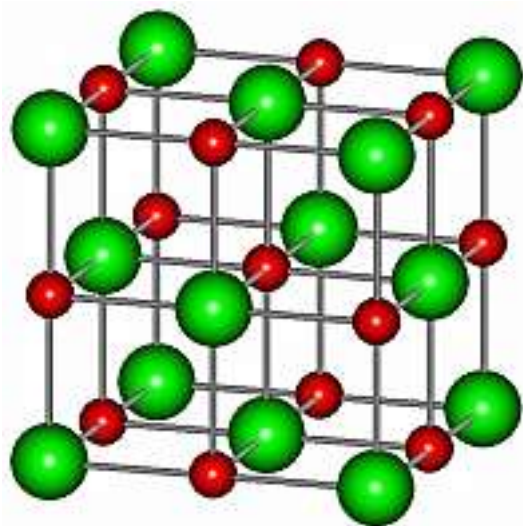


# Basis

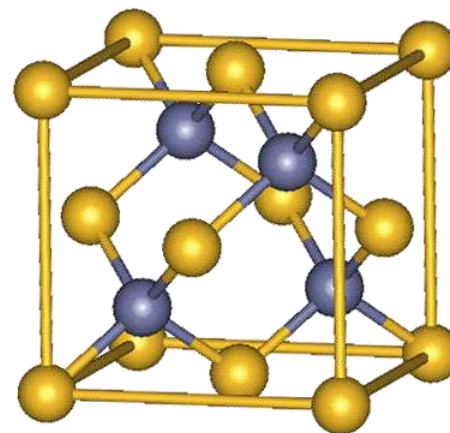
Fcc lattice



Math vs. physics



NaCl



ZnS

# Reciprocal lattice

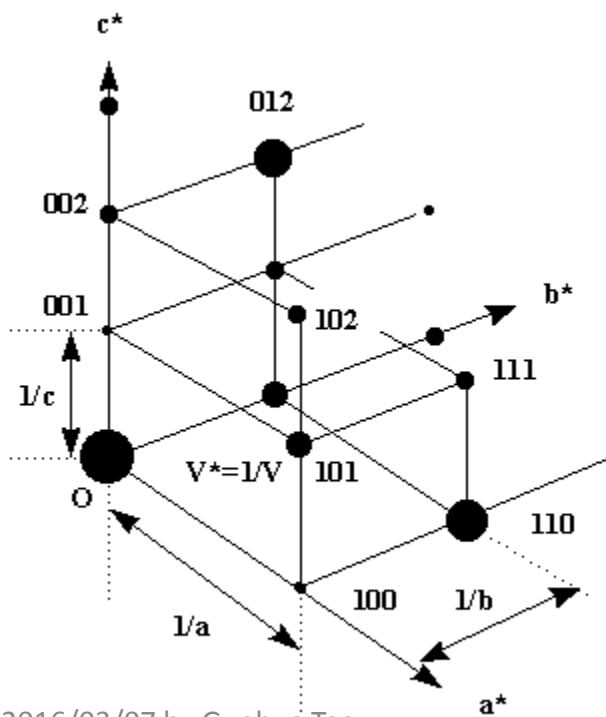
Space group = point group + translation group

$$T(n) \equiv T(n_1, n_2, \dots) = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + \dots$$

$$f[\mathbf{r} + T(n_1, n_2, \dots)] = f(\mathbf{r})$$

Translational symmetry

The inverse of the Bravais lattice consists of the set of wave vectors  $\mathbf{K}$



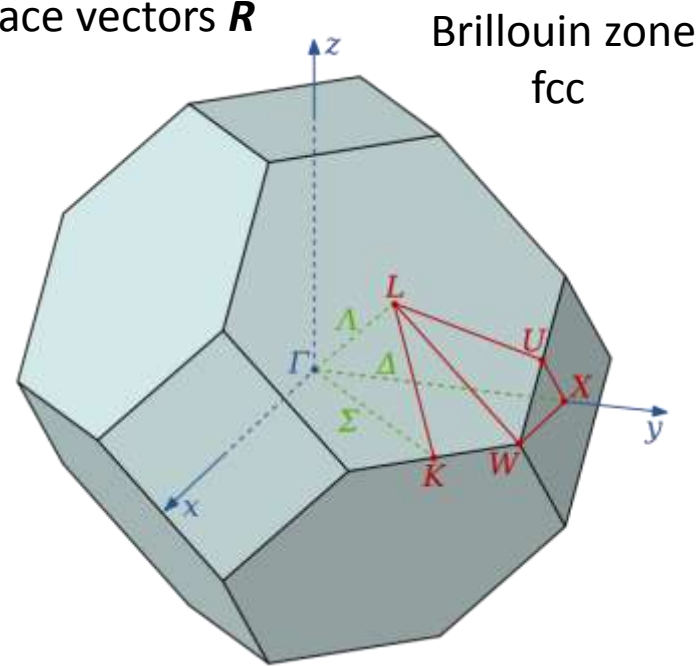
$$e^{i\mathbf{K} \cdot \mathbf{R}} = 1 \quad \text{for all real space vectors } \mathbf{R}$$

$$b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}$$

$$b_2 = 2\pi \frac{a_3 \times a_1}{a_2 \cdot (a_3 \times a_1)}$$

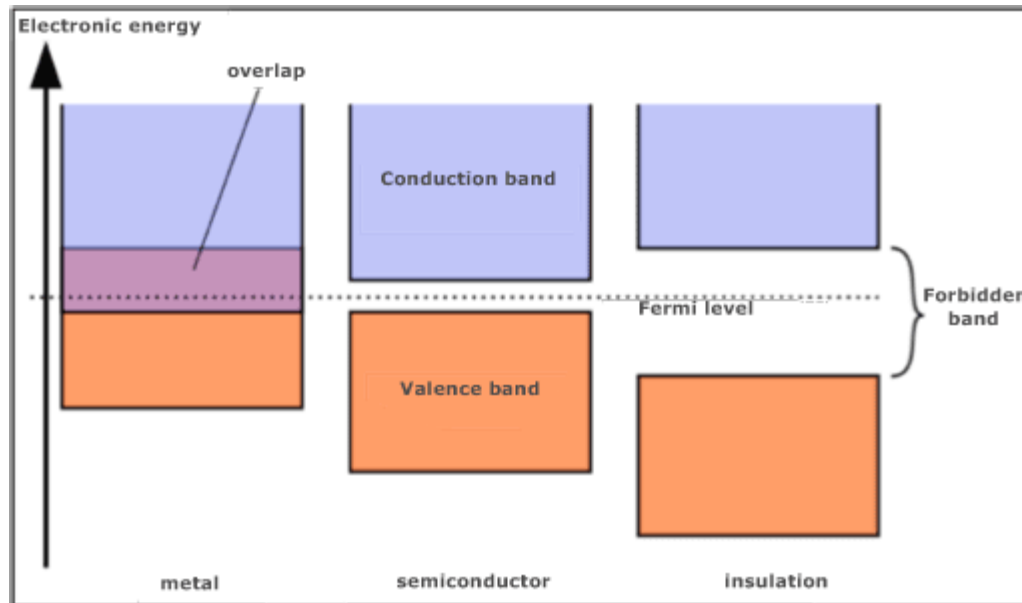
$$b_3 = 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_1 \times a_2)}$$

$$b_i \cdot a_j = 2\pi \delta_{ij}$$



# Band theory

1. Bloch theorem (1928) : electrons moves almost freely through the perfect lattice, scatted only by imperfections and phonons.
2. 1931, Wilson laid the foundation for the classification of metals, semiconductors and insulators.





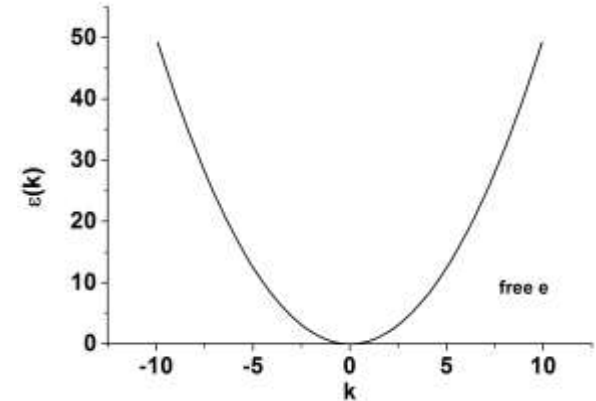
# Band gap

Free space:

$$H|\Psi\rangle = -\frac{\hbar^2}{2m}\nabla^2|\Psi\rangle = E|\Psi\rangle \quad H = \frac{\mathbf{p}^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

$$|\Psi(t)\rangle = e^{-\frac{i}{\hbar}\int_0^t H(t')dt'}|\Psi\rangle \quad \text{3D}$$

$$|\Psi\rangle = \frac{1}{\sqrt{2\pi}}e^{ikx-i\omega t}, k = \frac{p}{\hbar}, \omega = \frac{E}{\hbar} = \frac{p^2}{2m\hbar} = \frac{\hbar k^2}{2m}$$



1D

$$(\mathbf{k} + \mathbf{G})^2 = k^2$$

$$k = \pm \frac{1}{2}G = \pm n\pi/a$$

First Brillouin zone

Plane wave -> standing wave

$$k = \pm\pi/a$$

$$\psi(\pm) = \frac{1}{\sqrt{2\pi}}e^{\pm i\pi x/a} \quad \longrightarrow \quad \varphi(+)=\frac{1}{\sqrt{2\pi}}(e^{i\pi x/a}+e^{-i\pi x/a})=\sqrt{\frac{2}{\pi}}\cos(\pi x/a)$$

$$\varphi(-)=\frac{1}{\sqrt{2\pi}}(e^{i\pi x/a}-e^{-i\pi x/a})=\sqrt{\frac{2}{\pi}}\sin(\pi x/a)$$

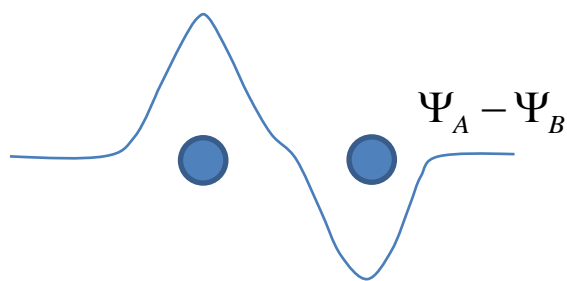
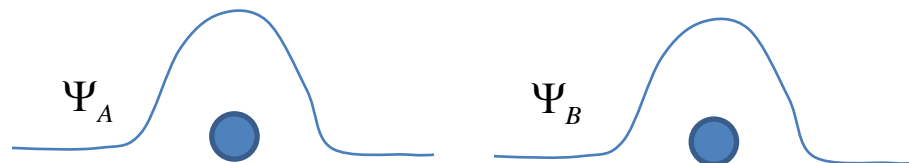
$$U(x) = U \cos(2\pi x/a)$$

$$E_g = \int_0^1 dx U(x) [|\varphi(+)|^2 - |\varphi(-)|^2] = \int_0^1 dx U \cos(2\pi x/a) [\cos^2(\pi x/a) - \sin^2(\pi x/a)] = U$$

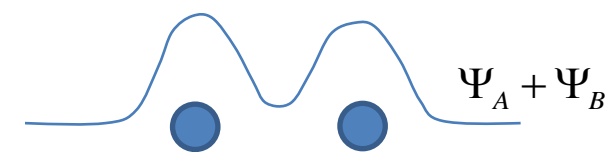


# Tight-binding

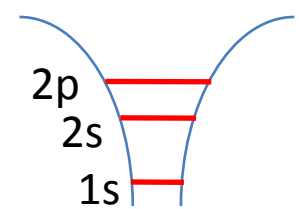
Linear combination of atomic orbital (LCAO)



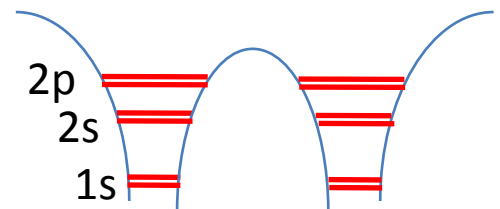
Excited state



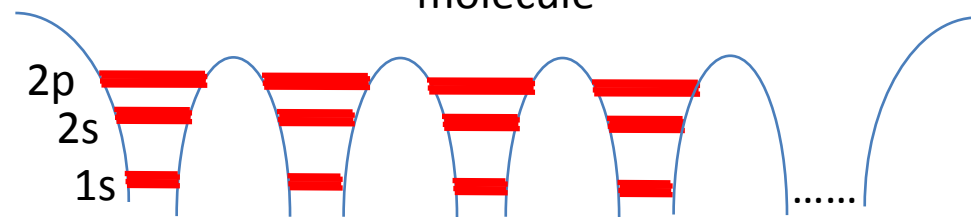
Ground state



atom



molecule



solid



# Bloch theorem

Free e:  $\psi_k(\mathbf{r}) = Ae^{i\mathbf{k}\cdot\mathbf{r}}$   
 atomic:  $\psi(\mathbf{r}) = Cu(\mathbf{r})$   
 crystal:  $\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r})$



$$u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R}_l)$$

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

Periodic potential

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

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R}_l) \quad \mathbf{R}_l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$$

Proof:

$$\psi_k(\mathbf{r}) = f(\mathbf{r})u_k(\mathbf{r})$$

$$u_k(\mathbf{r} + \mathbf{R}_n) = u_k(\mathbf{r})$$

$$|\psi(\mathbf{r})|^2 \text{ periodic} \implies |f(\mathbf{r} + \mathbf{R}_n)|^2 = |f(\mathbf{r})|^2 \quad \forall \mathbf{R}_n$$

$$f(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\implies \psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r})$$



# Detailed proof

Translational operator:

Ashcroft and Mermin, Solid state physics

$$T_{\alpha}f(\mathbf{r}) = f(\mathbf{r} + \mathbf{a}_{\alpha})$$

$$T_{\alpha}T_{\beta}f(\mathbf{r}) = T_{\alpha}f(\mathbf{r} + \mathbf{a}_{\beta}) = f(\mathbf{r} + \mathbf{a}_{\beta} + \mathbf{a}_{\alpha}) = T_{\beta}T_{\alpha}f(\mathbf{r})$$

Therefore  $[T_{\alpha}, T_{\beta}] = 0$

For independent particles: (may be generalized to correlated many body systems)

$$\begin{aligned} T_{\alpha}Hf(\mathbf{r}) &= T_{\alpha}\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + U(\mathbf{r})\right]f(\mathbf{r}) \\ &= \left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}+\mathbf{a}_{\alpha}}^2 + U(\mathbf{r} + \mathbf{a}_{\alpha})\right]f(\mathbf{r} + \mathbf{a}_{\alpha}) \\ &= \left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + U(\mathbf{r})\right]f(\mathbf{r} + \mathbf{a}_{\alpha}) \\ &= \left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + U(\mathbf{r})\right]T_{\alpha}f(\mathbf{r}) = HT_{\alpha}f(\mathbf{r}) \end{aligned} \quad \longrightarrow \quad [T_{\alpha}, H] = 0$$

# Detailed proof

Eigenfunctions:

$$\begin{cases} H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \\ T_\alpha\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{a}_\alpha) = \lambda_\alpha\psi(\mathbf{r}) \end{cases} \quad \alpha = 1, 2, 3$$

Periodic boundary conditions:

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + N_\alpha \mathbf{a}_\alpha) \quad \psi(\mathbf{r} + N_\alpha \mathbf{a}_\alpha) = T_\alpha^{N_\alpha} \psi(\mathbf{r}) = \lambda_\alpha^{N_\alpha} \psi(\mathbf{r}) = \psi(\mathbf{r})$$

$$\lambda_\alpha^{N_\alpha} = 1 = e^{i2\pi h_\alpha} \quad h_\alpha \text{ integer}, \quad \alpha = 1, 2, 3 \quad \lambda_\alpha = \exp\left(i \frac{2\pi h_\alpha}{N_\alpha}\right) \quad \lambda_\alpha = e^{i\mathbf{k} \cdot \mathbf{a}_\alpha}$$

Introduce reciprocal vector:

$$\mathbf{k} = \frac{h_1}{N_1} \mathbf{b}_1 + \frac{h_2}{N_2} \mathbf{b}_2 + \frac{h_3}{N_3} \mathbf{b}_3 \quad \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}$$

$$\psi(\mathbf{r} + \mathbf{R}_l) = \psi(\mathbf{r} + \ell_1 \mathbf{a}_1 + \ell_2 \mathbf{a}_2 + \ell_3 \mathbf{a}_3) \quad \longrightarrow \quad \psi(\mathbf{r} + \mathbf{R}_l) = e^{i\mathbf{k} \cdot \mathbf{r}} \psi(\mathbf{r})$$

$$= T_1^{\ell_1} T_2^{\ell_2} T_3^{\ell_3} \psi(\mathbf{r}) = \lambda_1^{\ell_1} \lambda_2^{\ell_2} \lambda_3^{\ell_3} \psi(\mathbf{r})$$

$$= \exp\left[i\mathbf{k} \cdot (\ell_1 \mathbf{a}_1 + \ell_2 \mathbf{a}_2 + \ell_3 \mathbf{a}_3)\right] \psi(\mathbf{r})$$

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

Easy to see  $u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_l) = u_{\mathbf{k}}(\mathbf{r})$

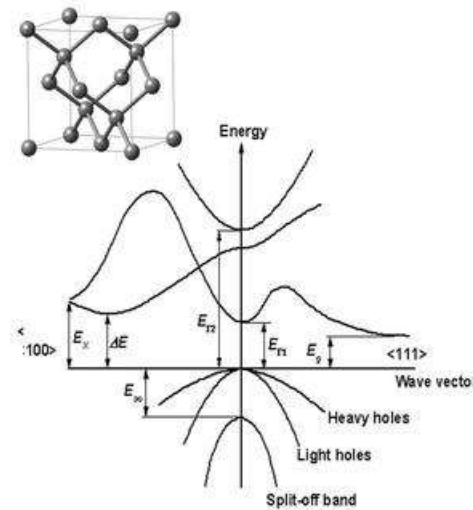
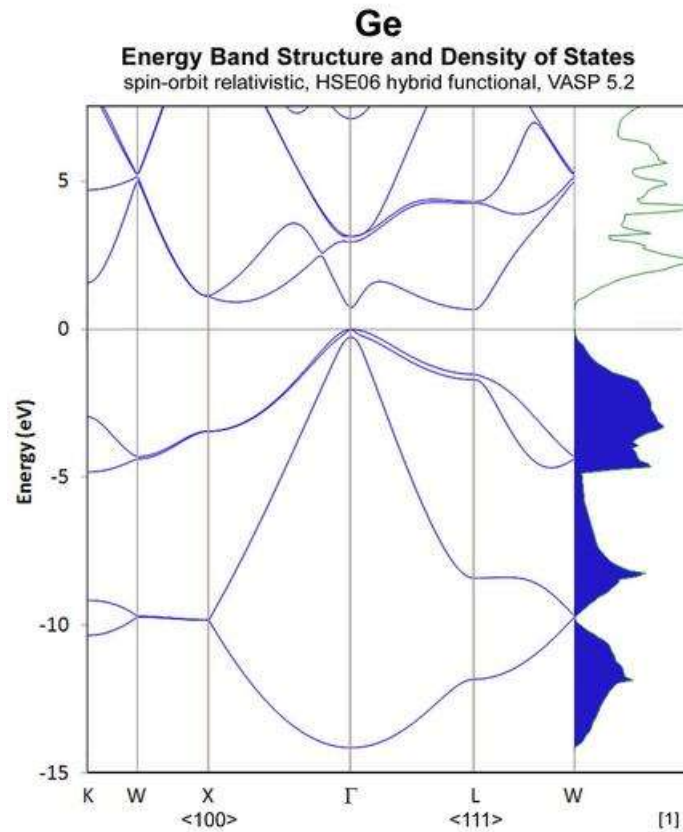


# Quantitative Calculation

1. [Self consistent field method](#), Hartree, 1928; Symmetry corrected by Fock in 1930, now known as Hartree-Fock method.
2. [Perturbation theory](#), ground state for two-electron systems, Hylleraas, 1930.
3. [The cellular method](#), Na metal, electronic energy and total energy, Wigner and Seitz, 1933; energy band, Wigner and Seitz, 1934; Slater, 1934. Cu bands, Krutter, 1935; NaCl, Shockley, 1936.
4. [Augmented plane waves](#), Slater, 1953.
5. [Orthogonalized plane waves \(OPW\)](#), Herring, 1940.
6. [Effective potential \(pseudopotentials\)](#), Fermi, 1934; Hellman, 1935.
7. Calculation on semiconductors, Ge, Herman and Callaway, 1953
8. [Density functional theory](#), Kohn and Sham, 1964

# Energy band structure

1. LDA results in a zero band gap, 0.07 eV from VASP by using HSE06.
2. Direct band gap 0.8 eV (exp), indirect band gap 0.66 eV (exp).



	Expt. [1]	Computed
300 K $E_g$	0.66 eV	0.66
$E_x$	1.2 eV	1.12
$E_{\Gamma 1}$	0.8 eV	0.73
$E_{\Gamma 2}$	3.22 eV	3.14
$\Delta E$	0.85 eV	0.91
$E_{\infty}$	0.29 eV	0.29

[1] <http://www.ioffe.rssi.ru/SVA/NSM/Semicond/Ge/bandstr.html>



# Challenge and advances

## \*Many body electron correlation.

Exchange energy and electron-electron interactions

### Experiments:

1. New materials: fullerenes, and graphenes.
2. New phenomena: superconductivity, quantum Hall effect etc.

### Theory:

1. BCS theory for superconductivity
2. DFT theory
3. Quantum Monte Carlo methods
4. Many body perturbation methods
5. Dynamical mean field theory

# Exercises

## Option 1:

Due: April 5, 2016

Energy band calculation for one of the following materials:

Copper:

1. Phys. Rev. **1935** 48 664
2. Phys. Rev. Lett. **1979** 43 82-85 E vs k and inverse lifetime of Cu(110)
3. Phys. Rev. **1963** 129 138-150 Energy band structure of copper.

Si/Ge:

1. Phys. Rev. B 48 17791-17805

Li, Na, K, Mg, Mo, Zn, Pt, Al  
B, Sn...

## Option 2:

Make Wigner-Seitz cells of bcc and fcc lattice (2 for each of them) by yourself using materials available.

