An introduction to solid-state physics

International summer School in electronic structure Theory: electron correlation in Physics and Chemistry

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Introduction

There are typically 10^{22} electrons per cm^3 in condensed matter systems. This is somehow too much for considering a solid as a big molecule. Fortunately, translation symmetries can help a lot in particular in the case of one-body Hamiltonian of the kind met in mean-field approaches (DFT, Hartree-Fock, tight-binding or extended-Hückel, etc.)

Figure: (Left) First silicon transistor (Bell Labs, Murray Hill, NJ) announced in 1951 by William Shockley; (Right) Silicon band structure. Shaded area indicates energy domains with no allowed states.

The unit cell and the periodic vectors

The unit cell is a portion of space that repeated periodically can reconstruct the entire crystal. A unit cell can contain several atoms (the motif). The lattice vectors: $\vec{R}_{ijk} = i\vec{a}_1 + j\vec{a}_2 + k\vec{a}_3$ allow to reconstruct the crystal from the atoms in the unit-cell with $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ the basis vectors. The minimum volume cell is a primitive cell.

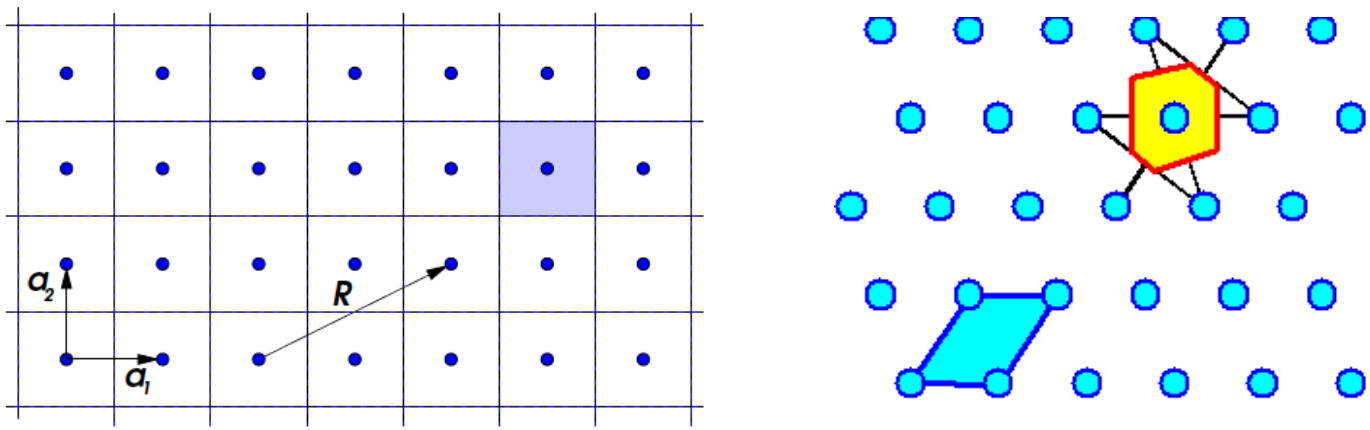
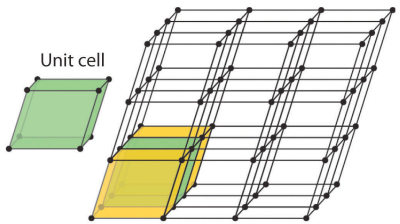


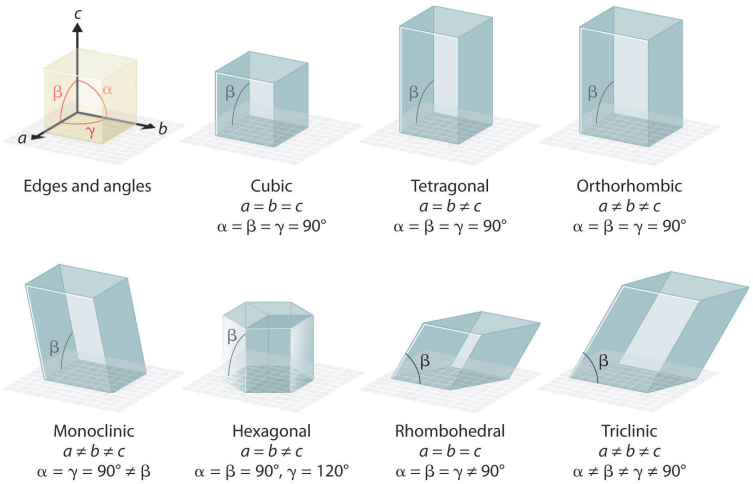
Figure: (Left) 2D square lattice with one atom per cell. A unit-cell is shaded in blue. (Right) 2D hexagonal cell with one atom per cell. Two different unit cells are represented. For the blue cell, 1/4th of each connected atom belong to this cell. The yellow one is called the Wigner-Seitz cell that is invariant with respect to the crystal symmetry point group.

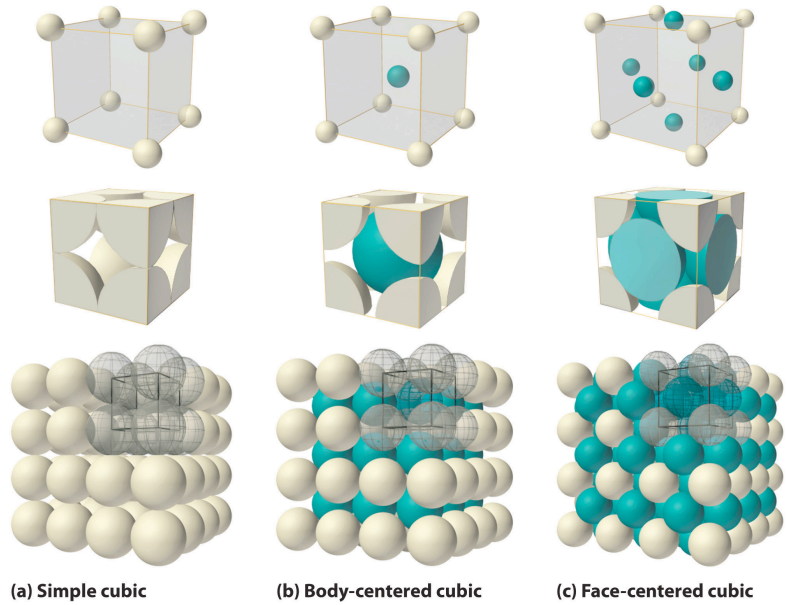
The 3D Bravais lattices and the motif



Depending on the shape of the unit-cell, one can categorize 3D crystal under 7 different "lattice systems", that yield 14 Bravais lattices depending on the disposition of atoms in the unit cell (the motif).

For example, a cubic lattice can be "simple", body-centered (BCC) or face-centered (FCC). Silicon and diamond are FCC lattices with 2 atoms per primitive cell.





Courtesy: *http : / / chemwiki . ucdavis . edu / Wikitexts / UC_Davis / UCD_Chem_2B / UCD_Chem_2B*

Symmetries, commutators and quantum numbers

Reminder: in the case of a spherically symmetric potential, the Hamiltonian commutes with the angular momentum L_z and L^2 operators (and L^2 commutes with L_z) which implies that there exists a common basis of eigenstates:

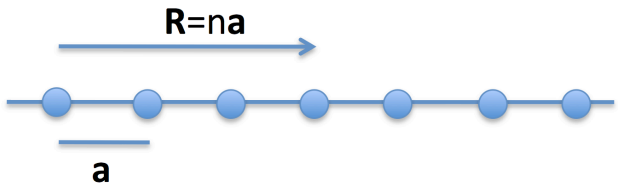
$$\begin{aligned} H|\psi_{nlm}> &= E_{nlm}|\psi_{nlm}> \\ L^2|\psi_{nlm}> &= l(l+1)\hbar|\psi_{nlm}> \\ L_z|\psi_{nlm}> &= m\hbar|\psi_{nlm}> \end{aligned}$$

We know that the solutions are of the type:

$$\psi_{nlm}(\vec{r}) = \psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi)$$

and that (nlm) are "good" quantum numbers: the Hamiltonian H acting on such states preserve the symmetry character of these eigenstates.

Bloch theorem in 1D: introduction



We consider now the case of a crystal with discrete (not infinitesimal) translation properties.

Assume that the potential is periodic: V(x+R)=V(x) (with R=na) and call (T_R) the translation operator. Then:

$$T_R\left[V(x)\psi(x)\right] = V(x-R)\psi(x-R) = V(x)T_R\psi(x)$$

which means that the potential, and thus the Hamiltonian, commute with the translation operator: $[T_R, H] = 0$. Then quantum mechanics says that one can find a common eigenbasis for the two operators.

$$\begin{aligned} H|\psi_k> &= E_k|\psi_k> \\ T_R|\psi_k> &= C_k(R)|\psi_k> \end{aligned}$$

Bloch theorem in 1D (II)

We can find the expression of the C_k by simple considerations. The translation operator should preserve the normalisation of ψ:

$$\int dx|\psi(x-R)|^2 = \int dx|\,T_R\psi(x)|^2 = \int dx|C(R)|^2|\psi(x)|^2 = \int dx|\psi(x)|^2$$

so $|C(R)|^2 = 1$ and $C(R) = e^{i\theta(R)}$. Further:

$$T_a\,T_a\psi(x) = \psi(x-2a) = T_{2a}\psi(x) \quad \Rightarrow \quad C(a)C(a) = C(2a)$$

The only mathematical function satisfying such conditions is:

$$C(a) = e^{-ika} \;\Rightarrow\; C(2a) = C(a)C(a) \quad \text{and} \quad C(R = na) = e^{-ikR}.$$

The quantum number (k) is associated with the translation operator.

Bloch theorem

We know therefore (generalizing to 3D) that one can find an eigenbasis of the Hamiltonian and of translation operators such that:

$$\boxed{\psi_{\vec{k}}(\vec{r}-\vec{R}) = T_{\vec{R}}\psi_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{R}}\psi_{\vec{k}}(\vec{r}) \quad \text{or} \quad \psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{\vec{k}}(\vec{r})}$$

This is a first formulation of Bloch theorem. A second formulation comes when considering the properties of $u_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\vec{r}}\psi_{\vec{k}}(\vec{r})$:

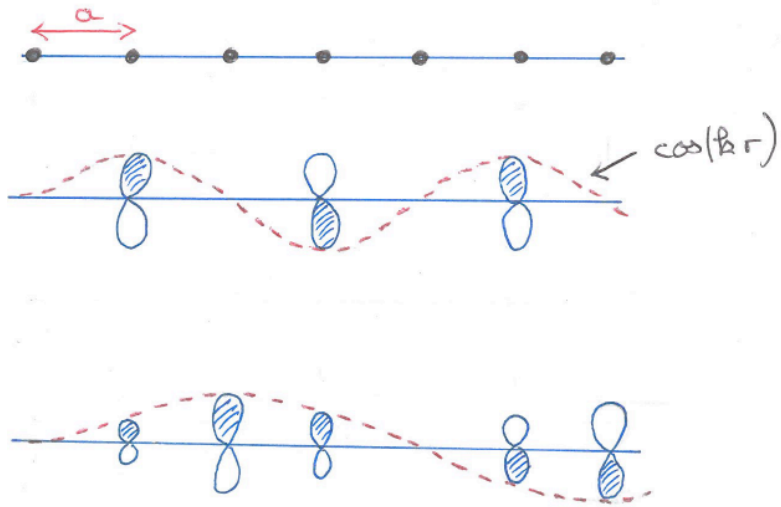
$$T_{\vec{R}}u_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot(\vec{r}-\vec{R})}\psi_{\vec{k}}(\vec{r}-\vec{R}) = e^{-i\vec{k}\cdot(\vec{r}-\vec{R})}e^{-i\vec{k}\cdot\vec{R}}\psi_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}}\psi_{\vec{k}}(\vec{r}).$$

Namely, the fonction $u_{\vec{k}}(\vec{r})$ is periodic and:

$$\boxed{\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}u_{\vec{k}}(\vec{r}), \quad \text{with} \quad u_{\vec{k}}(\vec{r}) \quad \text{periodic.}}$$

Bloch states with bare hands (literally)

The $e^{i\vec{k}\vec{r}}$ phase term can be regarded as an "envelope function" that modulates the periodic function $u_{\vec{k}}(\vec{r})$. In the 1D example here below, assume that each atom has one (p_z) orbital. One can create different Bloch states by changing the magnitude of the k-vector (we represent *e.g.* the real part of the wavefunctions).



For the first/second Bloch state, ($k = \pi/2a$) and ($k = \pi/4a$).

The reciprocal space

The $\vec{k}$-vectors are homogeneous to the inverse of a distance and lives in the "reciprocal space". If $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ are the periodic vector of the crystal, we choose to represent the $\vec{k}$-vectors as a function of the reciprocal space basis: $(\vec{b}_1, \vec{b}_2, \vec{b}_3)$ vectors such that:

$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_i \cdot (\vec{a}_j \times \vec{a}_k)} \quad \Rightarrow \quad \boxed{\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}}$$

Defining the reciprocal space vectors: $\boxed{\vec{G} = l_1\vec{b}_1 + l_2\vec{b}_2 + l_3\vec{b}_3}$, then the $e^{i\vec{G}\cdot\vec{r}}$ vectors form a basis for periodic functions since for any lattice vector in real space $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$,

$$e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r} + i\sum_\alpha n_\alpha l_\alpha \vec{a}_\alpha \cdot \vec{b}_\alpha} = e^{i\vec{G}\cdot\vec{r} + i\sum_\alpha n_\alpha l_\alpha 2\pi} = e^{i\vec{G}\cdot\vec{r}}$$

For example, $u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{\vec{k}}(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$, the planewave expansion of $u_{\vec{k}}(\vec{r})$.

The Brillouin zone

From the definition of (**G**):

$$e^{i(\vec{k}+\vec{G})\cdot\vec{R}} = e^{i\vec{k}\cdot\vec{R}} \quad \text{and} \quad \psi_{\vec{k}+\vec{G}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\left[e^{i\vec{G}\cdot\vec{r}}u_{\vec{k}+\vec{G}}(\vec{r})\right] = e^{i\vec{k}\cdot\vec{r}}\tilde{u}(\vec{r})$$

where $\tilde{u}$ is periodic: the Bloch states associated with the $e^{i\vec{k}\cdot\vec{r}}$ and $e^{i(\vec{k}+G)\cdot\vec{r}}$ phase factors are the same, and $e^{i\vec{k}\cdot\vec{R}}$ and $e^{i(\vec{k}+G)\cdot\vec{R}}$ are the same eigenvalues of $T_{\vec{R}}$.

The Brillouin zone (BZ) is the ensemble of independent $\vec{k}$-vectors (not connected by any $\vec{G}$-vector). It is the primitive cell of the reciprocal vectors lattice.

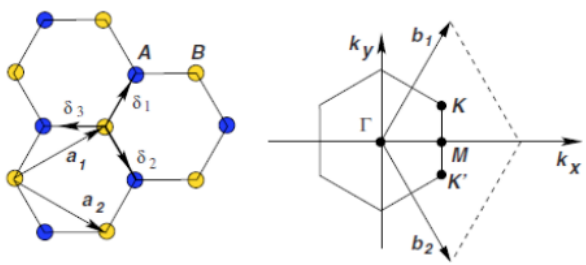


Figure: 2D hexagonal lattice with its first Brillouin-zone. The important k-points bear specific names (**Γ** is the zone-center, **K** is at the corner, etc.)

The Brillouin zone (II)

The Brillouin zone is usually taken to be the highest-symmetry primitive cell of the reciprocal lattice, namely the "Wigner-Seitz" primitive cell. Plot the planes normal to reciprocal lattice vectors cutting them "in the middle". The volume that such planes will define is the Brillouin zone. High symmetry directions and **k**-points have "standard" names.

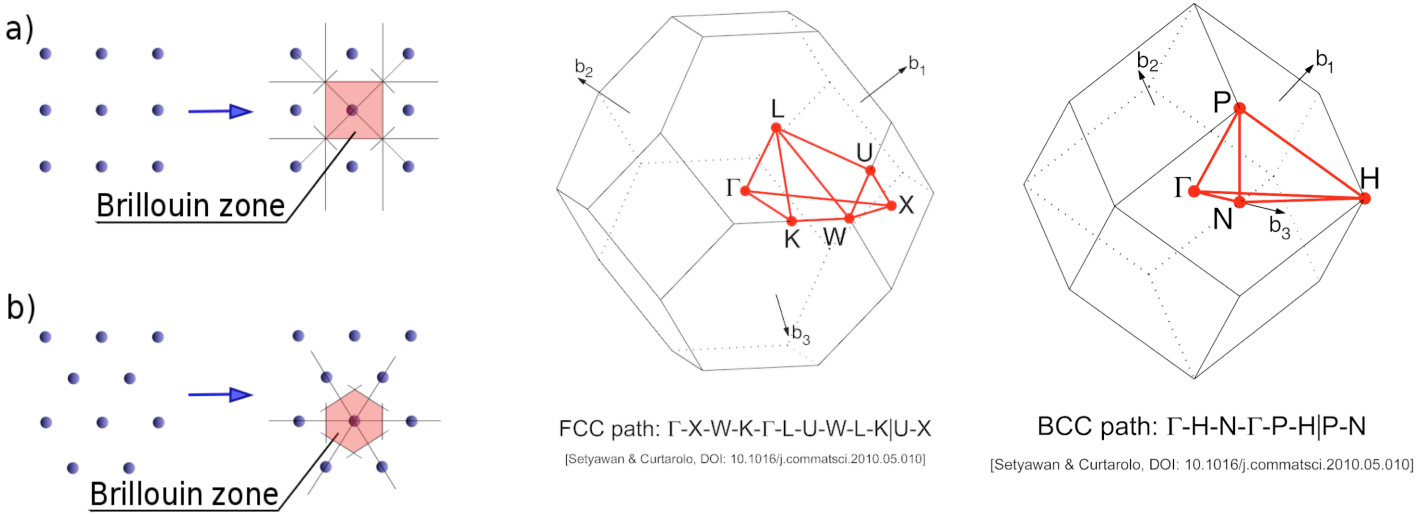


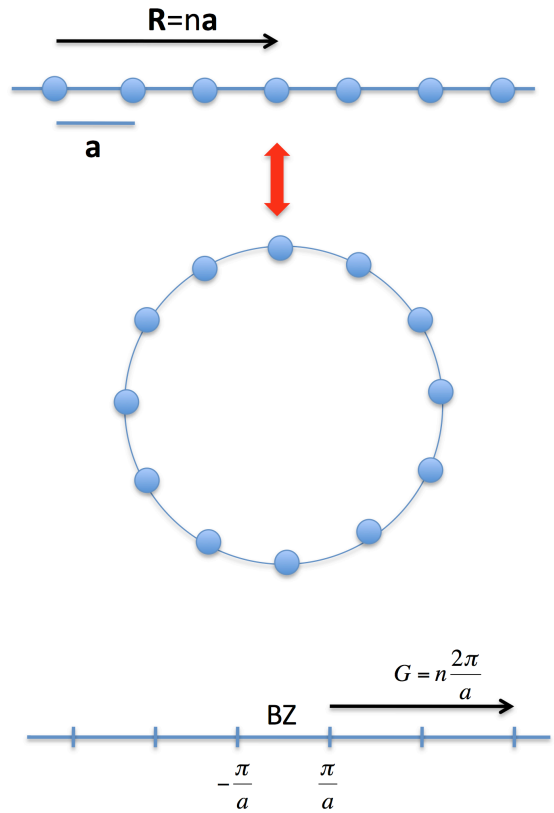
Figure: (Left) 2D square and hexagonal BZ. (Middle) The BZ of a face-centered cubic (FCC) lattice is a truncated octaedron. (Right) The BZ of a body-centered cubic lattice is a rhombic dodecahedron.

Number and nature of the **k**-vectors

For illustration, let's go back to 1D. The values of (k) are governed by the boundary conditions. Solid-state physicists adopt usually the Born and von Karman periodic boundary conditions where the solid "closes" onto itself. This means that with N cells, one has the condition:

$$\psi(x + Na) = \psi(x) \quad \Rightarrow \quad e^{ikNa} = 1$$
$$\Rightarrow \quad k = \text{integer} \times (2\pi/Na)$$

The first BZ is: $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$.



There are thus N k-vectors in the BZ, as many as unit cells.

Sum rule: $\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = \sum_{n=0}^{N-1} e^{ikna} = \frac{1-e^{ikNa}}{1-e^{ika}} = 0$ for $k \neq 0$ in the BZ.

Orthogonality of Bloch states

Let's demonstrate that Bloch states for different $(\vec{k})$-points in the BZ are orthogonal. One can write:

$$\langle \psi_{\vec{k}'} | \psi_{\vec{k}} \rangle = \int d\vec{r}\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} u^*_{\vec{k}'}(\vec{r}) u_{\vec{k}}(\vec{r})$$

which can be expressed in terms of Fourier components:

$$\frac{1}{8\pi^3} \int d\vec{r}\, e^{i(\vec{k}'-\vec{k}+\vec{G})\cdot\vec{r}} = \delta(\vec{k}' - \vec{k} + \vec{G}) = 0$$

since by definition for $(\vec{k})$ and $(\vec{k}')$ in the BZ, they cannot differ by a reciprocal-lattice vector $\vec{G}$. Alternatively by Bloch theorem:

$$\langle \psi_{\vec{k}'} | \psi_{\vec{k}} \rangle = \left(\sum_R e^{i(\vec{k}'-\vec{k})\cdot\vec{R}} \right) \int_{\Omega_{cell}} \psi^*_{\vec{k}'}(\vec{r}) \psi_{\vec{k}}(\vec{r}) = 0$$

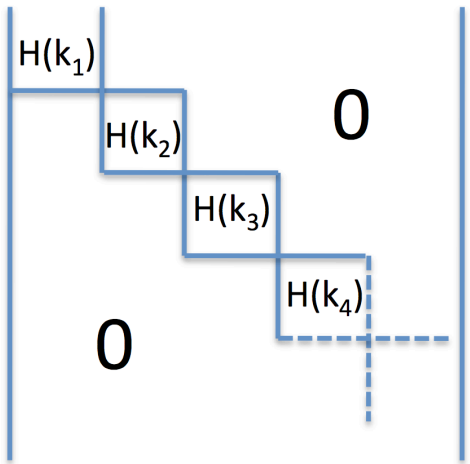
unless $\vec{k}' = \vec{k} + \vec{G}$ (including the condition: $\vec{k}' = \vec{k}$).

Block diagonalisation of the Hamiltonian

Since the Hamiltonian is periodic, then the arguments developed here above hold and:

$$\langle \psi_{n'\vec{k}'} | \hat{H} | \psi_{n\vec{k}} \rangle = \langle \psi_{n'\vec{k}} | \hat{H} | \psi_{n\vec{k}} \rangle \delta(\vec{k} - \vec{k}')$$

where the indices (n,n') serve to distinguish Bloch states with the same $\vec{k}$-vector (not necessarily eigenstates of $\hat{H}$, e.g. basis vectors).



The Hamiltonian does not couple Bloch states with different Bloch vectors.

This is the central result.

Since there are as many **k**-point in the BZ as there are unit cells in the crystal, in the absence of orthogonality and block diagonalization of the Hamiltonian, the Bloch representation would not have helped much.

Setting up $H(\vec{k})$

We start from Bloch theorem: $\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} u_{\vec{k}}(\vec{r})$, where $u_{n\vec{k}}(\vec{r})$ is periodic. Then:

$$\left[\frac{-\hbar^2\nabla^2}{2m} + V(\vec{r})\right] \psi_{n\vec{k}}(\vec{r}) = E_{n\vec{k}}\psi_{n\vec{k}}(\vec{r})$$

yields straighforwardly:

$$\left[\frac{(\vec{p}+\hbar\vec{k})^2}{2m} + V(\vec{r})\right] u_{n\vec{k}}(\vec{r}) = E_{n\vec{k}} u_{n\vec{k}}(\vec{r}), \quad \text{with} \quad \vec{p} = -i\hbar\nabla.$$

This is a $\vec{k}$-specific Hamiltonian: one has to set-up and diagonalize a different Hamiltonian for each $\vec{k}$-point of interest in the BZ.

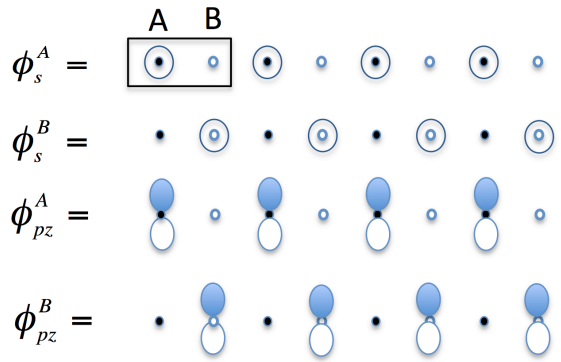
Compare e.g. to the hydrogen case where we had a specific radial equation for each l-quantum number, with the $(\mathbf{L}^2/2mr^2)$ centrifugal term coming from the kinetic operator in spherical coordinates.

Setting up $H(\vec{k})$ in a basis

LCAO basis: if each atom is described by a set of atomic orbitals $\alpha_{nlm}(\vec{r})$, then one can create a periodic crystal basis $\{\phi_{nlm}\}$ to describe the periodic function $u_{\vec{k}}(\vec{r})$ as follows:

$$\phi_{J,nlm}(\vec{r}) = \sum_{\vec{R}} \alpha_{J,nlm}(\vec{r} - \vec{\tau}_J - \vec{R})$$

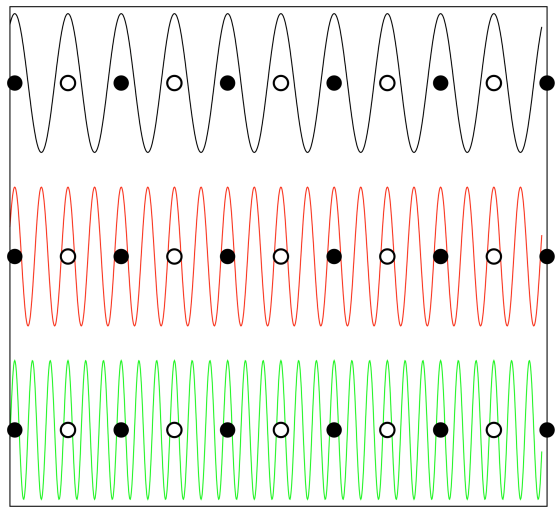
where $\vec{\tau}_J$ runs over the unit cell atoms.



PW basis: the planewave (PW) representation uses the Fourier expansion of $u_{n\vec{k}}(\vec{r})$ over the reciprocal lattice $\vec{G}$-vectors:

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c(\vec{G}) e^{i\vec{G}\vec{r}}, \quad \text{with:}$$

$$u_{\vec{k}}(\vec{G}) = \int \frac{d\vec{r}}{\Omega} u_{\vec{k}}(\vec{r}) e^{-i\vec{G}\vec{r}}$$



Linear combination of atomic orbitals versus planewaves

The question: "which is the best basis ?" (planewaves, Gaussians, real-space grid, wavelets, etc.) has probably no answer besides "it depends on the system you study !".

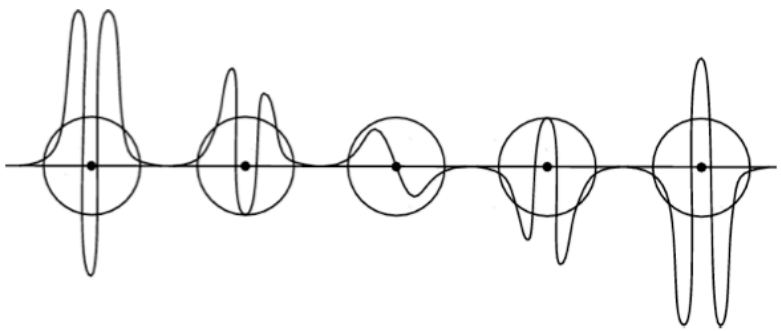


Figure 4.2: Atomic wave.

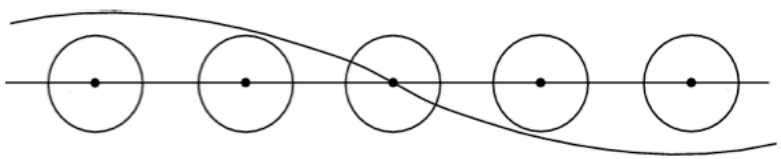


Figure 4.3: Plane wave.

Courtesy:
http://www.iue.tuwien.ac.at/phd/osintsev/disserch4.html

Atomic-like orbitals are extremely compact and allow a natural description of the variations of wavefunctions close to the atoms.

Plenewave basis are on the contrary not very good for describing strong variations of the density, but are more systematic and allow to sample the density far away from the atoms (e.g. diffuse orbitals, interstitial sites, etc.)

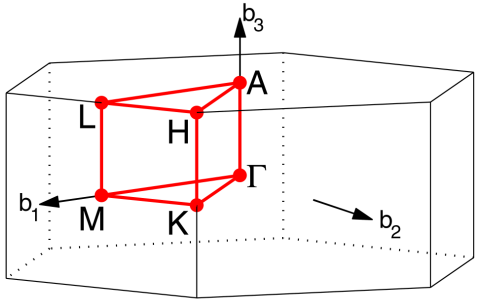
The full space group

Besides the translations, the crystal is invariant under various operations $\{g\}$ containing rotations, reflexions, inversion, etc. with respect to a point, an axis, or a plane, and combinations of such operations with translations: $(g|a)\vec{r} = g\star\vec{r} + \vec{\tau}$, with $\vec{\tau}$ not necessarily a lattice vector.

$$\psi_{\vec{k}}(g\star\vec{r} + \vec{\tau}) = e^{i\mathbf{k}\cdot(g\star\vec{r}+\vec{\tau})} u_{\mathbf{k}}(g\star\vec{r} + \vec{\tau}) = e^{ig^{-1}\mathbf{k}\cdot\vec{r}}\tilde{u}(\vec{r}), \quad \text{with} \quad \tilde{u}(\vec{r}) \text{ periodic.}$$

The eigenstates $\psi_{\vec{k}}(g\star\vec{r} + \vec{a})$ are also the eigenstates of $\hat{H}_{g^{-1}\mathbf{k}}$. In particular, the eigenvalues of $\hat{H}_{g^{-1}\mathbf{k}}$ and $\hat{H}_{\mathbf{k}}$ are the same.

The irreducible Brillouin zone defines the set of non-equivalent $\vec{k}$-points.



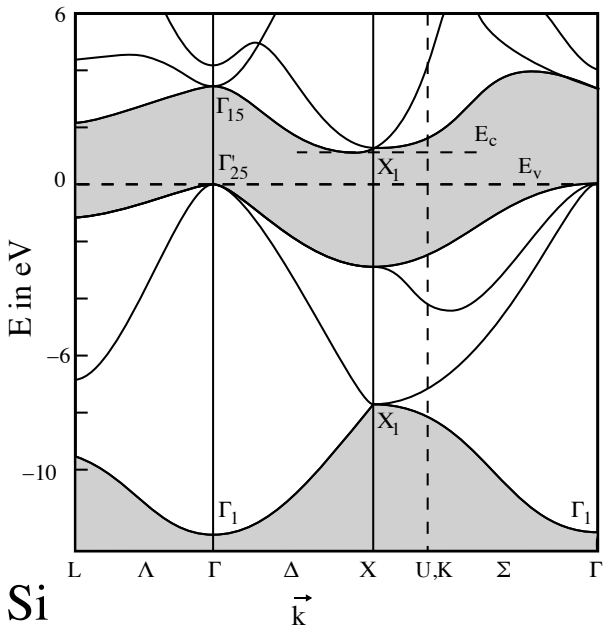
HEX path: Γ-M-K-Γ-A-L-H-A|L-M|K-H

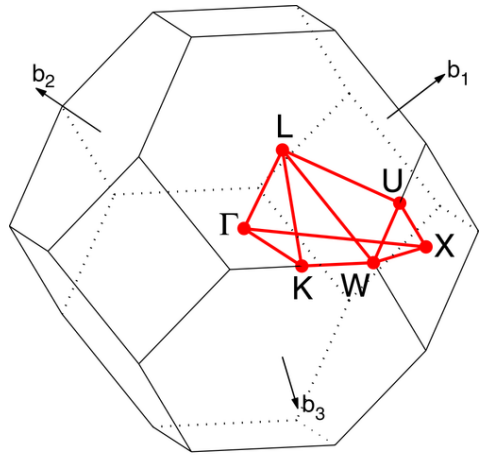
[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

Irreducible Brillouin zone (in red) for an hexagonal lattice. The irreducible BZ represents here 1/24 of the full Brillouin zone. Letters specify the name of the "high symmetry" $\vec{k}$-vector and directions. All other $\vec{k}$-vector in the BZ can be obtained by symmetry.

What is a band-structure ?

The plot of the $E_{n\vec{k}}$ eigenvalues of the Hamiltonian $\hat{H}_{\vec{k}}$ for $\vec{k}$-vectors moving along specific directions of the BZ represents the bandstructure.





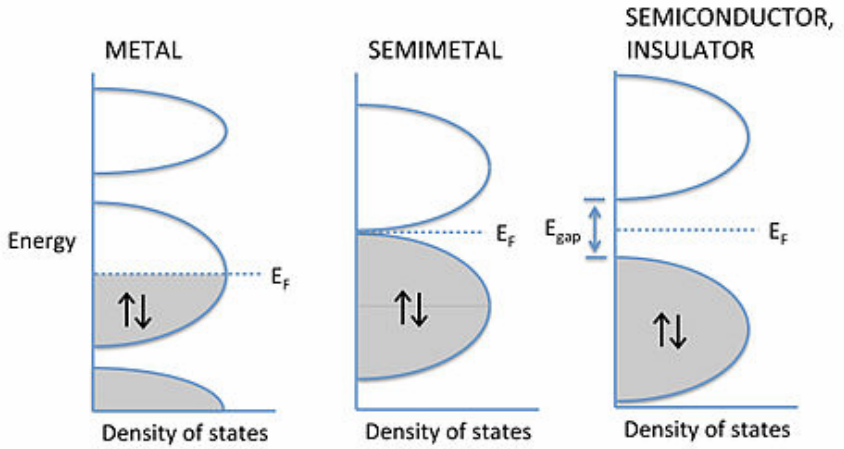
FCC path: Γ-X-W-K-Γ-L-U-W-L-K|U-X

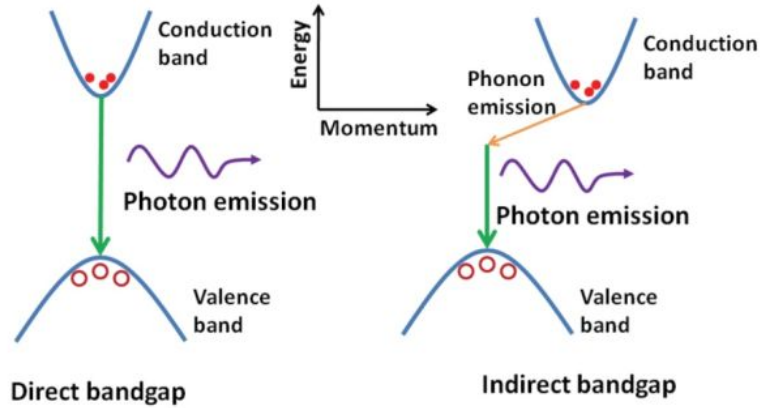
[Setyawan & Curtarolo, DOI: 10.1016/j.commatsci.2010.05.010]

Above: band structure of silicon (FCC lattice). The zero of energy has been set to the **top of the valence bands**. The shaded area above the (occupied) valence bands is **the gap**. Above the gap lie the **conduction bands** empty at 0 Kelvin. The shaded area below the valence bands is the gap in energy between the valence bands and the core levels.

Reading a band-structure

In a metal, there is no band gap: valence bands (VB) and conduction bands (CB) overlap. There is no need of energy for electrons to jump in empty energy levels.

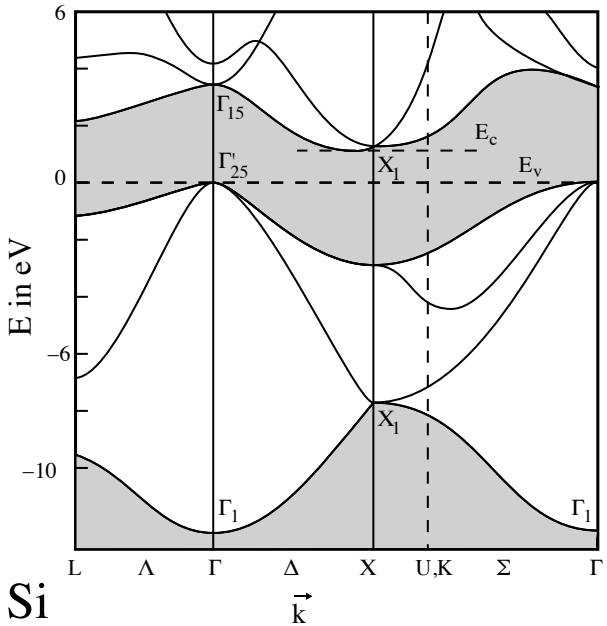




(From G.Sun (2010), N. Costa and A. Cartaxo (Ed.), ISBN: 978-953-307-088-9, DOI: 10.5772/8672).

In a **direct band gap**, the VB top and CB bottom are at the same $\vec{k}$-vector: a photon carrying close to zero momentum can promote an electron or be emitted by "hot" electron relaxation. In an **indirect band gap** semiconductor such as silicon, one need the momentum of a phonon to make transitions between the VB top and CB bottom.

The minimal band structure and the effective masse



Let's look at the band structure of Si and in particular the top of the valence bands at zone-center **Γ** and the bottom of the conduction bands along **ΓX**. Close to these minima/maxima, the bands are parabolic. In the vicinity of the extrema, we write the Bloch vectors as $(\mathbf{k}+\mathbf{q})$ where **k** is the Bloch vector at the band extremum and **q** is small. Then (with i,j=x,y,z):

$$\varepsilon_n(\mathbf{k}+\mathbf{q}) = \varepsilon_n(\mathbf{k}) + \frac{1}{2}\sum_{ij}\frac{\partial^2\varepsilon_n}{\partial k_i \partial k_j} q_i q_j + O(q^3)$$

For electrons or holes close to the bands maxima (remember than room temperature is 26 meV), then one can define an effective mass "tensor":

$$\frac{\hbar^2}{2m^*_{ij}} = \frac{1}{2}\frac{\partial^2\varepsilon_n}{\partial k_i \partial k_j}$$

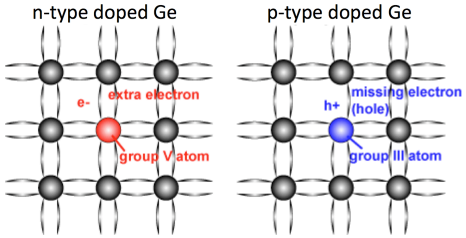
Usefulness of effective mass and interactions in crystal

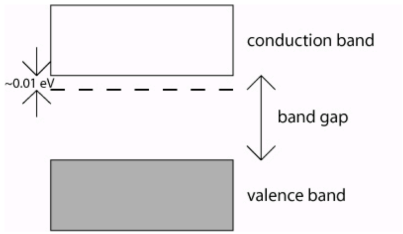
The effective mass tensor accounts for the effect of the interaction with the lattice and the other electrons that renormalize the electron mass: to lowest order, electrons and holes close to the band edges are free-electron with renormalized mass. Due to anisotropy, this is not as simple as the free-electron model, but one can keep in mind that an average effective mass in Si is roughly: $m^* \simeq 0.2 m_e$, where m_e is the "vacuum" mass of the electron.

Before exploring a few examples of the usefulness of such an effective mass, we will admit here - but that will be the subject of many discussions these two weeks - that another effect of the electron-electron interaction is to renormalize the long-range Coulomb interaction in semiconductors by an constant ϵ_M named the macroscopic dielectric constant. Namely:

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} \Rightarrow \frac{1}{\epsilon_M |\mathbf{r}-\mathbf{r}'|} \quad \text{beyond a (very) few nanometers.}$$

The hydrogenoid model of impurity





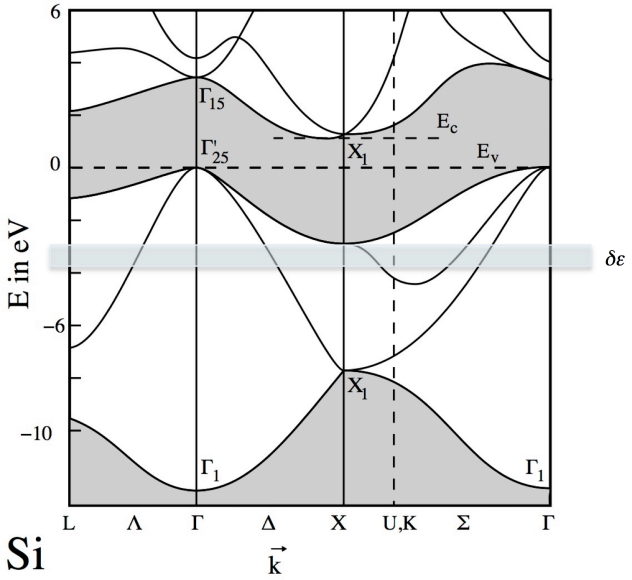
In e.g. n-type doped Ge by P, the crystal has an extra ionic charge ($Z_P = Z_{Ge} + 1$) and an extra electron that jumps into the conduction bands at room temperature. It is an effective hydrogenoid problem.

$$Rydb = \frac{e^4 m_e}{2\hbar^2} \Rightarrow E_{binding} = Rydb \left(\frac{1}{\epsilon_M^2}\right)\left(\frac{m^*}{m_e}\right) \simeq 9 \text{ meV}$$

$$bohr = \frac{\hbar^2}{m_e e^2} \Rightarrow a^* = (\epsilon_M)\left(\frac{m^*}{m_e}\right) bohr \simeq 80 \text{ bohrs.}$$

The experimental binding energy value for P:Ge is: $E_{binding} = 12$ meV, in nice agreement with the estimated value. The small binding energy and the large effective bohr radius justify the approximations used.

The density of states



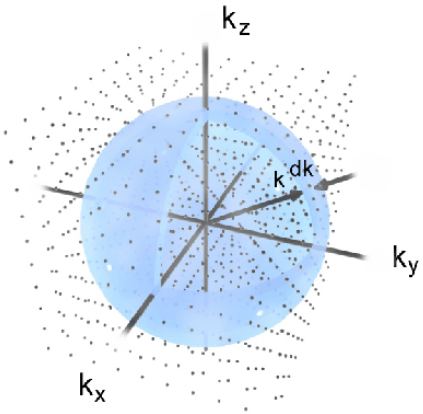
The density of states $g(\varepsilon)d\varepsilon$ counts the number of Bloch states with energy within $[\varepsilon, \varepsilon + d\varepsilon]$ and per unit volume. It is a crucial quantity since it tells you how many states are available at a given energy to absorb a photon, conduct electricity or heat (assuming that by doping or other means you can put your Fermi level at this energy).

The density of states requires a summation over the entire Brillouin zone (BZ), namely:

$$g(\varepsilon) = \frac{1}{\Omega} \int_{BZ} \frac{d\mathbf{k}}{\Delta\mathbf{k}} \sum_n \delta(\varepsilon - \varepsilon_{n\mathbf{k}}), \quad \text{with} \quad \Delta\mathbf{k} = \frac{\Omega_{BZ}}{N} = \frac{8\pi^3}{N\Omega_{cell}} = \frac{8\pi^3}{\Omega},$$

where $\Delta\mathbf{k}$ is the elementary volume in reciprocal space allowing for one Bloch state (2 if adding spin variable).

Parabolic bands density of states (0D,1D,2D,3D)

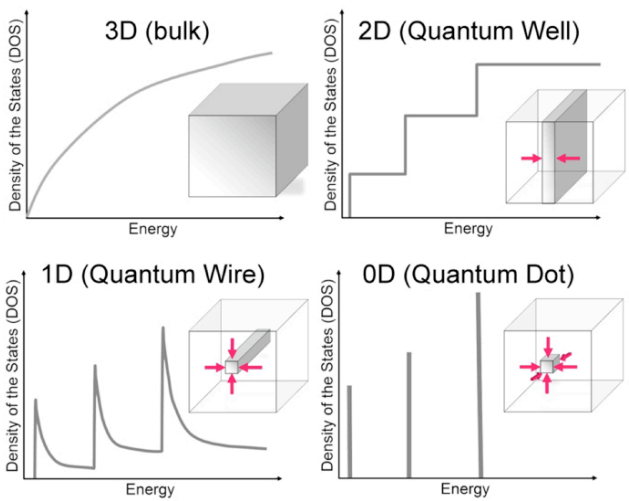


In the case of parabolic bands, it is a standard exercise to count the number of allowed Bloch vectors up to an energy E and its corresponding k-vector amplitude such that $E = \hbar^2 k^2 / 2m_e$:

$$N(E) = 2_{spin} \frac{(4\pi k^3/3)}{(8\pi^3/\Omega)} \Rightarrow \frac{N}{\Omega} \propto E^{3/2}$$

so that $g(\varepsilon) = \frac{1}{\Omega} dN(E)/dE \propto \sqrt{E}$.

(Exercise: the kinetic energy per volume scales as $\rho^{5/3}$, ρ the density.)

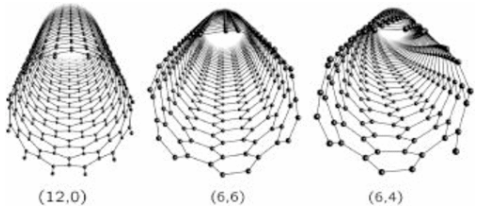


It is also standard to redo the exercise at various space dimension to show that:

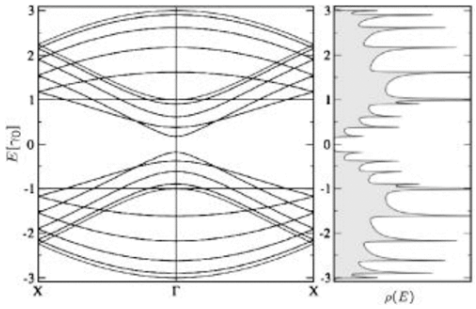
- $g_{2D}(\varepsilon) \propto constante$,
- $g_{1D}(\varepsilon) \propto 1/\sqrt{\varepsilon}$,
- $g_{0D}(\varepsilon) \propto \sum_n \delta(\varepsilon - \varepsilon_n)$.

Figure courtesy Lorenzo Mino et al 2013 J. Phys. D: Appl. Phys. 46 423001

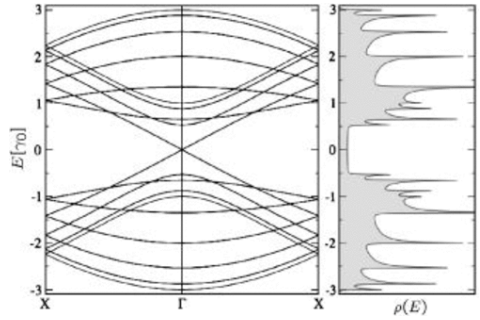
A well-known example: the nanotubes



Nanotubes have allowed exploring in much better details physics at "1D" (together with nanowires, etc.)



Band structure (DFT/LDA)and electronic density of states (eDos) of a semiconducting (10,0) nanotube. At the onset of parabolic bands, the eDos varies clearly as $1/\sqrt{\epsilon}$.



Band structure and eDos of a metallic (9,9) nanotube. At the Fermi level, the dispersion is linear, not parabolic: the eDos is constant around E_F.

Courtesy Charlier et al. Rev. Mod. Phys. 2007

Formation of bands and band gaps

The quasi-continuum of $\{\varepsilon_{n\mathbf{k}}\}$ energies produces a manifold a states. But how can we interpret the formation of bands and band gaps ? Why is graphene semi-metallic and diamond insulating ? Why is hexagonal boron-nitride insulating ? Why does the band gap close from diamond to silicon, both crystallizing in the same FCC structure ?

Bands from the free-electron gas model

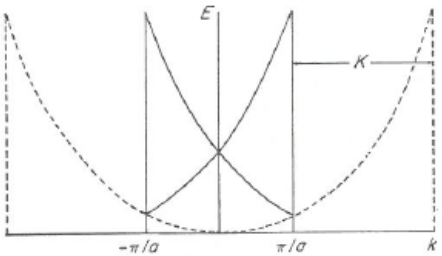


FIGURE 1.11. Free-electron $E(\mathbf{k})$ relation. Dashed curve outside $|\mathbf{k}| = \pi/a$ represents extended zone scheme. Solid curves give energy in reduced zone scheme. $K = 2\pi/a$ is primitive translation of one-dimensional reciprocal lattice.

It is instructing to start from the 1D free-electron model in a box of length L ($L \to +\infty$) of which the eigenstates are $\psi(k) = e^{ikr}/\sqrt{L}$ and the energies are $\varepsilon(k) = \hbar^2 k^2/2m$.

(Figure from Jones and March, Theoretical Solid State Physics, p. 41, Dover Eds.)

We can always say that the free-electron gas is invariant by a translation $T(a)$ and define a reciprocal-space with a Brillouin zone: $|k| \leq \pi/a$ and reciprocal-lattice vectors G $= n(2\pi/a)$.

Scheme: take a **k**-vector in the BZ and get the energy of all $e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$ eigenvectors of $\hat{H}_{\mathbf{k}}$ (u periodic) $\Rightarrow$ these are the $e^{i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{G}\cdot\mathbf{r}}$ states !!

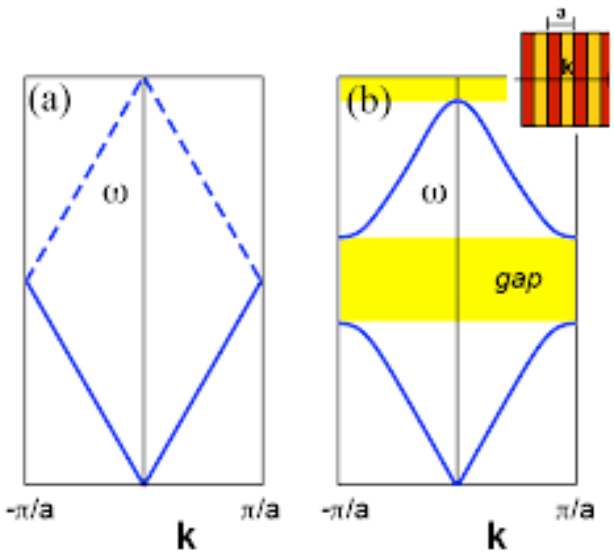
For a given (**k**) in the BZ, plot all the $\hbar^2|\mathbf{k}+\mathbf{G}|^2/2m$ energy levels.

In the Bloch states band-structure picture, all free-electron states are "folded back" into the BZ.

Bands from the free-electron gas model (II)

We can now switch the periodic potential V yielding:

$$\frac{\hbar^2}{2m}(k+G)^2 c_n(k+G)\delta_{G,G'} + \sum_{G'} c_n(k+G-G')V(G') = E_{nk}c_{nk}(G).$$



Close to the $(k = \pi/a)$ zone-boundary, the e^{ikr} and $e^{i(k+G)r}$ (with $G = -2\pi/a$) states - degenerate in energy without V - mix strongly through $U = V(2\pi/a) \Rightarrow$ solve:

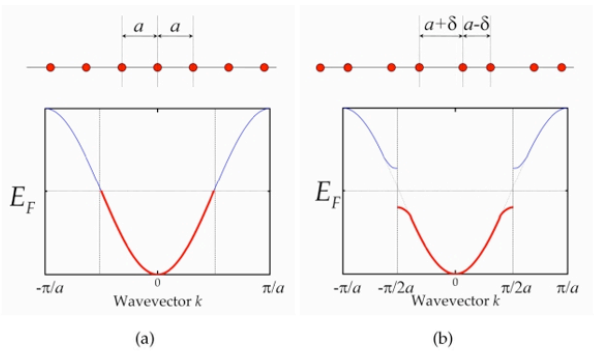
$$\left(\frac{\hbar^2}{2m}k^2 - \varepsilon\right)c(k) + Uc(k+G) = 0$$
$$\left(\frac{\hbar^2}{2m}(k+G)^2 - \varepsilon\right)c(k+G) + Uc(k) = 0$$

yielding to lowest order (see Kittel, chapter 7):

$$\varepsilon(\frac{\pi}{a} + \delta k) = \varepsilon_0 + \frac{\hbar^2\delta\mathbf{k}^2}{2m} \pm U\left[1 + 2\left(\frac{\varepsilon_0}{U^2}\right)\frac{\hbar^2\delta\mathbf{k}^2}{2m}\right], \text{ with } \varepsilon_0 = \frac{\hbar^2\delta\mathbf{k}^2}{2m}(\frac{\pi}{a})^2.$$

Complement: the Peierls distorsion

The above discussion can be applied to understand the Peierls distorsion, which can be viewed as a solid-state physics version of the molecular Jahn-Teller effect. Assume a simple 1D band model at half-filling with the Fermi wavevetor at halfway the zone-boundary ($k_F = \pi/2a$).



A dimerisation of the lattice will double the unit-cell size (a⇒2a) divide by 2 the BZ ($2\pi/a \Rightarrow 2\pi/2a$), introducing Fourier components of the potential V at $G = \pi/a$ that can couple the two states at $\pm k_F$.

The crucial argument now is that the penalty in elastic energy is quadratic in the (δa) distortion, while the electronic energy gain is linear with U (see previous slide), that is with the distortion strength ⇒ the distortion always win at small (δa).

From the atomic limit to the solid

Rather than starting from the free-electron gas model, it is very intuitive to start from the atomic limit in the standard picture of the atomic-orbitals interaction and the formation of bonding-antibonding states, generalizing this approach to a large number of atoms in interaction. In many important cases, its is however difficult to recognize the solid limit from the atomic limit !!

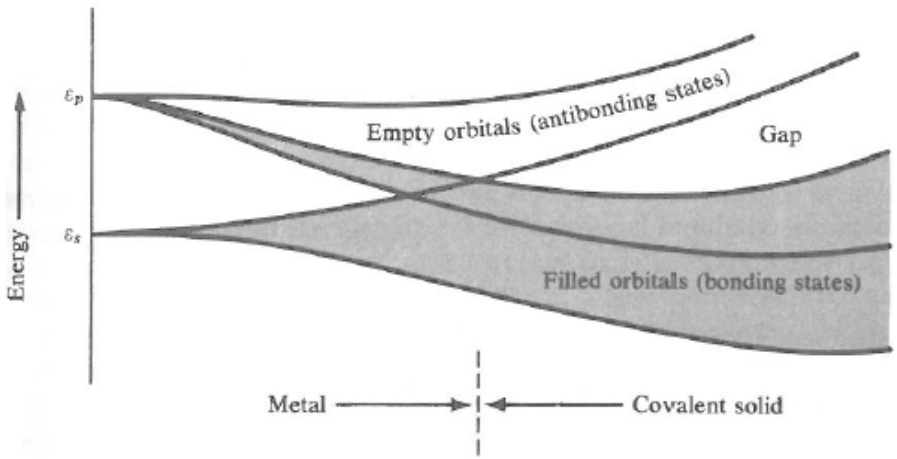


FIGURE 2-3
The formation of bands in a homopolar tetrahedral semiconductor as the atoms are brought together. Internuclear distance decreases to the right.

Figure: evolution of the energy bands from the atomic limit to the solid as a function of (decreasing) interatomic distance. (From: "Electronic structure and the properties of solids", Walter A. Harrison, Dover Ed.)

In the solid limit for silicon, one starts from well defined (2s) and (2p) atomic states, to intertwined hybridized sp_3 bands.

The tight binding (or extended Hückel) formalism

Assume atomic orbitals $\phi_m(\vec{r})$ per site, typically eigenstates of the isolated atom Hamiltonian. "m" here can represent (nlm) indexes.

One can form crystal extended Bloch basis states as a linear combination of atomic orbitals (LCAO): $\psi_m(\vec{r}) = \sum_{\vec{R}_n} a_m(\vec{R}_n)\phi_m(\vec{r} - \vec{R}_n)$.

For $\psi(\vec{r})$ to satisfy the Bloch theorem: $\psi(\vec{r} + \vec{R}_l) = e^{i\vec{k}\cdot\vec{R}_l}\psi(\vec{r})$, one finds that: $a_m(\vec{R}_n) = e^{i\vec{k}\cdot\vec{R}_n} a_m(\vec{R}_0 = \vec{0})$.

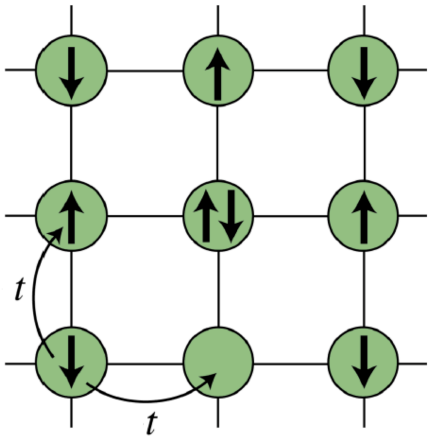
By normalization, assuming that: $\langle\phi_m(\vec{r} - \vec{R}_n)|\phi_m(\vec{r} - \vec{R}_l)\rangle = \delta_{nl}$, that is we assume localized orbitals, then: $a_m(\vec{R}_0) \simeq 1/\sqrt{N}$ and:

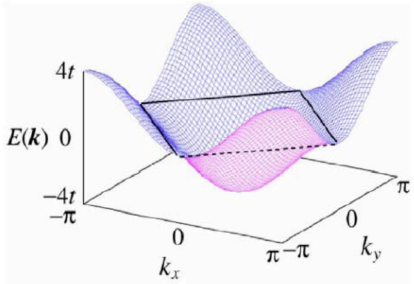
$$\psi_{m\vec{k}}(\vec{r}) \simeq \frac{1}{\sqrt{N}} \sum_{\vec{R}_n} e^{i\vec{k}\cdot\vec{R}_n}\phi_m(\vec{r} - \vec{R}_n).$$

Such a basis Bloch state can be e.g. an *s*-orbital repeated periodically with a $e^{i\vec{k}\cdot\vec{R}_n}$ phase factor. The phase factor is the standard $e^{i\vec{k}\cdot\vec{r}}$ Bloch phase taken to be zero only at atomic sites.

The 2D square lattice

Assume one orbital $\phi(\vec{r})$ per site and interatomic distance (a):





Onsite energy set to zero:

$$E_0 = \langle \phi(\vec{r}) | \hat{H} | \phi(\vec{r}) \rangle = 0,$$

First-nearest neighbor hopping energy:

$$t = -\langle \phi(\vec{r}) | \hat{H} | \phi(\vec{r} + \vec{a}_{1/2}) \rangle.$$

Then the tight-binding approach can be set up as follows:

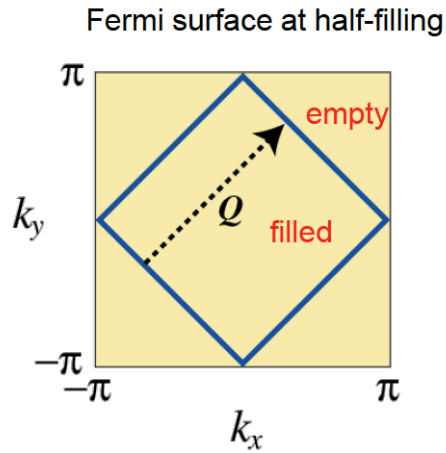
$$E(k_x, k_y) = \langle \psi_{\vec{k}}(\vec{r}) | \hat{H} | \psi_{\vec{k}}(\vec{r}) \rangle \quad \text{with} \quad \psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{n,m} e^{i\vec{k}\cdot\vec{R}_{nm}} \phi(\vec{r} - \vec{R}_{nm})$$

where $\vec{R}_{nm} = n\vec{a}_1 + m\vec{a}_2$, and yields the following band structure:

$$E(k_x, k_y) = -t \left(e^{\pm i k_x a} + e^{\pm i k_y a} \right) = -2t \left[cos(k_x a) + cos(k_y a) \right].$$

Square lattice at half filling: Fermi surface nesting

Assume one electron per site, namely a situation of half-filling where only half of the band is occupied. Then the Fermi surface is a square ! The Fermi surface is said to be nested: specific wavevectors $\mathbf{Q}$ can connect large portions of the Fermi surface.

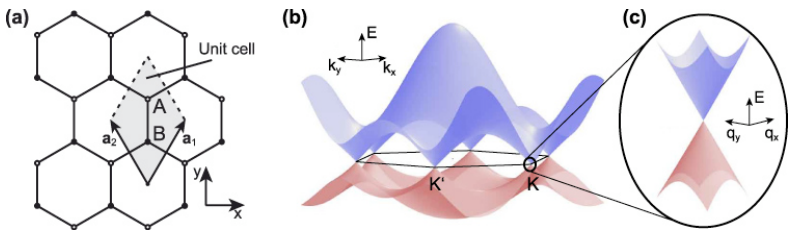


This may lead to instabilities of the Fermi surface. Assume a perturbation $\delta V_{\mathbf{Q}}$ (phonon, magnon, etc.) with wavector $\mathbf{Q}$. Then a very large number and initial and final states are available for scattering, inducing a huge response of the system to the perturbation.

Such a model is a minimal model for the cuprate (CuO) planes close to the Fermi level with strong Cu ($d_{x^2-y^2}$) character.

The graphene

Close to E_F the graphene band structure is dominated by p_z orbitals. With two atoms per cell at positions τ_A and τ_B in the unit-cell one can build two basis Bloch states per $\mathbf{k}$: $\psi_{\mathbf{k}}^{A/B} = \sum_n \phi_z(\mathbf{r} - \tau_{A/B} - \mathbf{R}_n) e^{i\mathbf{k}\cdot\mathbf{R}_n}$.



Courtesy J Gttinger et al 2012 Rep. Prog. Phys. 75 126502

We define:

- $\langle \phi_z(\mathbf{r} - \tau_{A/B}) | \hat{H} | \phi_z(\mathbf{r} - \tau_{A/B}) \rangle = 0$ (energy reference)
- $\langle \phi_z(\mathbf{r} - \tau_A) | \hat{H} | \phi_z(\mathbf{r} - \tau_B) \rangle = \gamma$

One then diagonalize the 2x2 Hamiltonian with the $\langle \psi_{\mathbf{k}}^{A/B} | \hat{H} | \psi_{\mathbf{k}}^{A/B} \rangle$ matrix elements, keeping only first-nearest-neigbour interactions, yielding:

$$E^{\pm}(\mathbf{k}) = \pm\gamma |\alpha(\mathbf{k})|^2, \quad \alpha(\mathbf{k}) = 1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2}$$

which cancels at the ($\mathbf{k} = \mathbf{K}$) BZ corners.

(see The band theory of graphite, P. R. Wallace Phys. Rev. 71, 622, 1947).

The ionicity gap of hexagonal BN

Hexagonal BN cristallized as graphene, but atom "A" and "B" are different : one is boron, the other nitrogen. We follow the very same treatment than graphene, but the onsite energies must be different for boron and nitrogen: $\langle \phi_z(\mathbf{r} - \tau_{A/B}) | \hat{H} | \phi_z(\mathbf{r} - \tau_{A/B}) \rangle = \Delta/2$ for boron and -$\Delta/2$ for nitrogen which is more electronegative.

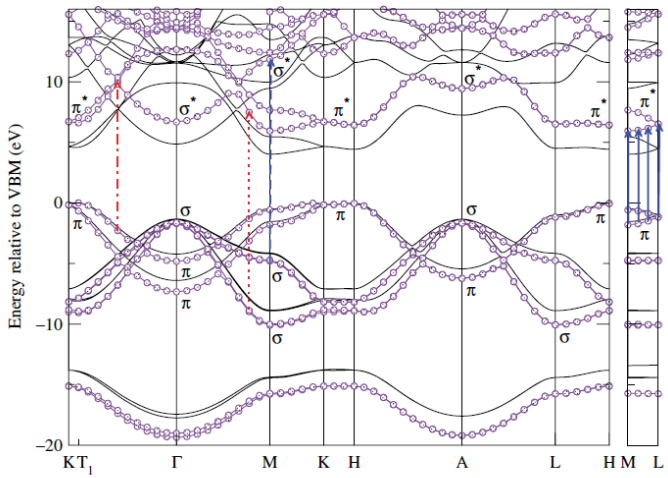


Figure 14. Quasiparticle band structure for bulk h-BN (Reprinted figure with permission from Arnaud *et al.*, Physics Review Letters, 96, 026402, 2006 [197]. Copyright © (2006) by the American Chemical Society.). The solid lines are the result of DFT-LDA calculations. Open (violet) circles represent the GW calculations. The two band structures have been aligned at the valence bands maximum (T_1 point near K along the Γ–K direction). The vertical arrows indicate optical transitions contributing to the main optical absorption spectrum features.

Courtesy Arenal et al, Adv. Phys. 2010

Then solving again the 2x2 Hamiltonian problem, one finds:

$$E^{\pm}(\mathbf{k}) = \pm\sqrt{\Delta^2/4\gamma^2 + |\alpha(\mathbf{k})|^2}$$

Even when $\alpha(\mathbf{k})$ cancels due to the hexagonal geometry, as in graphene, the difference of ionicity Δ leaves the gap opened.

Complement: insulator-to-metal transition by doping

A nice illustration of the formation of a band is given by the physics of "degenerate" semiconductors which are semiconductors, or insulators, than turned metallic due to high doping: upon increasing dopant concentration, the impurity states start overlapping and form a band which becomes larger and larger. When the impurity band overlap with the valence of conduction bands, the system becomes metallic !

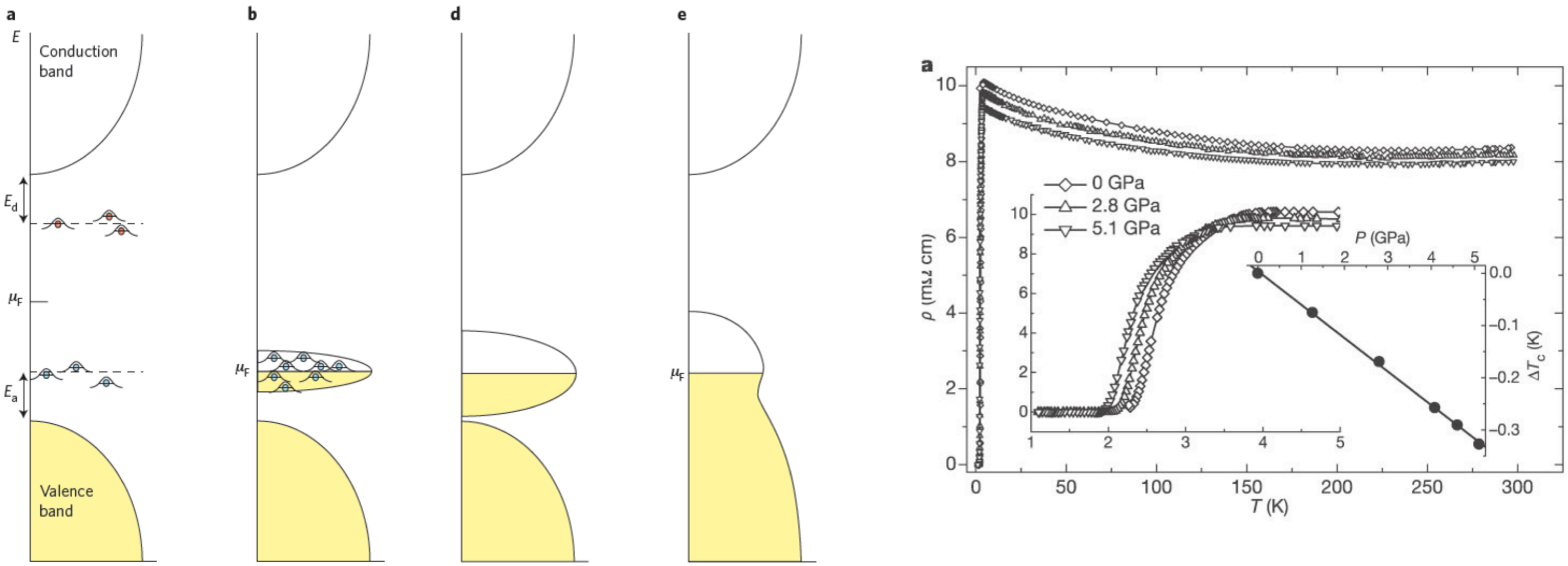


Figure. (Left) Insulator to metal transition by doping (Blase et al., Nature Mater. 8, 375, 2009) (Right) Superconducting transition in B-doped diamond (Ekimov et al., Nature 428, 542-545, 2004).

Vibrational modes in solids: phonons

Another important use of periodicity concerns the vibrational modes in crystals: the phonons. The theory starts from the Taylor expansion of the total energy around the atomic equilibrium positions:

$$E(\{\mathbf{R}_I\}) = E(\left\{\mathbf{R}_I^0\right\}) + \frac{1}{2}\sum_{I\alpha,J\beta}\left(\frac{\partial^2 E}{\partial u_{I\alpha}\partial u_{J\beta}}\right)_{u=0} u_{I\alpha}u_{J\beta} + O(u^3)$$

where e.g. $(u_{I\alpha})$ is the displacement along the direction $(\alpha = x, y, z)$ around its equilibrium direction of atom (I) in the crystal. Using Newton's equation with classical ions of mass M_I, namely: $\boxed{M_I d^2 u_{I\alpha}/dt^2 = -\partial E/\partial u_{I\alpha}}$, the search for harmonic solutions: $u_I(t) = v_I exp(i\omega t)/\sqrt{M_I}$ yields:

$$\omega^2 v_{I\alpha} = \sum_{J\beta} D_{I\alpha,J\beta} v_{J\beta} \quad \text{with:} \quad D_{I\alpha,J\beta} = \frac{1}{\sqrt{M_I M_J}}\left(\frac{\partial^2 E}{\partial u_{I\alpha}\partial u_{J\beta}}\right)$$

$\left(\partial^2 E/\partial u_{I\alpha}\partial u_{J\beta}\right)$ is the force constant matrix, namely "the spring constant" between the two atoms (I) and (J), and $D_{I\alpha,J\beta}$ is the dynamical matrix.

The frozen phonon approach

In a molecule, the dynamical matrix ($D_{I\alpha,J\beta}$) can be calculated by finite differences displacing explicitely all atoms by a small distance $\pm\delta u$ (say 0.1 bohr) in each direction of space. This comes at the price of $6N_{at}$ total energy calculations, where N_{at} is the number of atoms.

In a solid, $N_{at} \to +\infty$! The textbook approach is to look for solutions that are planewave like, or propagating waves, namely: $\mathbf{u}(\mathbf{R},t) = \vec{\epsilon} \times e^{i(\mathbf{q}\cdot\mathbf{R}-\omega t)}$ with $\mathbf{u}(\mathbf{R},t)$ the displacement of atom $\mathbf{R}$ at time (t). $\vec{\epsilon}$ is the polarization vector. The reason for that really is that the dynamical matrix depends only on the distance $(\mathbf{R}_I - \mathbf{R}_J)$ thanks to periodicity:

$$\omega^2 v_\alpha(\mathbf{R}) = \sum_{\mathbf{R}'} \sum_{\beta} D_{\alpha,\beta}(\mathbf{R}-\mathbf{R}') v_\beta(\mathbf{R})$$

where the right-hand-side is a convolution product that yields a direct product by Fourier transform:

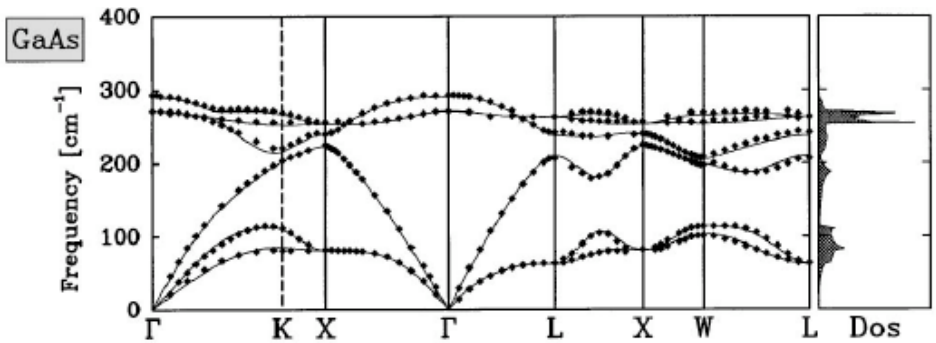
$$\omega^2 v_\alpha(\mathbf{q}) = \sum_{\beta} D_{\alpha,\beta}(\mathbf{q}) v_\beta(\mathbf{q}), \qquad D_{\alpha,\beta}(\mathbf{q}) = \sum_{\mathbf{R}} D_{\alpha,\beta}(\mathbf{R}) e^{-i\mathbf{q}\cdot\mathbf{R}}$$

Phonon band structures: acoustic and optical modes

Phonon modes with different **q**-vectors "cannot mix" (in the harmonic approximation) and only **q**-vector in the Brillouin zone should be considered, since again:

$$\mathbf{u}_{\mathbf{q}+\mathbf{G}}(\mathbf{R},t) = \vec{\epsilon} \times e^{i((\mathbf{q}+\mathbf{G})\cdot\mathbf{R}-\omega t)} = \vec{\epsilon} \times e^{i(\mathbf{q}\cdot\mathbf{R}-\omega t)} = \mathbf{u}_{\mathbf{q}}(\mathbf{R},t)$$

Periodicity has allowed to block-diagonalize the dynamical matrix allowing the efficient calculation of vibrational modes in solids.



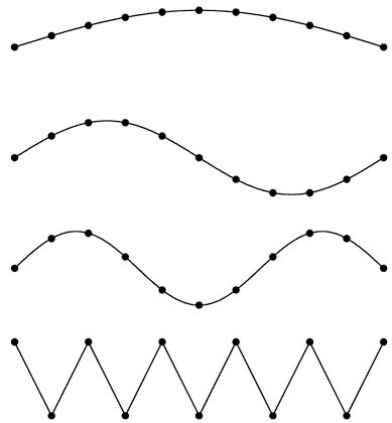
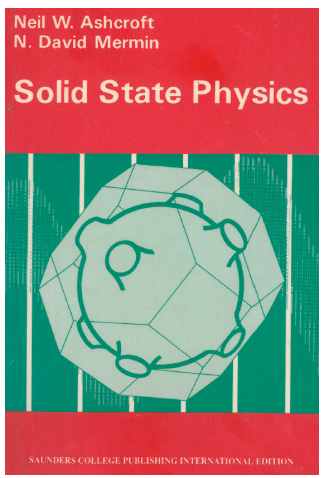


Figure (Left). DFT and experimental (dots) phonon band structure for GaAs (Baroni et al. Rev. Mod. Phys. 2001). There are N_{at}^{cell}=2 atoms/cell and thus 6 modes per **q**-point. (Right) Schematic representation of phonons with various wavevectors.

Complement: The Fermi surface

The Fermi surface is the energy surface in the Brillouin zone such that $\varepsilon_{n\mathbf{k}} = E_F$, where E_F is the Fermi level. At zero Kelvin, all states at lower energy are occupied, all states above are empty.



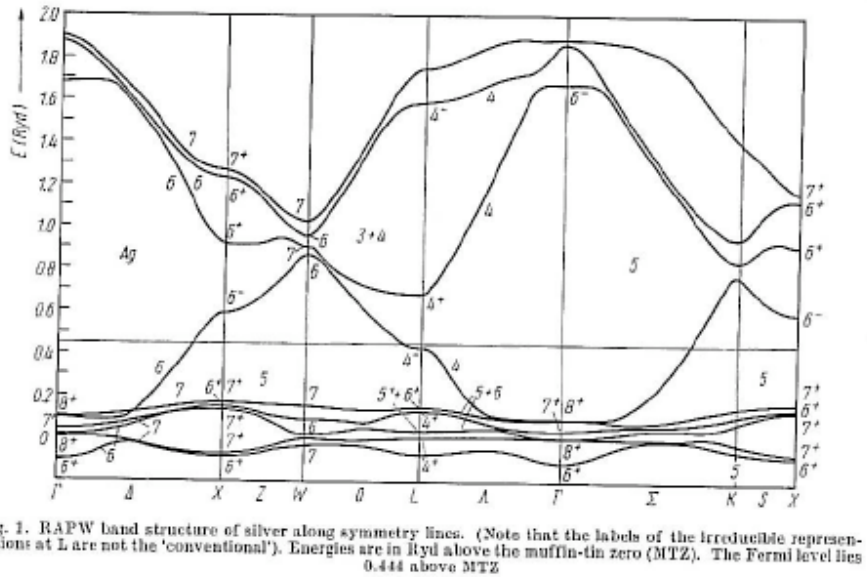
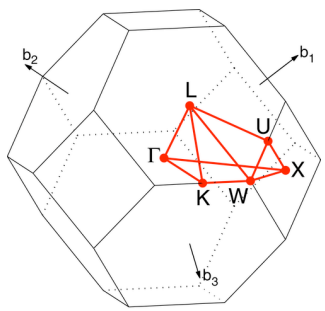


Fig. 1. RAPW band structure of silver along symmetry lines. (Note that the labels of the irreducible representations at L are not the 'conventional'). Energies are in Ryd above the muffin-tin zero (MTZ). The Fermi level lies 0.444 above MTZ

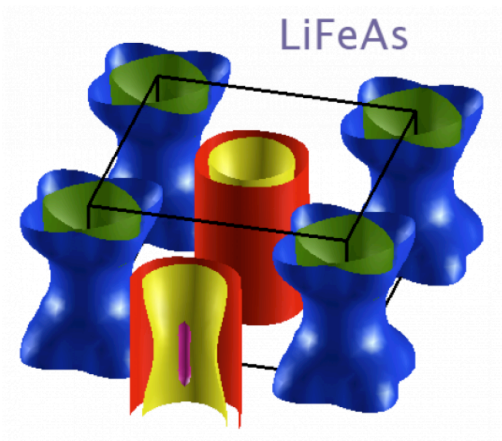


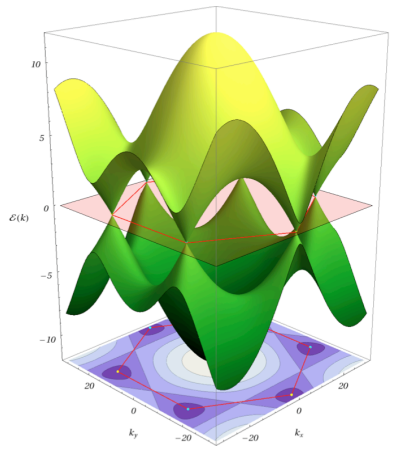
FCC Brillouin zone.

Figure (Left) The cover of Ashcroft and Mermin, Solid State Physics, Saunders College Publishing, showing the Fermi surface of silver. (Right) An historical band structure of silver using relativistic augmented planewave method (N.E. Christensen, TU Denmark, Phys. Stat. sol. (b) **54**, 651 (1972).

The Fermi surface

The Fermi surface characterizes the charge carriers at room temperature ($k_B T$=25 meV), in connection with the electronic and thermal conduction properties. Any perturbation bringing little energy to the system, as compared to electronic band dispersions (namely a few eV), such as phonons or magnons, will scatter electron from one-point of the Fermi surface to another.





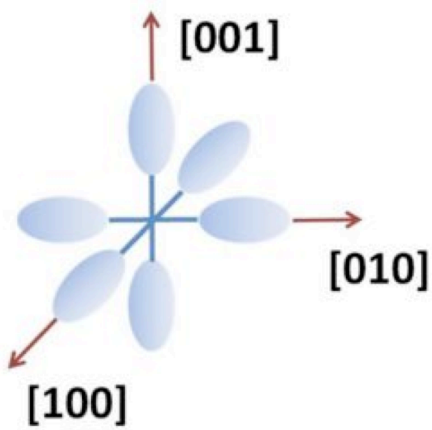


Figure (Left) LiFeAs Fermi "multiple" surface: several bands cross the Fermi level. (Centre and left) Do you recognize the materials with such Fermi surfaces ?

Complement: Impulsion operators as generators of translations

Start with a 1D infinitesimal translation by a distance (da):

$$\hat{T}_{da}\psi(x) = \psi(x - da) = \psi(x) - da\frac{d\psi}{dx} = \left(\hat{I} - \frac{i}{\hbar}da\frac{\hbar}{i}\frac{d}{dx}\right)\psi(x)$$

so that: $\hat{T}_{da} = \hat{I} - \frac{i}{\hbar}(da)\hat{p}_x$. This leads to a general relation:

$$\boxed{\hat{T}_{\vec{a}} = \exp\left(-\frac{i}{\hbar}\hat{\vec{p}}\cdot\vec{a}\right).}$$

If a system is invariant by infinitesimal translations, then the Hamiltonian commutes with $\hat{T}_{da}$, that is with the impulsion operator. By Ehrenfest, the impulsion is conserved.

$$\frac{d\langle\hat{p}_x\rangle}{dt} = \langle\frac{\partial\hat{p}_x}{\partial t}\rangle + \frac{1}{i\hbar}\langle\left[\hat{p}_x, \hat{H}\right]\rangle = 0 + 0$$