An introduction to solid-state physics

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

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Bibliography

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- Quantum Theory of Solids, Charles Kittel, John Wiley and Sons.

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.

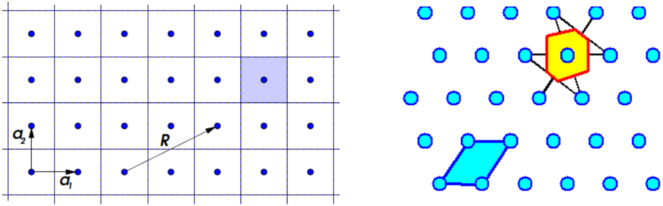
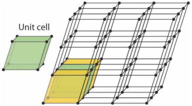


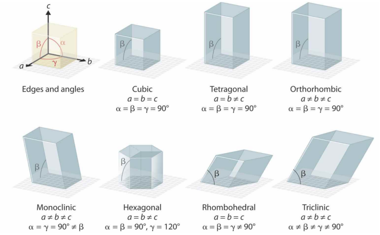
Figure: (Left) 2D square lattice with one atom per cell. A unit-cell is shaded in blue. (Right) 2D hexagonal cell with one atom per cell. Two different unit cells are represented. For the blue cell, 1/4th of each connected atom belong to this cell. The yellow one is called the Wigner-Seitz cell that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

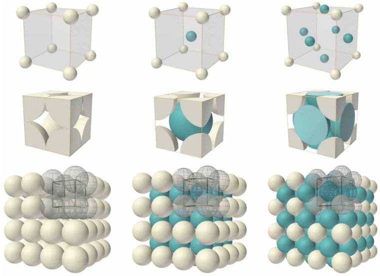
The 3D Bravais lattices and the motif



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.





(a) Simple cubic **(b) Body-centered cubic** **(c) Face-centered cubic**

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:

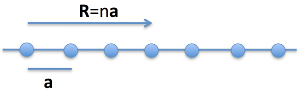
$$
\begin{aligned}
H|\psi_{nlm}>= E_{nlm}|\psi_{nlm}> \\
L^2|\psi_{nlm}>= l(l+1)\hbar|\psi_{nlm}> \\
L_z|\psi_{nlm}>= m\hbar|\psi_{nlm}>
\end{aligned}
$$

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:

$$T_R V(x)\psi(x) = V(x-R)\psi(x-R) = V(x)T_R\psi(x)$$

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.

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

Common eigenvectors to H and T_R are called Bloch states. (Felix Bloch: Swiss-American Nobel prize for NMR.)

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

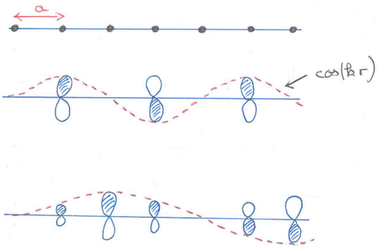
$$T_{\vec{R}}u_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot(\vec{r}-\vec{R})}\psi_{\vec{k}}(\vec{r}-\vec{R}) = e^{-i\vec{k}\cdot(\vec{r}-\vec{R})}e^{-i\vec{k}\cdot\vec{R}}\psi_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}}\psi_{\vec{k}}(\vec{r}).$$

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 ($k = \pi/4a$).

Setting up $H(\vec{k})$ for the periodic u_k

We start from Bloch theorem: $\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} u_{n\vec{k}}(\vec{r})$ plugged in:

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

to obtain straighforwardly for $u_{n\vec{k}}(\vec{r})$ the periodic part:

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

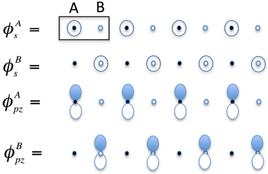
This is a $\vec{k}$-specific Hamiltonian: one has to set-up and diagonalize a different Hamiltonian for each $\vec{k}$ quantum number (a vector). We have added the "n" index to point to all possible solutions for a given $\vec{k}$.

Compare to hydrogen case with a specific radial equation for each l-quantum number, with the $l(l+1)\hbar^2/2mr^2$ centrifugal term coming from the kinetic operator in spherical coordinates.

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

LCAO basis: Take an AO basis $\alpha_\mu(\vec{r})$ for the atoms in unit cell and then create a basis $\{u_\mu\}$ of periodic functions to expand the $u_{n\vec{k}}(\vec{r})$ with:

$$u_\mu(\vec{r}) = \sum_{\vec{R}} \alpha_\mu(\vec{r} - \vec{R})$$

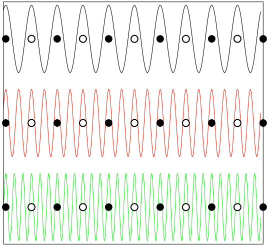


The number of AO per unit cell gives the number of $u_{n\vec{k}}(\vec{r})$ for a given $\vec{k}$.

PW basis: the planewave (PW) representation uses the Fourier series expansion of $u_{n\vec{k}}(\vec{r})$ over the $e^{i\vec{G}\vec{r}}$ planewaves

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}(\vec{G}) e^{i\vec{G}\vec{r}}$$

The $\vec{G}$ are such that the $e^{i\vec{G}\vec{r}}$ are periodic: they are called reciprocal lattice vectors.



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 !".

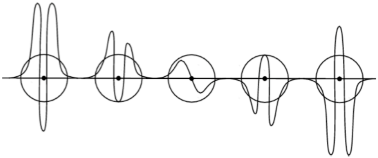


Figure 4.2: Atomic wave.

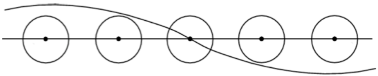


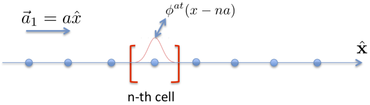
Figure 4.3: Plane wave.

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 1D-chain of atoms with one atomic orbital per atom



Assume N identical atoms with interatomic distance "a" forming a 1D chain. Assume one $\phi^{at}(x-na)$ atomic orbital per atom in position (na).

Wavefunctions built as linear combination of atomic orbitals (LCAO):

$$\psi(x) = \sum_{n=1}^{N} c_n \phi^{at}(x-na) \quad \Longrightarrow \quad N \simeq 10^{23} \text{ unknown}\{c_n\} \text{ coefficients}$$

Use Bloch theorem: $\psi_{\tilde{n}k}(x) = e^{ikx} u_{\tilde{n}k}(x)$ with $u_{\tilde{n}k}$ periodic

The only periodic LCAO is obtained for c_n all equals (basically $c_n = 1/\sqrt{N}$ by normalization). The only possible wavefunctions are:

$$u(x) = \sum_{n=1}^{N} \frac{1}{\sqrt{N}} \phi^{at}(x-na) \quad \text{and} \quad \psi_k(x) = \sum_{n=1}^{N} \frac{e^{ikx}}{\sqrt{N}} \phi^{at}(x-na)$$

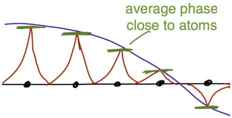
We removed the $\tilde{n}$-index since one state per k with one AO per cell.

The 1D-chain energy levels in the tight-binding limit

Assume localized atomic orbitals $=> e^{ikx}\phi^{at}(x-na) \simeq e^{ikna}\phi^{at}(x-na)$. Then the energy of ψ_k is just:

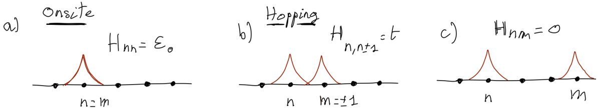
$$\varepsilon_k = \langle\psi_k|\hat{H}|\psi_k\rangle = \frac{1}{N}\sum_{n,m}^{N} e^{ik(m-n)a} H_{nm}$$

$$H_{nm} = \langle\phi^{at}(x-na)|\hat{H}|\phi^{at}(x-ma)\rangle$$



H_{nm} = Hamiltonian matrix elements in the AO basis. In the tight-binding limit (AO localized)

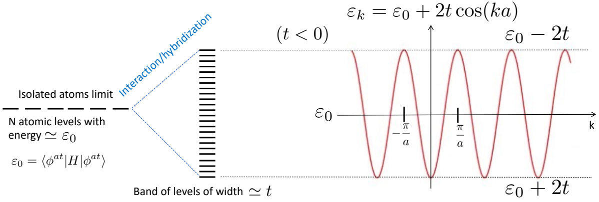
- $(m=n)$ $H_{nm}=\varepsilon_0$ on-site energy
- $(m=n\pm1)$ $H_{nm}=t$ hopping energy
- $|m-n|>1$ $H_{nm}=0$ (tight-binding limit)



The 1D-chain energy levels in the tight-binding limit (II)

In the tight-binding limit, one obtains straighforwardly:

$$\varepsilon_k = \langle \psi_k | \hat{H} | \psi_k \rangle = \frac{1}{N} N(\varepsilon_0 + te^{ika} + te^{-ika}) = \varepsilon_0 + 2t\cos(ka)$$

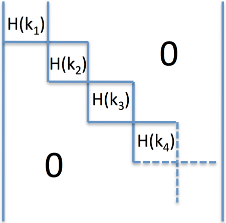


Question 1: for N-atoms with one atomic orbital per atom, one should get N energy levels !! But the quantum number k is continuous ??

Question 2 : why don't we build the full Hamiltonian $\langle \phi_k | H | \psi_{k'} \rangle$ in the space of Bloch states with various k ?

Block diagonalisation of the Hamiltonian in k-space

It is a common result of quantum mechanics that if $\hat{A}$ and $\hat{B}$ commute and $|\psi_1\rangle$ and $|\psi_2\rangle$ are eigenstates of $\hat{A}$ with different eigenvalues, then $\langle\psi_1|\hat{B}|\psi_2\rangle = 0$ (just calculate $\langle\psi_1|[\hat{A},\hat{B}]|\psi_2\rangle$). Now the ψ_k with ”different k” are eigenstates of translation operators with different eigenvalues so that they are orthogonal through $\hat{H}$.



The Hamiltonian does not couple Bloch states with different Bloch vectors. This is the central result that allows to decoupling degrees of freedom and reducing the complexity of the problem.

We still have an *a priori* infinite number of k-vectors !

Introduction to the Brillouin zone for k-vectors

It is easy to see that if $k' = k + 2\pi/a$ then :

$$\varepsilon_{k'} = \varepsilon_0 + 2t\cos(ka + \frac{2\pi}{a}a) = \varepsilon_k$$

$$\psi_{k'}(x) = \frac{1}{N}\sum_n^N e^{ika+i\frac{2\pi}{a}a}\phi^{at}(x-na) = \psi_k(x)$$

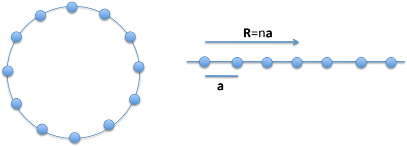
Two quantum number (k') and (k) such that (k'-k) is a multiple of $2\pi/a$ index the same quantum state(s) ! One can restrict (k) to $[-\frac{\pi}{a}, \frac{\pi}{a}[$

The restriction in k-space to independent k-vectors is called the first Brillouin zone (Léon Brillouin, French physicist emigrated to the US in 1940).

This is very similar to the idea that in Y_{lm} spherical harmonics, one just needs to sample (m) within $[-l, l]$.

Discretizing the k (the 1D chain continued)

The values of (k) are governed by the boundary conditions. Solid-state physicists adopt usually the Born-von Karman periodic boundary conditions where the solid (the 1D chain here) closes onto itself:



This means that with N atoms, one has the condition:

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

As such, in the first Brillouin zone, there are $\frac{2\pi/a}{2\pi/Na}=N$ discretized independent k-vectors.

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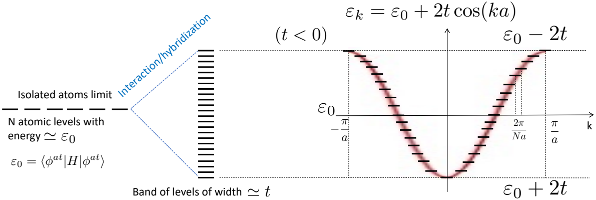

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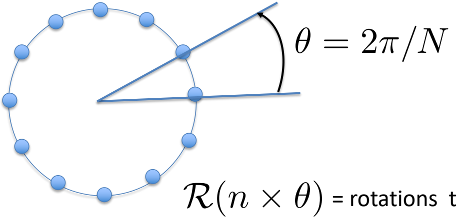
Exercise: From physics to chemistry

The same algebra can be achieved in the "chain of atoms around a circle" using point group symmetries rather than translations.



$\mathcal{R}(n \times \theta)$ = rotations that commute with $\hat{H}$

The reciprocal space (the space for the $\vec{k}$-vectors)

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:

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

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

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

Any periodic function, such as the potential $V(\vec{r})$, can be expressed as a Fourier serie over the $e^{i\vec{G}\cdot\vec{r}}$ basis (which is a "planewave" basis).

The first Brilllouin zone

Remember that the $\psi_{\vec{k}}$ eigenstates of H are also eigenstates of the translation operators with eigenvalue $e^{i\vec{k}\cdot\vec{r}}$. But:

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

This means that the $(\vec{k})$ and $(\vec{k}+\vec{G})$ are the same quantum numbers, leading to same eigenvalues of the translation operator. The Brillouin zone (BZ) is the ensemble of independent $\vec{k}$-vectors (not connected by any $\vec{G}$-vector). It is the unit cell of the reciprocal vectors lattice.

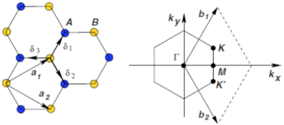
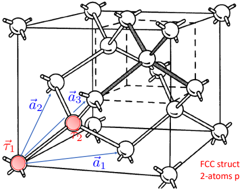


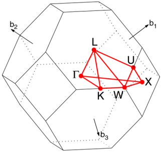
Figure: 2D hexagonal lattice with its first Brillouin-zone. The important k-points bear specific names (**Γ** is the zone-center, **K** is at the corner, etc.)

The silicon band structure

Silicon is an FCC structure with 2-atoms per unit cell (with positions τ_l, l=1,2, in the unit cell). The band structure if the plot of $\varepsilon_{\mathbf{k}}$ energy levels along specific directions in the BZ. The band gap (minimum energy between occupied and unoccupied levels) is of about 1.2 eV.

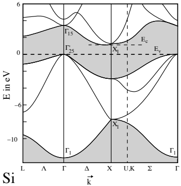


FCC structure with
2-atoms per cell



FCC path: Γ-X-W-K-Γ-L-U-W-L-K|U-X

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



It is an indirect gap semiconductor : the top of the valence (occupied) bands is not at the same $\vec{k}$-vector as the bottom of the conduction (empty) bands. A photon (negligible momentum) cannot be adsorbed at the gap energy. The direct band gap is of about 3.4 eV . As such, a lot of solar photons cannot be adsorbed. Not good for solar cell efficiency.

The silicon band structure (LCAO)

We can adopt a very minimal atomic orbital (AO) basis with one set of $\alpha = (3s, 3p_x, 3p_y, 3p_z)$ atomic orbitals per atom (we forget here about core electrons). As such there are 8 atomic orbitals in one unit cell since there are two atoms with position $\vec{\tau}_I$ (I=1,2) in one cell. By repeating each atomic orbital periodically, one can make 8 periodic functions:

$$u_{I\alpha}(\mathbf{r}) = \frac{1}{\sqrt{N_{cells}}} \sum_{n}^{N_{cells}} \phi^{at}_{I\alpha}(\mathbf{r} - \mathbf{R}_n - \tau_I)$$

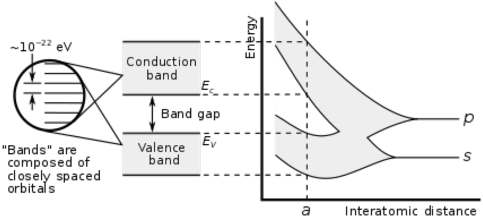
and Bloch states will be a linear combination of these 8 periodic functions:

$$\psi_{n\vec{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{I\alpha} C_n(I\alpha) u_{I\alpha}(\mathbf{r})$$

This will yield 8 levels per $\vec{k}$-vector => 4 are occupied by the 8 $(3s^2, 3p^2)$ electrons per unit cell and 4 are unoccupied.

Silicon from the atomic limit : metallic to semiconducting

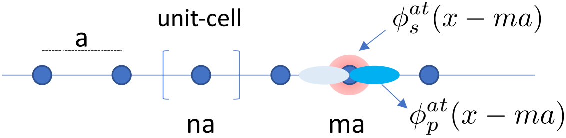
When silicon is formed from the atomic limit by approaching the atoms, first the 3*s* and 3*p* bands forms (the 3*s* is filled the 3*p* is metallic). Then the 2 subbands overlap. Surprizingly, a gap reopens when approaching the experimental interatomic distance, forming a semiconductor. This is the sp^3 rehybridization.



Courtesy wikipedia.

Exercise : 1D silicon and *sp* hybridization

Assume again a 1D chain of N atoms with 1-atom per cell but now one *s* and one p_x orbital per atom.



One can form two periodic functions, one made of *s* atomic orbitals, the second made of *p* atomic orbitals, and form the corresponding Bloch states with proper phase factor:

$$u_{s/p}(x) = \frac{1}{\sqrt{N}} \sum_n^N \phi_{s/p}^{at}(x - na) \quad \text{and} \quad \psi_k^{s/p}(x) = \sum_n^N \frac{e^{ikna}}{\sqrt{N}} \phi_{s/p}^{at}(x - na)$$

Any Bloch state is a linear combination: $\psi_k(x) = \alpha_k \psi_k^s(x) + \beta_k \psi_k^p(x)$.

Exercise : 1D silicon and *sp* hybridization (II)

Project eigenvalue equation: $\hat{H}|\psi_k\rangle = \varepsilon_k|\psi_k\rangle$ onto $\langle\psi_k^s|$ and $\langle\psi_k^p|$:

$$\begin{pmatrix} H_{ss} & H_{sp} \\ H_{ps} & H_{pp} \end{pmatrix} \begin{pmatrix} \alpha_k \\ \beta_k \end{pmatrix} = \varepsilon_k \begin{pmatrix} \alpha_k \\ \beta_k \end{pmatrix}$$

with:

$$\begin{aligned} H_{ss} &= \langle\psi_k^s|H|\psi_k^s\rangle = -\varepsilon_0 - 2\gamma\cos(ka) \\ H_{pp} &= \langle\psi_k^p|H|\psi_k^p\rangle = +\varepsilon_0 + 2\gamma\cos(ka) \\ H_{sp} &= \langle\psi_k^s|H|\psi_k^p\rangle = 2\gamma i\sin(ka) \end{aligned}$$

where we assumed that onsite *s* energy is $-\epsilon_0$ and onsite *p* energy is $+\epsilon_0$ and hopping integrals are as follows:

with onsite *sp* coupling zero by symmetry.

Exercise : 1D silicon and *sp* hybridization (III)

The solution yields:

$$\varepsilon_k = \pm\sqrt{\varepsilon_0^2 + 4\gamma\varepsilon_0 \cos(ka) + 4\gamma^2} \qquad \text{with} \qquad k \subset \left[\frac{-\pi}{a}, \frac{\pi}{a}\right[$$

that yields the following band structure with increasing γ (hopping energy) when atoms come closer and closer:

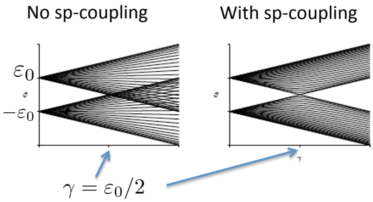
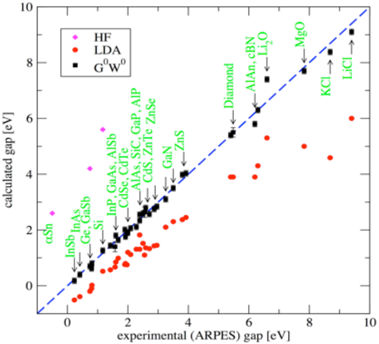


Fig: Evolution of band structure as a function of the strength of the hopping coupling γ with (Left) no *sp* coupling and (Right) a *sp* coupling equal to $\pm\gamma$. For each value of γ, we plot a few energy levels corresponding to 20 k-values in the Brillouin zone.

To conclude : band gaps with DFT (Kohn-Sham)

We compile here below the DFT-LDA Kohn-Sham gap of semiconductors and insulators (red dots; courtesy Valério Olévano) that we compare to the experimental values (first diagonal). We also provide the Hartree-Fock gap (pink dots).



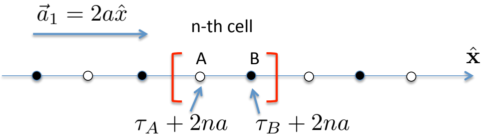
Clearly, the DFT Kohn-Sham gap is too small !! On the contrary, the Hartree-Fock gap is too large. As an important example, the LDA, HF and experimental band gap of silicon are: 0.6 eV, 6.5 eV, and ... 1.2 eV.

The black dots are the results of perturbation theory correcting the Kohn-Sham energies: the *GW* formalism will be the subject of some of next week lectures.

Thanks

Exercise : The ionicity gap

Assume now a 1D chain of N cells with 2-atoms per cell and one atomic orbital per atom.



One can form two periodic functions, one made of atomic orbitals on atoms A, the second made of atomic orbitals on atoms B, and form the corresponding Bloch states with proper phase factor:

$$u_A(x) = \frac{1}{\sqrt{N}} \sum_n^N \phi_A^{at}(x - 2na - \tau_A) \quad \text{and} \quad \psi_k^A(x) = \sum_n^N \frac{e^{ikna}}{\sqrt{N}} \phi_A^{at}(x - 2na - \tau_A)$$

and idem for B orbitals.

Exercise : The ionicity gap (II)

Any Bloch state is a linear combination: $\psi_k(x) = \alpha_k \psi_k^A(x) + \beta_k \psi_k^B(x)$.
Project eigenvalue equation: $\hat{H}|\psi_k\rangle = \varepsilon_k |\psi_k\rangle$ onto $\langle\psi_k^s|$ and $\langle\psi_k^d|$:

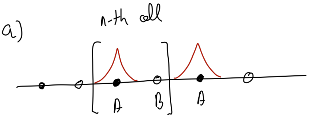
$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} \alpha_k \\ \beta_k \end{pmatrix} = \varepsilon_k \begin{pmatrix} \alpha_k \\ \beta_k \end{pmatrix}$$

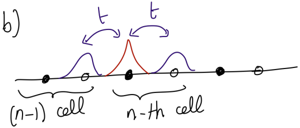
with:

$H_{AA} = \langle\psi_k^A|H|\psi_k^A\rangle = \varepsilon_0^A$ (A atoms are 2nd neighbours => no hopping)

$H_{BB} = \langle\psi_k^B|H|\psi_k^B\rangle = \varepsilon_0^B$ (B atoms are 2nd neighbours => no hopping)

$H_{AB} = \langle\psi_k^A|H|\psi_k^B\rangle = 2t\cos(ka)$ (hopping between nearest neighbors atoms)



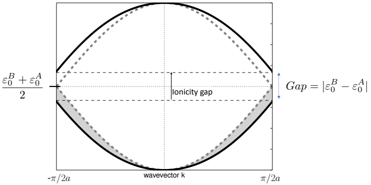


Exercise : The ionicity gap (III)

The equation to solve is $(\varepsilon_k - \varepsilon_0^A)(\varepsilon_k - \varepsilon_0^B) = 4t^2\cos^2(ka)$ yielding:

$$\varepsilon_k = \frac{\varepsilon_0^A + \varepsilon_0^B}{2} \pm \sqrt{4t^2\cos^2(ka) + (\varepsilon_0^B - \varepsilon_0^A)^2/4} \quad \text{with} \quad k \subset \left[\frac{-\pi}{2a}, \frac{\pi}{2a}\right[$$

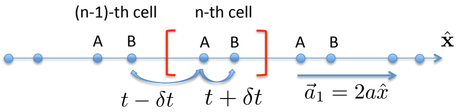
that yields a band structure with a gap $|\varepsilon_0^B - \varepsilon_0^A|$ opening at the BZ boundary due to ionicity (different onsite energies on atoms A and B) :



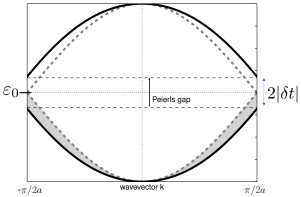
The magnitude of the gap is controlled by the ionicity. The grey dashed line is the band structure in the absence of onsite difference. This exercise may explain the difference between graphene and h-BN.

Exercise : The Peierls distortion

Assume now a 1D chain with 2 identical atoms per cell and one atomic orbital per atom but with bond alternation. Assume onsite energy $\varepsilon_0 = 0$.



$$\text{Then:} \quad \varepsilon_k = \pm 2t\sqrt{\cos^2(ka) + (\delta t/t)^2 \sin 2(ka)} \qquad \text{with} \quad k \subset \left[\frac{-\pi}{2a}, \frac{\pi}{2a}\right[$$



A gap opens at BZ boundary with a magnitude controlled by the bond alternation. The shaded area is the energy gained by the electrons if the lower subband was filled and the upper subband empty.