1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2011

Part II – Quantum Mechanical Methods : Lecture 5

Quantum Modeling of Solids: Basic Properties

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Part II Outline

theory & practice

1. It's A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. From Atoms to Solids
5. Quantum Modeling of Solids: Basic Properties
6. Advanced Prop. of Materials: What else can we do?

example applications

7. Nanotechnology
8. Solar Photovoltaics: Converting Photons into Electrons
9. Thermoelectrics: Converting Heat into Electricity
10. Solar Fuels: Pushing Electrons up a Hill
11. Hydrogen Storage: the Strength of Weak Interactions
12. Review

Motivation

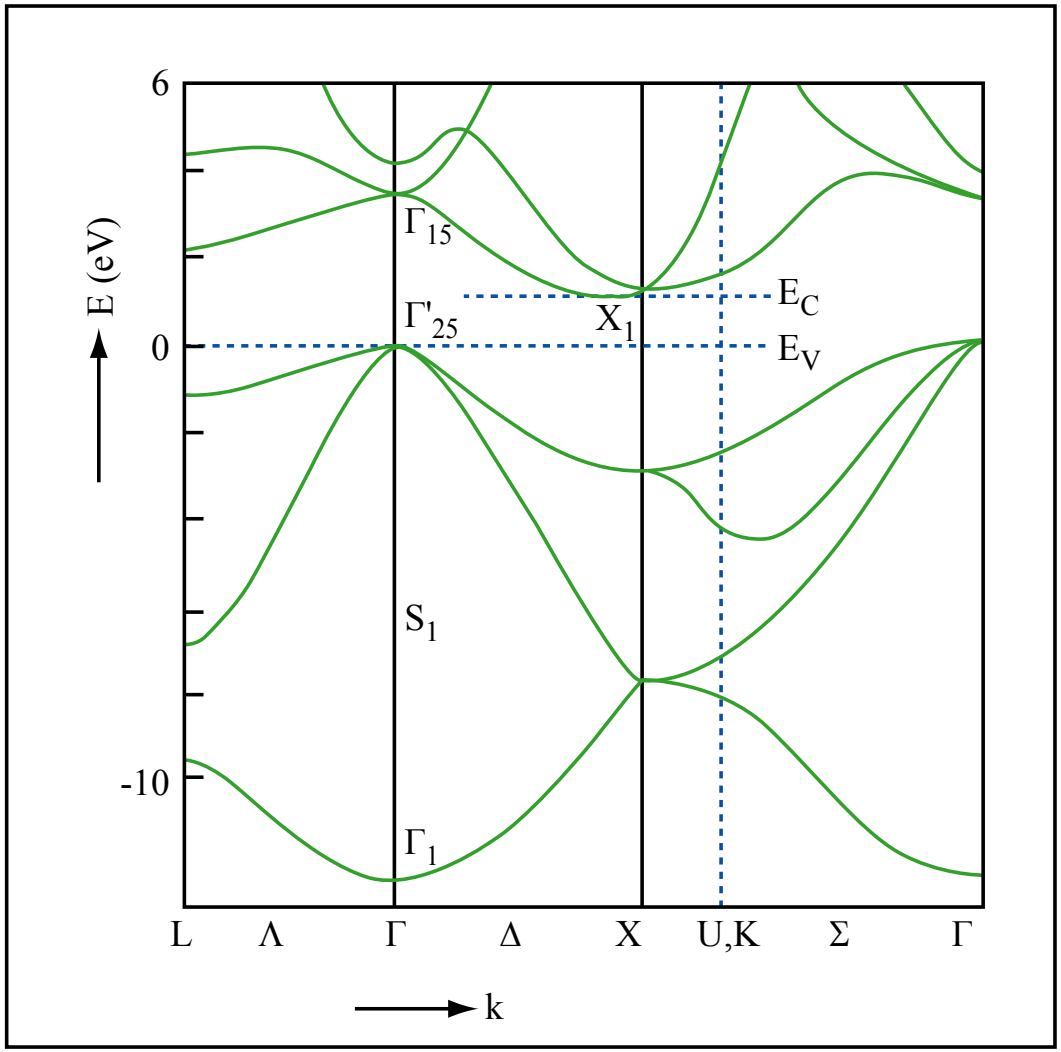
? mechanical properties

? electrical properties

? optical properties

Lesson outline

- Review
- structural properties
- Calc. the band structure
- Calc. the DOS
- Metal/insulator
- Magnetization



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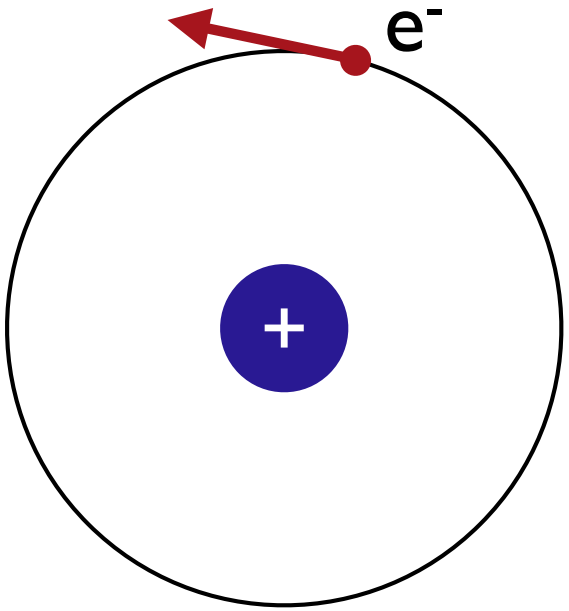
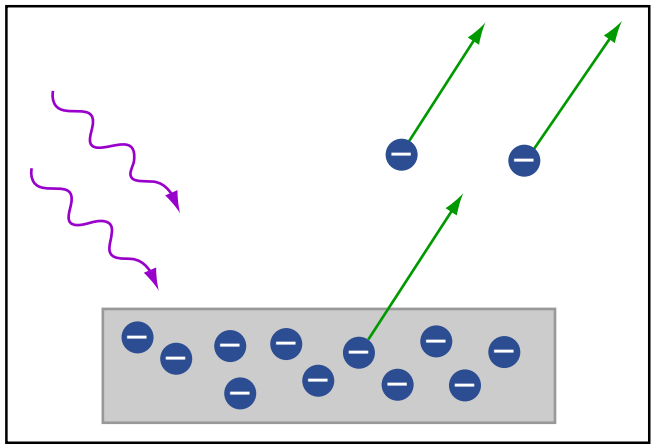
Let's take a walk through memory lane for a moment...

In the Beginning....

There were some strange observations by some very smart people.





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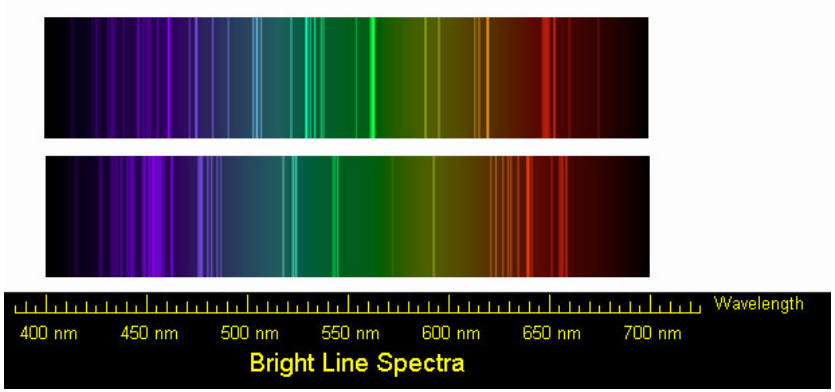


Image courtesy NASA.

In the Beginning....

The weirdness just kept going.

Image removed due to copyright restrictions. See the image here: http://icanhascheezburger.com/2007/06/02/im-in-ur-quantum-box/.

It Became Clear...

...that matter behaved like waves (and vice versa).

And that we had to lose our "classical" concepts of absolute position and momentum.

And instead consider a particle as a wave, whose square is the probability of finding it.

$$\Psi(\mathbf{r},t) = A\exp[i(\mathbf{k}\bullet\mathbf{r} - \omega t)]$$

But how would we describe the behavior of this wave?

Then, F=ma for Quantum Mechanics

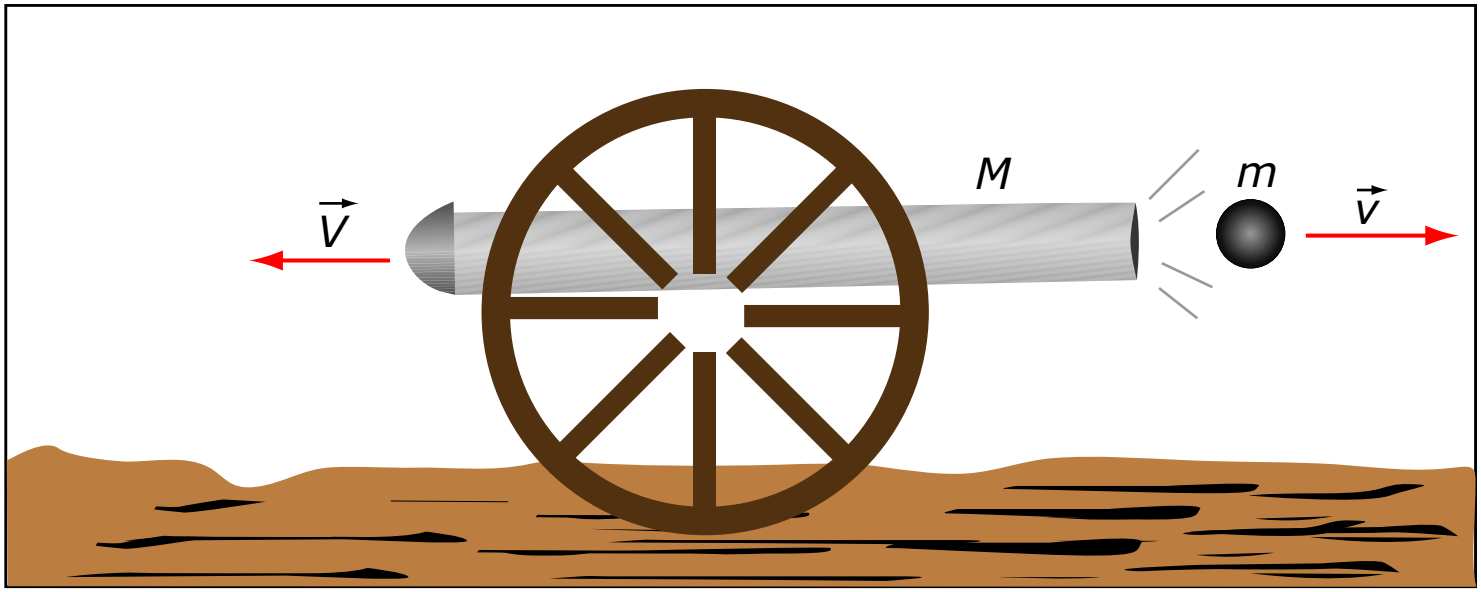
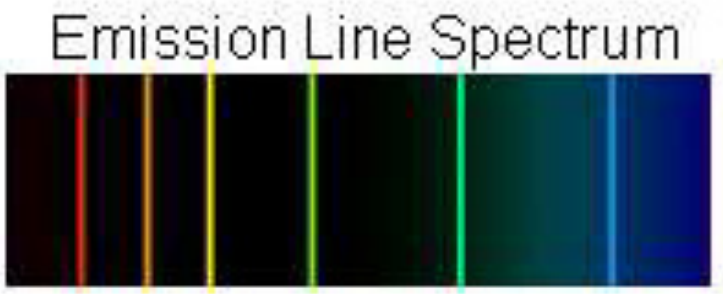


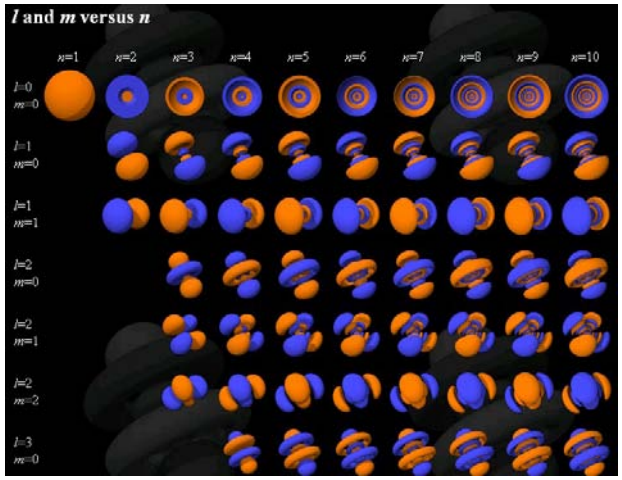
Image by MIT OpenCourseWare.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t) \right] \psi(\vec{r},t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r},t)$$

It Was Wonderful

It explained many things.





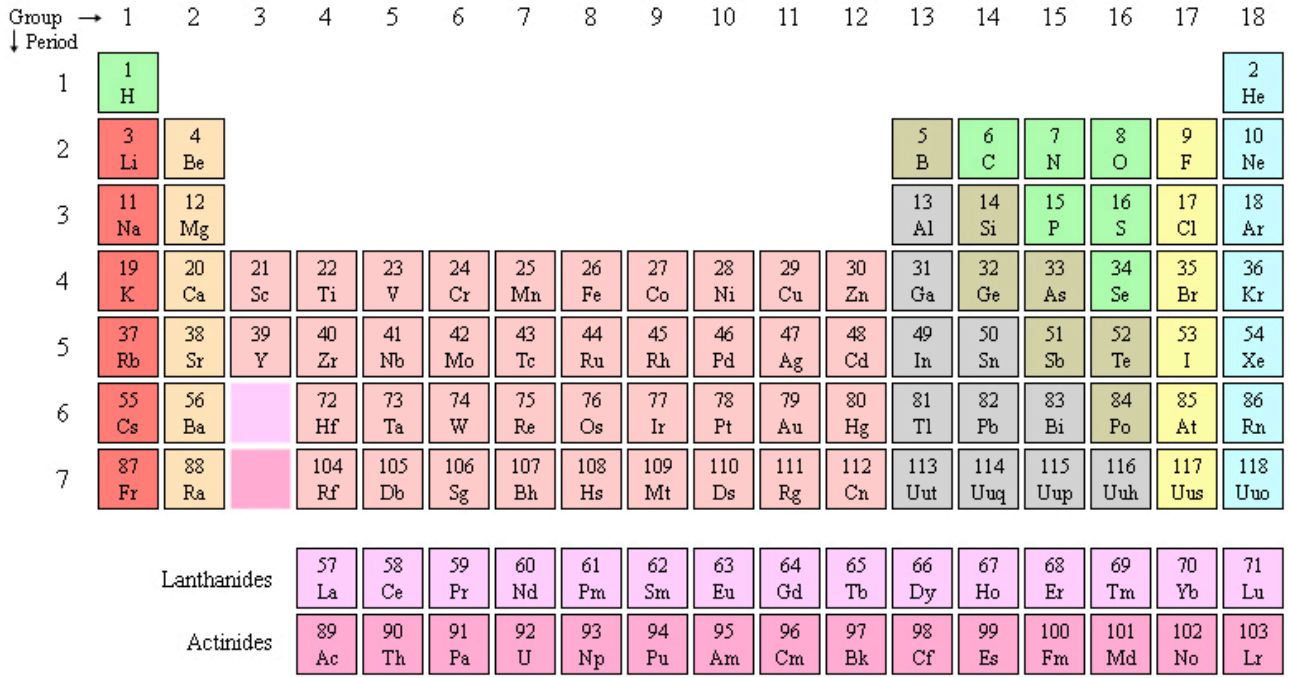
Courtesy of David Manthey. Used with permission.
Source: http://www.orbitals.com/orb/orbtable.htm.

It gave us atomic orbitals.

It predicted the energy levels in hydrogen.

It Was Wonderful

It gave us the means to understand much of chemistry.



BUT...

Nature Does > 1 electron!

It was impossible to solve for more than a single electron.

Enter (stage left) computational quantum mechanics!

But...

We Don't Have The Age of the Universe

Which is how long it would take currently to solve the Schrodinger equation exactly on a computer.

So...we looked at this guy's back.

Screenshot of article removed due to copyright restrictions; see the article online:
http://blogs.discovermagazine.com/loom/2009/05/23/sigmas-from-shoulder-to-shoulder-science-tattoos/.

And started making some approximations.

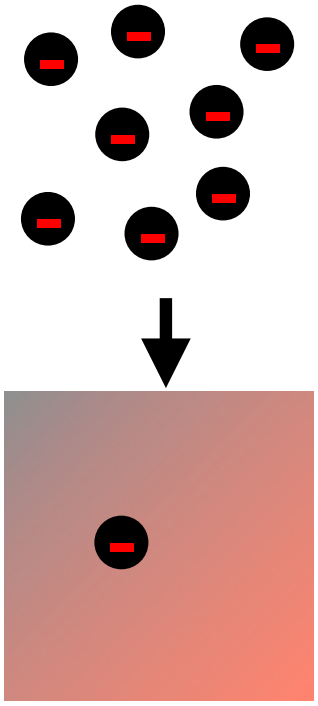
The Two Paths

Ψ is a wave function of all positions & time.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right]\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)$$

Chemists (mostly)

Physicists (mostly)



Ψ = something simpler

H = something simpler

"mean field" methods

Working with the Density

$$E[n] = T[n] + V_{ii} + V_{ie}[n] + V_{ee}[n]$$

kinetic — ion-electron — ion-ion — electron-electron

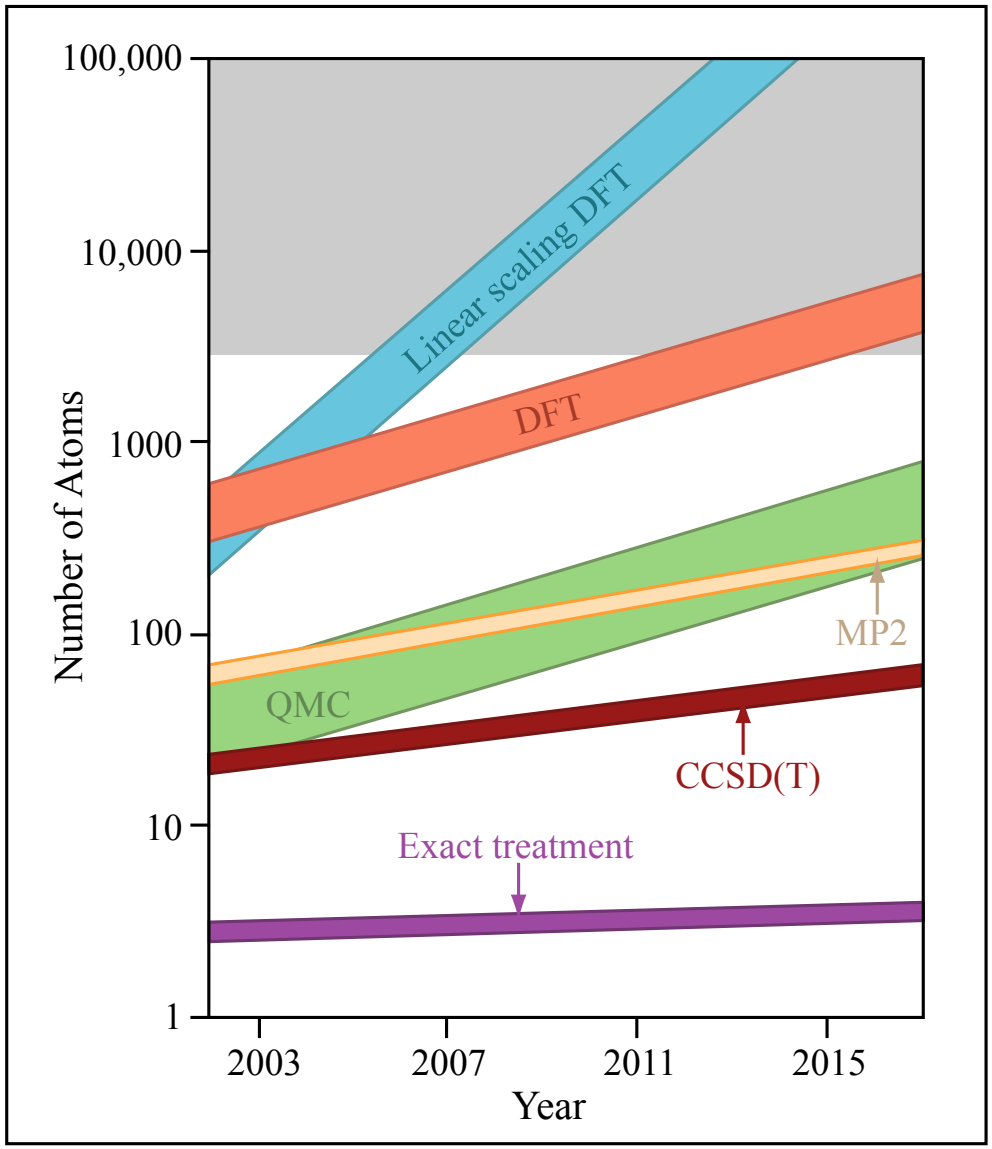
n=#	$\Psi(N^{3n})$	$\rho(N^3)$
1	8	8
10	10^9	8
100	10^{90}	8
1,000	10^{900}	8

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

ion potential — Hartree potential — exchange-correlation potential

Review: Why DFT?



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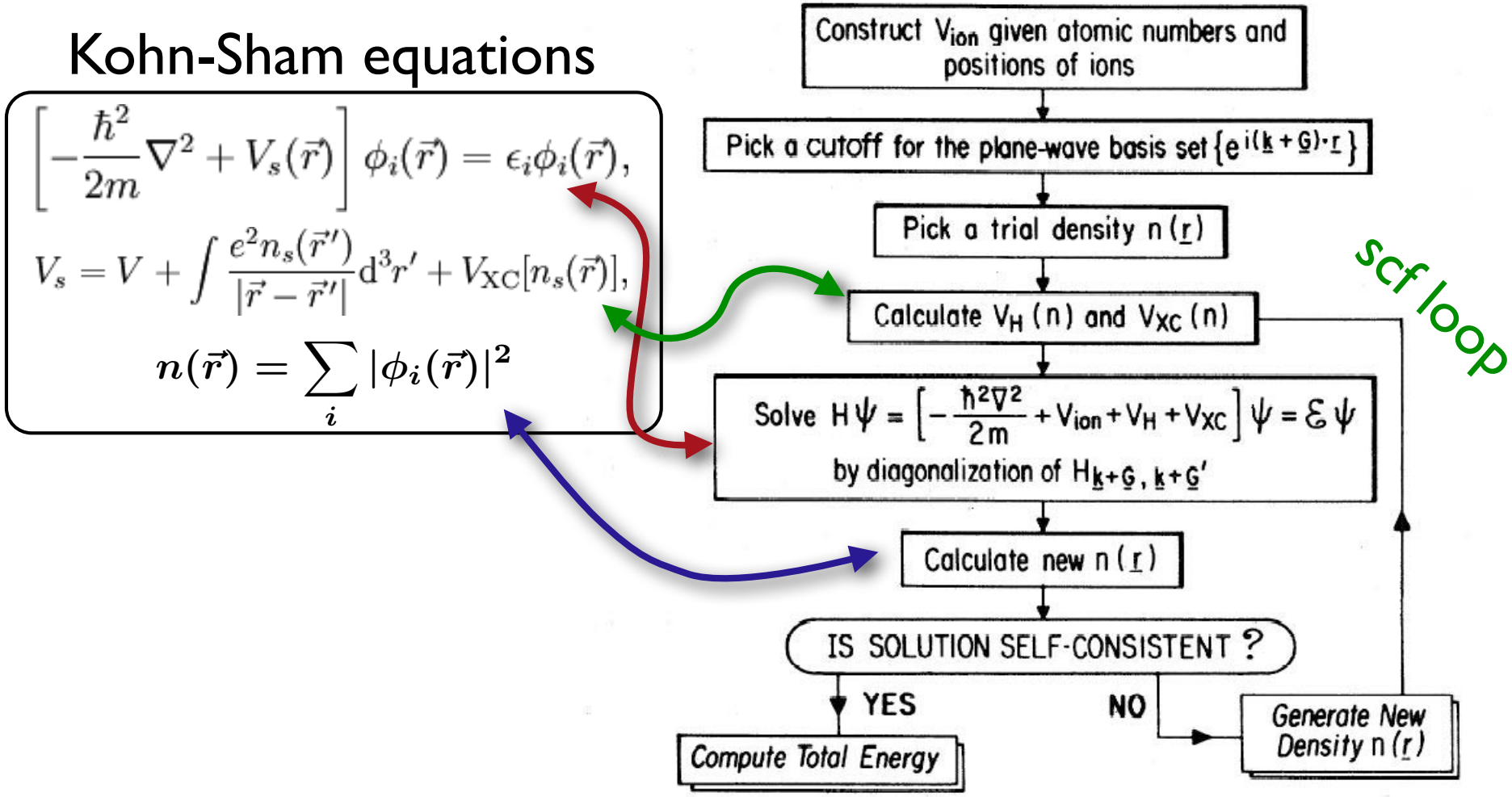
Review: Self-consistent cycle

Kohn-Sham equations

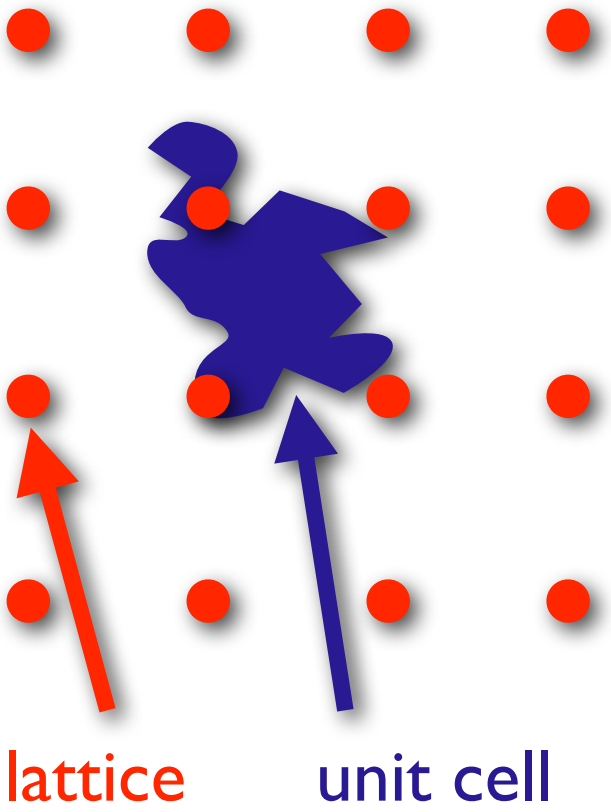
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$



Review: Crystal symmetries



A crystal is built up
of a unit cell and
periodic replicas thereof.

Image of M. C. Escher's "Mobius with Birds" removed due to copyright restrictions.

Review: Crystal symmetries

4 Lattice Types

7 Crystal Classes

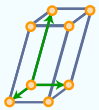
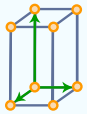
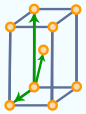
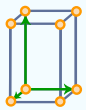
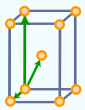
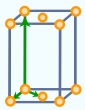
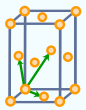
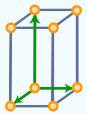
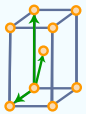
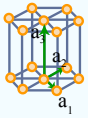
Bravais Lattice	Parameters	Simple (P)	Volume Centered (I)	Base Centered (C)	Face Centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^0$ $\alpha_{12} \neq 90^0$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^0$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^0$ $\alpha_{23} = \alpha_{31} = 90^0$				

Image by MIT OpenCourseWare.

Bravais

The most common Bravais lattices are the cubic ones (simple, body-centered, and face-centered) plus the hexagonal close-packed arrangement.

...why?

Reciprocal Lattice & Brillouin Zone

Associated with each real space lattice, there exists something we call a reciprocal lattice.

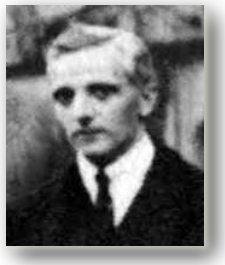
The reciprocal lattice is the set of wave-vectors which are commensurate with the real space lattice.

It is defined by a set of vectors a*, b*, and c* such that a* is perpendicular to b and c of the Bravais lattice, and the product a* x a is 1.

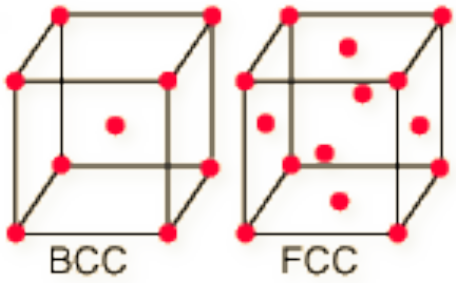
Reciprocal Lattice & Brillouin Zone

It is defined by a set of vectors a*, b*, and c* such that a* is perpendicular to b and c of the Bravais lattice, and the product a* x a is 1.

In particular: $$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$



Brillouin



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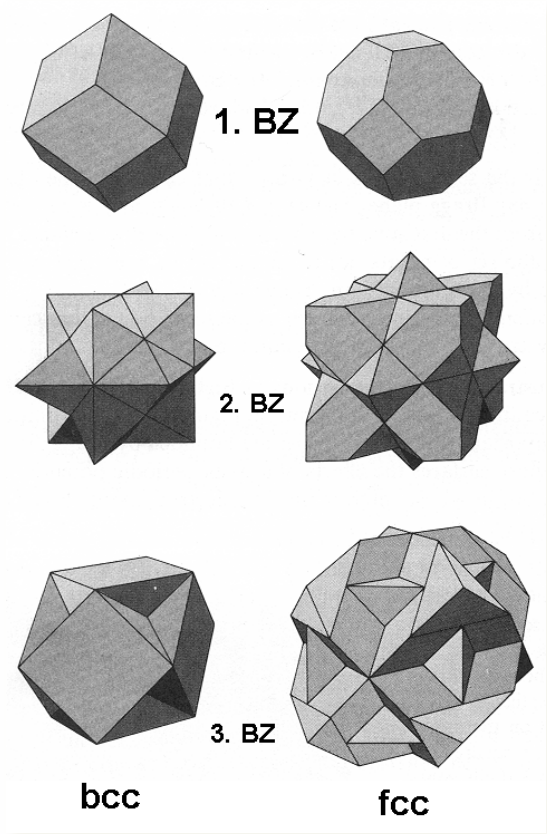
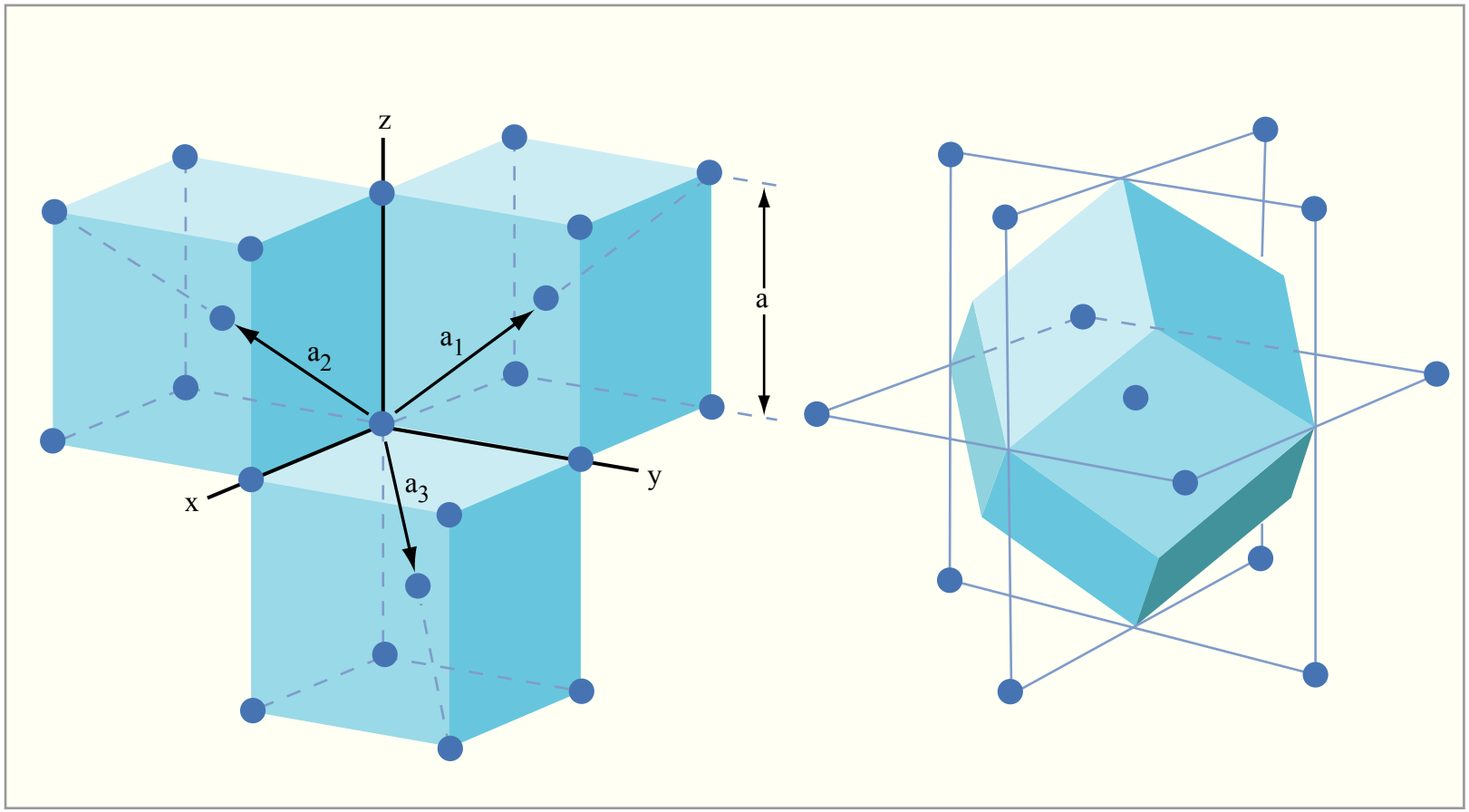
$$\longrightarrow \quad \mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad \longrightarrow$$



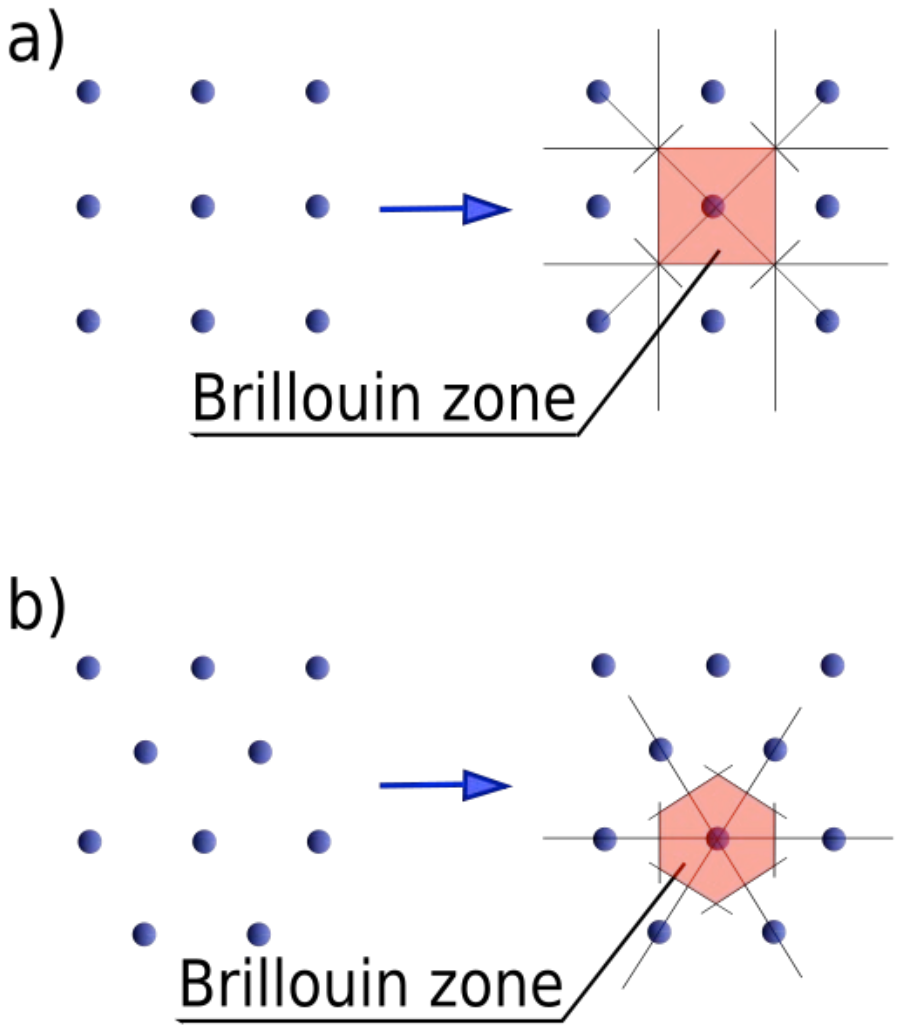
Review: The inverse lattice

real space lattice (BCC) inverse lattice (FCC)



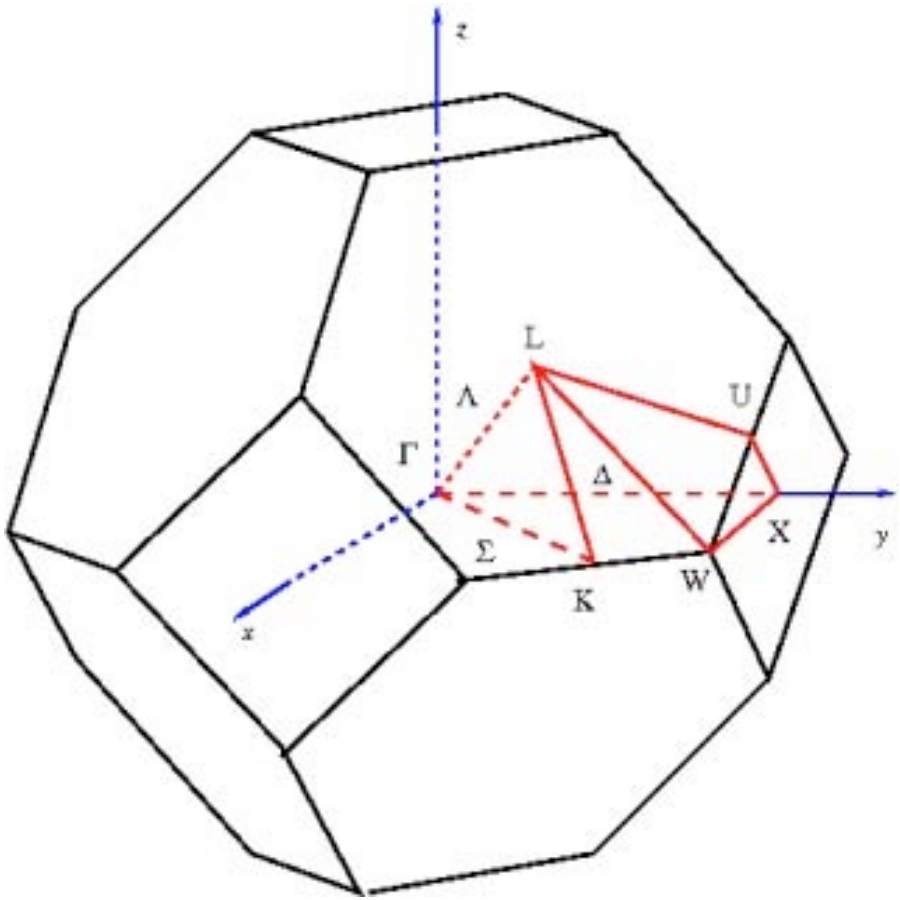
The Brillouin zone

inverse lattice



The Brillouin zone is a special unit cell of the inverse lattice.

The Brillouin zone



Brillouin zone of the FCC lattice

Bloch's Theorem (Take 2)

Reciprocal lattice vectors have special properties of particular value for calculations of solids.

Remember that we write the reciprocal lattice vector:

$$\mathbf{G} = 2\pi n\mathbf{a}^* + 2\pi m\mathbf{b}^* + 2\pi o\mathbf{c}^*$$

We added the 2 simply for convenience, and the n, m, o, are integers.

Now consider the behavior of the function exp(iGr).

Bloch's Theorem (Take 2)

$$\exp(i\mathbf{G}\cdot\mathbf{r}) = \exp\left[i(2\pi n\mathbf{a}^* + 2\pi m\mathbf{b}^* + 2\pi o\mathbf{c}^*)\cdot(\alpha\mathbf{a} + \beta\mathbf{b} + \gamma\mathbf{c})\right]$$

$$= \exp\left[i(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)\right]$$

$$= \cos(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma) + i\sin(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)$$

As **r** is varied, lattice vector coefficients (α,β,γ) change between 0 and 1 and the function exp(i**G**·**r**) changes too.

However, since n, m, and o are integral, exp(i**G**·**r**) will always vary with the periodicity of the real-space lattice.

$$e^{i\vec{G}\cdot\vec{R}} = 1 \quad \longrightarrow \quad \psi(\vec{r}) = \sum_j c_j e^{i\vec{G}_j\cdot\vec{r}}$$

automatically periodic in R!

Bloch's Theorem (Take 2)

The periodicity of the lattice in a solid means that the values of a function (e.g., density) will be identical at equivalent points on the lattice.

The wavefunction, on the other hand, is periodic but only when multiplied by a phase factor.

This is known as Bloch's theorem.

NEW quantum number k that lives in the inverse lattice!

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

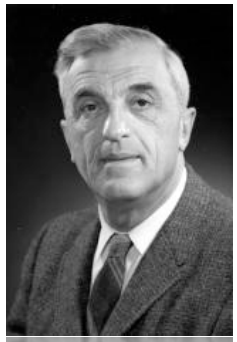
$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

Periodic potentials

Results of the Bloch theorem:

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

$$|\psi_{\vec{k}}(\vec{r}+\vec{R})|^2 = |\psi_{\vec{k}}(\vec{r})|^2$$



charge density
is lattice periodic

if solution $\psi_{\vec{k}}(\vec{r}) \longrightarrow \psi_{\vec{k}+\vec{G}}(\vec{r})$ also solution

with $E_{\vec{k}} = E_{\vec{k}+\vec{G}}$

Periodic potentials

Schrödinger equation	certain symmetry	quantum number
hydrogen atom	spherical symmetry $[H, L^2] = HL^2 - L^2H = 0$ $[H, L_z] = 0$	$\psi_{n,l,m}(\vec{r})$
periodic solid	translational symmetry $[H, T] = 0$	$\psi_{n,\vec{k}}(\vec{r})$

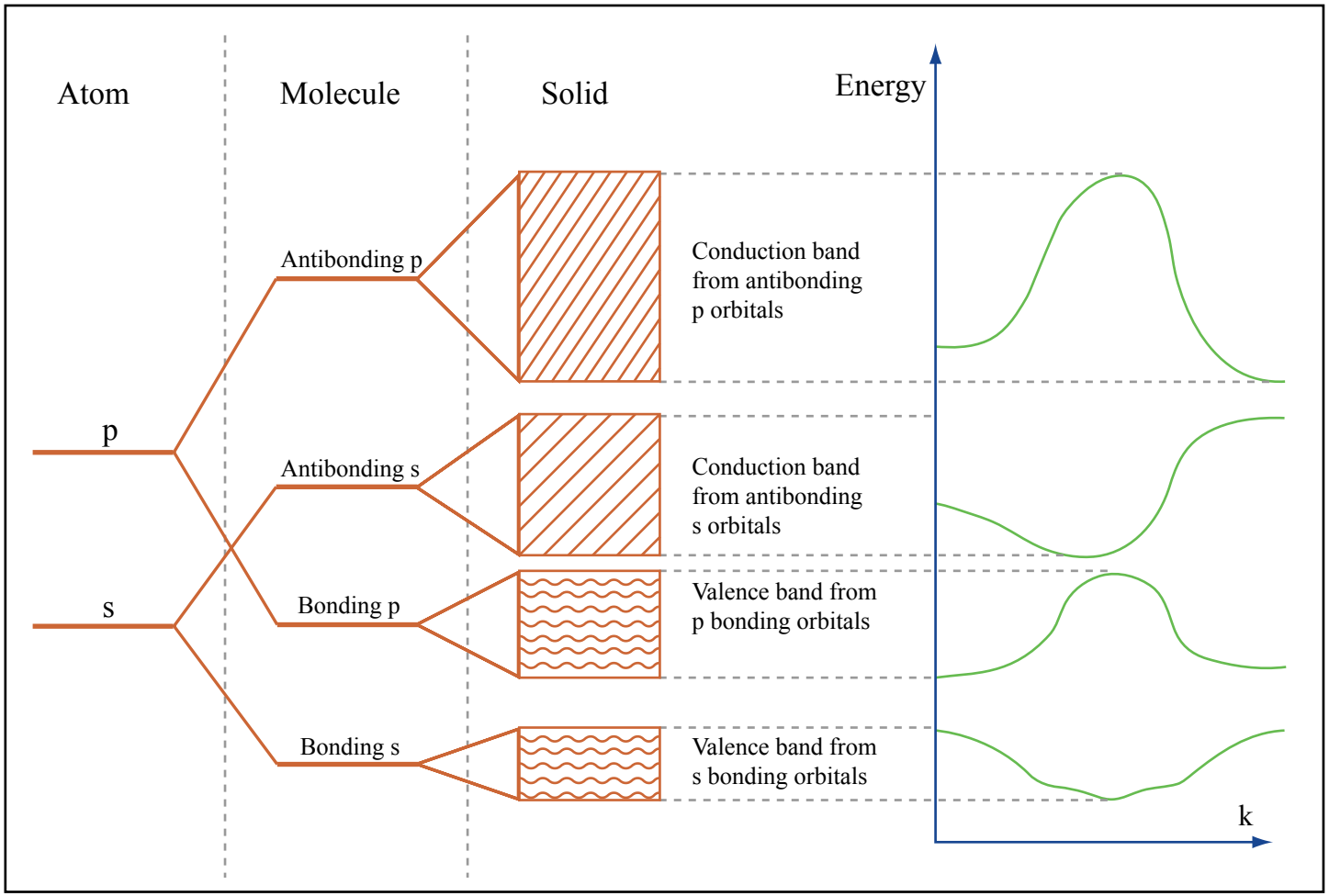
The band structure

Different wave functions can satisfy the Bloch theorem for the same ***k***: eigenfunctions and eigenvalues labelled with ***k*** and the index n

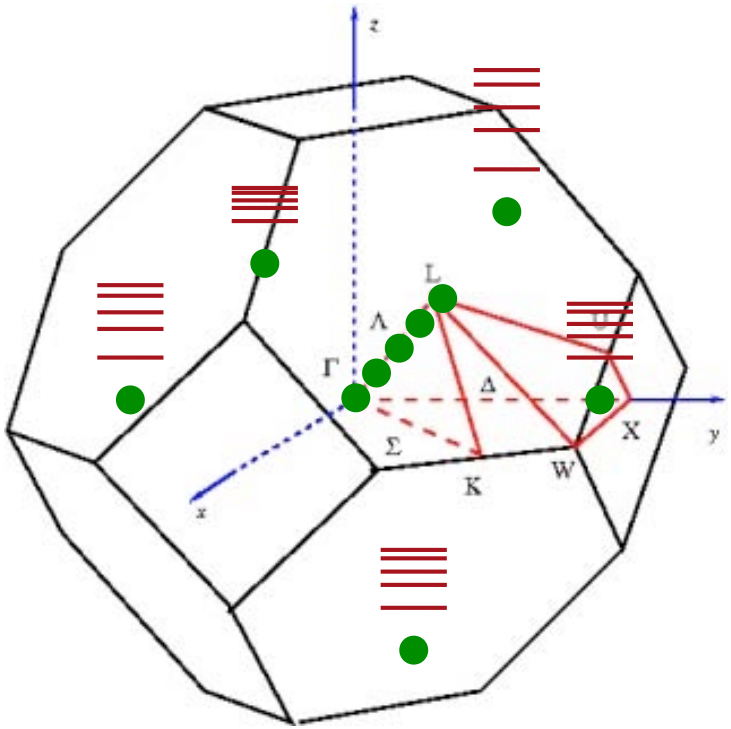
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}\psi_{\vec{k}}(\vec{r}) \longrightarrow \begin{matrix}\psi_{n,\vec{k}}(\vec{r}) \\ \epsilon_{n,\vec{k}}\end{matrix}$$

energy bands

The band structure

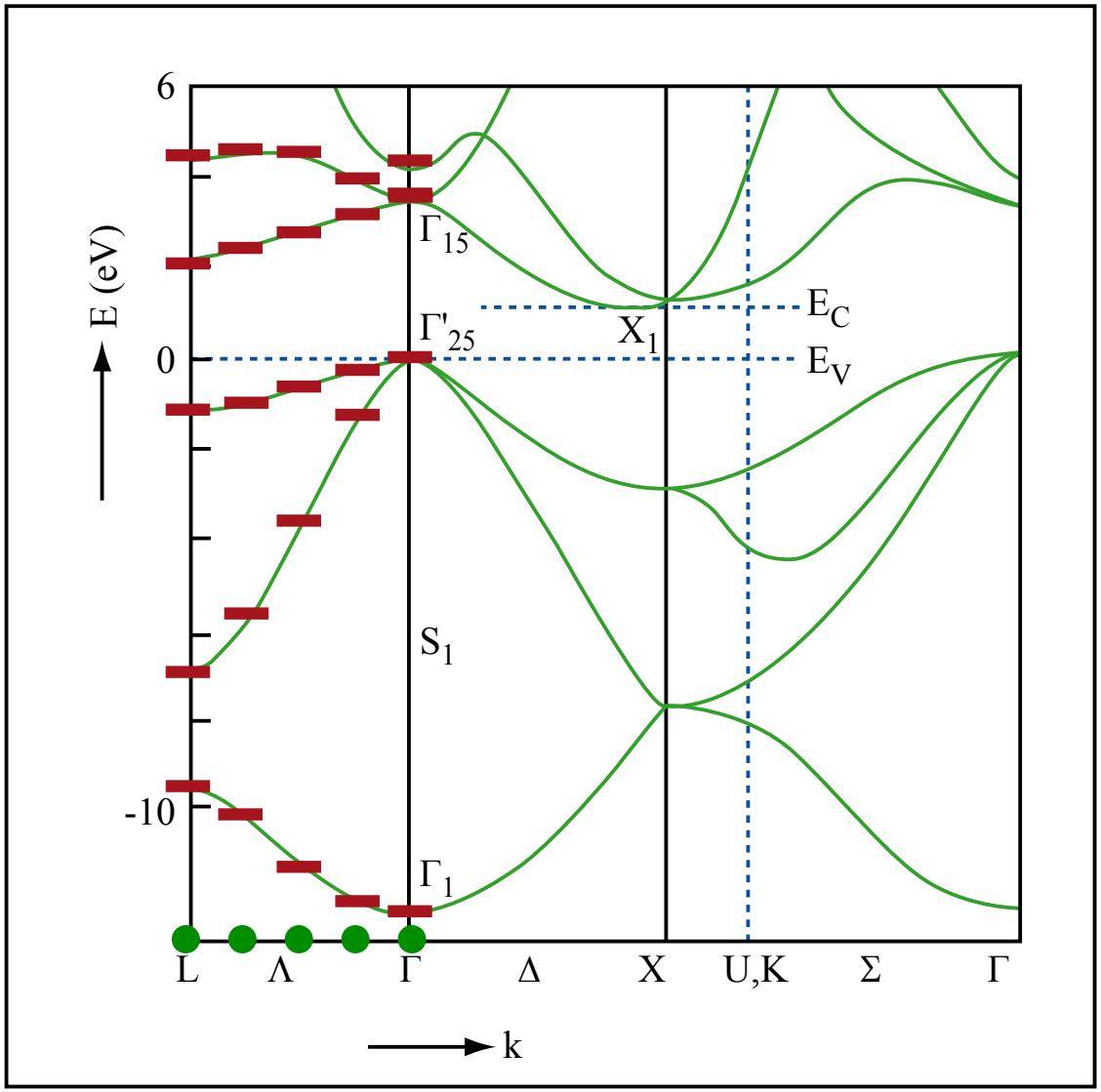


The band structure

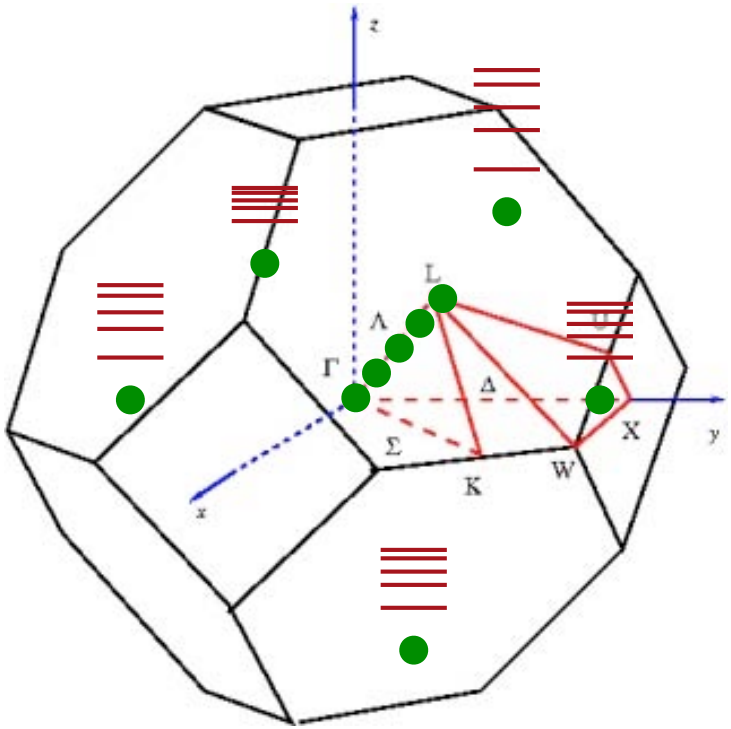


energy levels
in the Brillouin zone

Silicon



The band structure



energy levels
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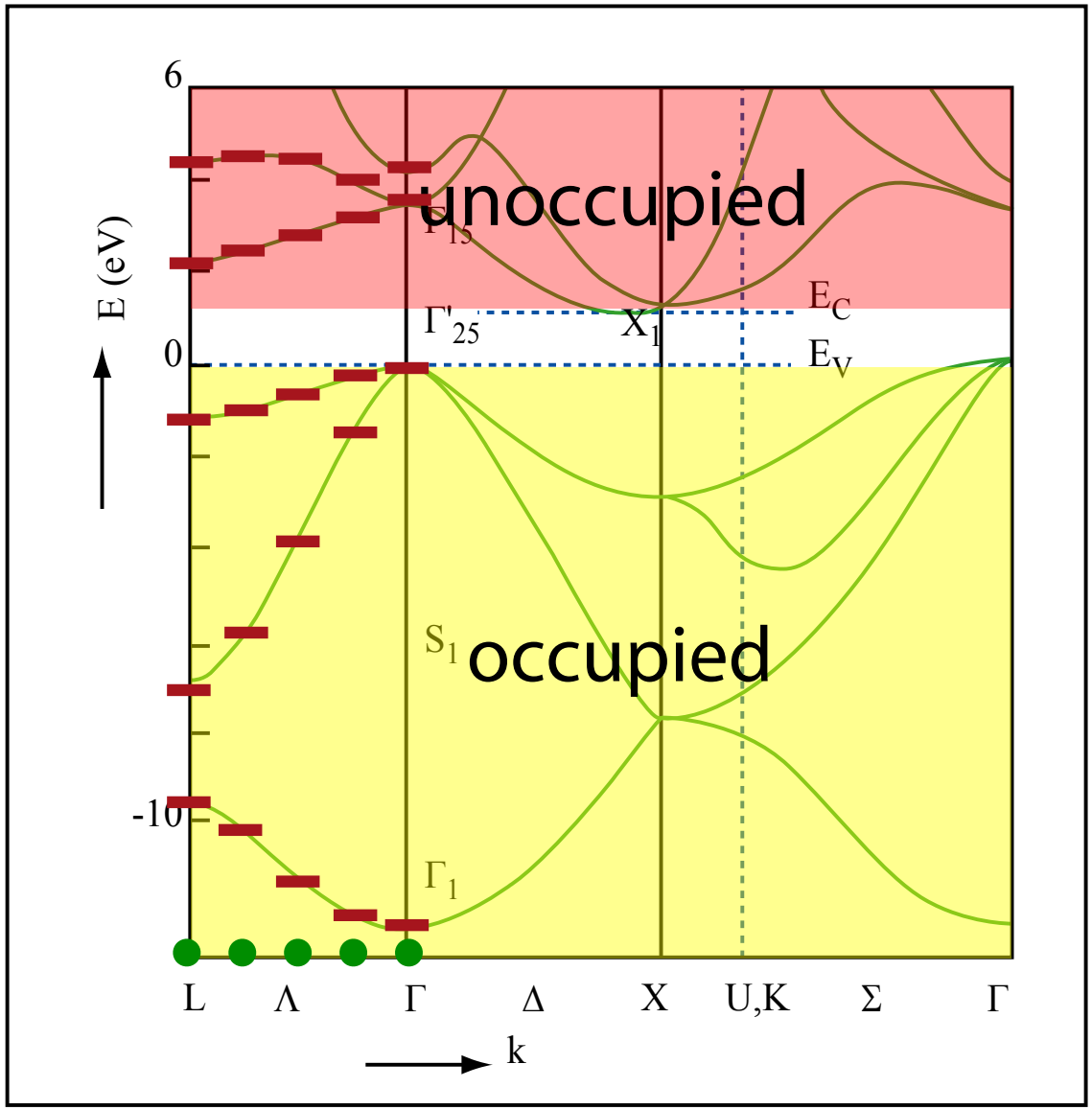
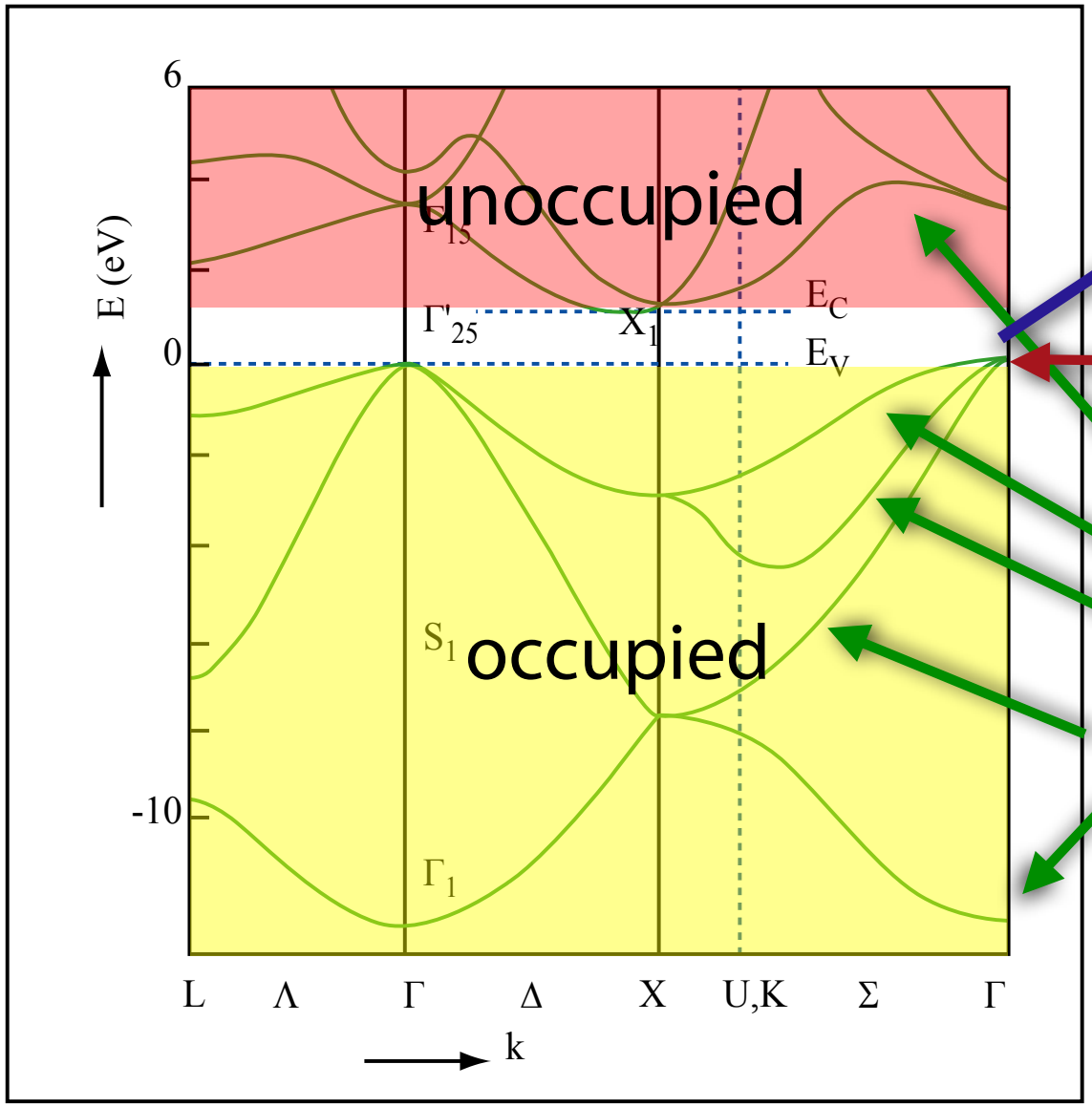
Silicon



The Fermi energy



gap: also visible in the DOS

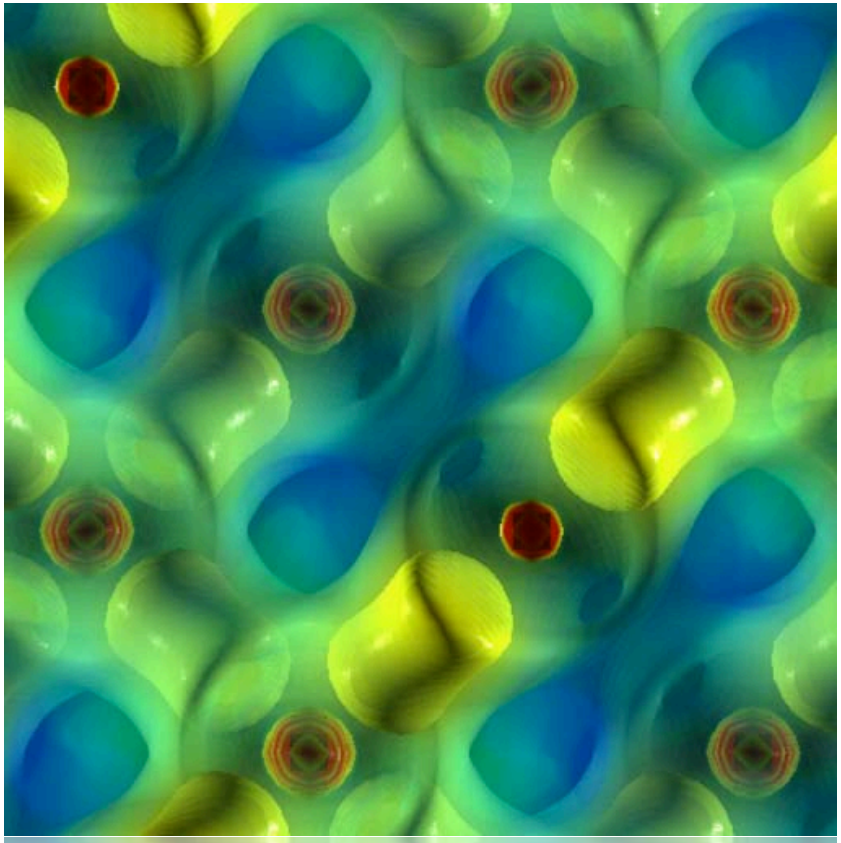
Fermi energy

one band can hold two electrons (spin up and down)

Image by MIT OpenCourseWare.

The electron density

electron
density
of silicon



Structural properties

Forces on the atoms can be calculated with the Hellmann–Feynman theorem:

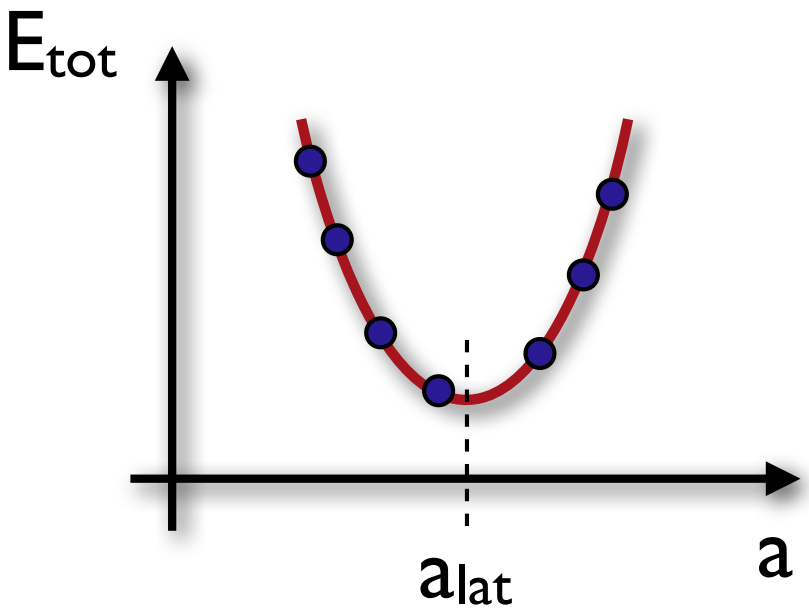
$$\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau$$

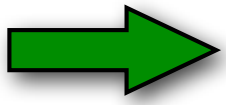
For λ=atomic position, we get the force on that atom.

Forces automatically in most codes.

Structural properties

finding the
equilibrium
lattice constant



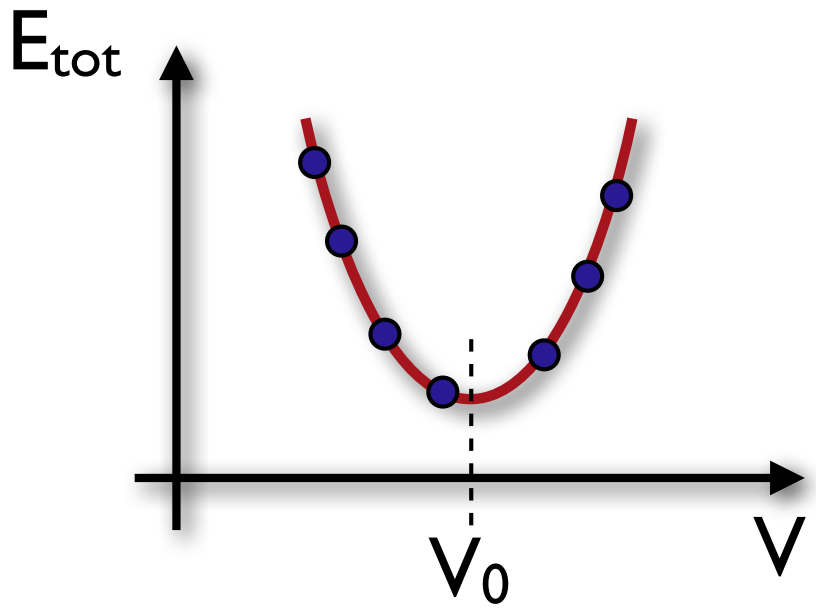


mass density

$m_u = 1.66054\ 10^{-27}$ Kg

Structural properties

finding the stress/pressure and the bulk modulus



$$p = -\frac{\partial E}{\partial V}$$

$$\sigma_{\text{bulk}} = -V\frac{\partial p}{\partial V} = V\frac{\partial^2 E}{\partial V^2}$$

Calculating the band structure

3-step procedure

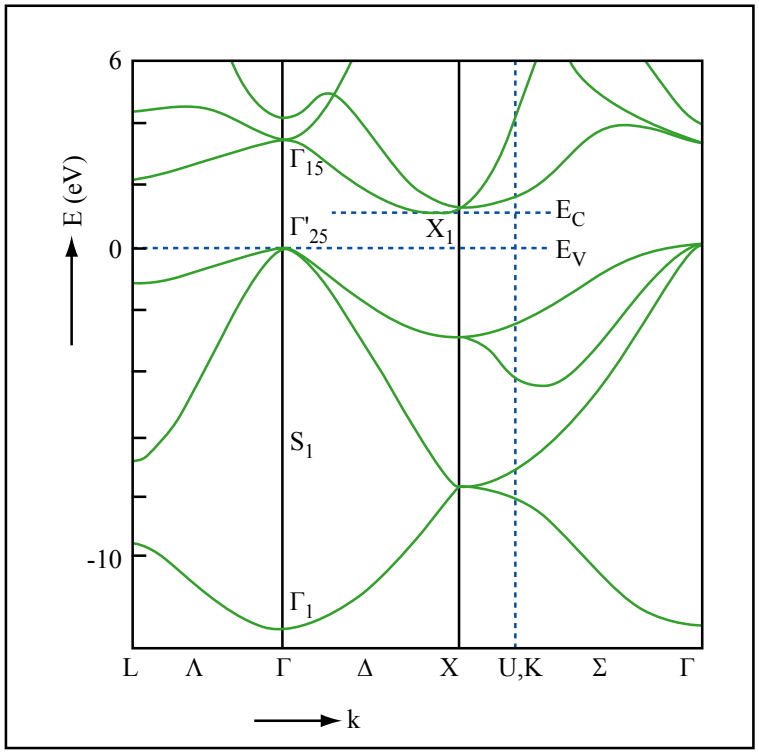
1. Find the converged ground state density and potential.
2. For the converged potential calculate the energies at k-points along lines.
3. Use some software to plot the band structure.

Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$



Calculating the DOS

3-step procedure

1. Find the converged ground state density and potential.
2. For the converged potential calculate energies at a VERY dense k-mesh.
3. Use some software to plot the DOS.

Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$

Image removed due to copyright restrictions. Please see Fig. 3 in Yu, R., and X. F. Zhang. "Platinum Nitride with Fluorite Structure." *Applied Physics Letters* 86 (2005): 121913.

Metal/insulator

silicon

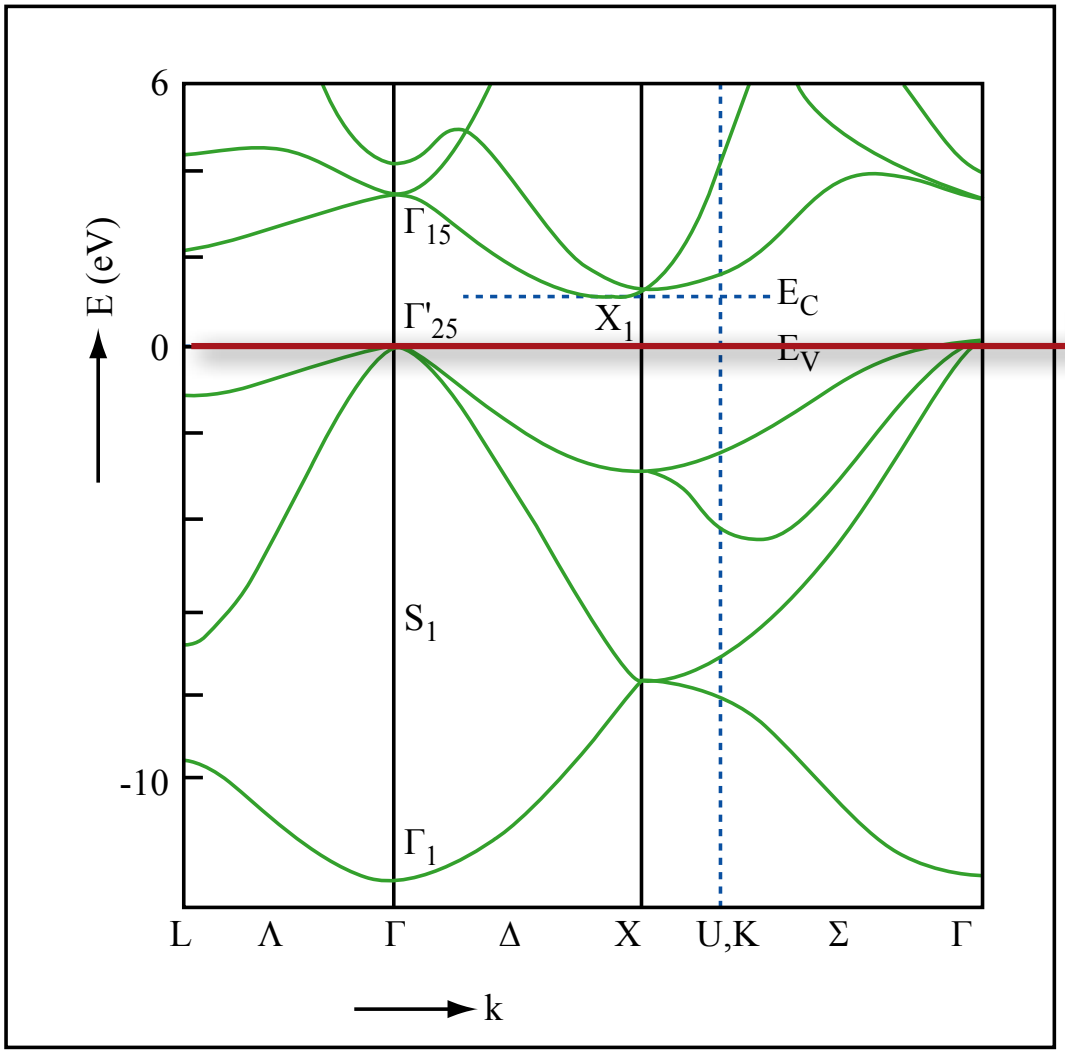


Image by MIT OpenCourseWare.

Are any bands crossing the Fermi energy?

YES: METAL

NO: INSULATOR

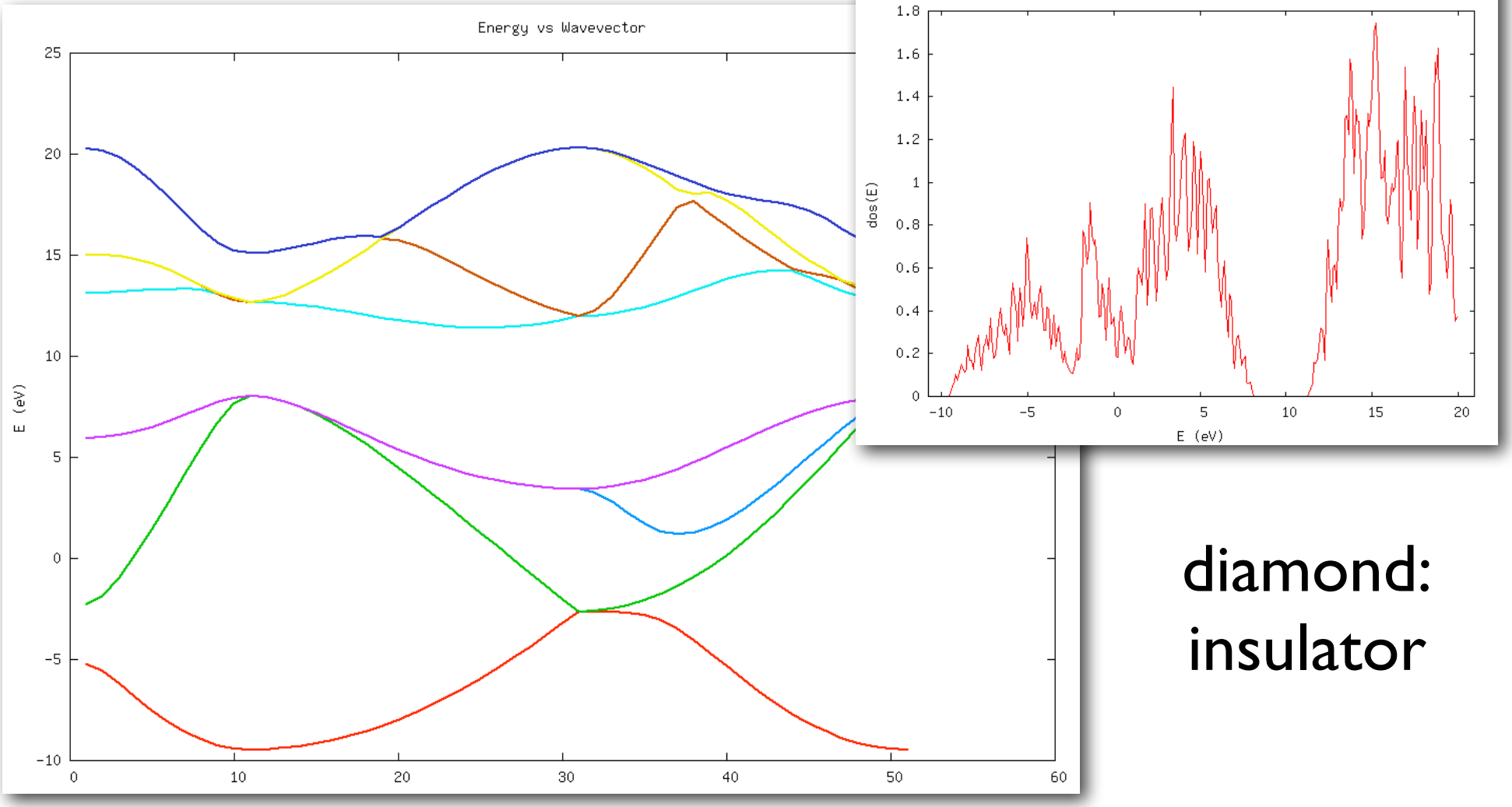
Fermi energy

Number of electrons in unit cell:

EVEN: MAYBE INSULATOR

ODD: FOR SURE METAL

Metal/insulator



diamond:
insulator

Metal/insulator

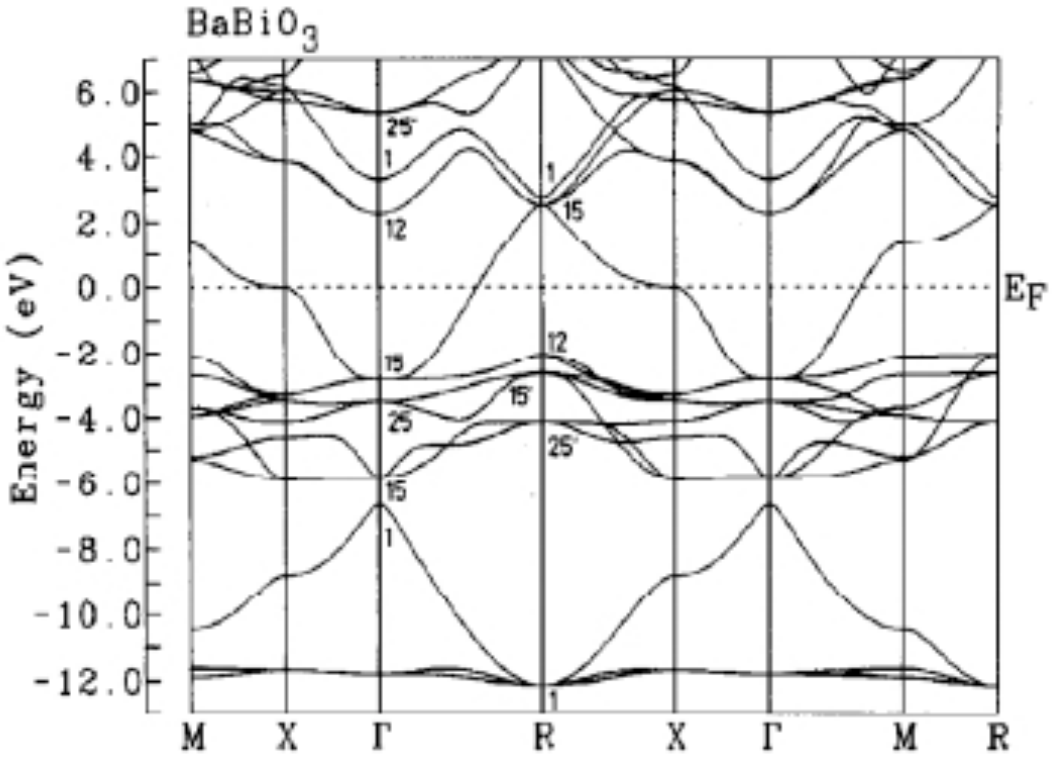
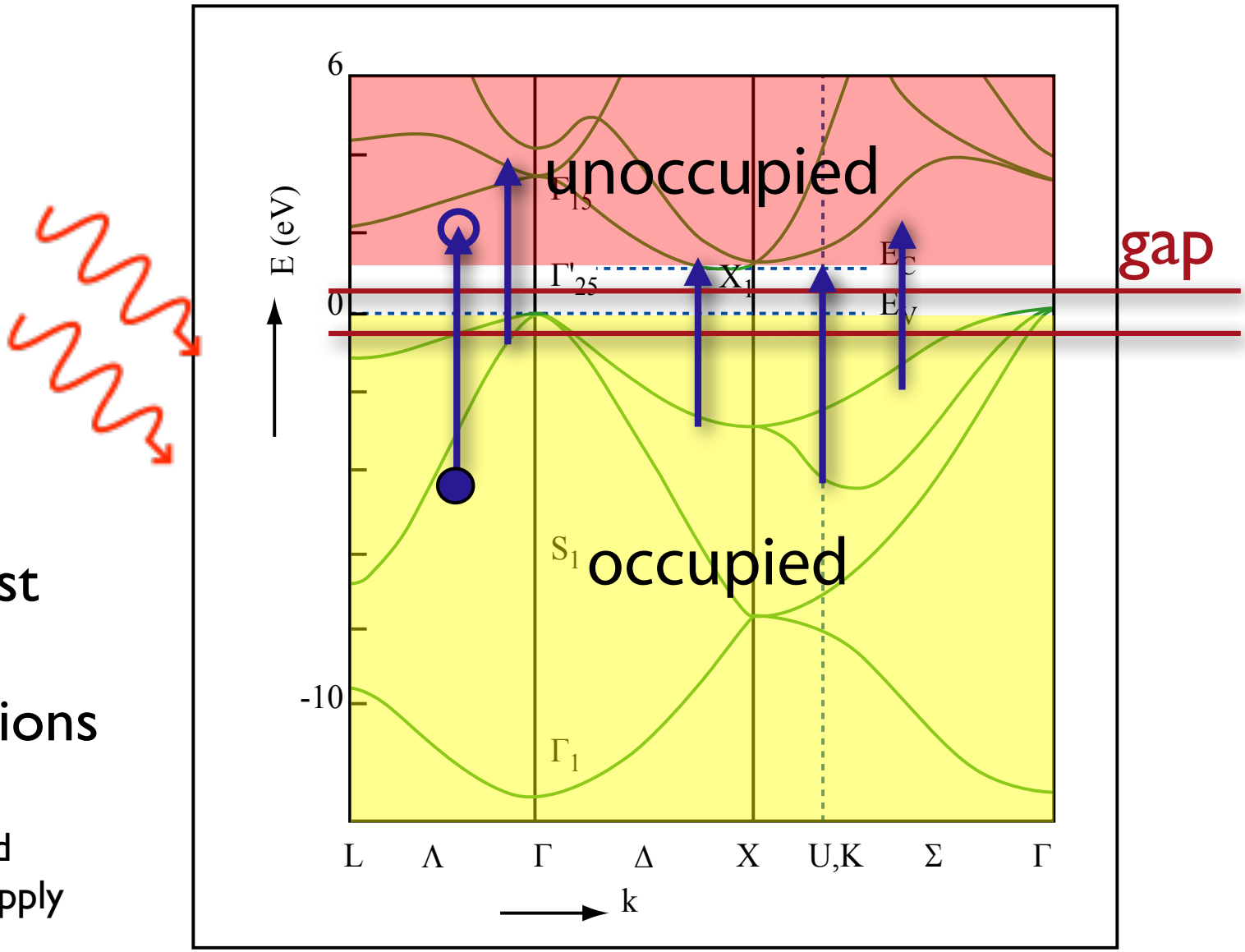


Fig. 3. Self-consistent APW energy band structure for $BaBiO_3$.

$BaBiO_3$: metal

Simple optical properties

E=hv



photon has almost
no momentum:
only vertical transitions
possible

energy conversation and
momentum conversation apply

Silicon Solar Cells Have to Be Thick ($$$)

It's all in the band-structure!

Please see graph at http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/illustr/si_banddiagram.gif.

Literature

- Charles Kittel, Introduction to Solid State Physics
- Ashcroft and Mermin, Solid State Physics
- wikipedia, “solid state physics”, “condensed matter physics”, ...

3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modeling and Simulation
Spring 2011