1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2012

Part II – Quantum Mechanical Methods : Lecture 7

Quantum Modeling of Solids: Basic Properties

Jeffrey C. Grossman

Department of Materials Science and Engineering
Massachusetts Institute of Technology

Part II Topics

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. Application of Quantum Modeling of Molecules: Solar Thermal Fuels
5. Application of Quantum Modeling of Molecules: Hydrogen Storage
6. From Atoms to Solids
7. Quantum Modeling of Solids: Basic Properties
8. Advanced Prop. of Materials: What else can we do?
9. Application of Quantum Modeling of Solids: Solar Cells Part I
10. Application of Quantum Modeling of Solids: Solar Cells Part II
11. Application of Quantum Modeling of Solids: Nanotechnology

"The purpose of computing is insight, not numbers."

Richard Hamming

"What are the most important problems in your field? Are you working on one of them? Why not?"

"It is better to solve the right problem the wrong way than to solve the wrong problem the right way."

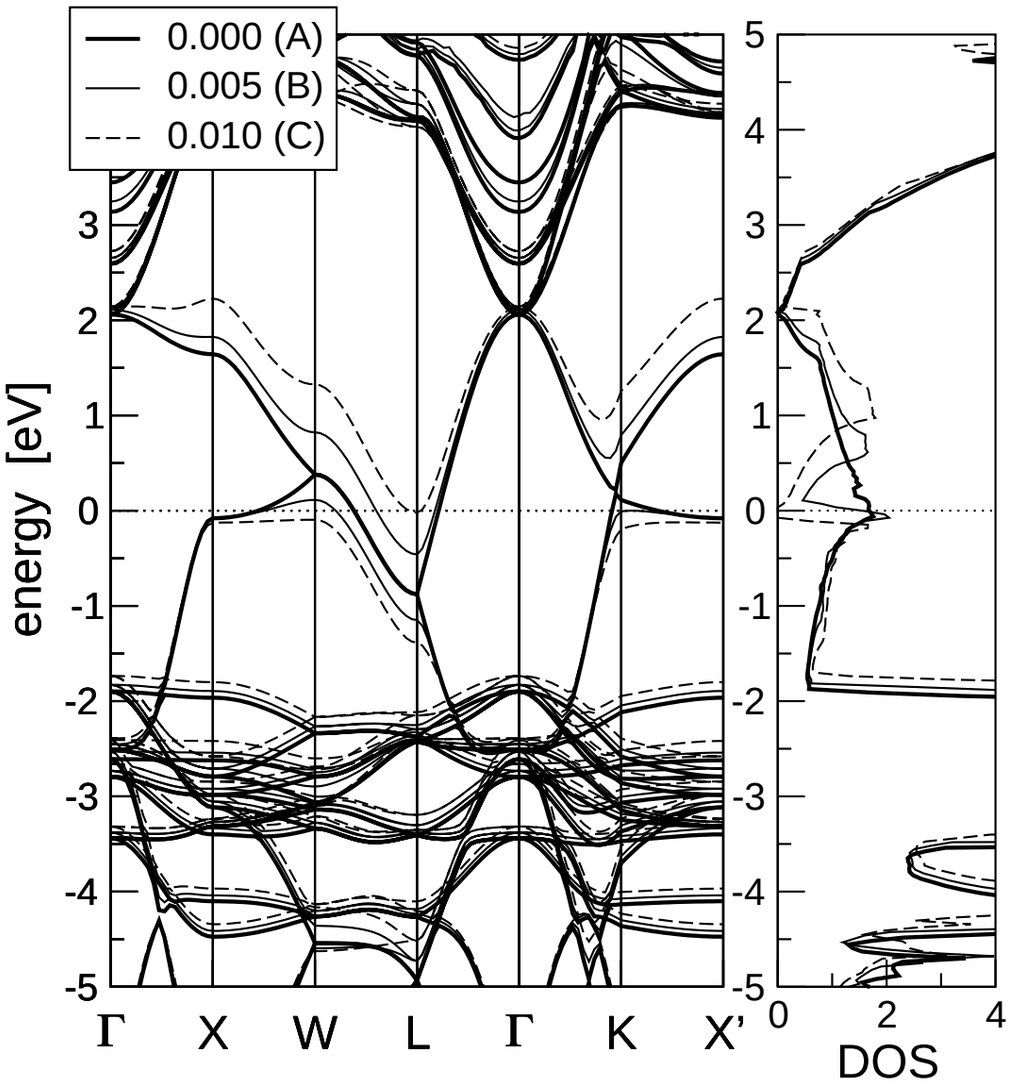
"In research, if you know what you are doing, then you shouldn't be doing it."

"Machines should work. People should think."

...and related: "With great power comes great responsibility." (Spiderman's Uncle)

Lesson outline

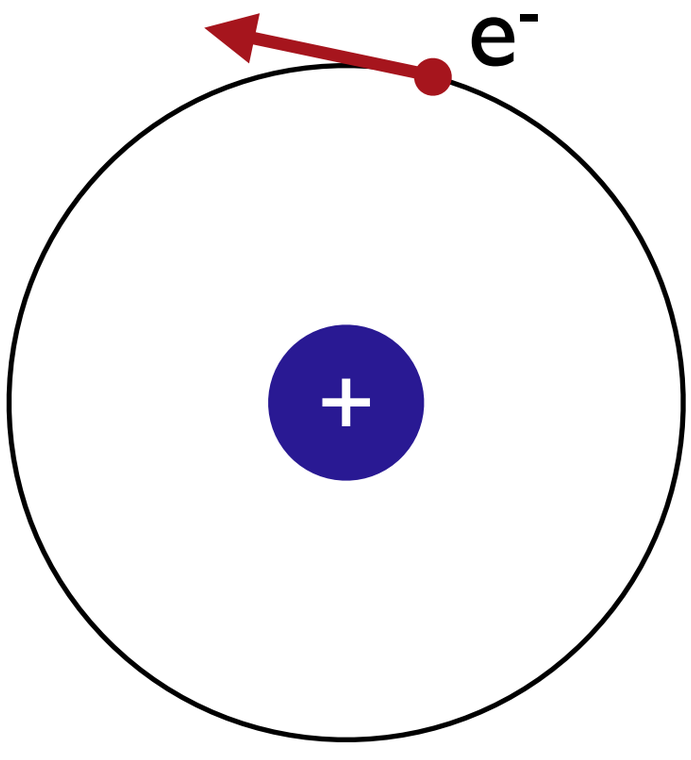
- Review
- structural properties
- Band Structure
- DOS
- Metal/insulator
- Magnetization

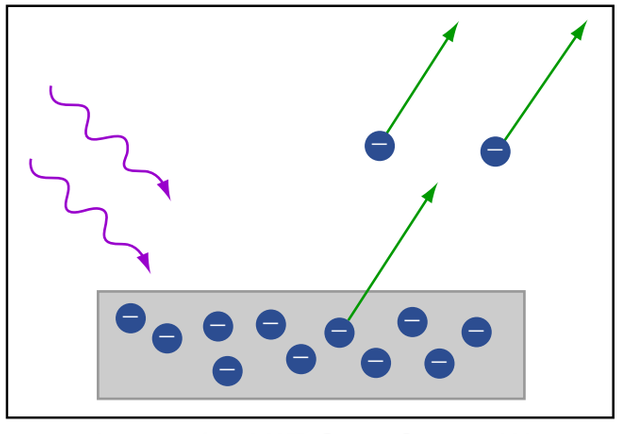


Let's take a walk through memory lane for a moment...

In the Beginning....

There were some strange observations by some very smart people.





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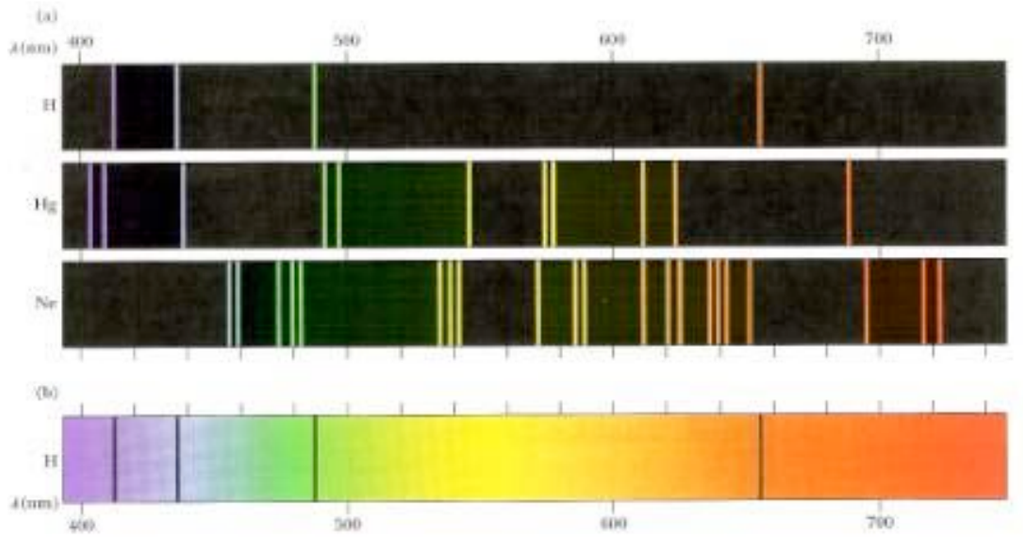
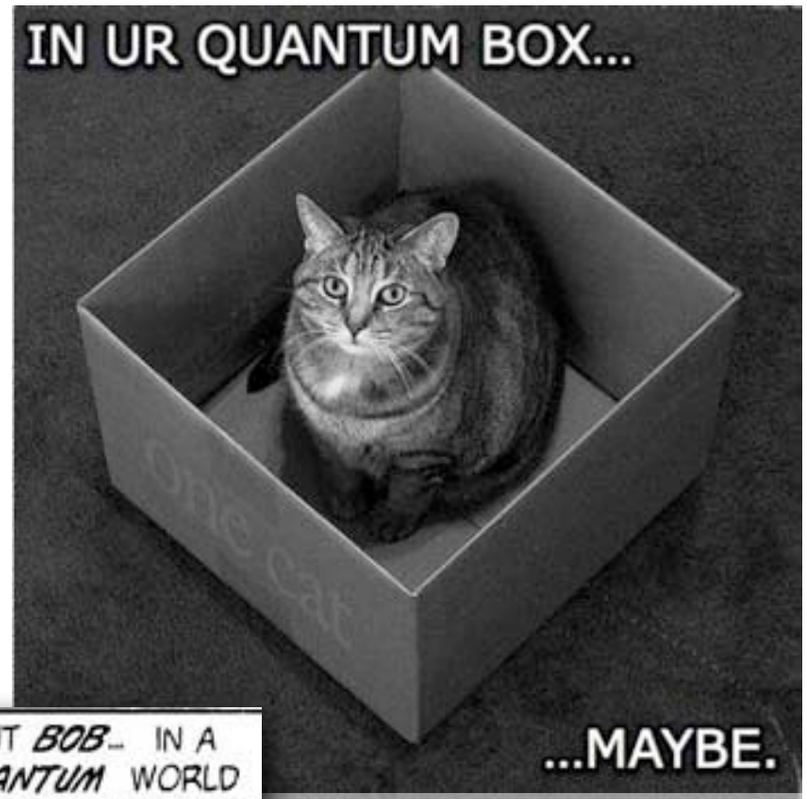


In the Beginning....

The weirdness just kept going.



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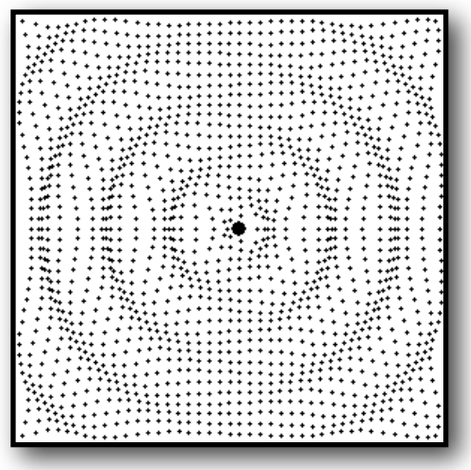
It Became Clear...

...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

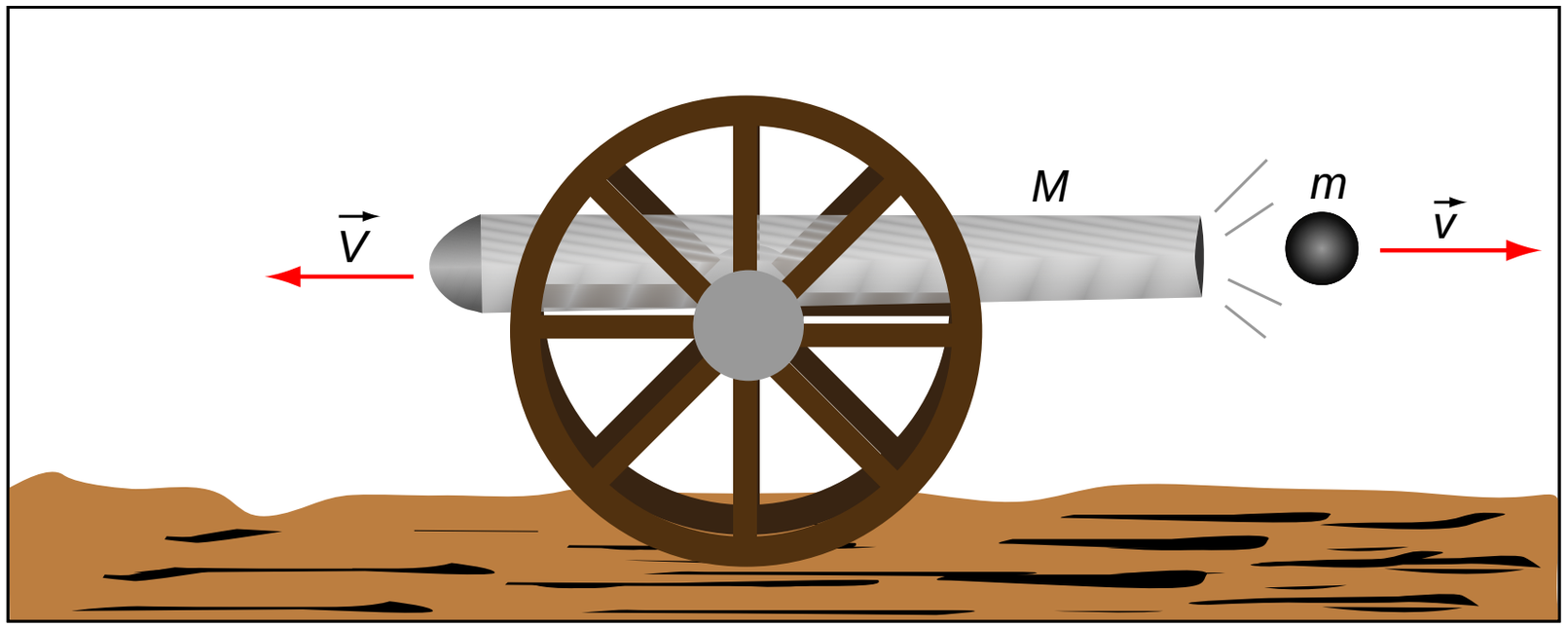
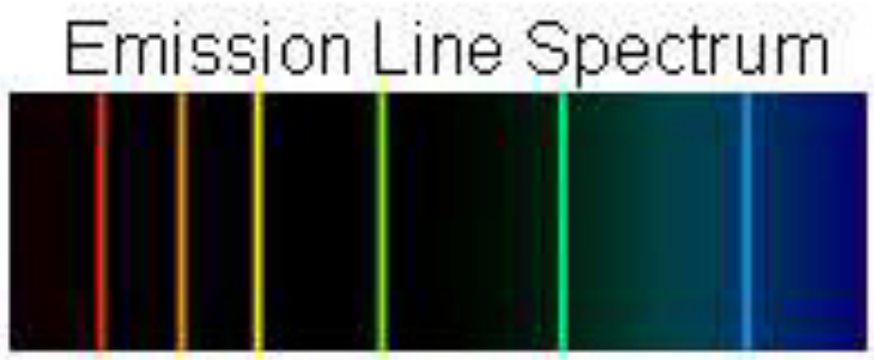


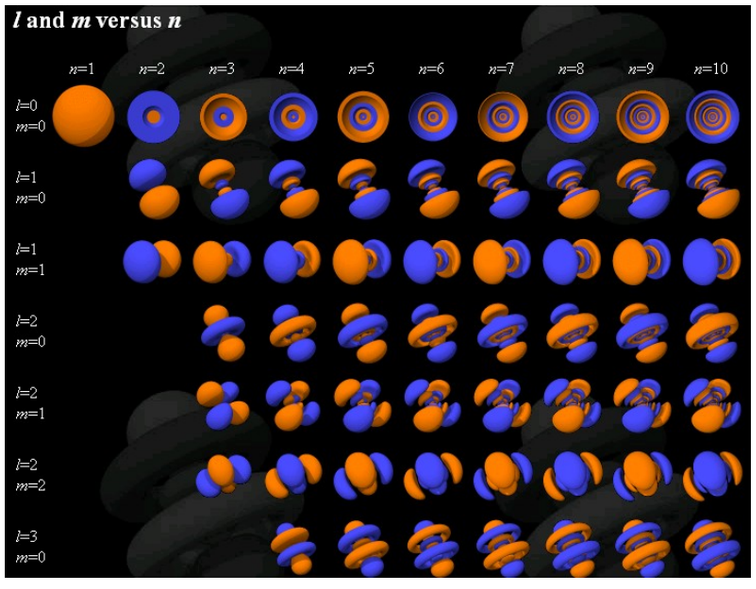
Image by MIT OpenCourseWare.

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

It Was Wonderful

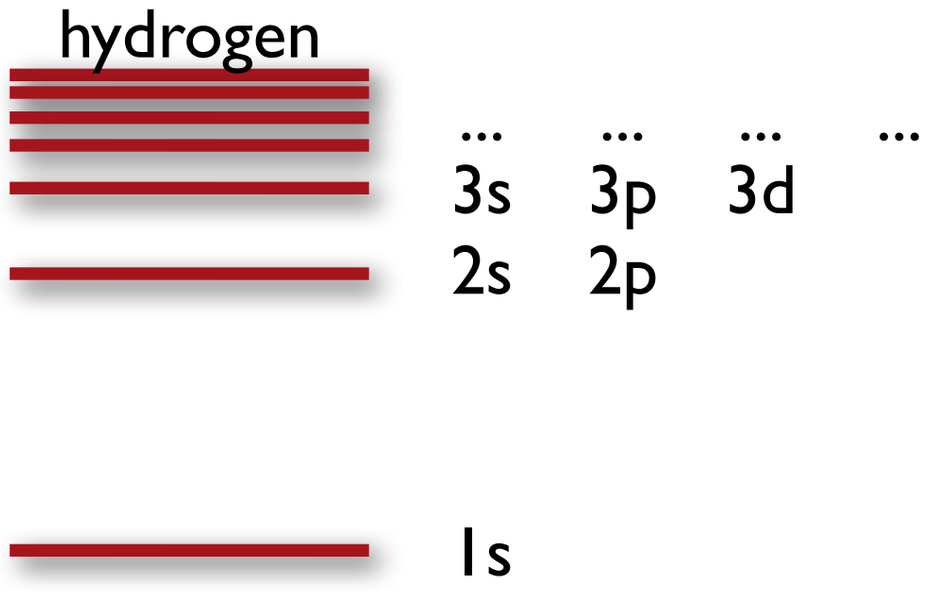
It explained many things.





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

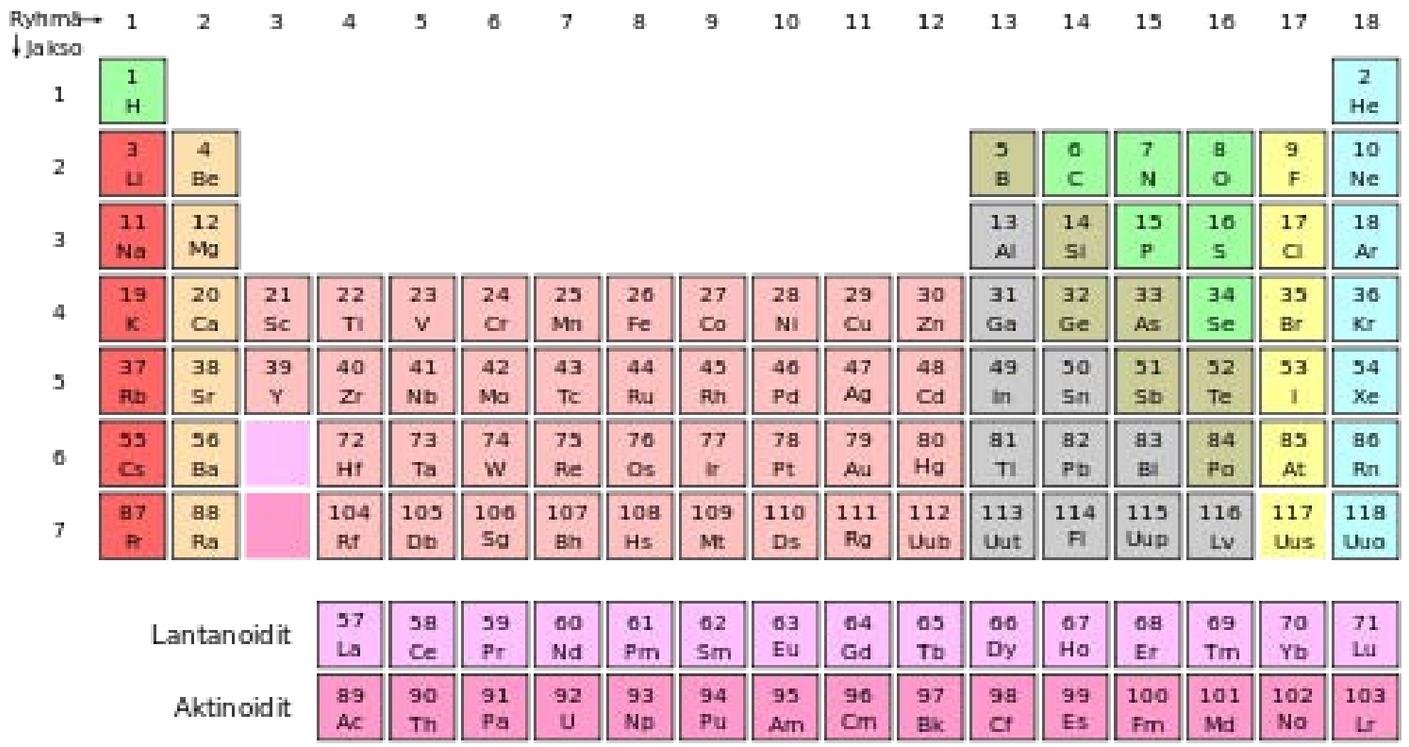
It gave us atomic orbitals.



It predicted the energy levels in hydrogen.

It Was Wonderful

It gave us the means to understand much of chemistry.



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BUT...

Nature Does > 1 electron!

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

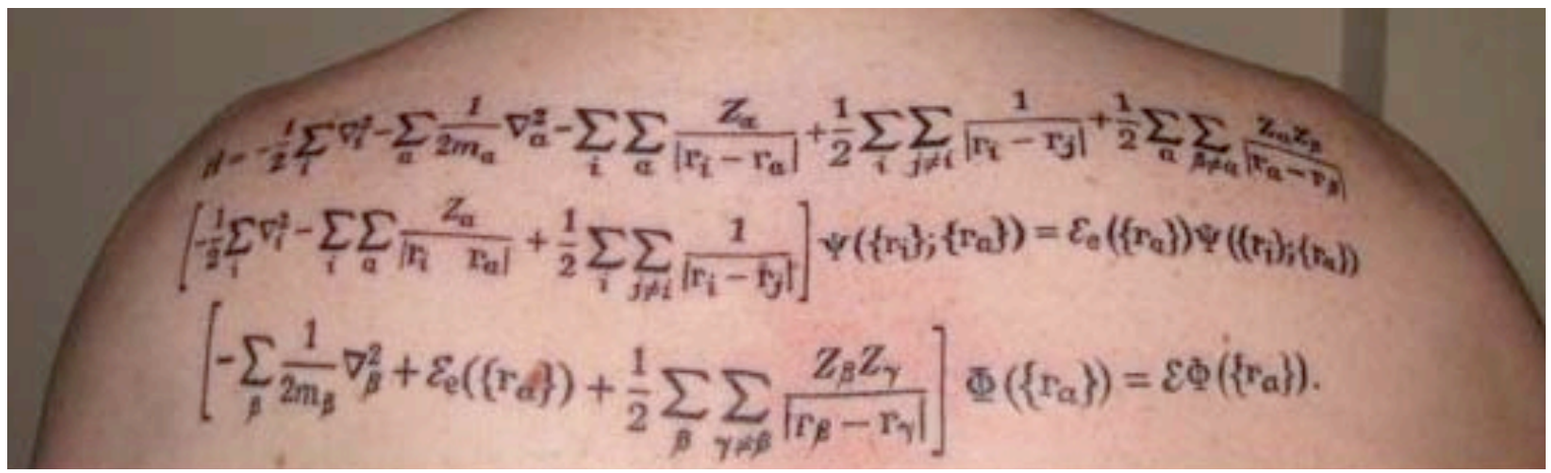
Enter computational quantum mechanics!

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.



And started making some approximations.

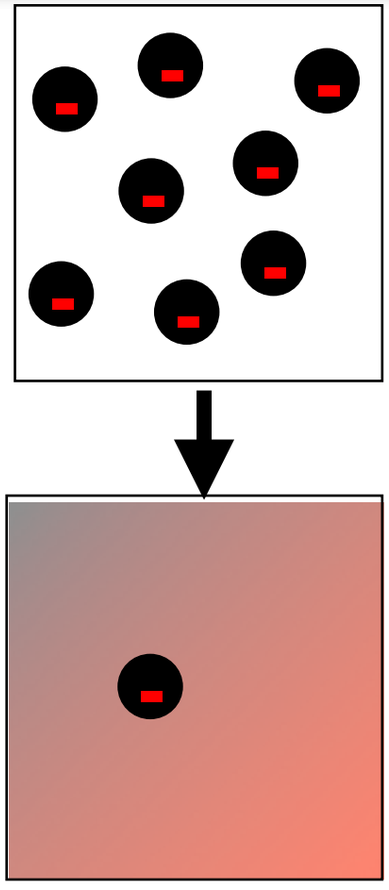
The Two Paths

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

Walter Kohn

Working with the Density

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

kinetic ion-ion ion-electron electron-electron

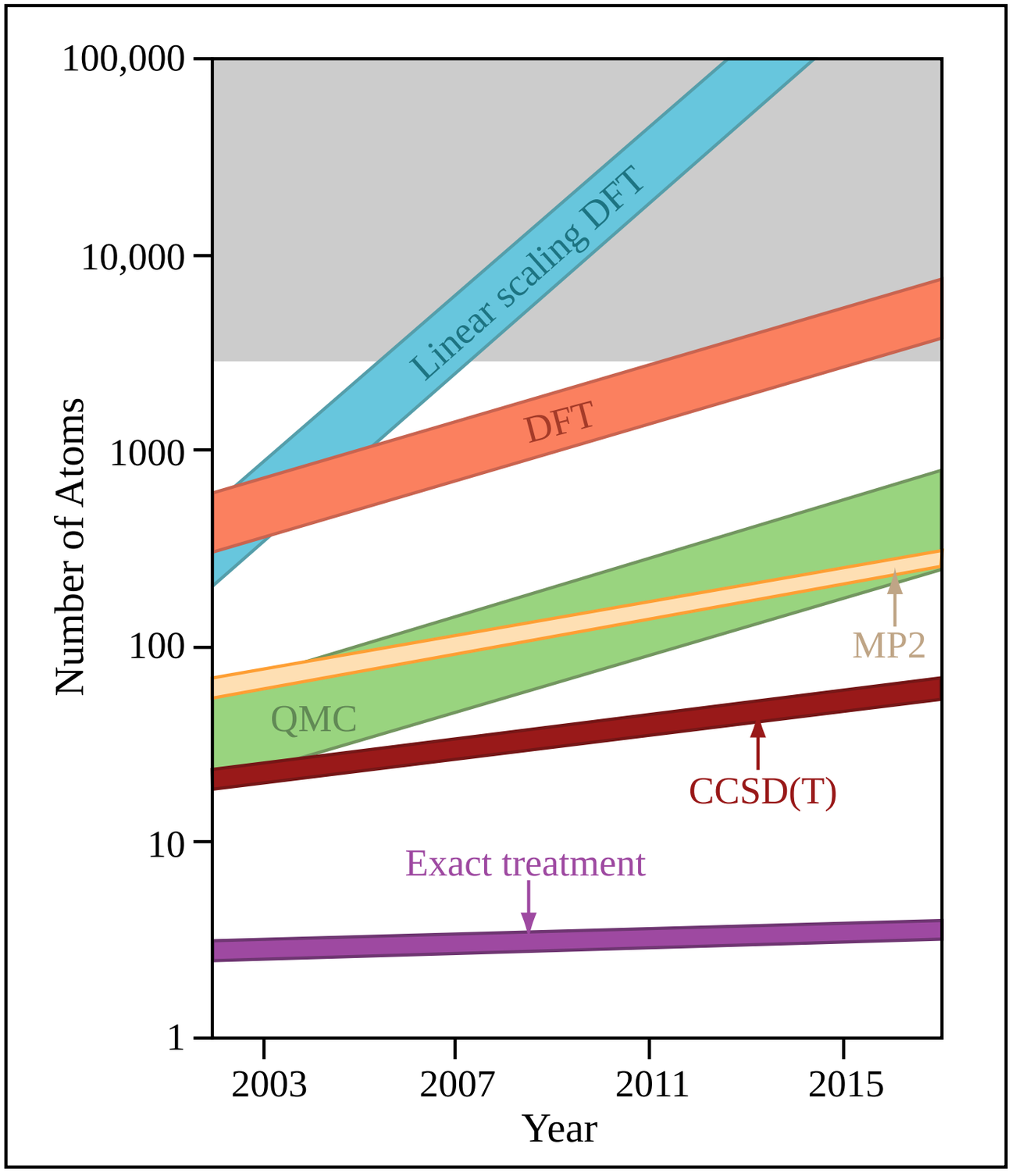
n=#	$\Psi(N^{3n})$	$\rho(N^3)$
1	8	8
10	10^9	8
100	10^{90}	8
1,000	10^{900}	8

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

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

ion potential Hartree potential exchange-correlation potential

Review: Why DFT?



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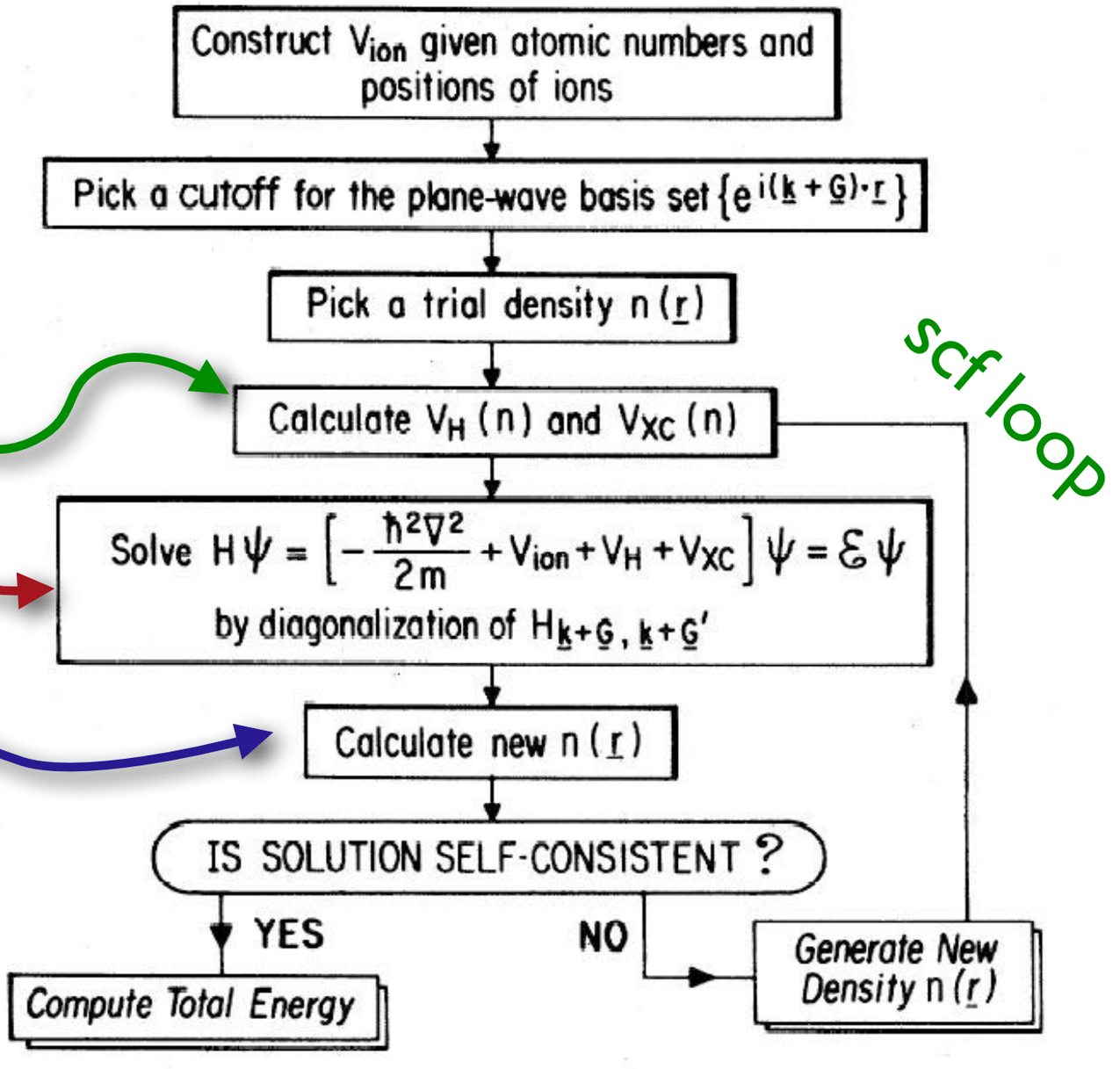
Review: Self-consistent cycle

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

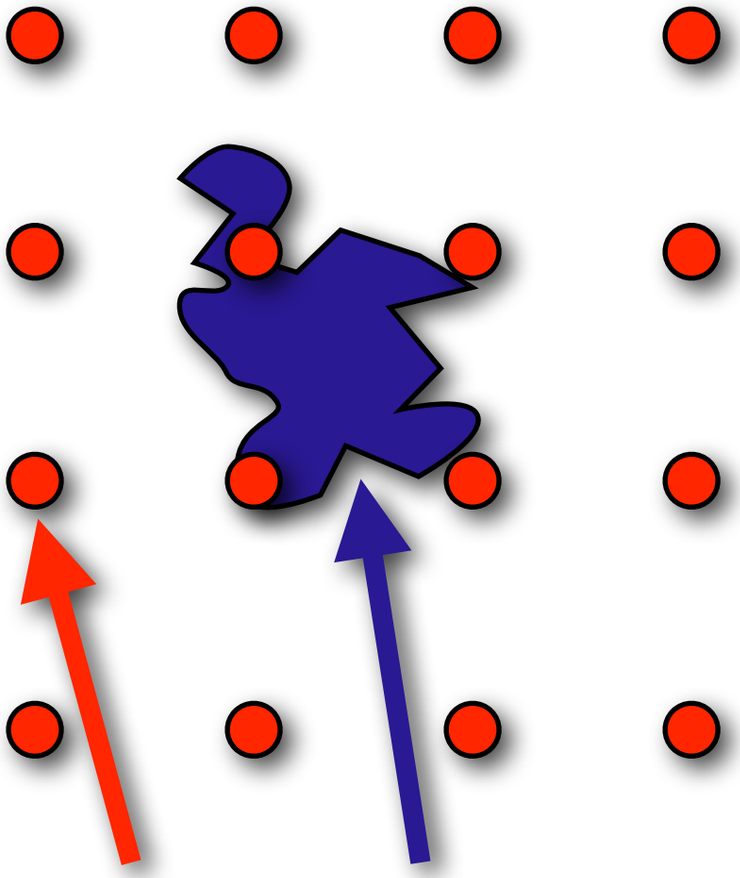


Image of Sketch 96 (Swans) by M.C. Escher removed due to copyright restrictions.

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

Review: Crystal symmetries

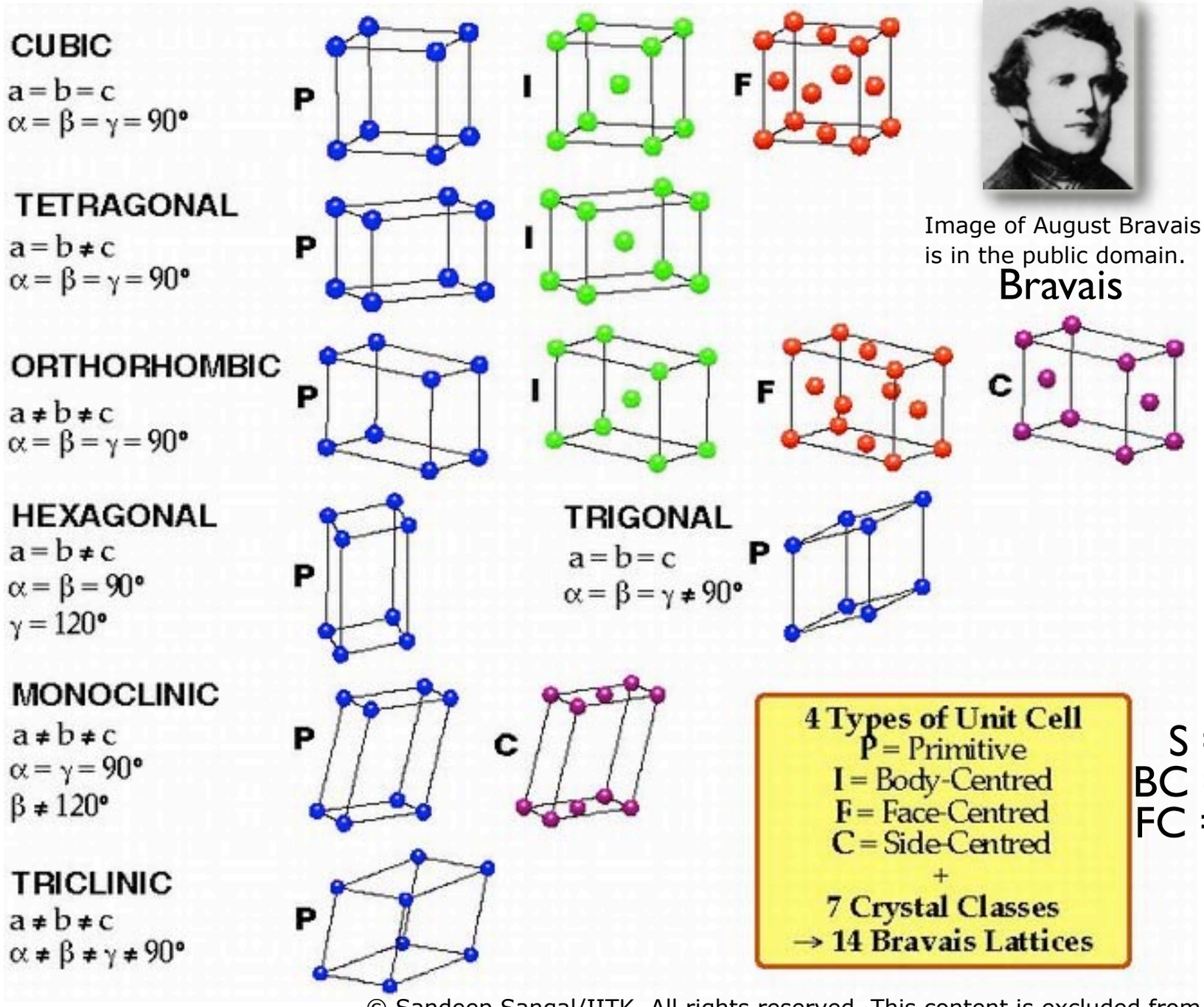


Image of August Bravais is in the public domain.

Bravais

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

...why?

S = simple
BC = body centered
FC = face centered

Reciprocal Lattice & Brillouin Zone

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

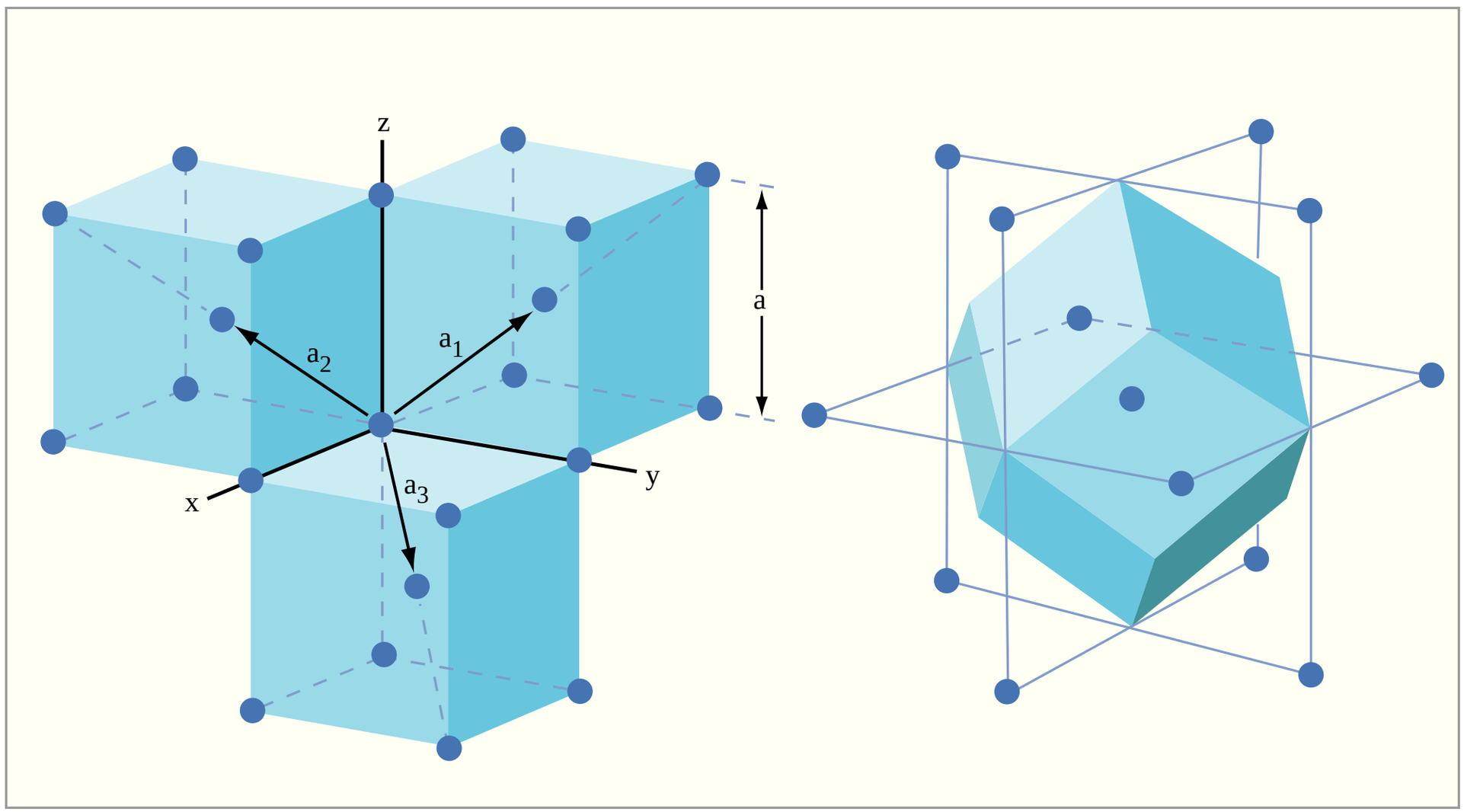
The reciprocal lattice is the set of wave-vectors which are commensurate with the real space lattice.
Sometimes we like to call it "G".

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.

Review: The inverse lattice

real space lattice (BCC)

inverse lattice (FCC)



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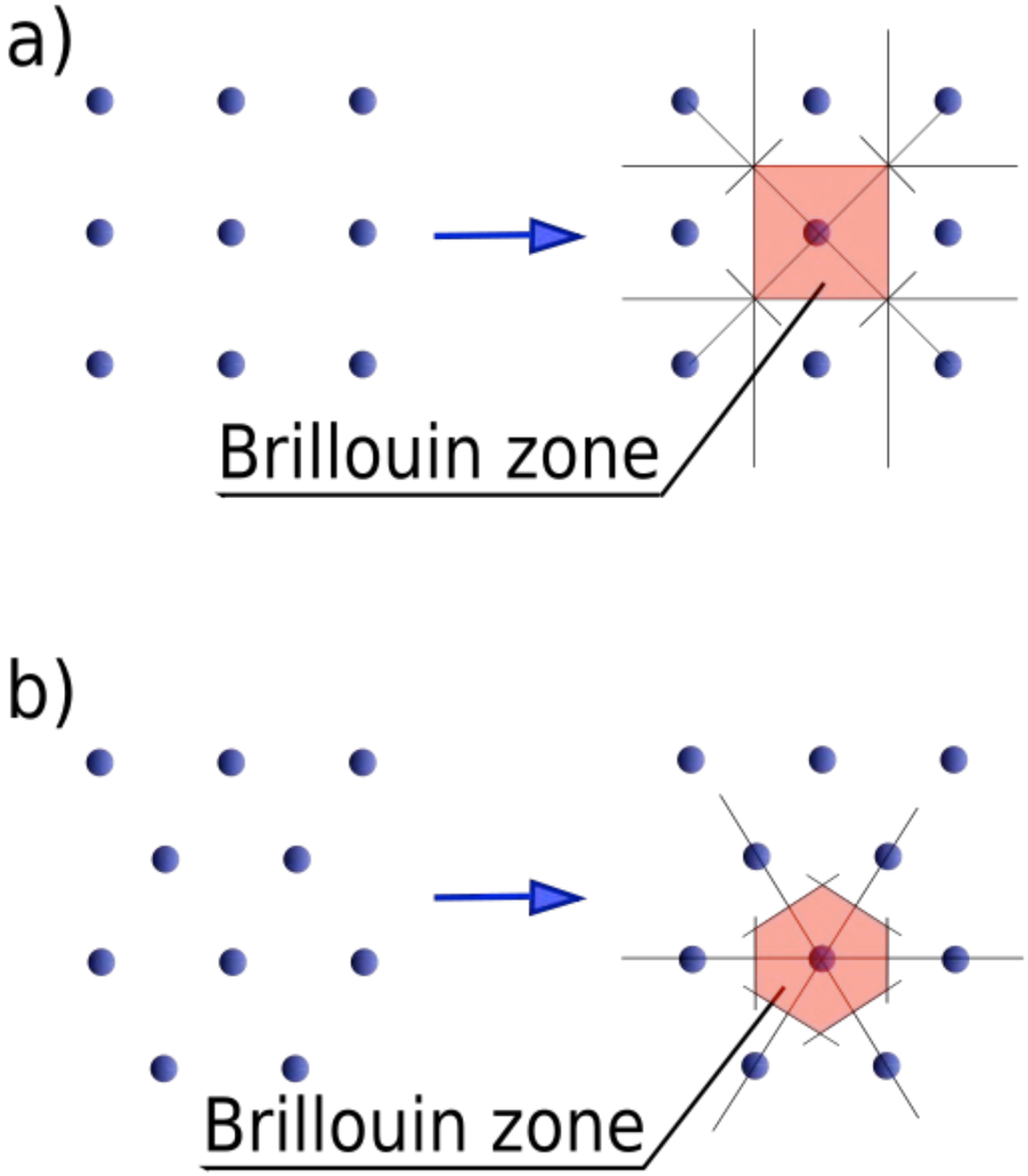
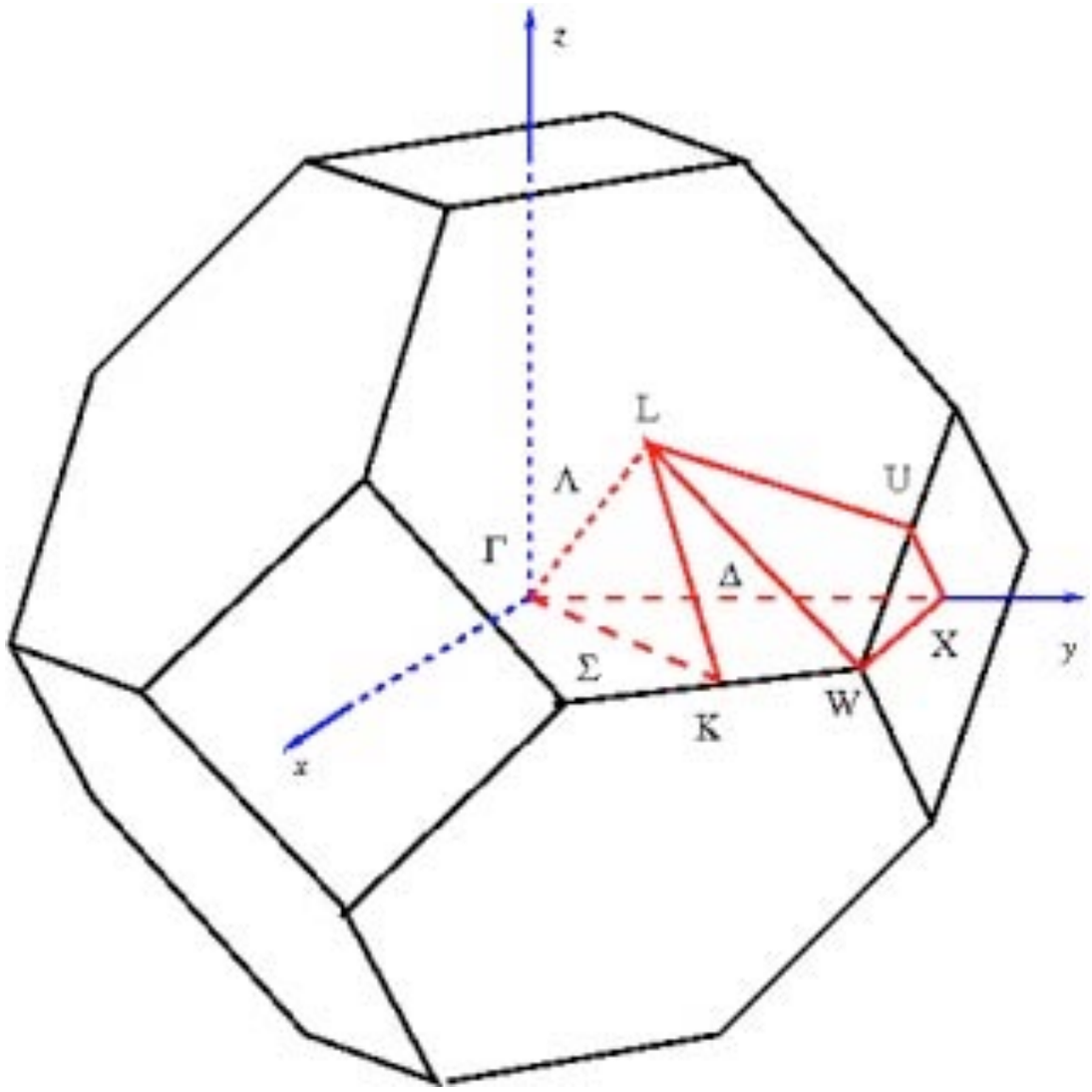
The Brillouin zone

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

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 → $\psi_{n,l,m}(\vec{r})$

$$[H, L^2] = HL^2 - L^2H = 0$$

$$[H, L_z] = 0$$

periodic solid → translational symmetry → $\psi_{n,\vec{k}}(\vec{r})$

$$[H, T] = 0$$

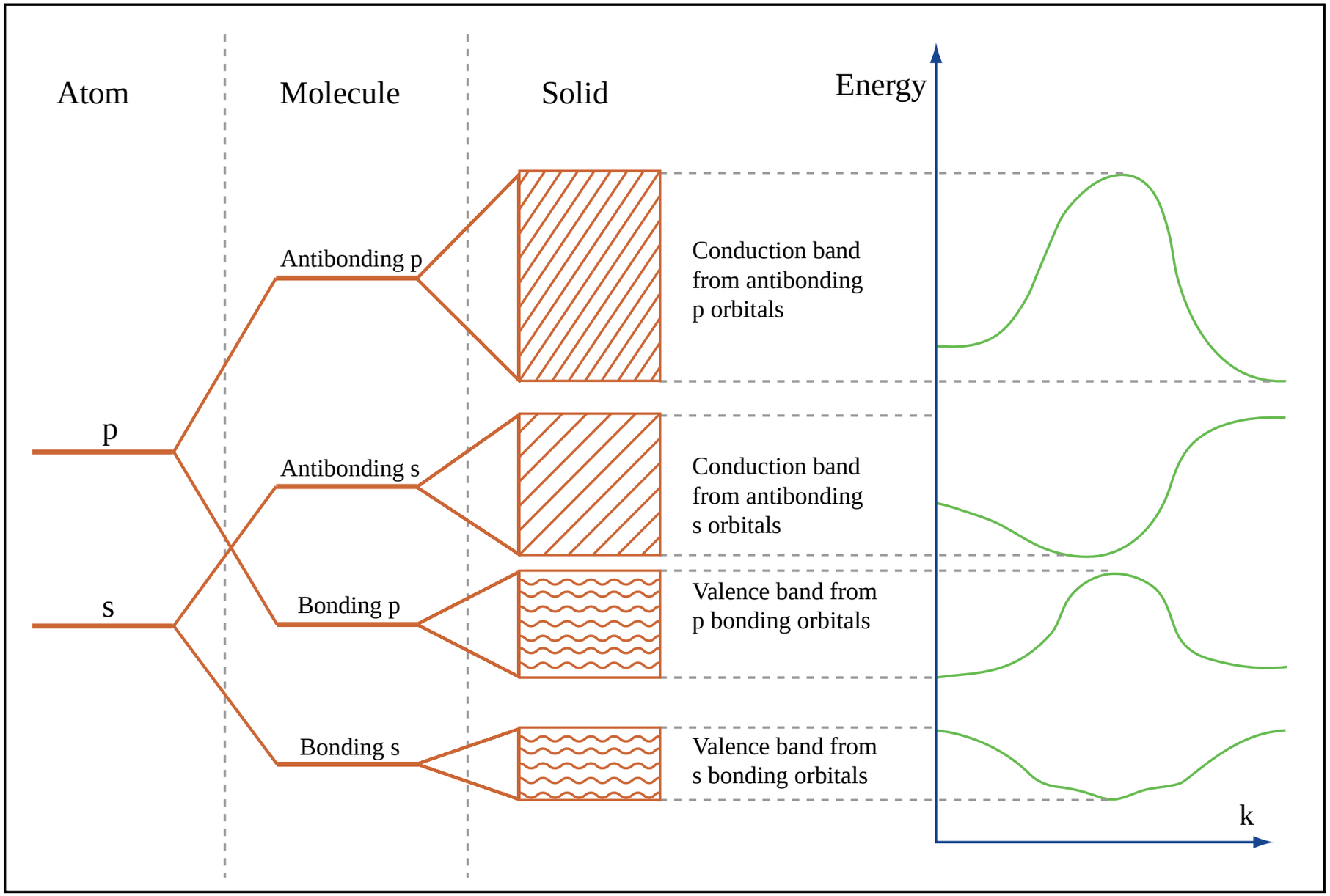
Origin of band structure

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

From atoms to bands



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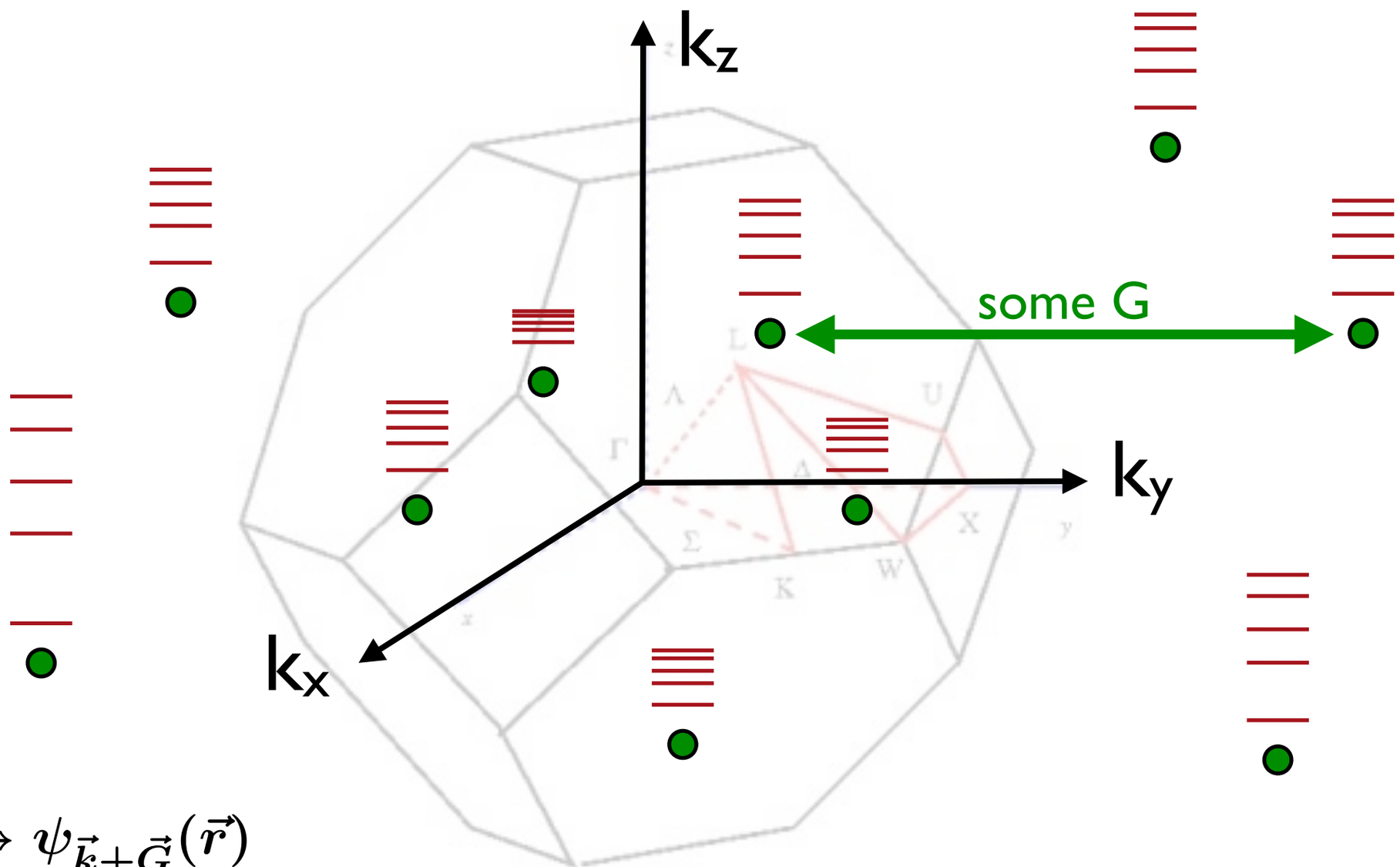
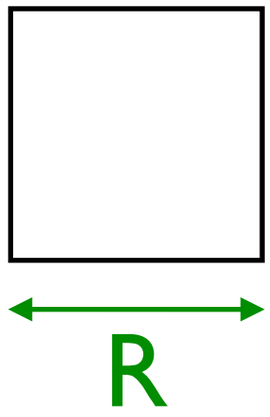
The inverse lattice



$$\psi_{\vec{k}}(\vec{r}) \quad \rightarrow \psi_{\vec{k}+\vec{G}}(\vec{r})$$

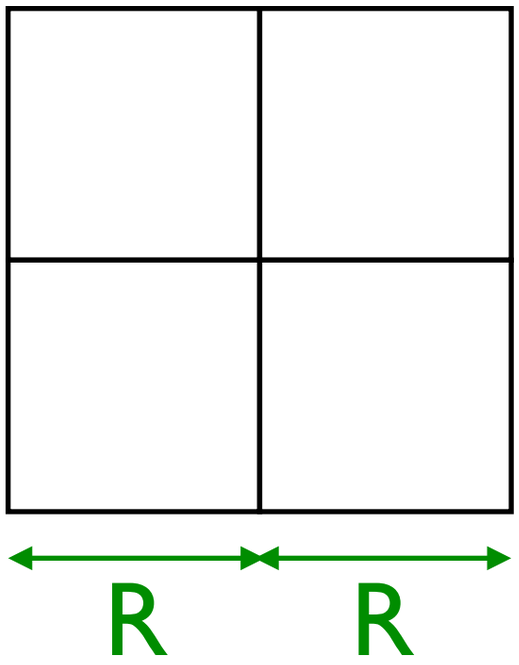
$$E_{\vec{k}} = E_{\vec{k}+\vec{G}}$$

The inverse lattice



$$\psi_0(\vec{r} + \vec{R}) = \psi_0(\vec{r})$$

periodic over unit cell

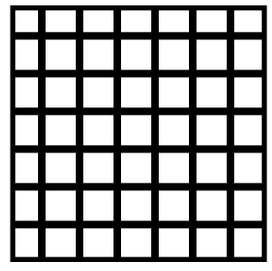


$$\psi_{\vec{G}/2}(\vec{r} + 2\vec{R}) = \psi_{\vec{G}/2}(\vec{r})$$

periodic over larger domain

The inverse lattice

choose certain
k-mesh e.g. 8x8x8
N=512



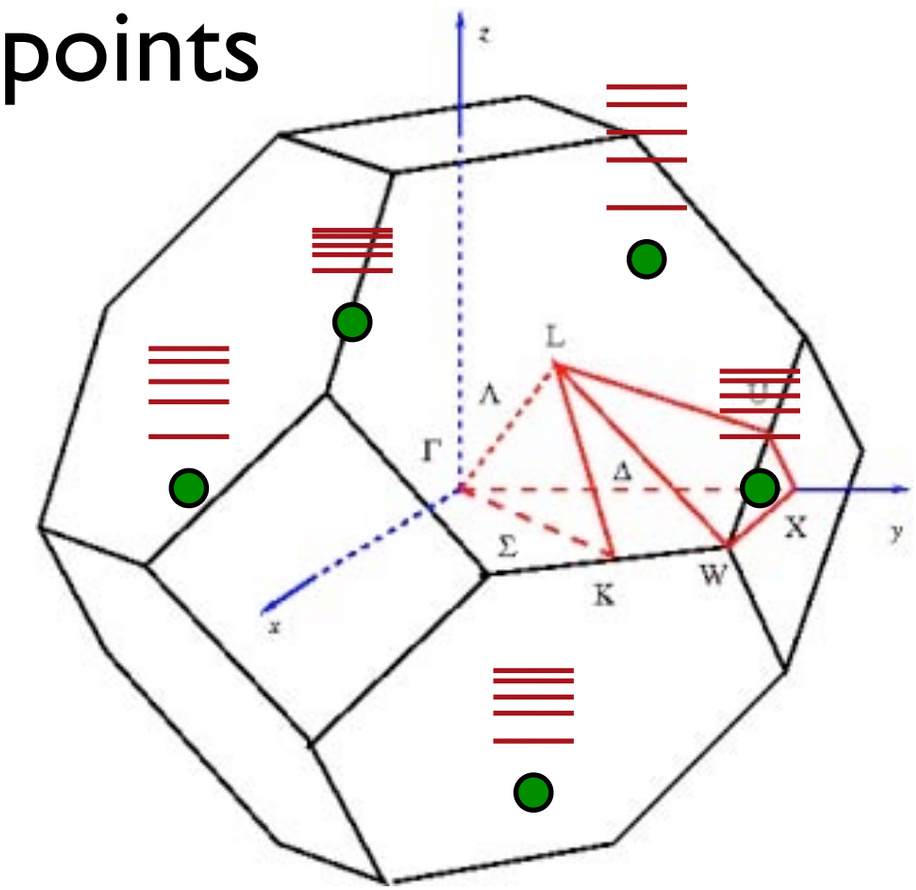
number of
k-points (N)

unit cells in
the periodic
domain (N)

The inverse lattice

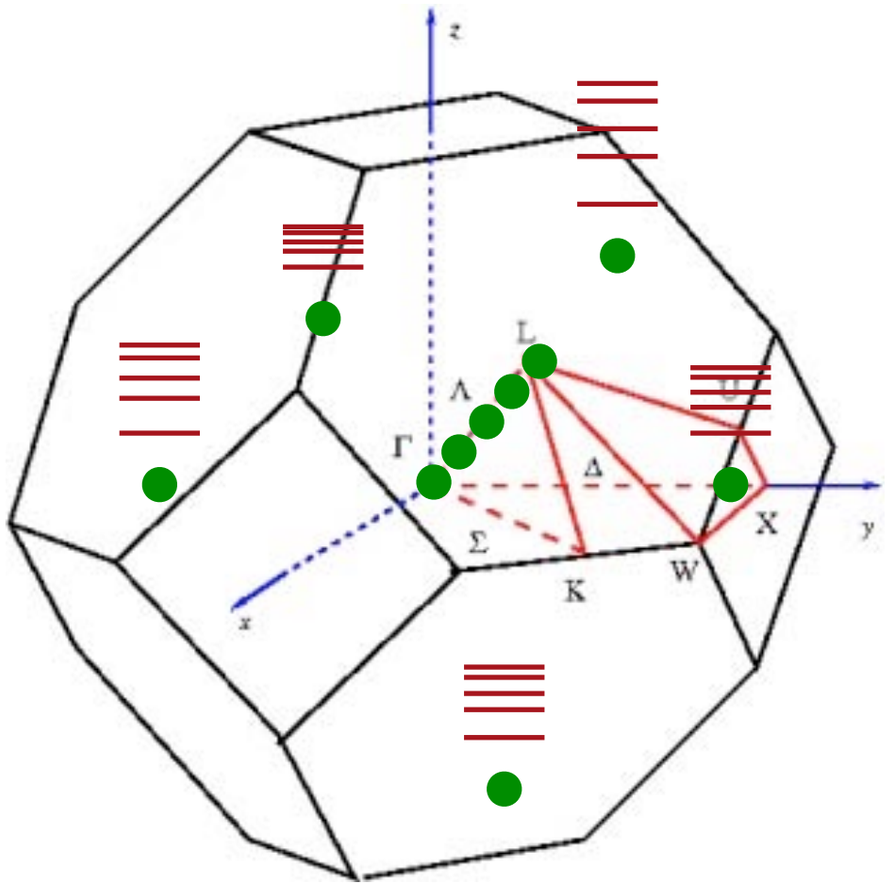
Distribute all electrons over the lowest states.

N k-points



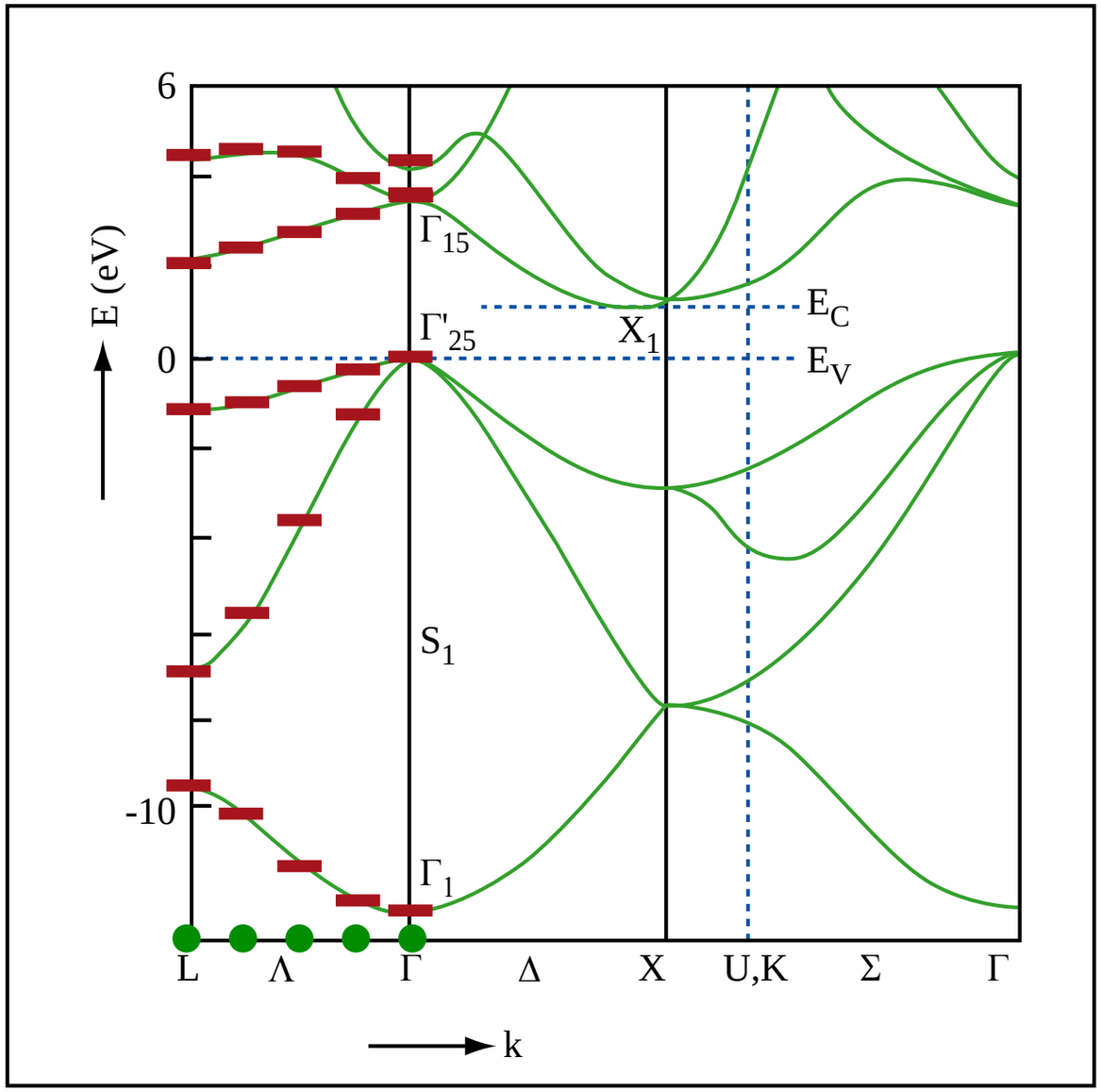
You have
(electrons per unit cell)*N
electrons to distribute!

The band structure



- energy levels in the Brillouin zone
- k is a continuous variable

Silicon



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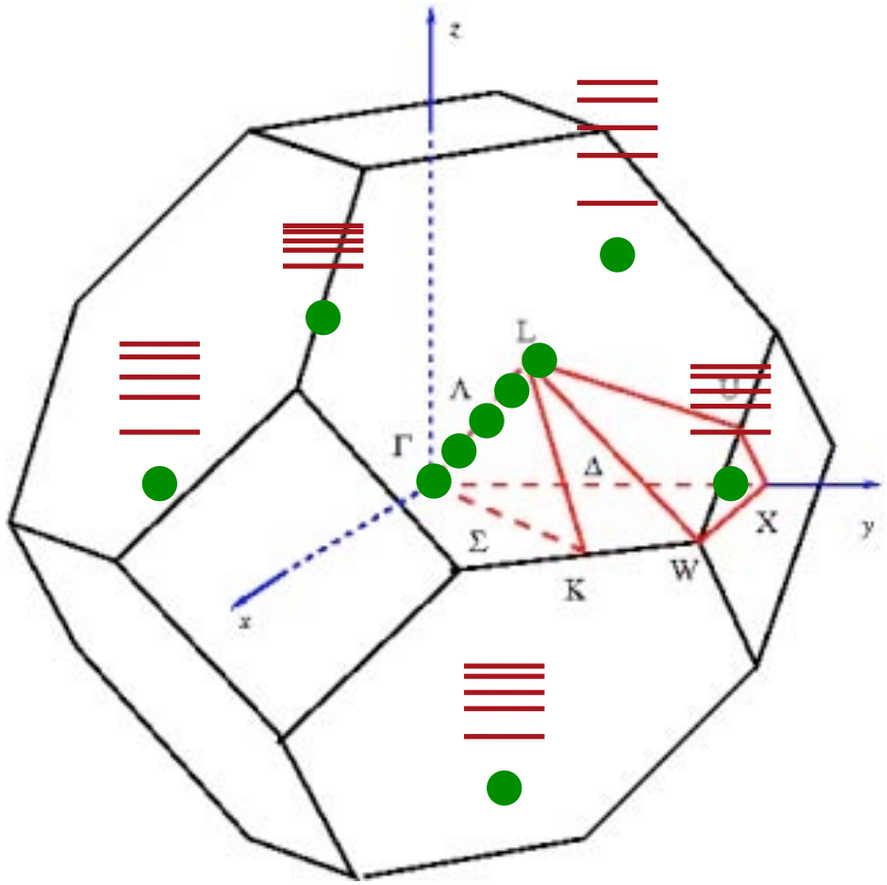
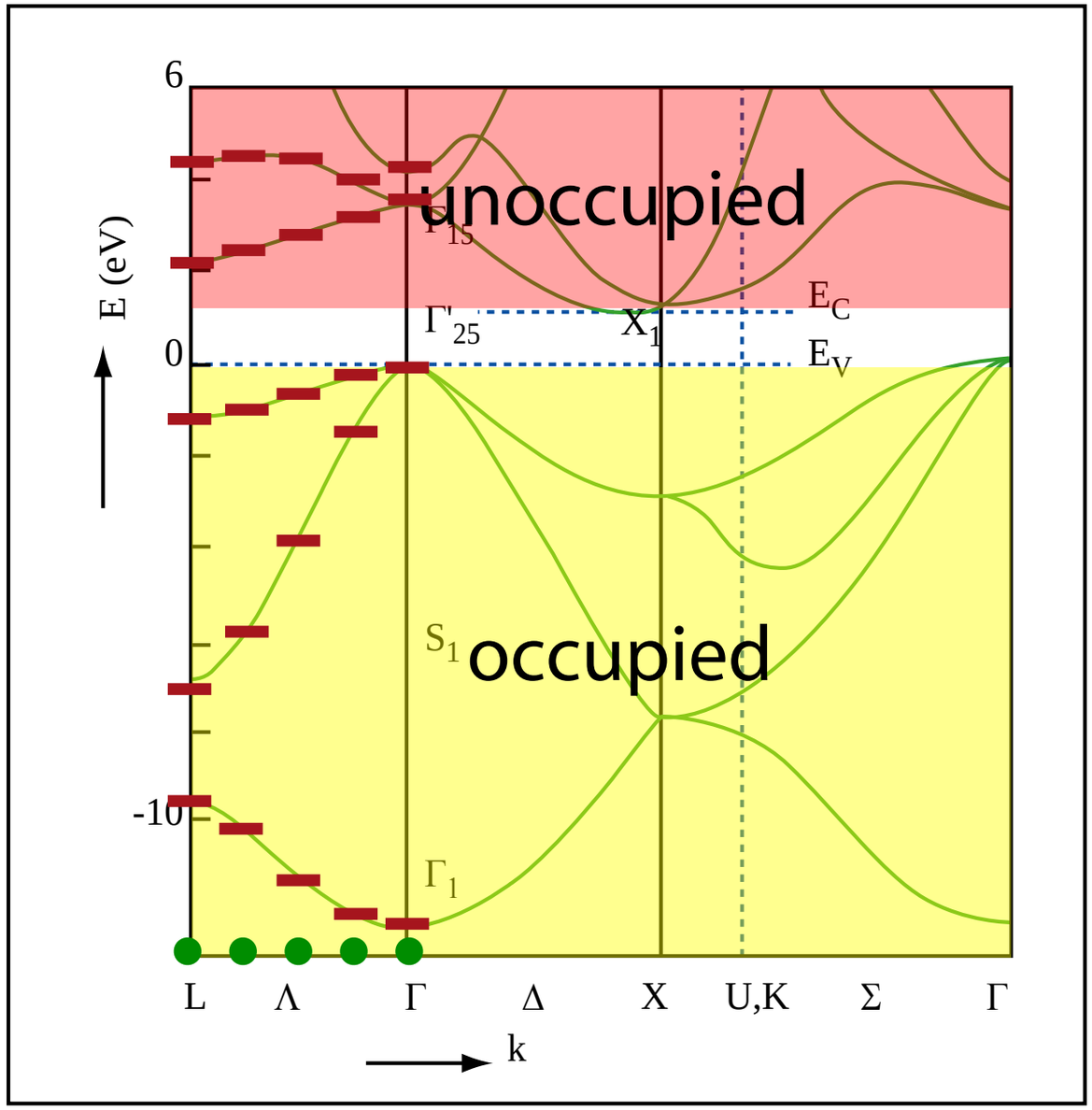
The band structure



- energy levels in the Brillouin zone
- k is a continuous variable

Silicon



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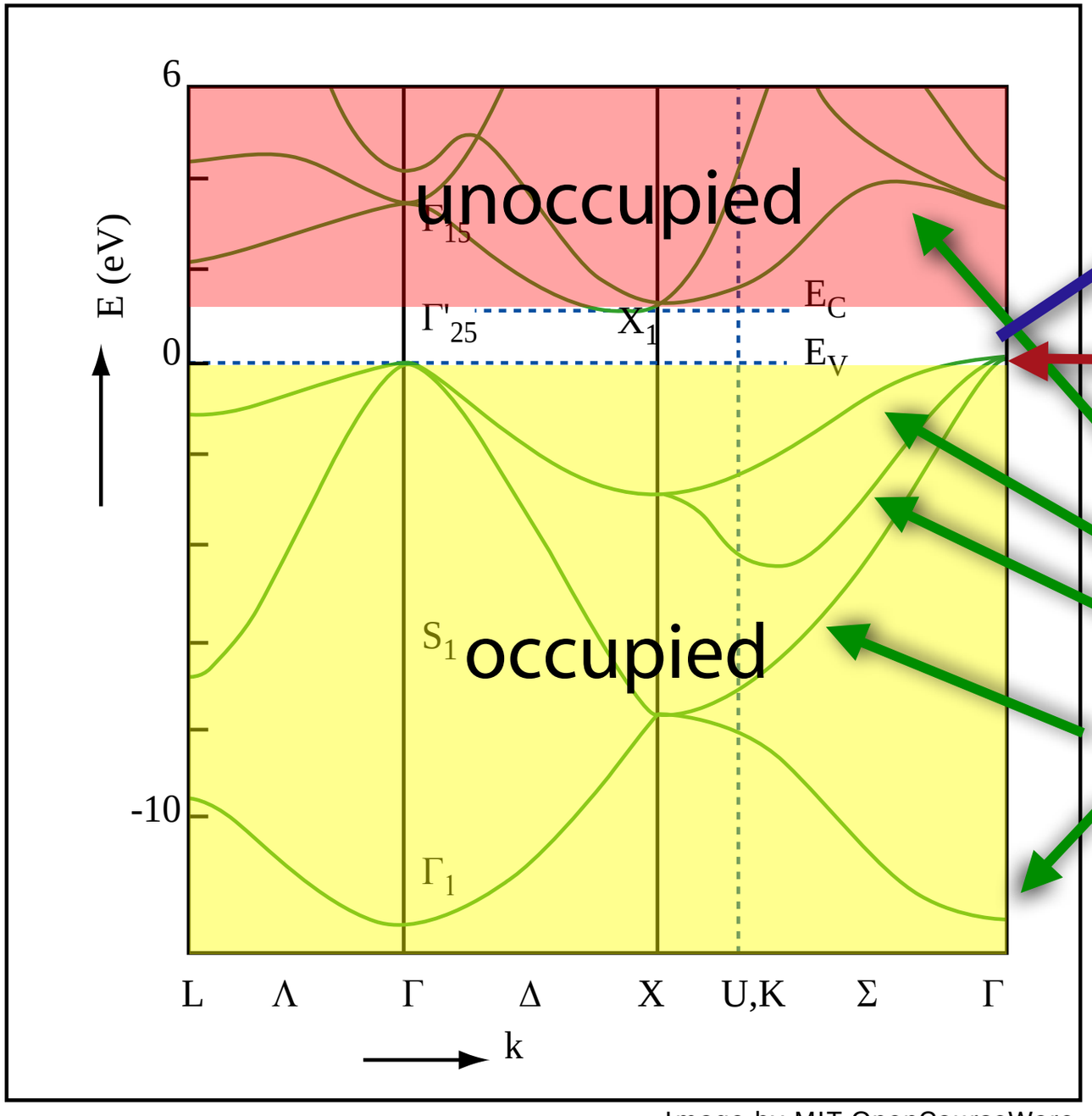
The Fermi energy



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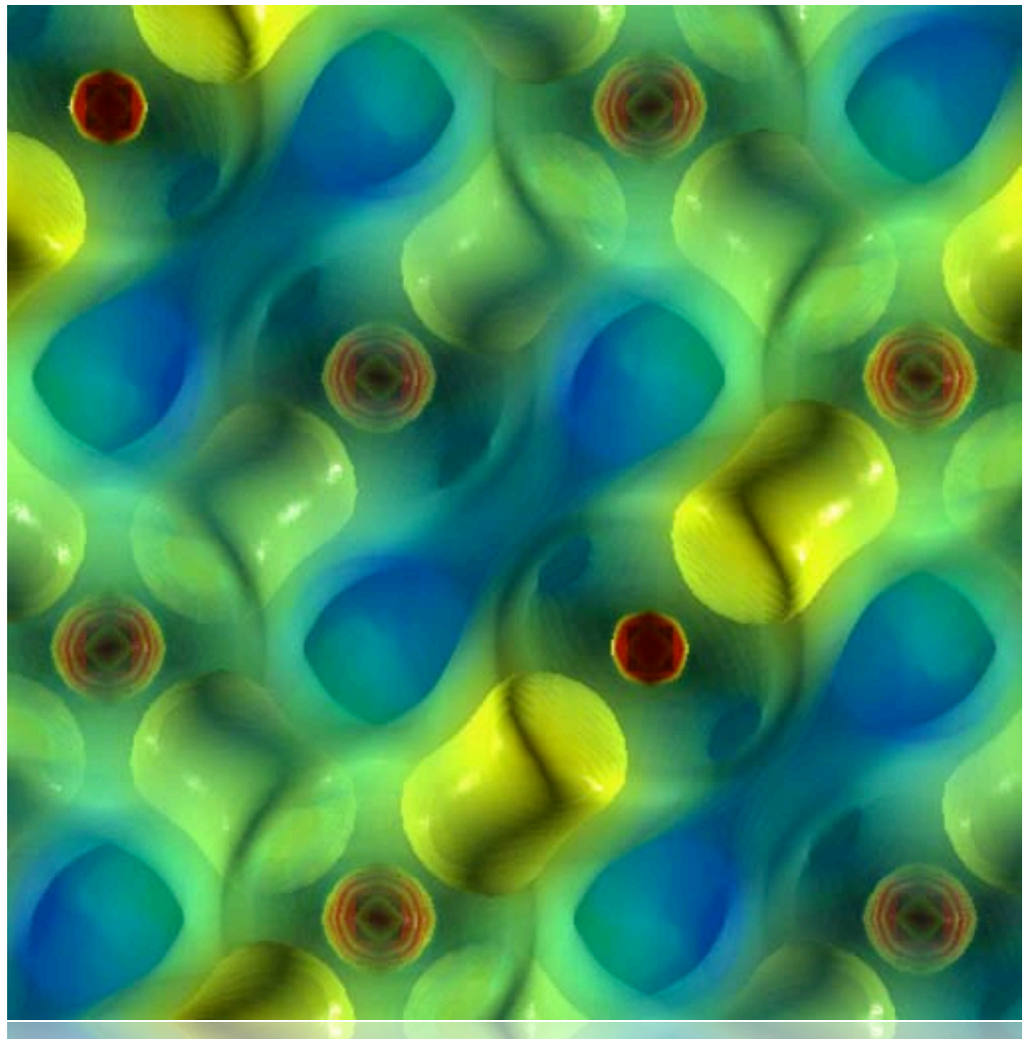
gap: also visible in the DOS

Fermi energy

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

The electron density

electron density of silicon



Structural properties

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

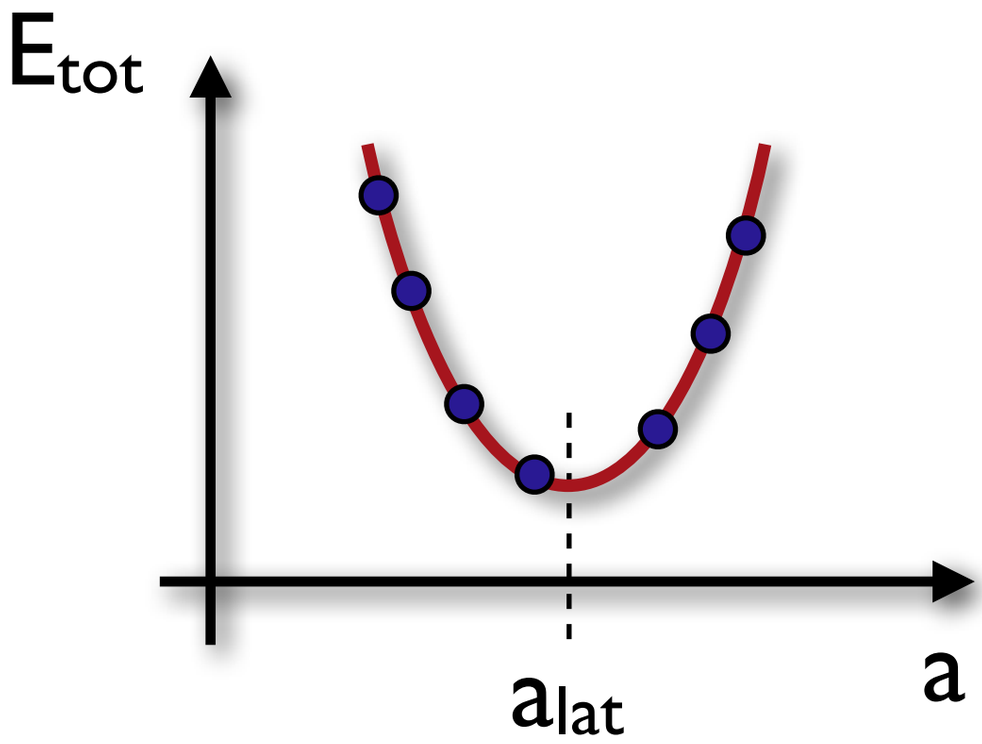
$$\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau$$

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

Forces automatically in most codes.

Structural properties

finding the
equilibrium
lattice constant

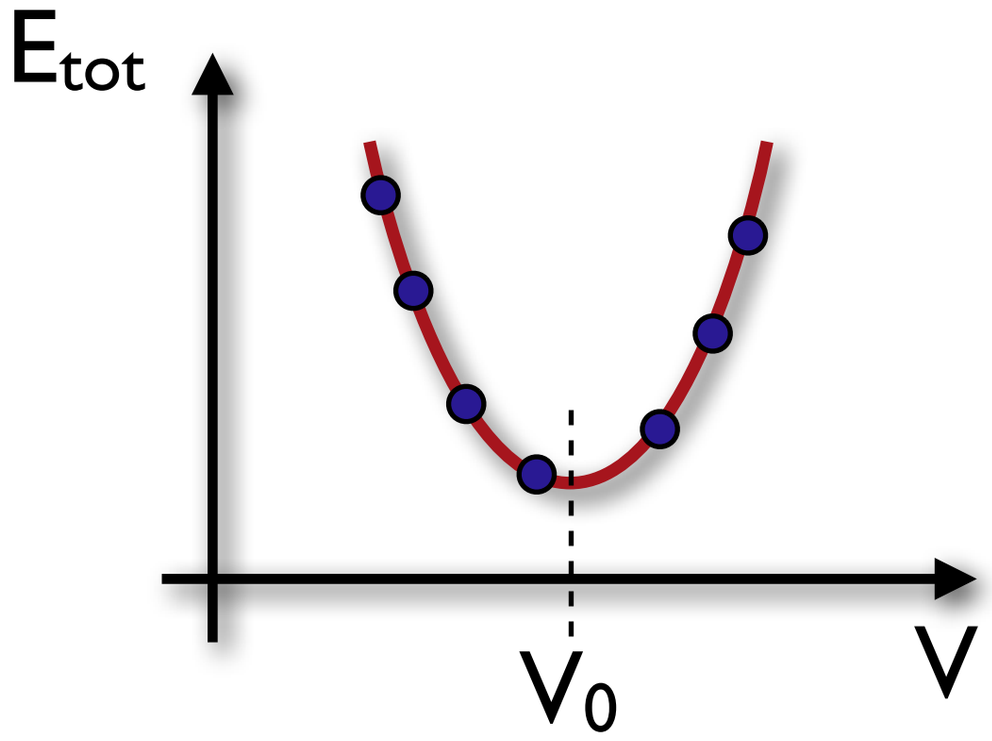


mass density

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

Structural properties

finding the stress/pressure and the bulk modulus



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

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

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

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

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

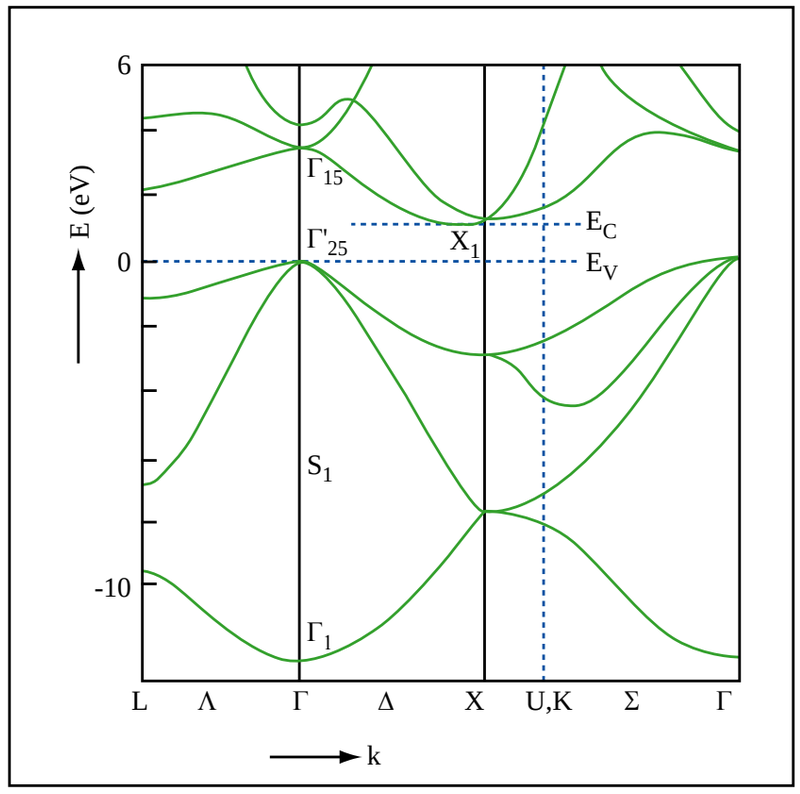


Image by MIT OpenCourseWare.

Calculating the DOS

3-step procedure

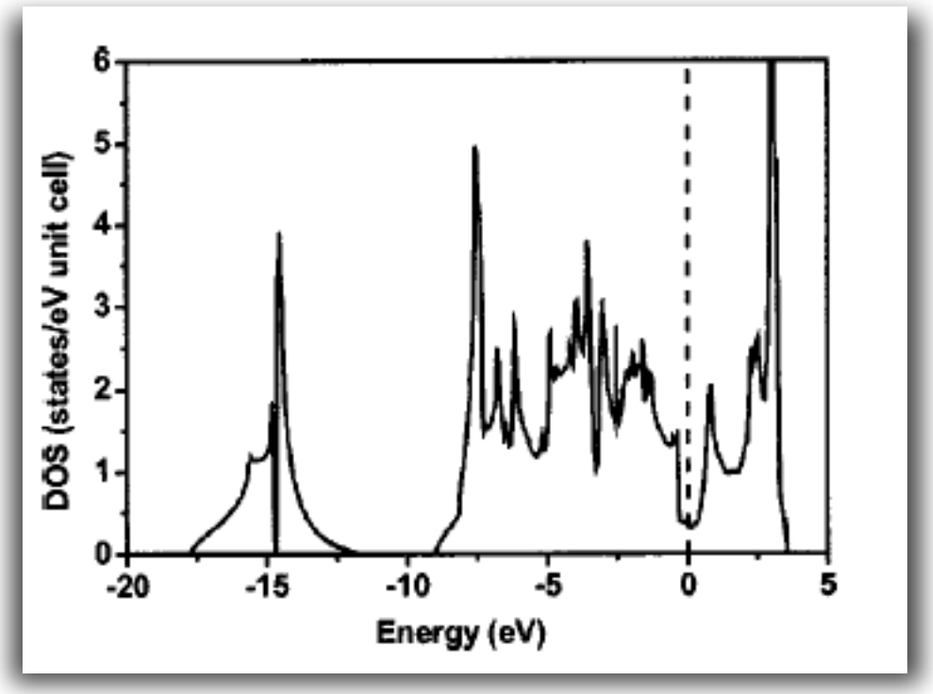
1. Find the converged ground state density and potential.
2. For the converged potential calculate energies at a VERY dense k-mesh.
3. Use some software to plot the DOS.

Kohn-Sham equations

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

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

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



Metal/insulator

silicon

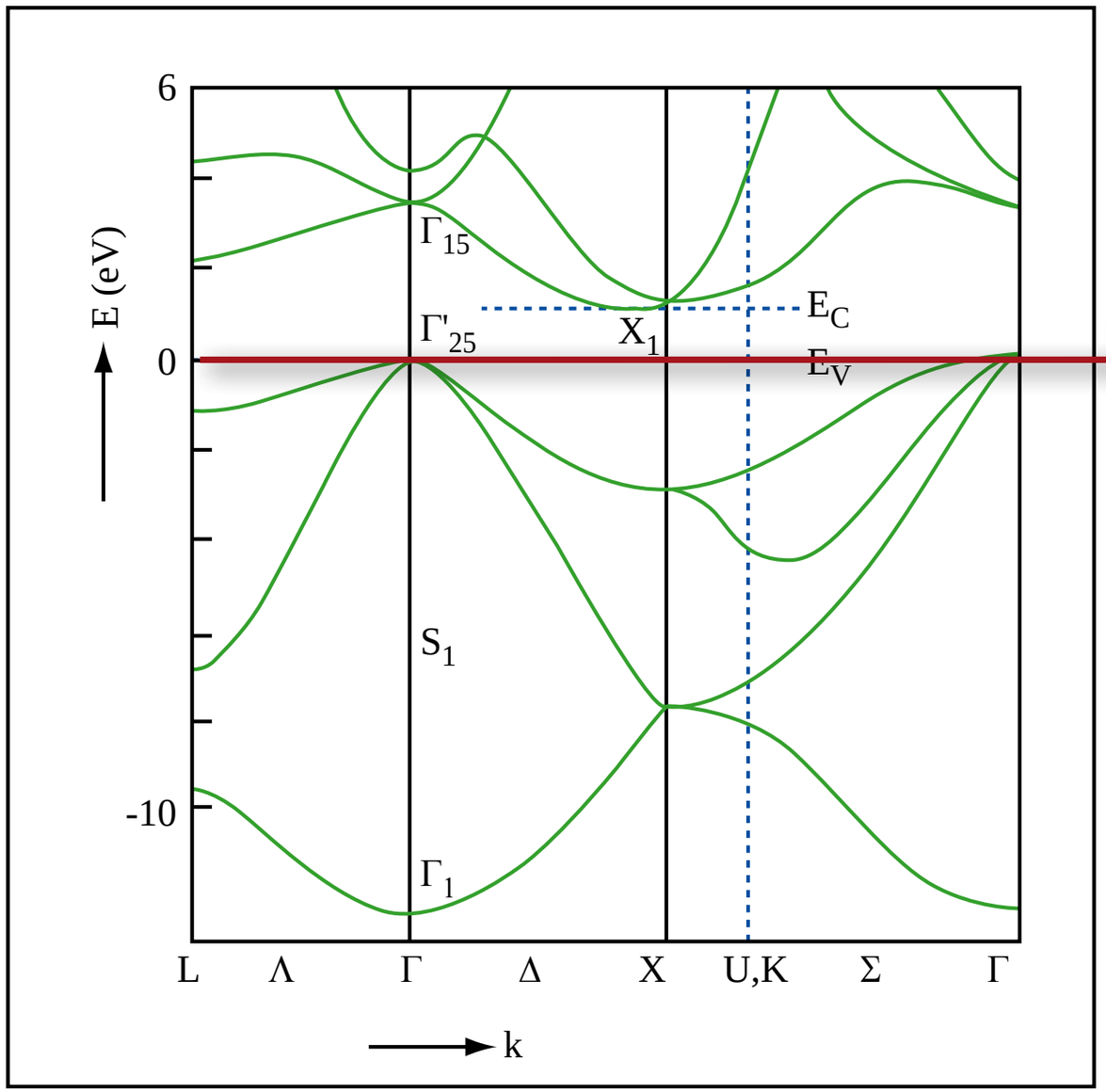


Image by MIT OpenCourseWare.

Are any bands crossing the Fermi energy?

YES: METAL

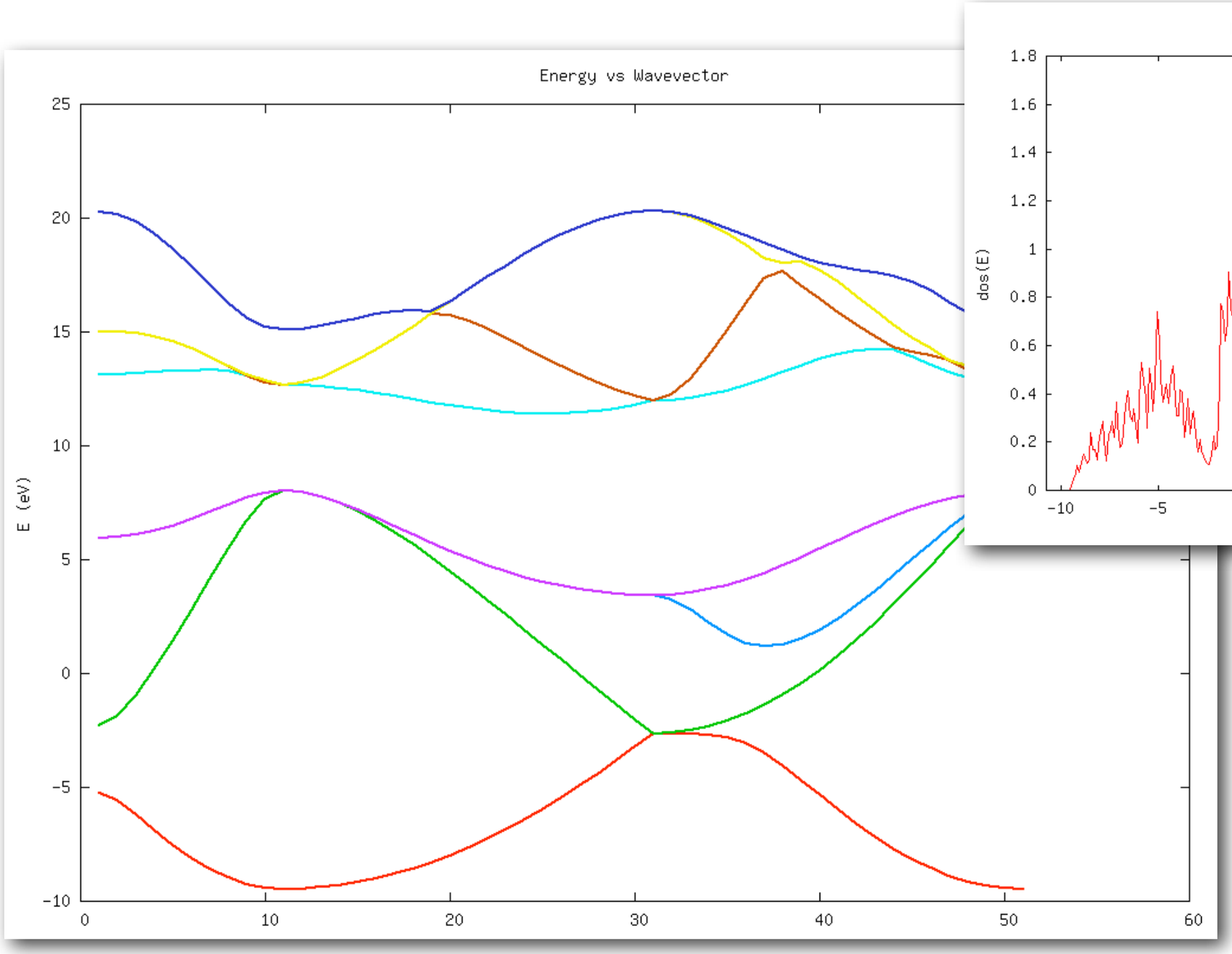
NO: INSULATOR

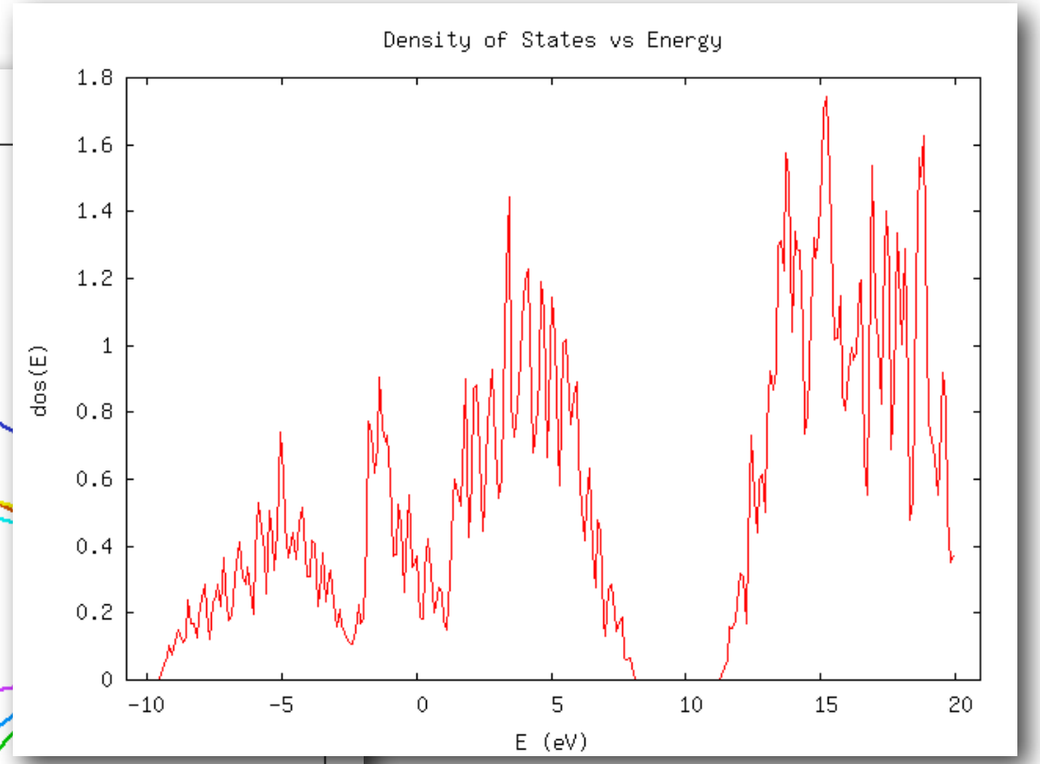
Number of electrons in unit cell:

EVEN: MAYBE INSULATOR

ODD: FOR SURE METAL

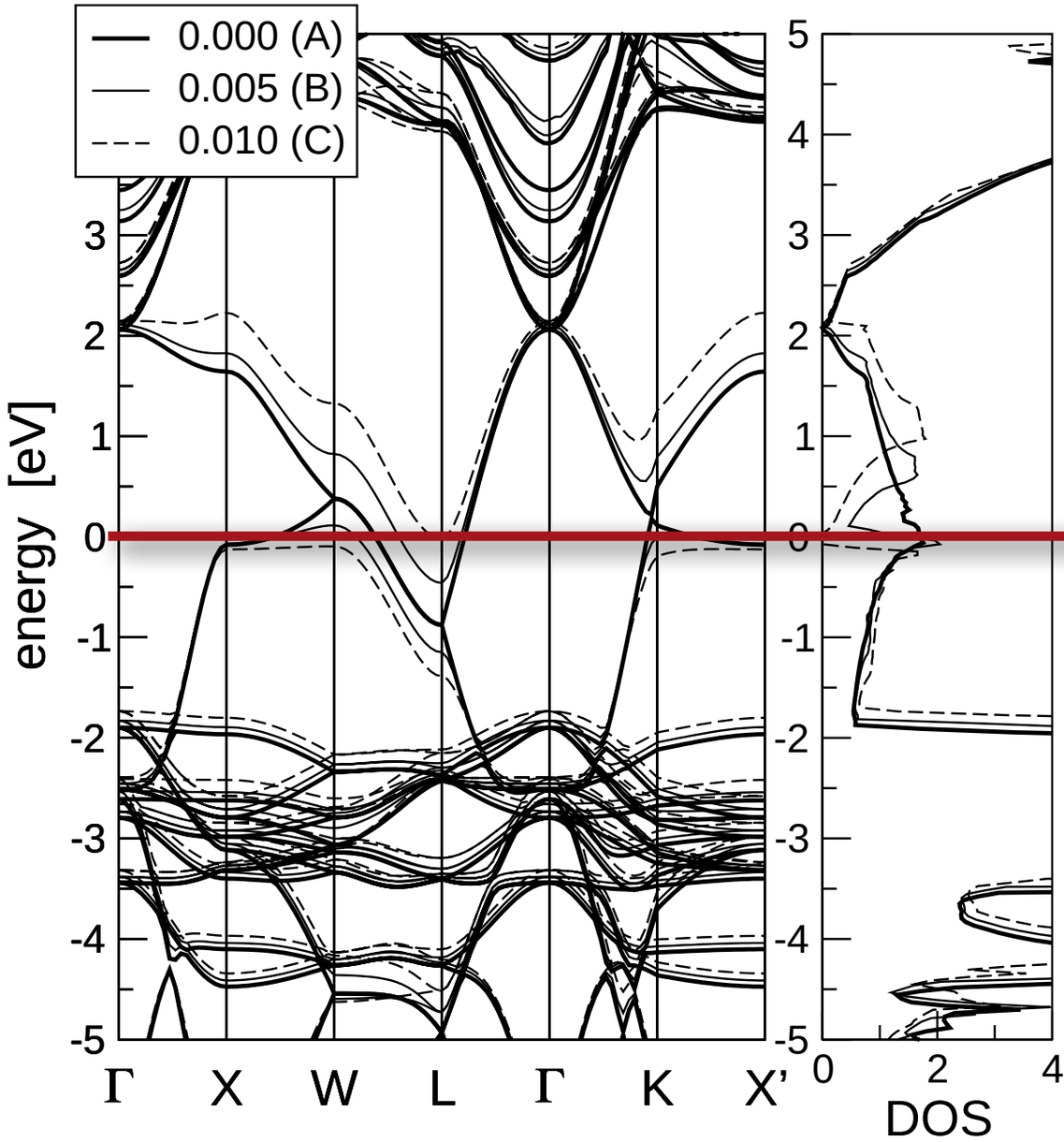
Metal/insulator





diamond: insulator

Metal/insulator



$BaBiO_3$: metal

Fermi energy

Simple optical properties

E=hν

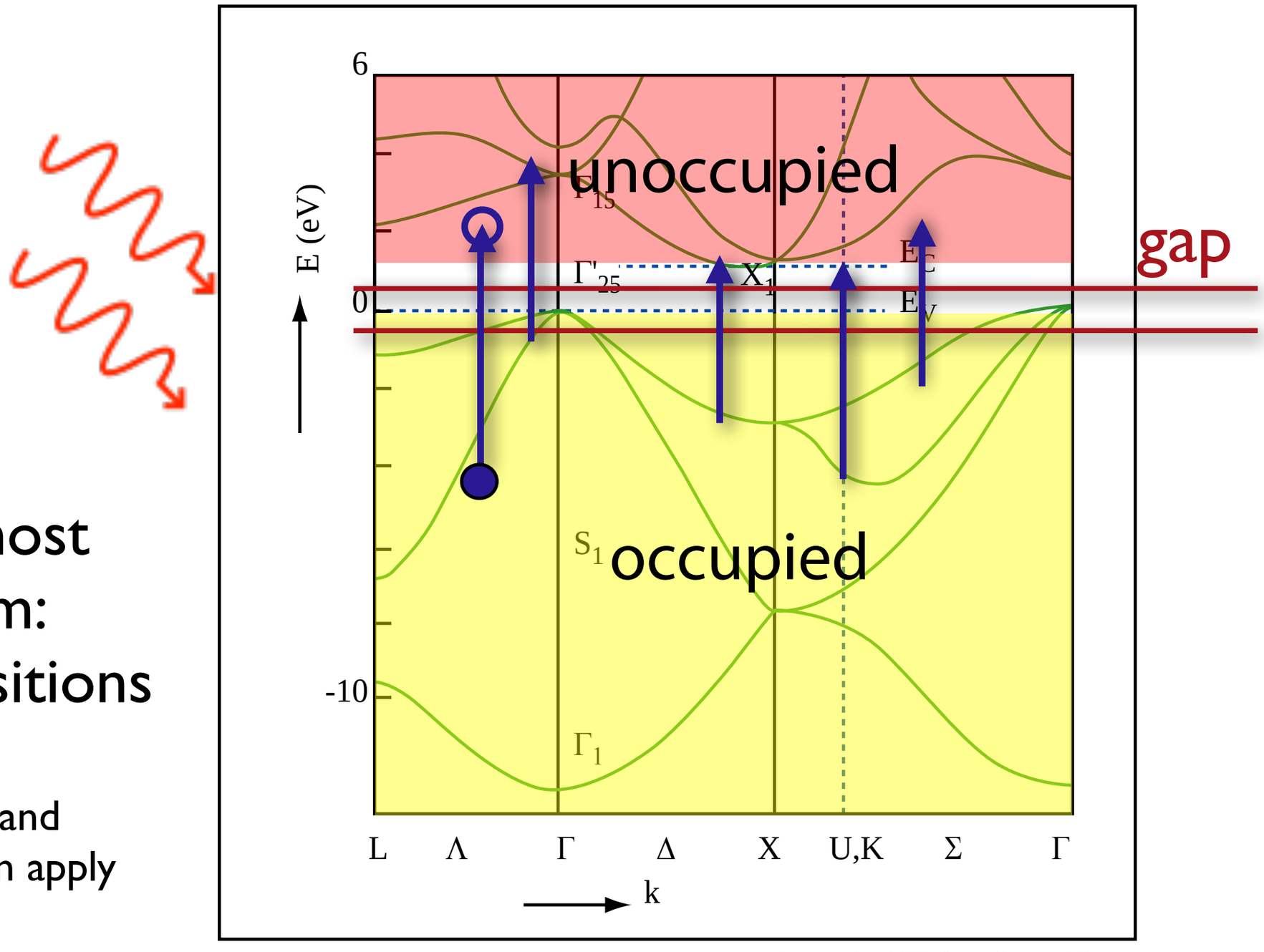


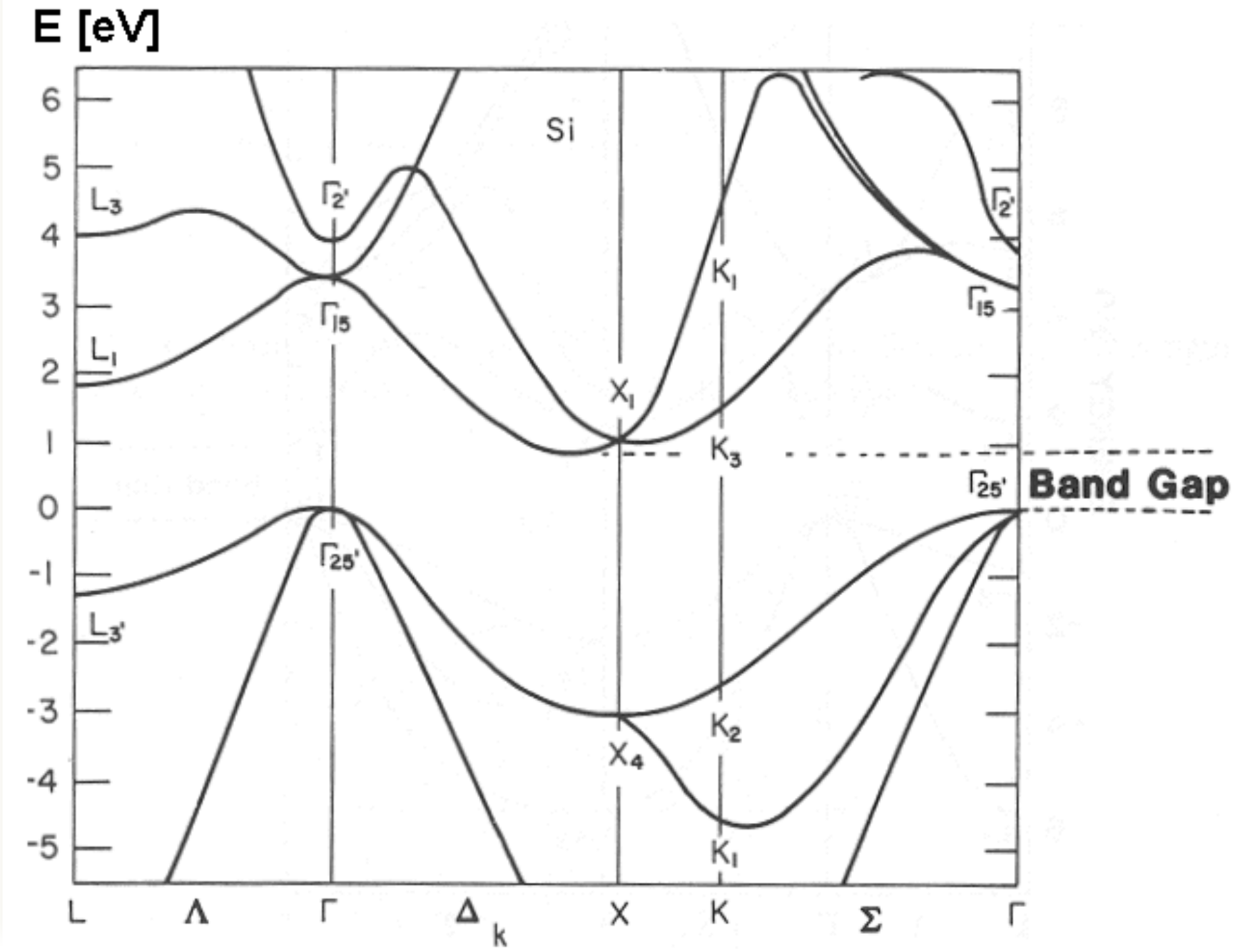
Image by MIT OpenCourseWare.

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!



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 Modelling and Simulation
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