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

Part II – Quantum Mechanical Methods : Lecture 9

Some Review & Introduction to Solar PV

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

Lesson outline

- Discussion of PSET
- Review for the Quiz
- Introduction to Solar PV

Motivation: ab-initio modeling!

?
mechanical properties

?
electrical properties

?
optical properties

Vision without Action is a *Dream*

Action without Vision is a *Nightmare*

Japanese proverb

Why quantum mechanics?

Problems in classical physics that led to quantum mechanics:

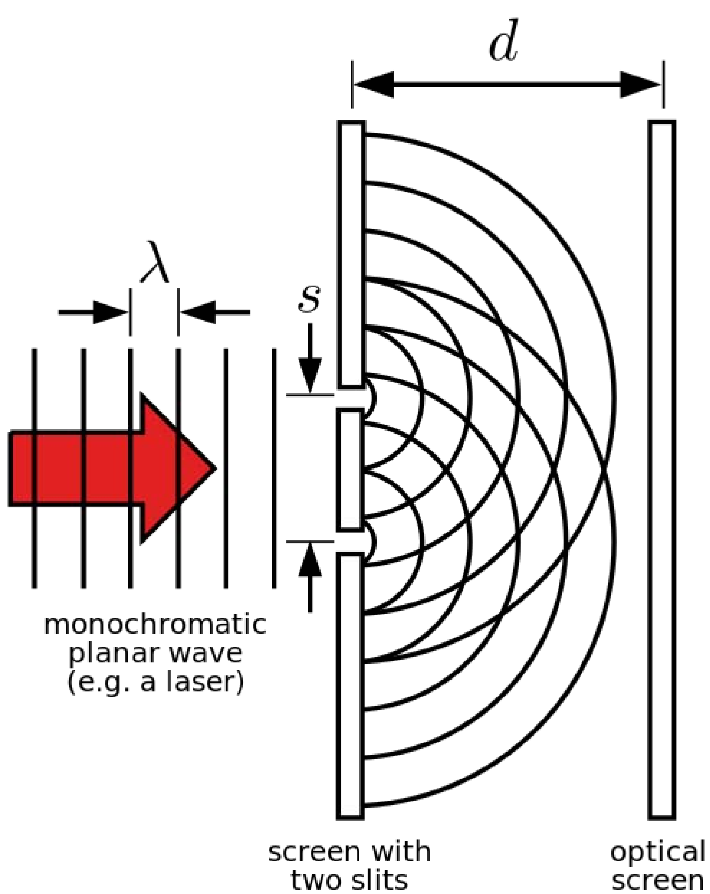
- “classical atom”
- quantization of properties
- wave aspect of matter
- (black-body radiation), ...

Wave aspect of matter

light
matter

wave character

particle character



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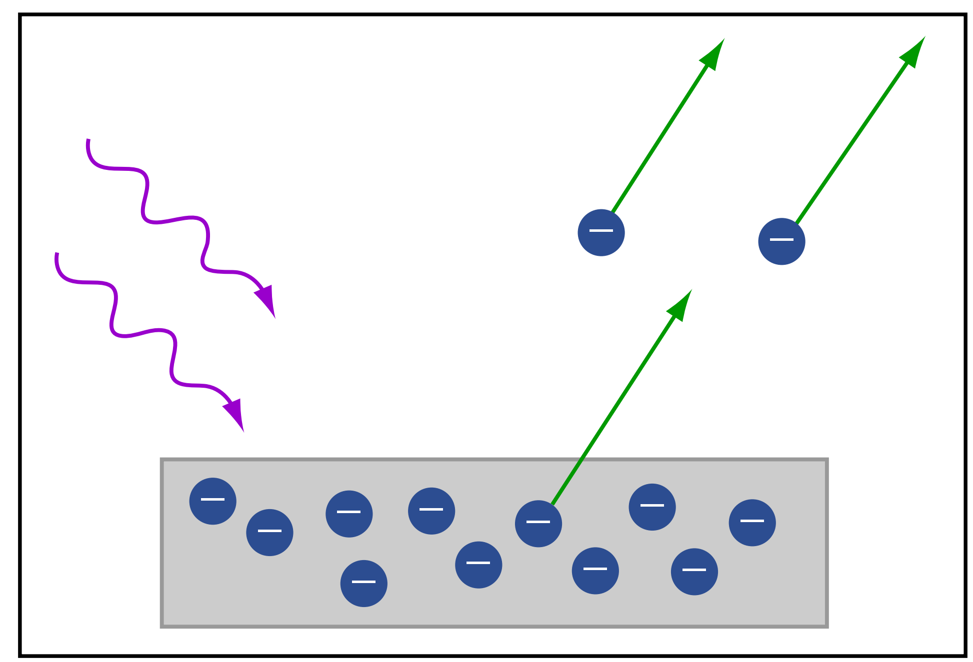

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Wave aspect of matter

particle: E and momentum $\vec{p}$

wave: frequency ν and wavevector $\vec{k}$

$$E = h\nu = \hbar\omega$$

$$\vec{p} = \hbar\vec{k} = \frac{h}{\lambda}\frac{\vec{k}}{|\vec{k}|}$$

de Broglie: free particle can be described a as planewave with

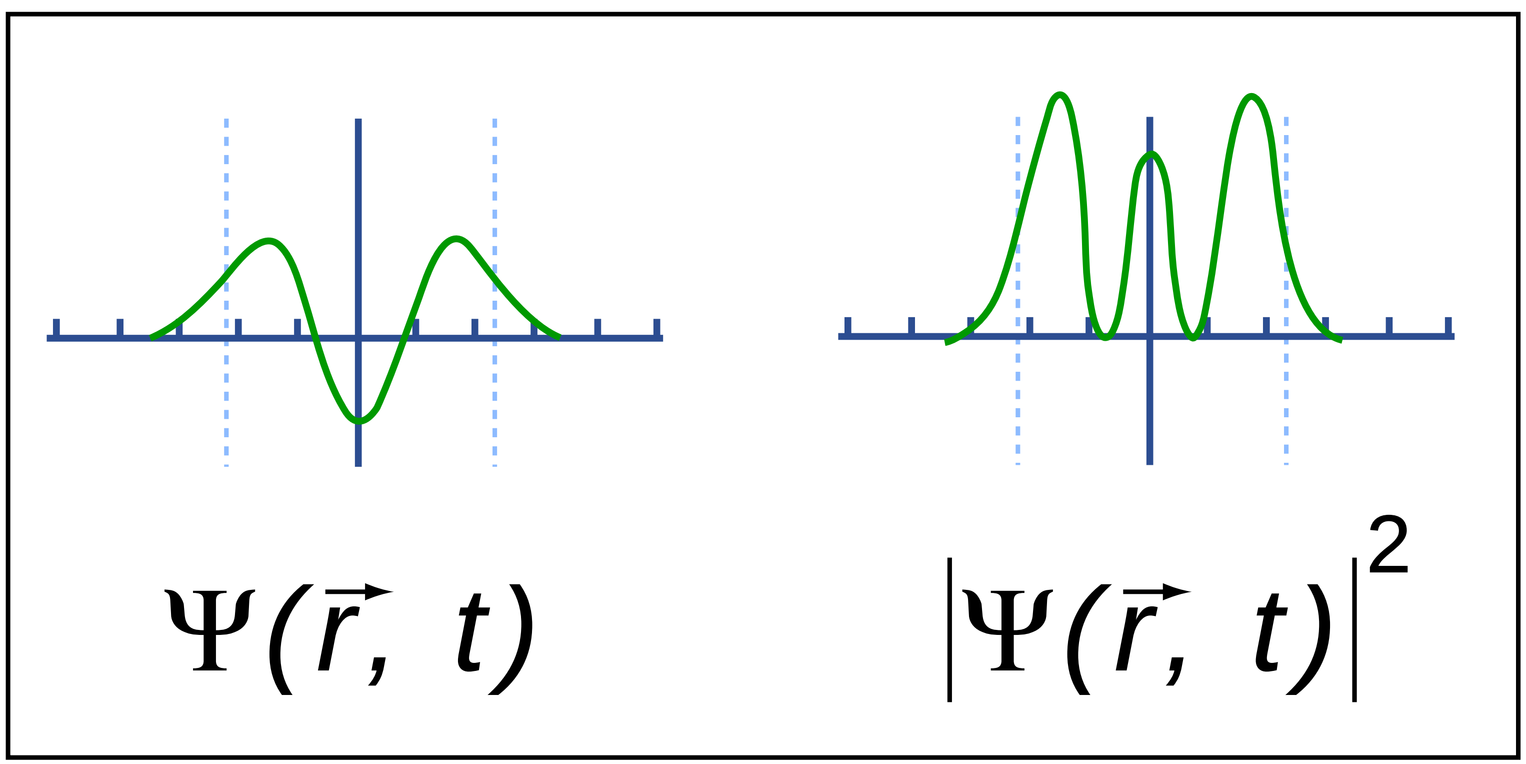
$$\psi(\vec{r},t) = Ae^{i(\vec{k}\cdot\vec{r}-\omega t)}.$$

$$\lambda = \frac{h}{mv}$$

Interpretation of a wavefunction

$\psi(\vec{r}, t)$ → wave function (complex)

$|\psi|^2 = \psi\psi^*$ → interpretation as probability to find particle!



$$\int_{-\infty}^{\infty} \psi\psi^* dV = 1$$

Image by MIT OpenCourseWare.

Schrödinger equation

H time independent: $\psi(\vec{r},t) = \psi(\vec{r}) \cdot f(t)$

$$i\hbar \frac{\dot{f}(t)}{f(t)} = \frac{H\psi(\vec{r})}{\psi(\vec{r})} = \text{const.} = E$$

$$\boxed{H\psi(\vec{r}) = E\psi(\vec{r})}$$

$$\psi(\vec{r},t) = \psi(\vec{r}) \cdot e^{-\frac{i}{\hbar}Et}$$

time independent Schrödinger equation
stationary Schrödinger equation

The hydrogen atom

stationary
Schrödinger equation

$$H\psi = E\psi$$

$$\left[\, T + V \,\right]\psi = E\psi$$

just solve ☺

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

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(\vec{r}) = E\psi(\vec{r})$$

The hydrogen atom

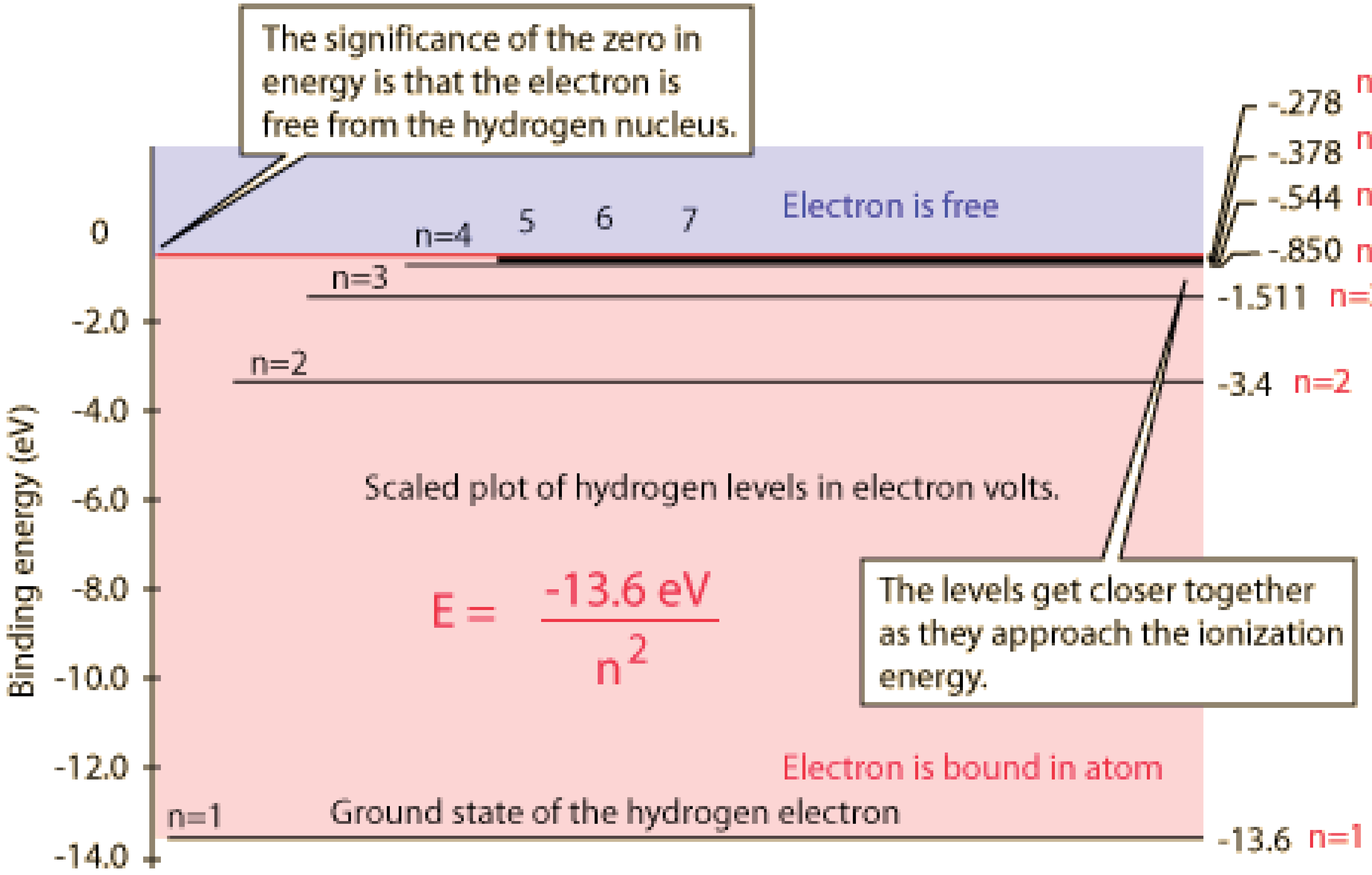
quantum numbers

n	l	m_l	$F(\phi)$	$P(\theta)$	$R(r)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\,a_0^{3/2}}\left[2-\frac{r}{a_0}\right] e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0} e^{-r/2a_0}$

Image by MIT OpenCourseWare.

The hydrogen atom

Energies: $$E_n = \frac{-me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = \frac{-13.6eV}{n^2} \qquad n = 1,2,3,...$$



Atomic units

1 eV = 1.6021765^{-19} J

1 Rydberg = 13.605692 eV = 2.1798719^{-18} J

1 Hartree = 2 Rydberg

1 Bohr =5.2917721^{-11} m

Atomic units (a.u.):

Energies in Ry
Distances in Bohr

Also in use: 1Å=10^{-10}m, nm= 10^{-9}m

Everything is spinning ...

$$
\begin{aligned}
\vec{F} &= -\nabla E \\
&= \nabla\, \vec{m} \cdot \vec{B}
\end{aligned}
$$

Stern–Gerlach experiment (1922)

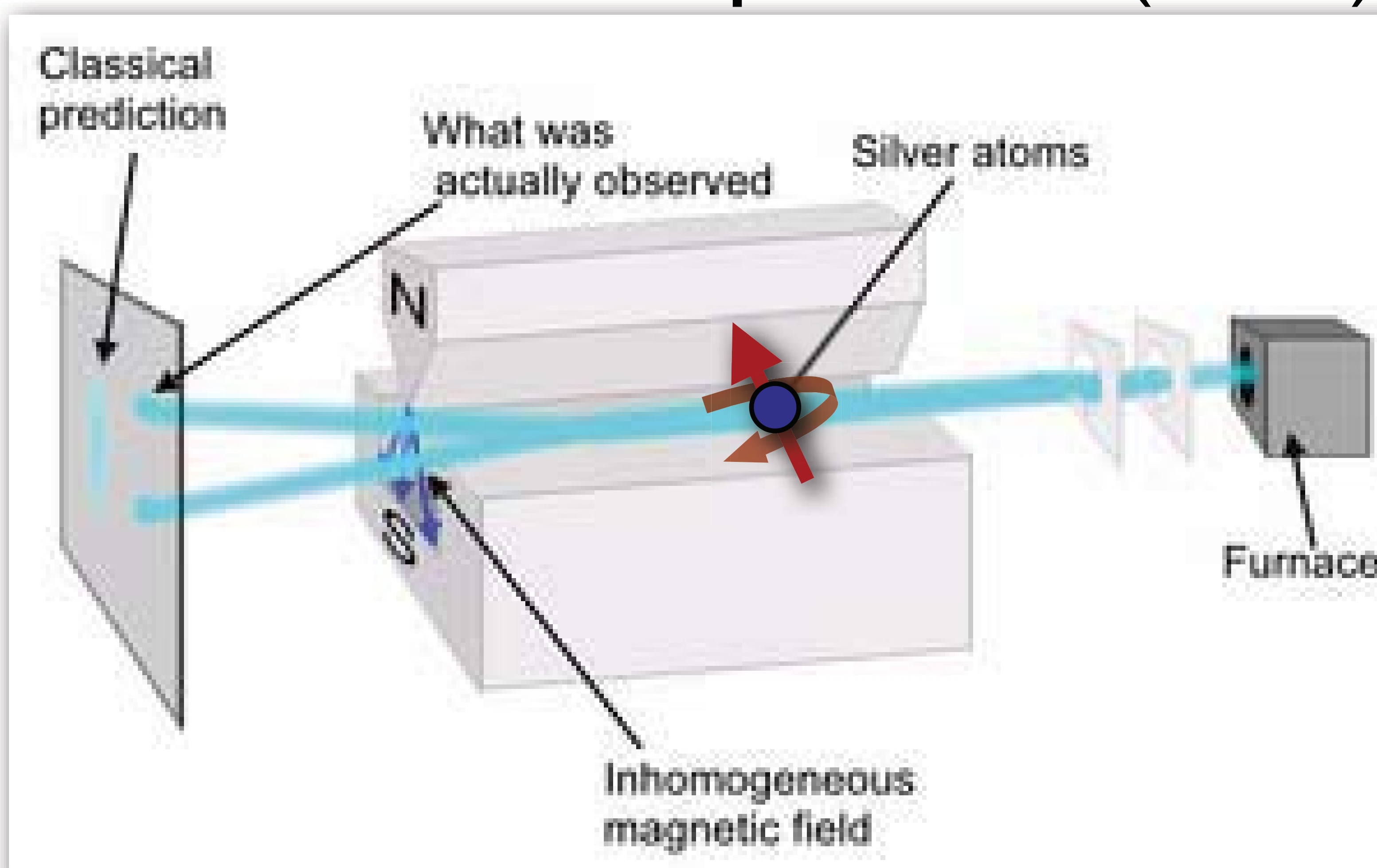


Image courtesy of Teresa Knott.

Everything is spinning ...

new quantum number: spin quantum number

for electrons: spin quantum number can ONLY be

up

down

Pauli’s exclusion principle

Two electrons in a system cannot have the same quantum numbers!

quantum numbers:

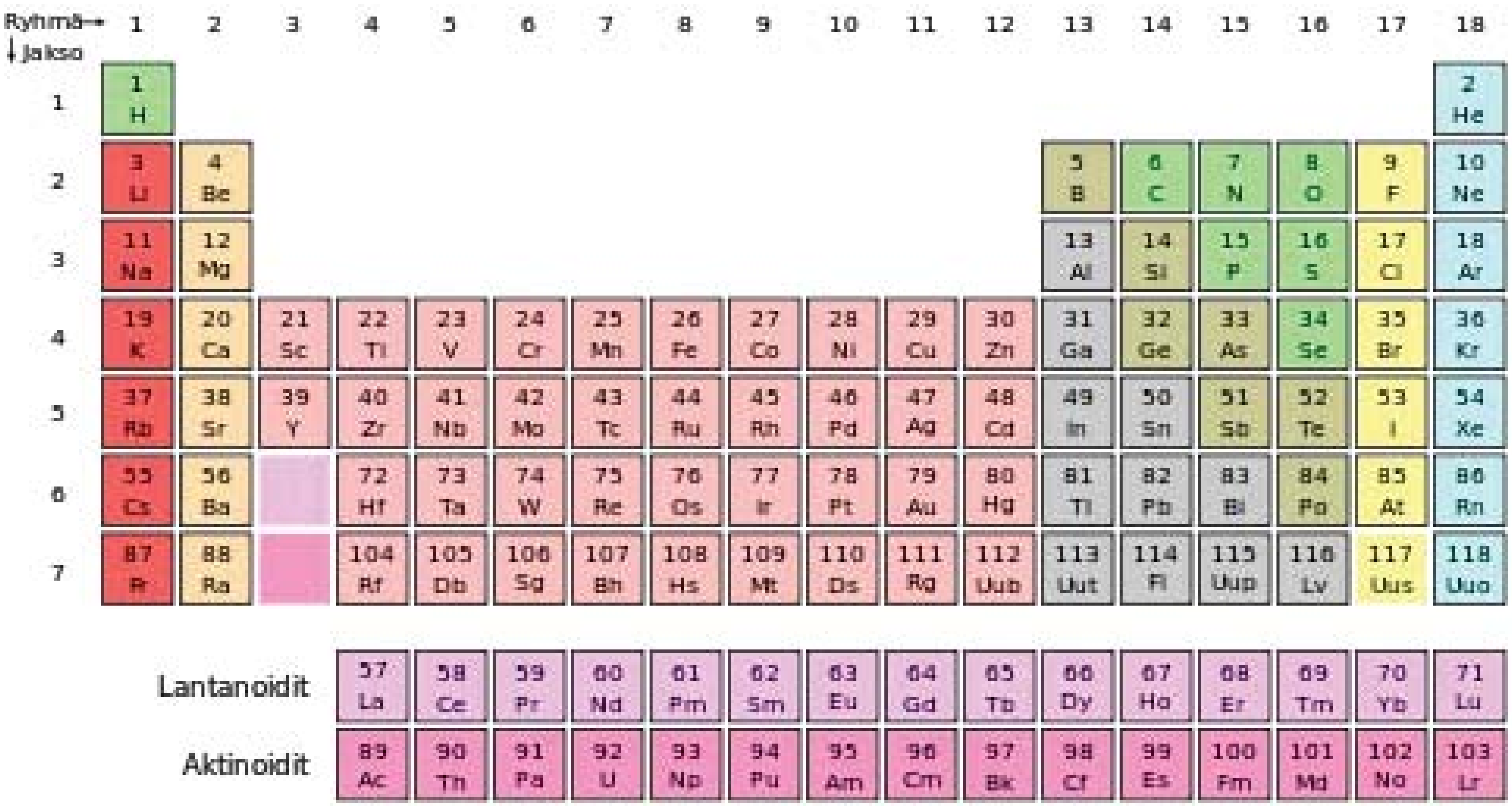
main n: 1,2,3 ...

orbital l: 0,1,...,n-1

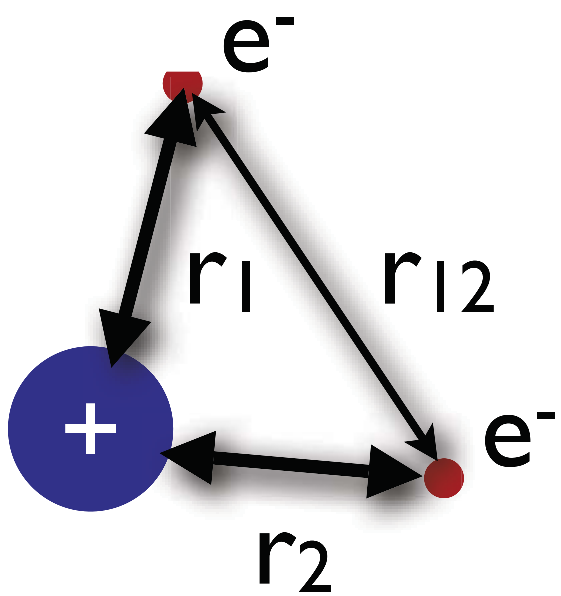
magnetic m: -l,...,l

spin: up, down

Periodic table of elements



Next? Helium?



$$H\psi = E\psi$$

$$\Big[H_1 + H_2 + W\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

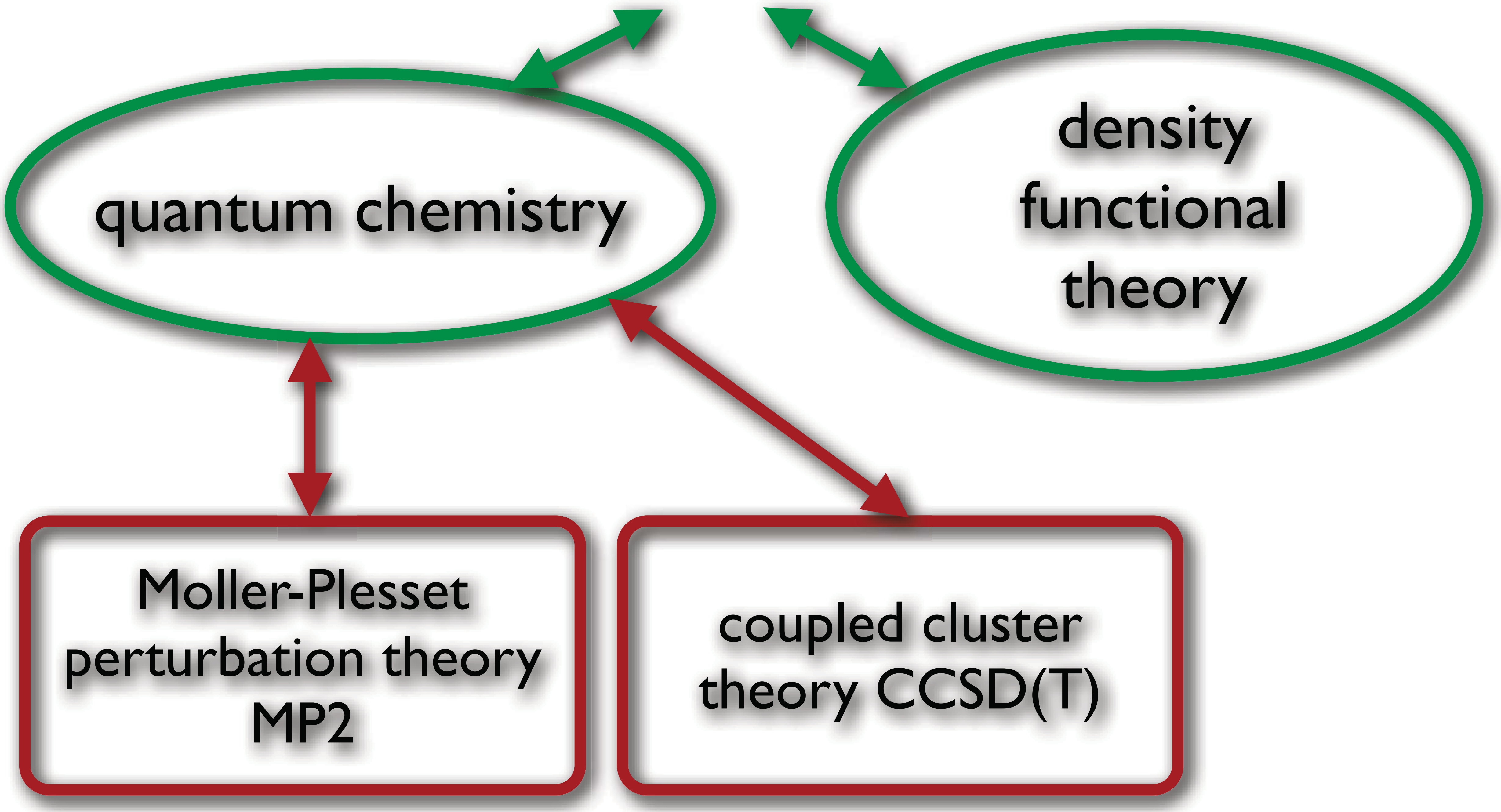
$$\Big[T_1 + V_1 + T_2 + V_2 + W\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\Big[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

cannot be solved analytically

problem!

Solutions


quantum chemistry
density functional theory
Moller-Plesset perturbation theory MP2
coupled cluster theory CCSD(T)

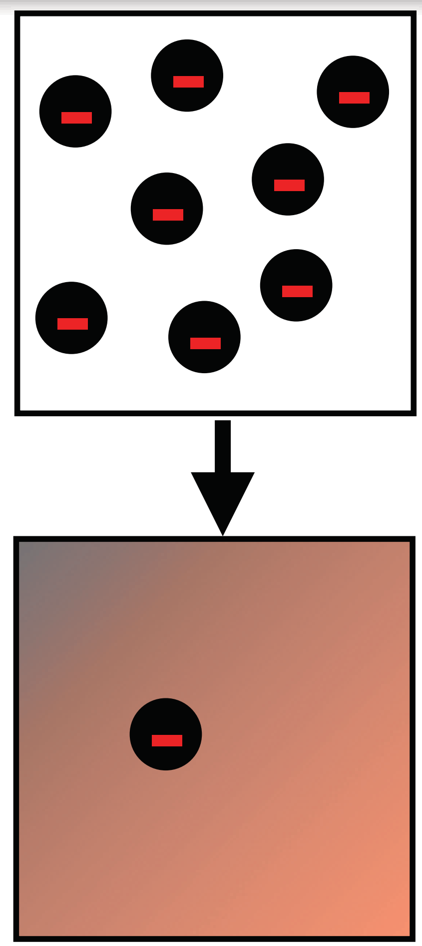
The Two Paths

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)

Ψ = something simpler



"mean field" methods

Physicists (mostly)

H = something simpler

Walter Kohn

Working with the Density

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

kinetic ion-electron

ion-ion electron-electron

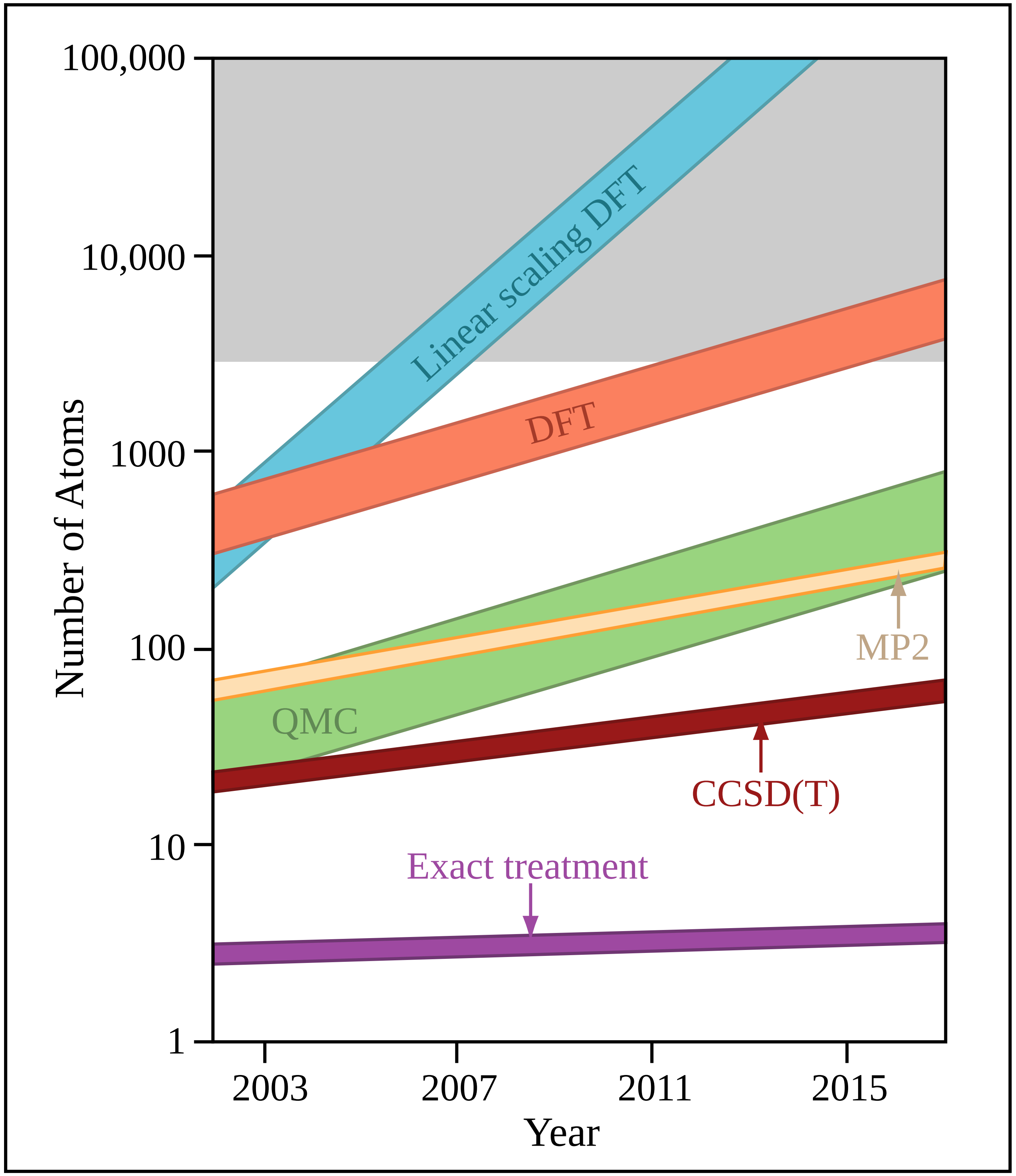
n=#	$\Psi(N^{3n})$	$\rho(N^3)$
1	8	8
10	10^9	8
100	10^{90}	8
1,000	10^{900}	8

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

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

ion potential Hartree potential exchange-correlation potential

Why DFT?



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Density functional theory

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

kinetic ion-ion ion-electron electron-electron

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

$$E_{\text{ground state}} = \min_{\phi} E[n]$$

Find the wave functions that minimize the energy using a functional derivative.

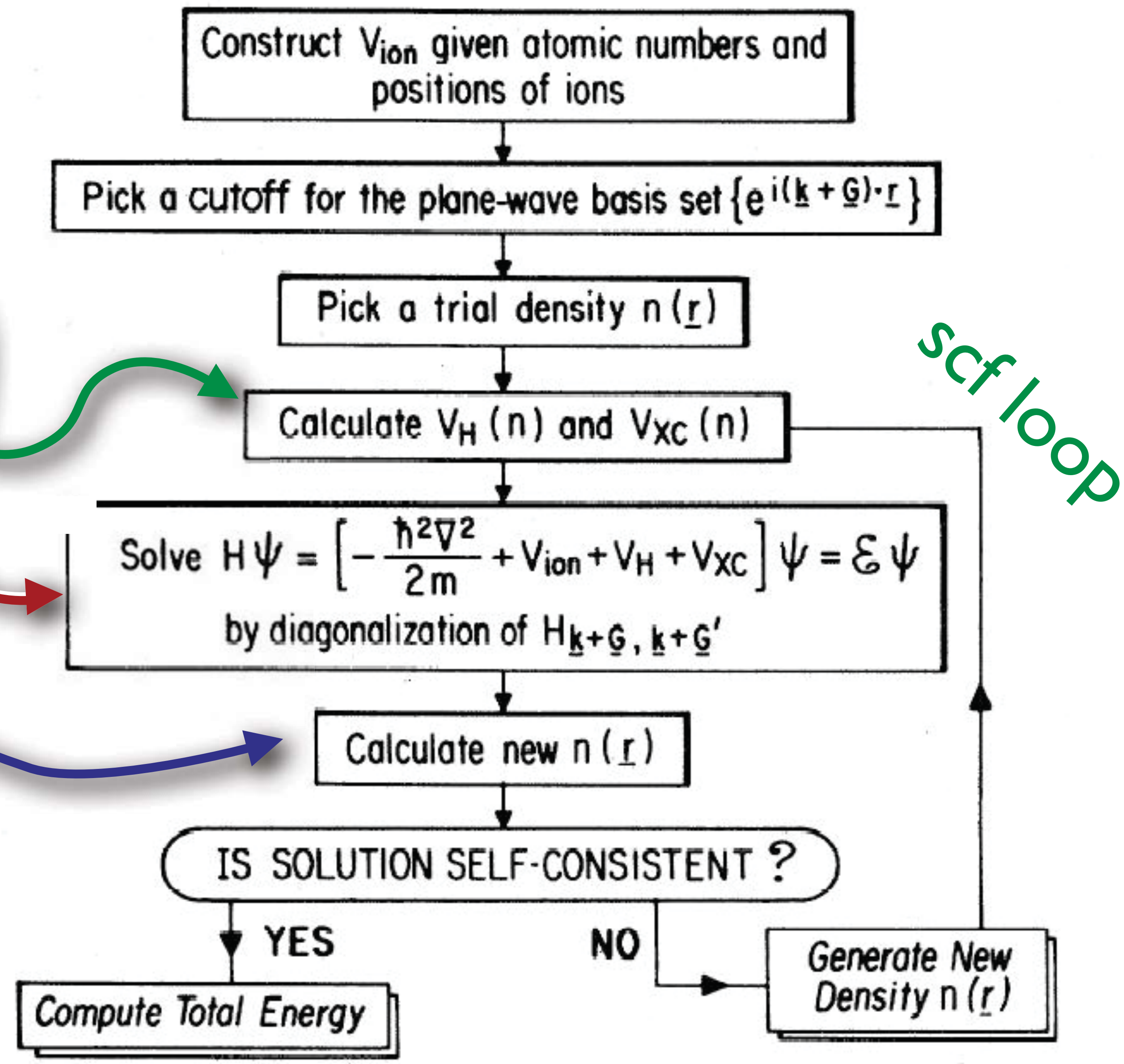
Self-consistent cycle

Kohn-Sham equations

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

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

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



Density functional theory

Only one problem: v_{xc} not known!!!

approximations necessary

local density approximation LDA

general gradient approximation GGA

- structure
- bulk modulus
- shear modulus
- elastic constants
- vibrational properties
- sound velocity

- binding energies
- reaction paths
- forces
- pressure
- stress
- ...

Convergence for molecules

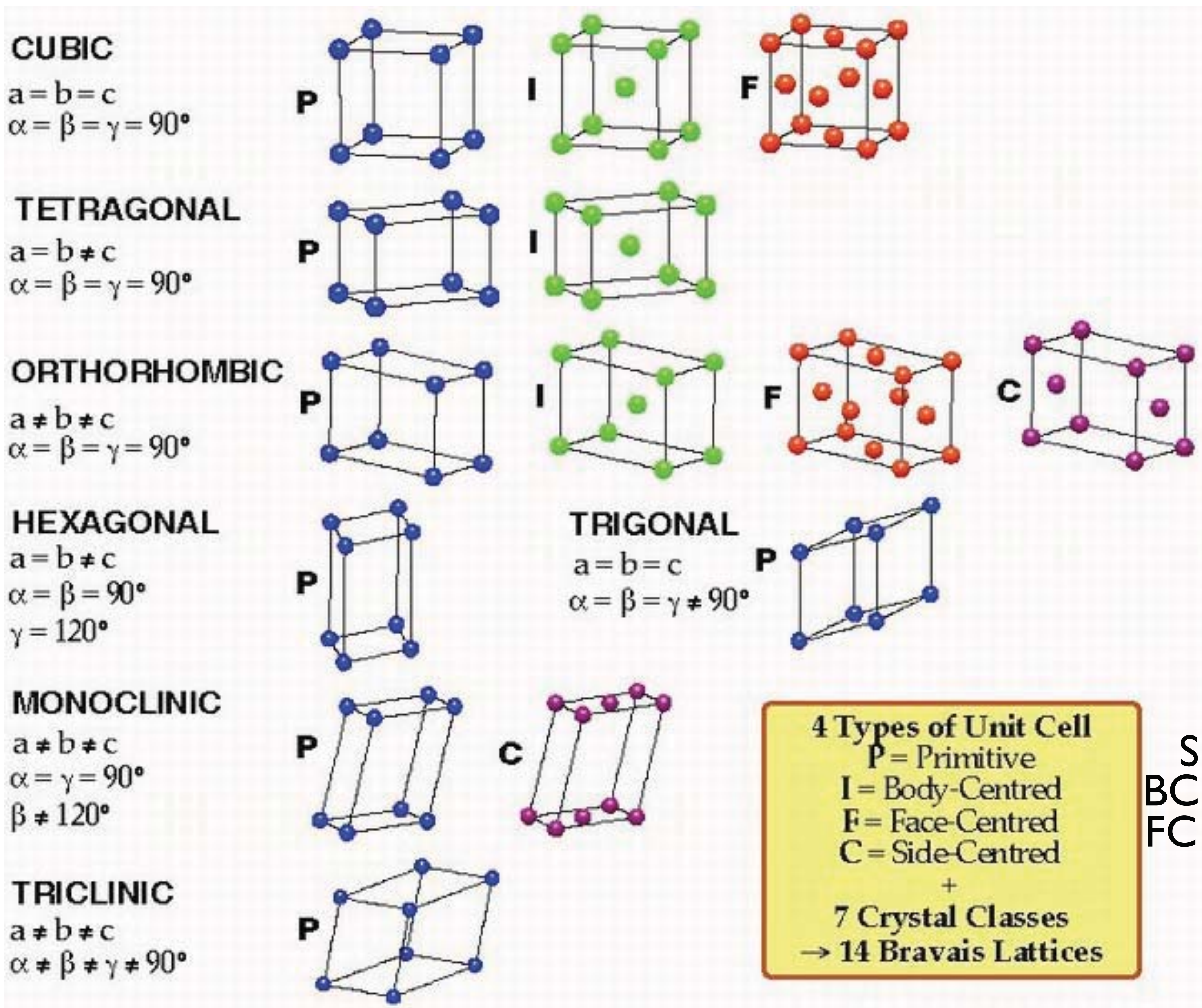
Was my box big enough?

?

Was my basis big enough?

Did I exit the scf loop at the right point?

Crystal symmetries



S = simple
BC = body centered
FC = face centered

The inverse lattice

The real space lattice is described by three basis vectors:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

The inverse lattice is described by three basis vectors:

$$\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$$

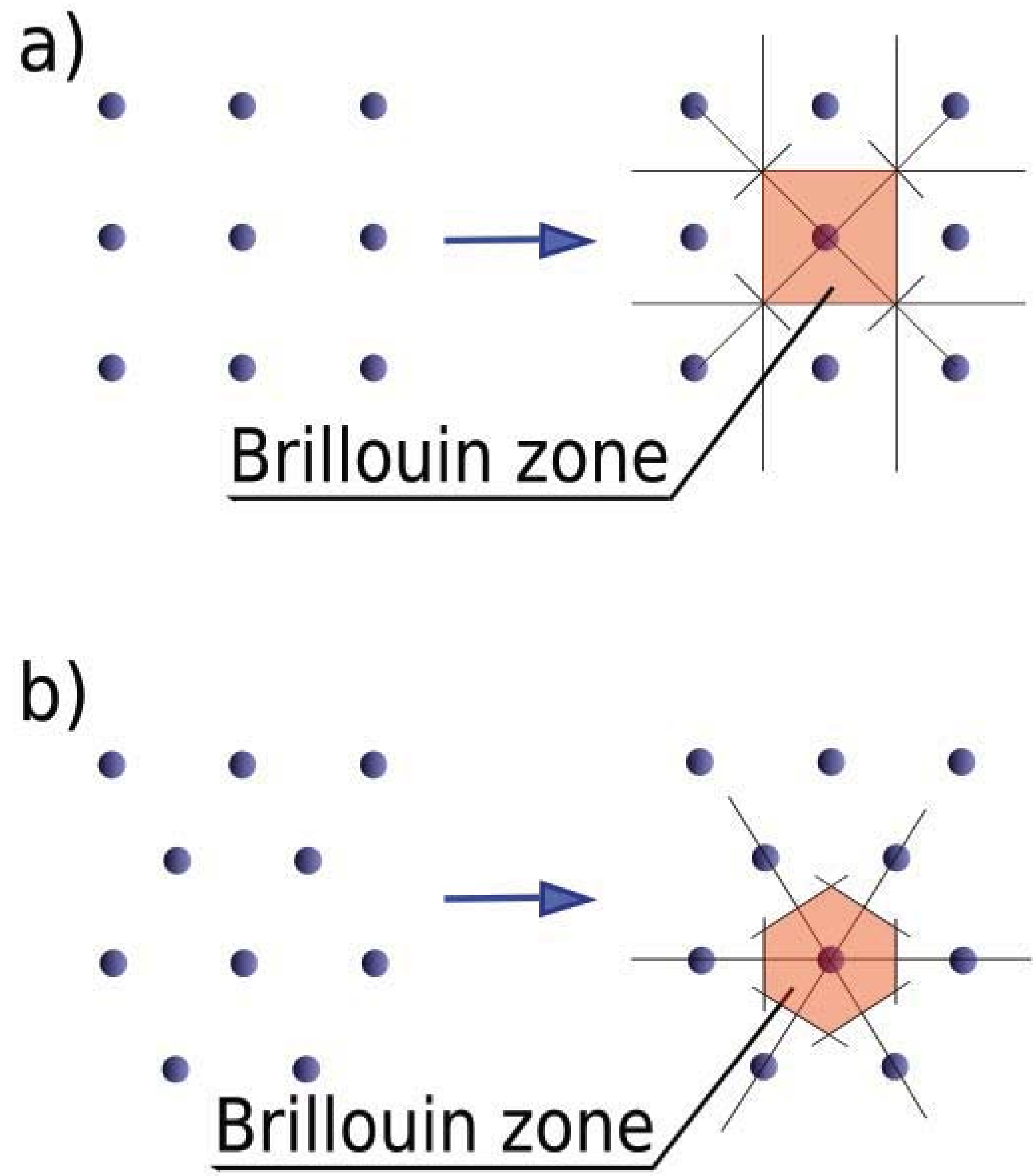
$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)} \qquad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$

$$e^{iG\cdot R} = 1 \longrightarrow \psi(\vec{r}) = \sum_j c_j e^{iG_j\cdot r}$$

automatically periodic in R!

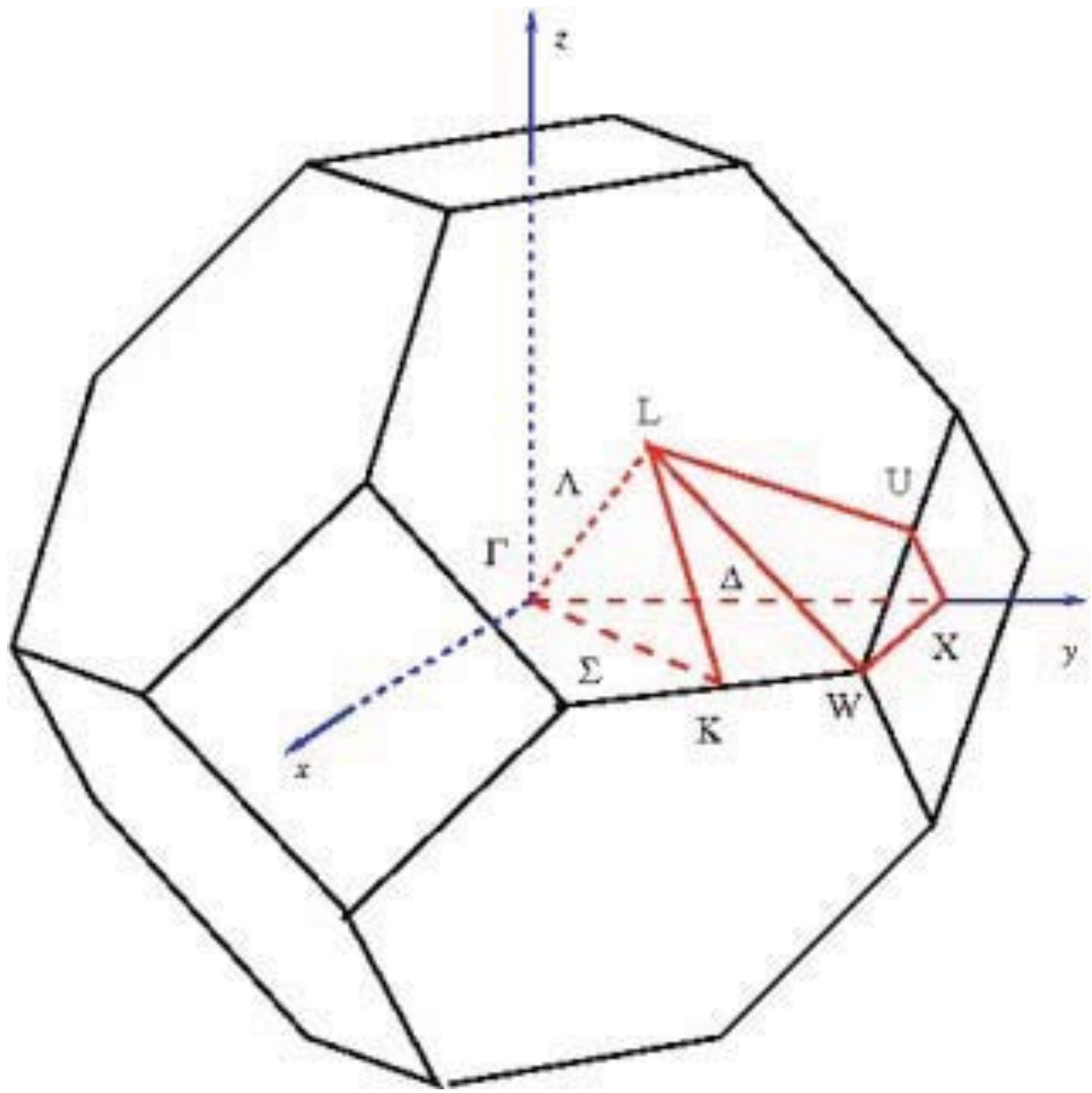
The Brillouin zone

inverse lattice



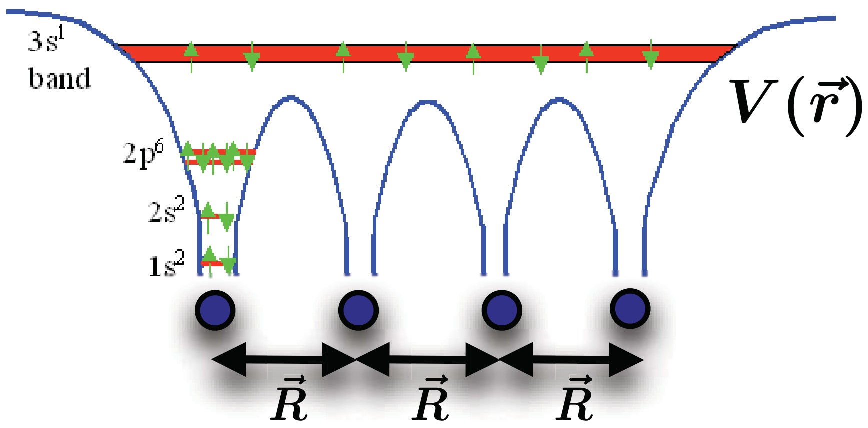
The Brillouin zone is a special unit cell of the inverse lattice.

The Brillouin zone



Brillouin zone of the FCC lattice

Periodic potentials



lattice vector

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

NEW quantum number k that lives in the inverse lattice!

Bloch's theorem

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

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

Inverse lattice

Results of Bloch's theorem:

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

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

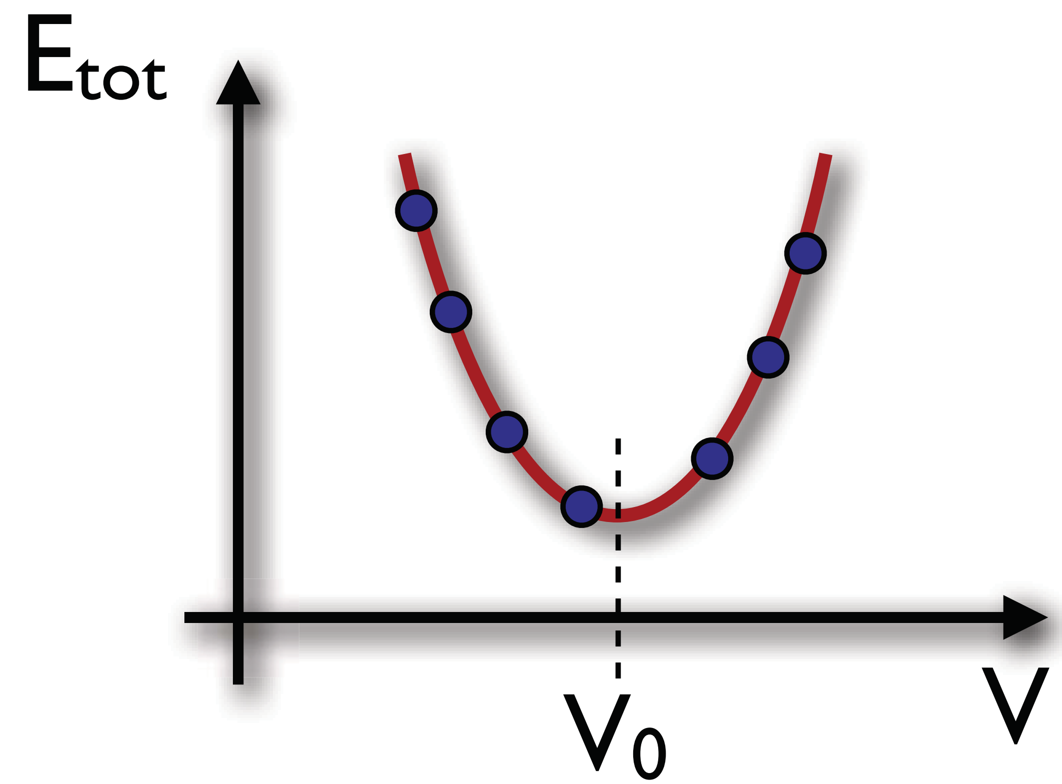
charge density
is lattice periodic

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

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

Structural properties

finding the stress/pressure and the bulk modulus



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

Calculating the band structure

3-step procedure

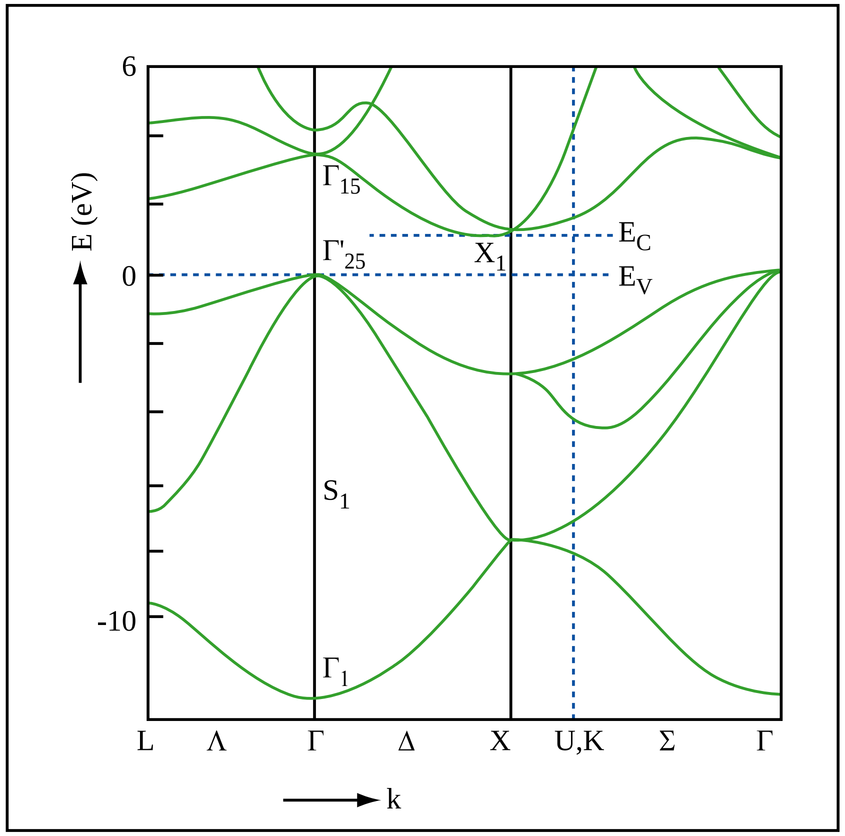
1. Find the converged ground state density and potential.
2. For the converged potential calculate the energies at k-points along lines.
3. Use some software to plot the band structure.

Kohn-Sham equations

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

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

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



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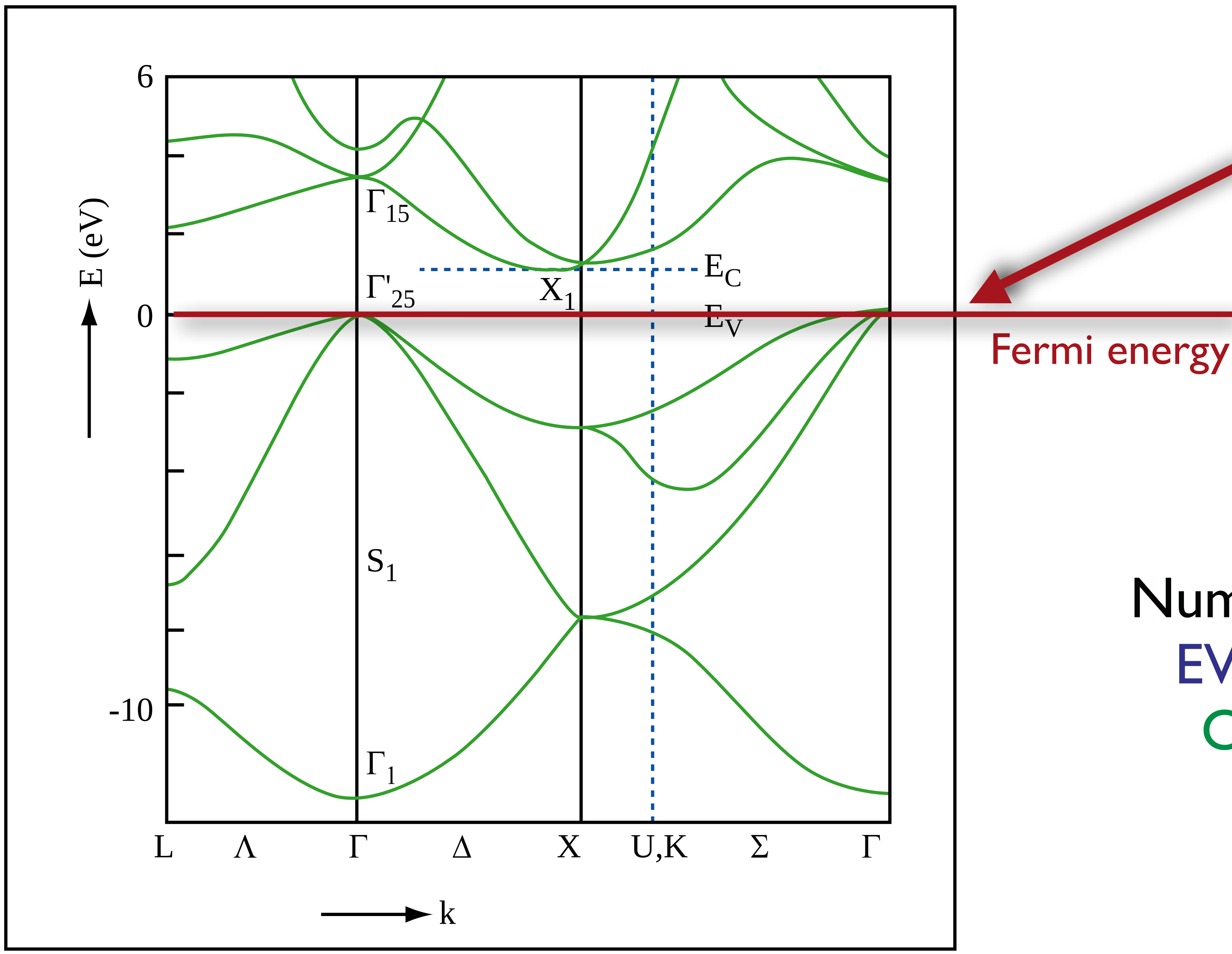
Metal/insulator

silicon



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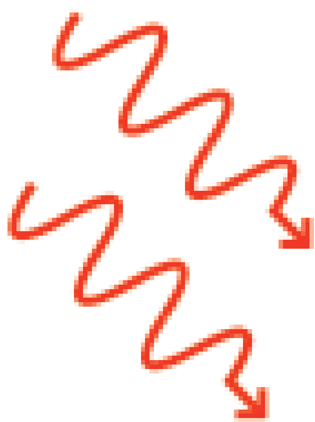
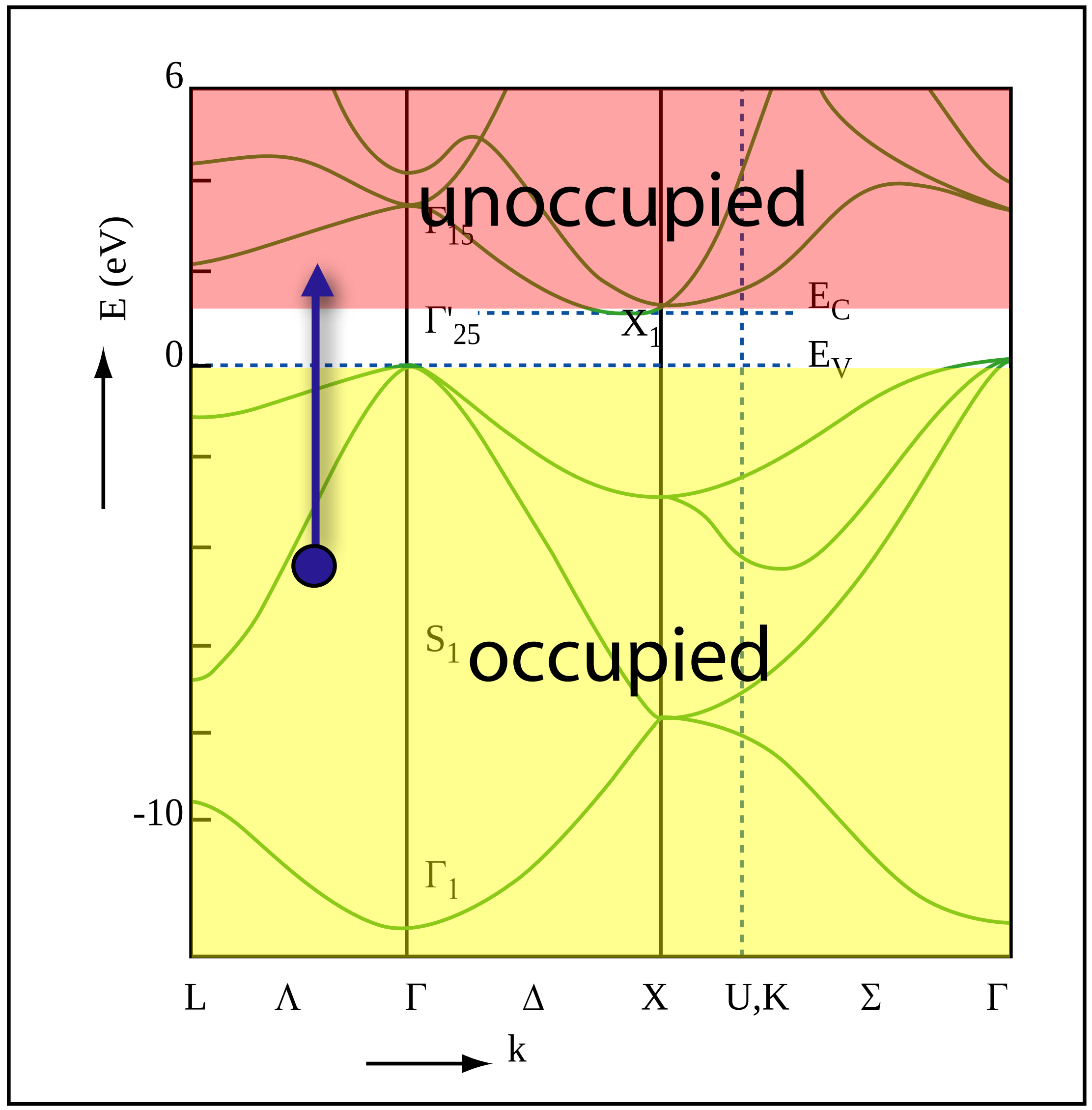
Are any bands crossing the Fermi energy?
YES: METAL
NO: INSULATOR

Number of electron in unit cell:
EVEN: MAYBE INSULATOR
ODD: FOR SURE METAL

Simple optical properties

E=hν





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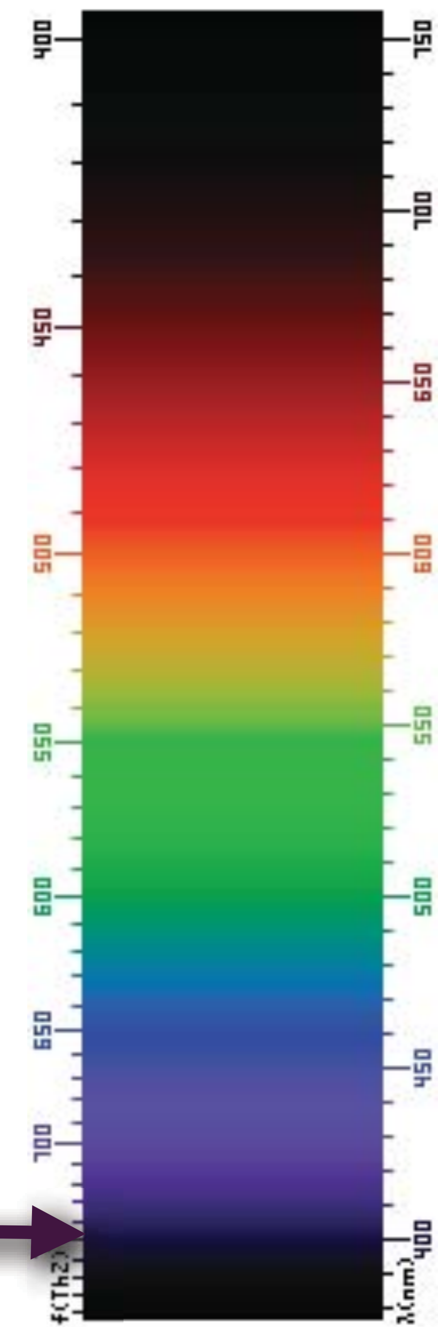

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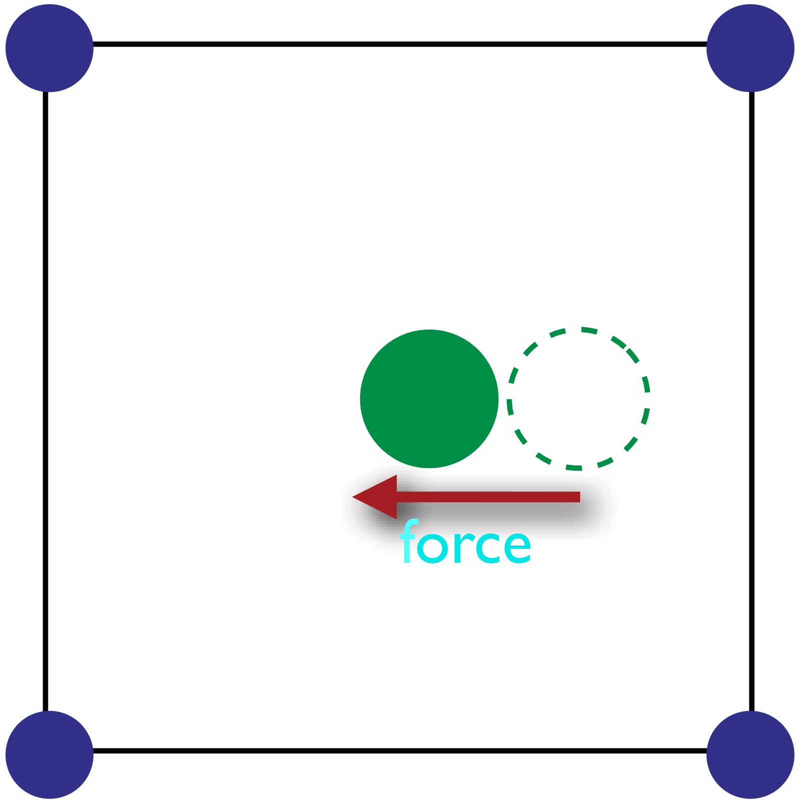
shortest wave length visible 400 nm ; corresponds to photon with E=3.1 eV

Vibrational properties

lattice vibrations
are called: phonons



What is the frequency of this vibration?

Magnetization

iron

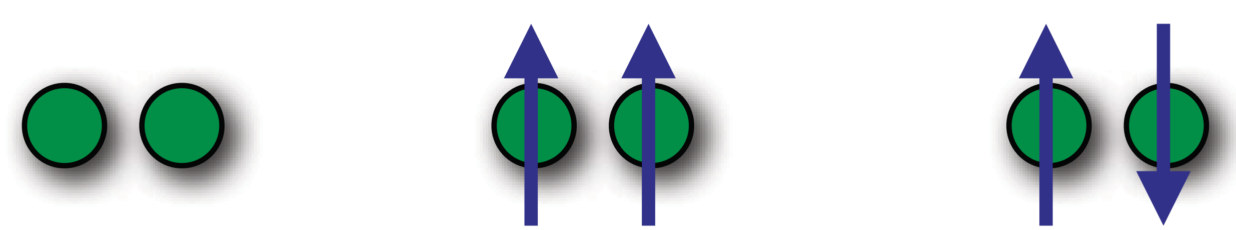
```
&control
  calculation = 'scf',
  pseudo_dir = ''
/
&system
  ibrav=3,
  celldm(1)=5.25,
  nat=1,
  ntyp=1,
  ecutwfc=25.0,
  occupations='smearing'
  smearing='gauss',
  degauss=0.05,
  nspin=1
  starting_magnetization(1)=0.0
/
&electrons
  conv_thr=1.0d-10
/
ATOMIC_SPECIES
Fe 55.847 iron.UPF
ATOMIC_POSITIONS {crystal}
Fe 0.0 0.0 0.0
K_POINTS {automatic}
4 4 4 1 1 1
```

nspin=1: non spin-polarized
nspin=2: spin-polarized

starting magnetization
for each atom

perform three calculations
and find lowest energy:

non spin-polarized   spin-polarized



ferromagnetic   anti-ferromagnetic

With the band structure and DOS we find:

- electrical conductivity (insulator/metal/semiconductor)
- thermal conductivity
- optical properties
- magnetization/polarization
- magnetic/electric properties
- ...

Convergence for solids

Was my k-mesh fine enough?

Was my basis big enough?

?

Did I exit the scf loop at the right point?

Summary of properties

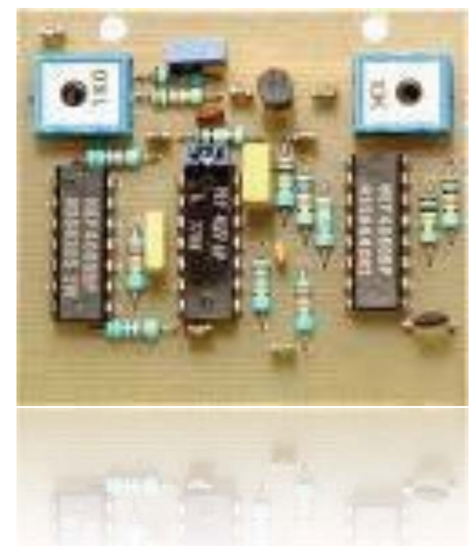
structural properties

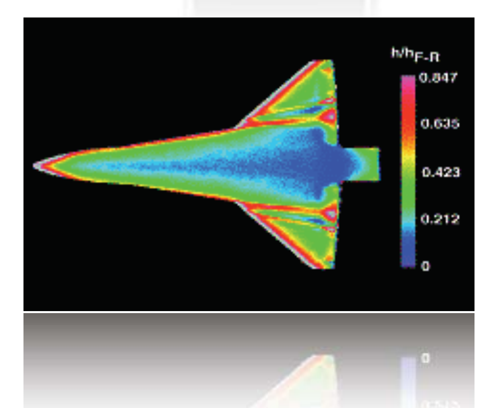
electrical properties

optical properties

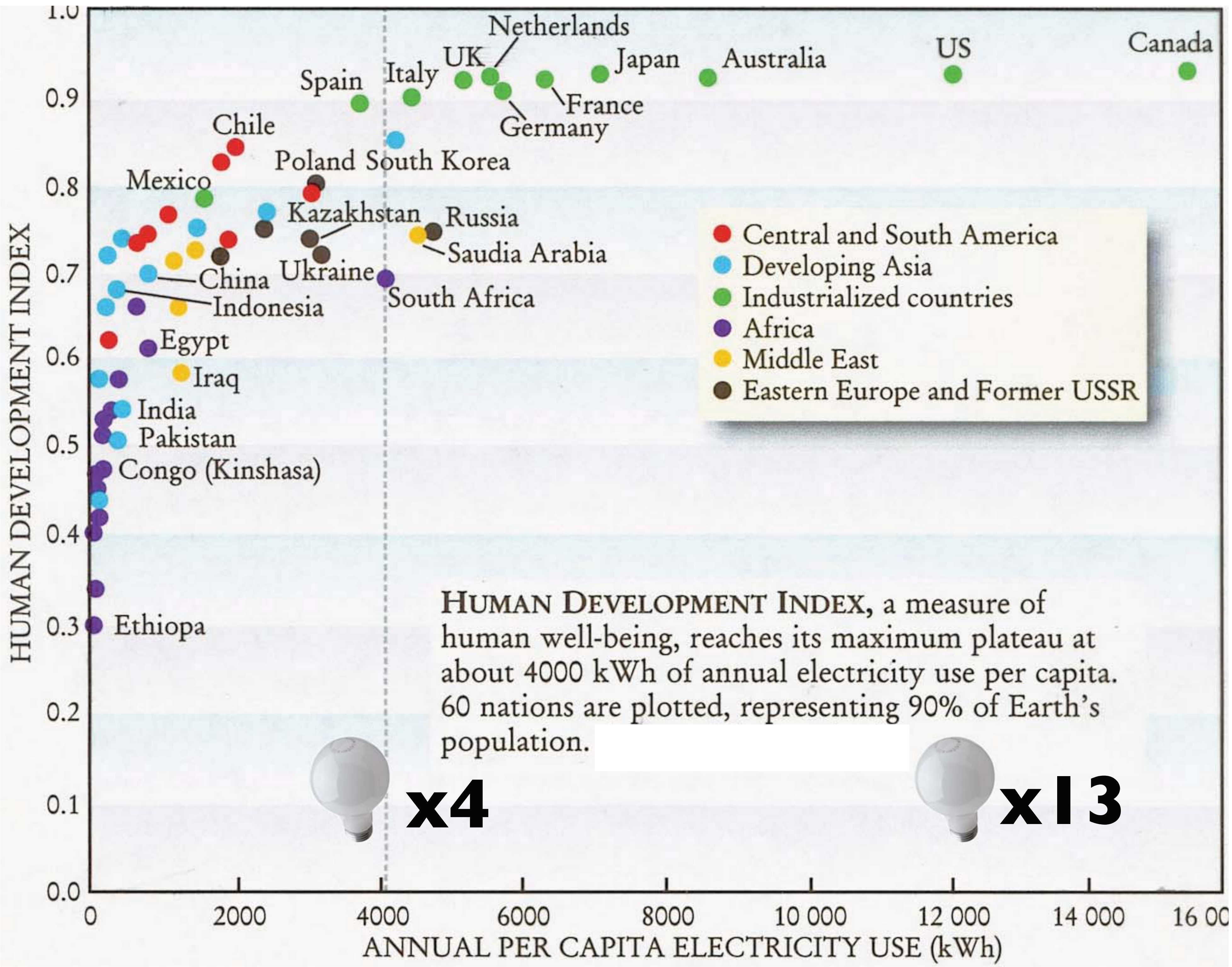
magnetic properties

vibrational properties





It's Not *Only* About Warming: Abundance of Affordable Energy Resources Can Uplift the World



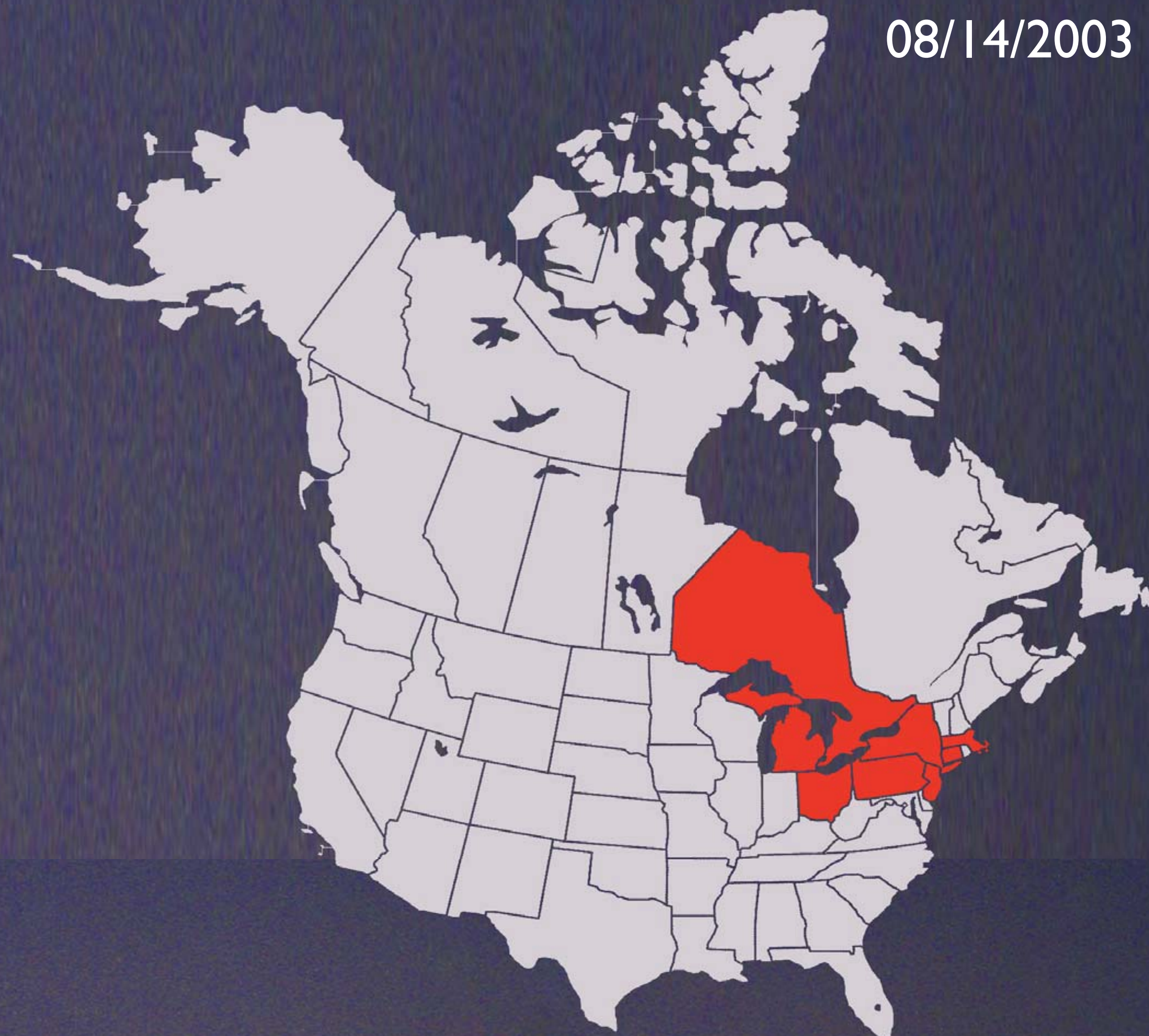
HUMAN WELL-BEING INCREASES WITH INCREASED PER-CAPITA ENERGY USE

Courtesy: Vladimir Bulovic

It's Not *Only* About Warming: Abundance of Affordable Energy Resources Can Uplift the World

North American Electrical Blackout

08/14/2003



… August 15 …
just 24 hours into blackout
Air Pollution was Reduced

SO_2 >90%

O_3 ~50%

Light Scattering
Particles ~70%

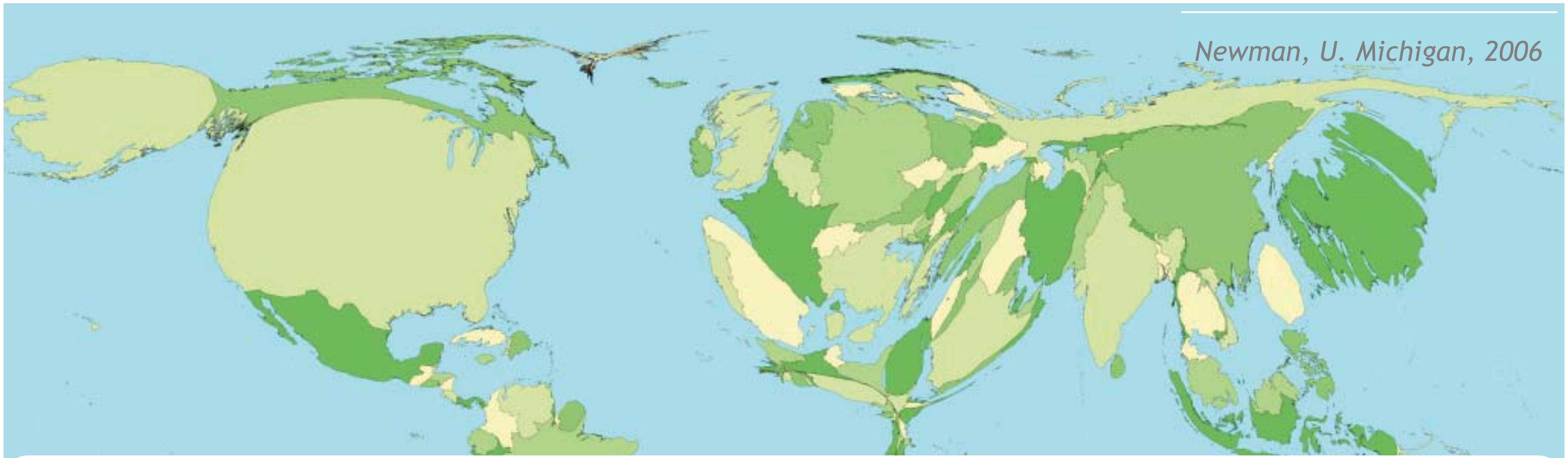
"This clean air benefit was realized over much of eastern U.S."

Marufu et al., Geophysical Research Letters 2004

by 4:13 pm 256 power plants were off-line

Courtesy: Vladimir Bulovic

Map of the World Scaled to Energy Consumption by Country

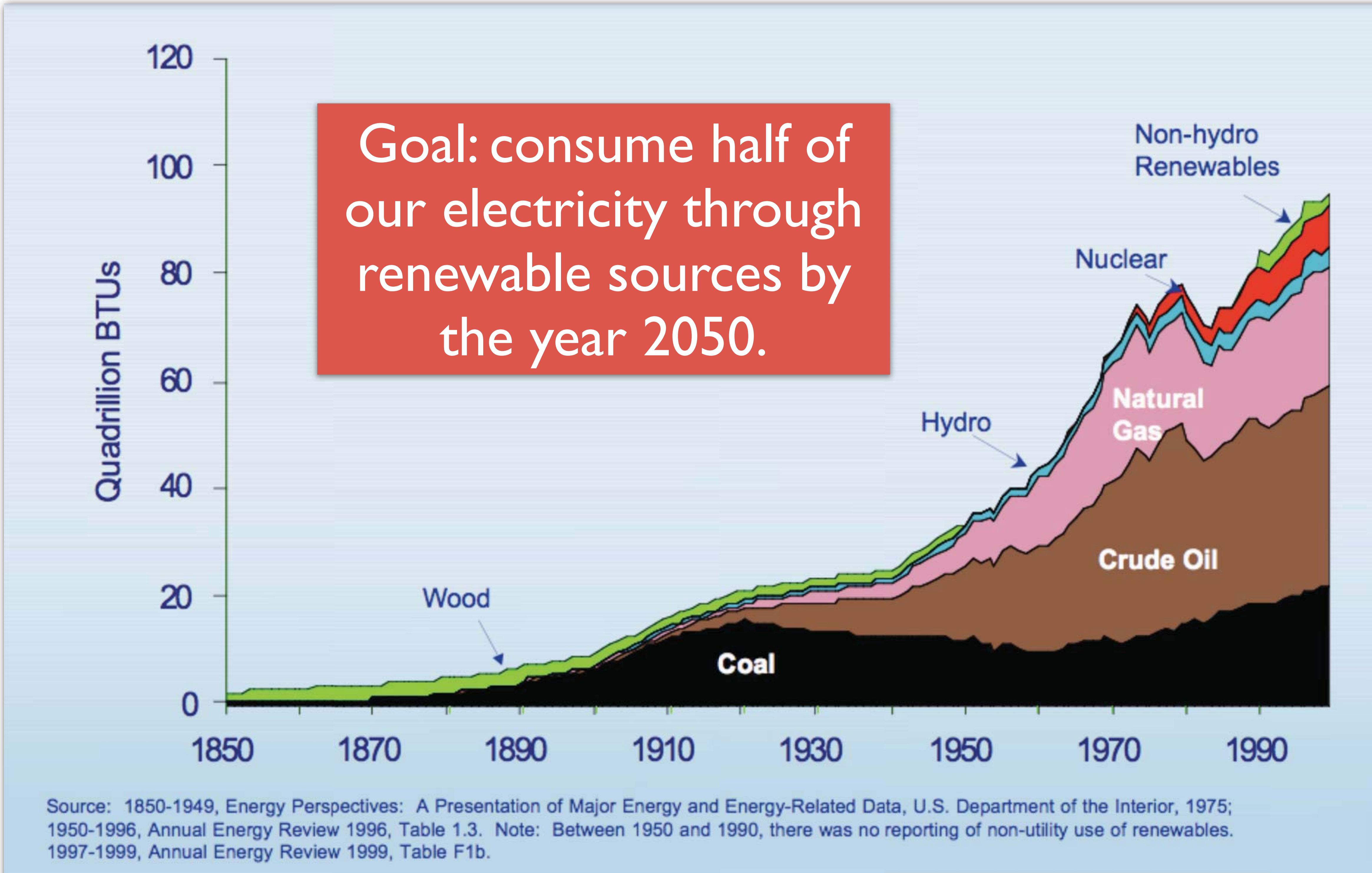


Courtesy of M. E. J. Newman.

- In 2002 the world burned energy at a rate of 13.5 TW
- How fast will we burn energy in 2050?
- (assume 9 billion people)
- If we use energy like in U.S. we will need 102 TW
- Conservative estimate: 28~35 TW

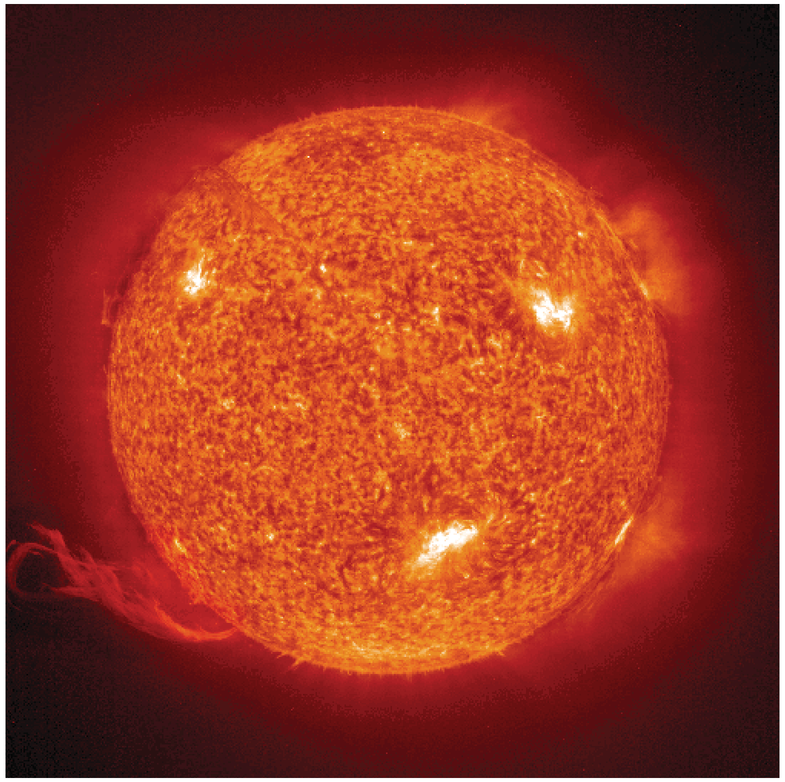
Energy use estimates from Nocera, Daedalus 2006 & Lewis and Nocera, PNAS 2006

U.S. Energy Consumption



Energy from the Sun

- Energy released by an earthquake of magnitude 8 (10^{17} J):
  - the sun delivers this in one second
- Energy humans use annually (10^{20} J):
  - sun delivers this in one hour
- Earth's total resources of oil (3 trillion barrels, 10^{22} J):
  - the sun delivers this in two days



Courtesy of SOHO/EIT (ESA & NASA) consortium.