Density Functional Theory and General Notions of First-Principles Codes

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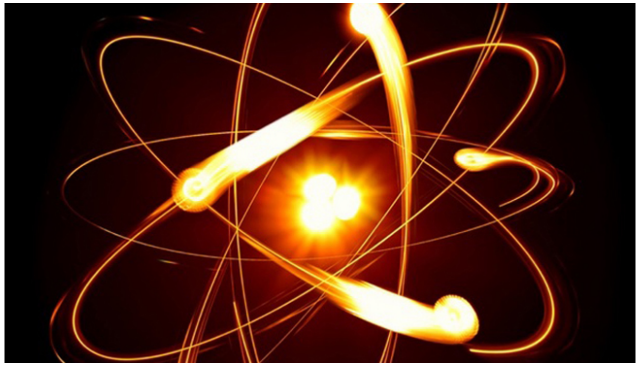
The physics of low-energy matter



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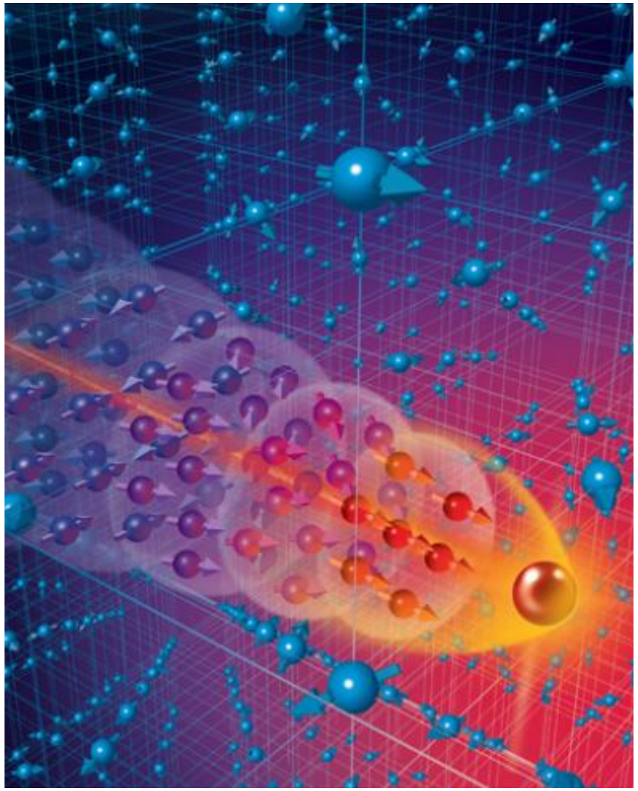
Made of electrons & nuclei
(interacting with photons)

matter at T up to several millon K

(except for nuclear fission and radioactive decay)

- Atomic & molecular physics
- Condensed matter physics (solids, liquids)
- Plasma physics

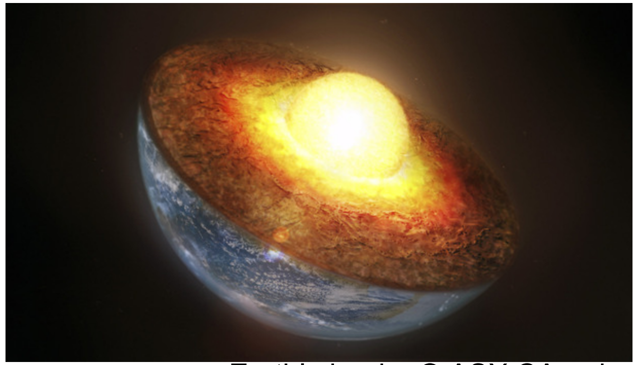


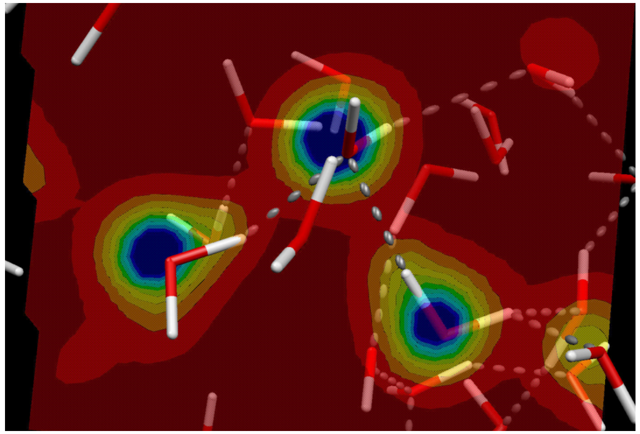
Low energy in the sense of
not probing inner structure of nuclei

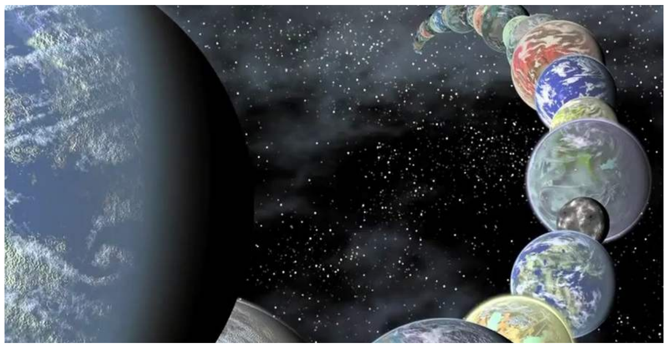
The physics of low-energy matter

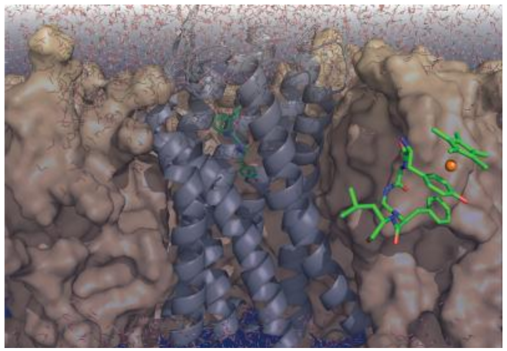
Behind properties and processes in

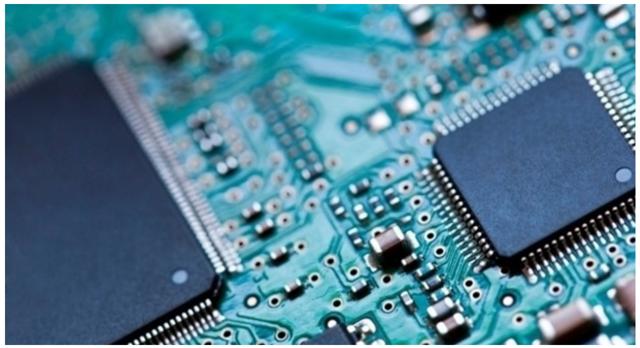
- *Chemistry*
- *Biomedicine (biochem, biophys, molecular bio)*
- *Geo (geophyiscs, geochemistry)*
- *Lots of astrophysics (planets, exoplanets)*
- *Engineering (materials, electronics …)*
- *Energy research*
- *Nanoscience and technlogy*


Earth’s inerior © ASX CAnada


Liquid water © MV Fernandez-Serra







Even a white dwarf
Carbon at high T and P

T. Metcalfe, M. Montgomery & K. Kaana
Astrophys. J. Lett. (2004)

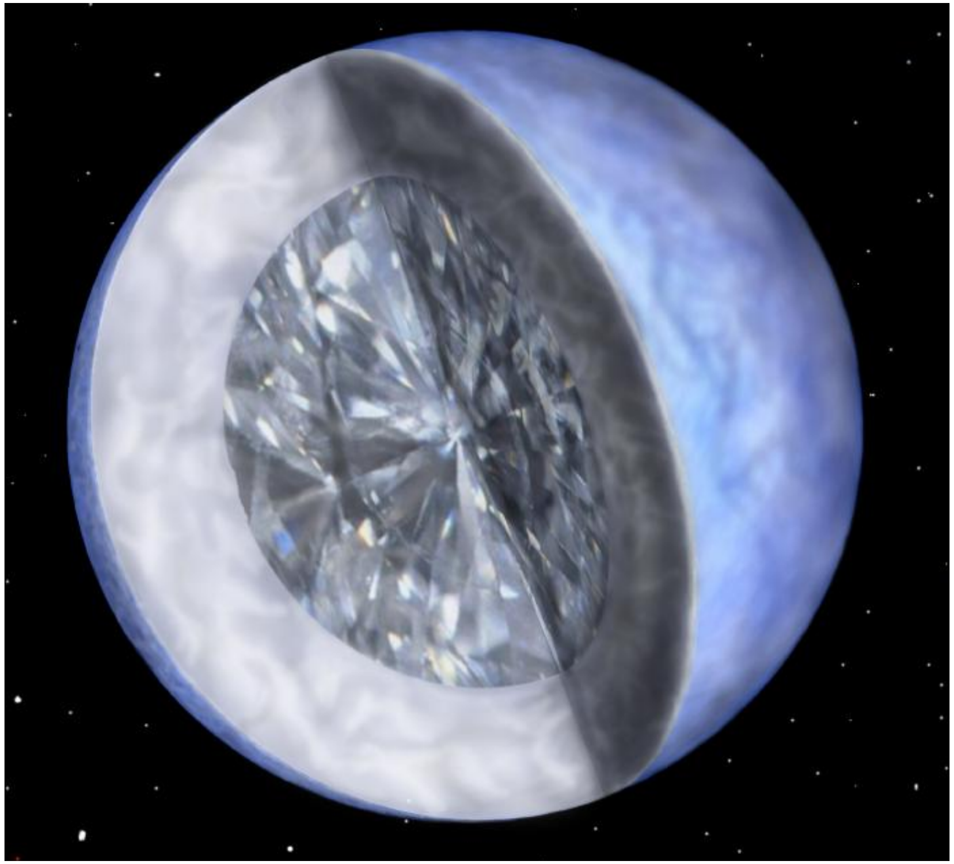
White dwarf (dead star) in Centaur (50 light-years away)

R = 2000 Km (< Earth)

M = 300,000 x M_{Earth}

T = 2 million K

Density = 10^6 gr/cc



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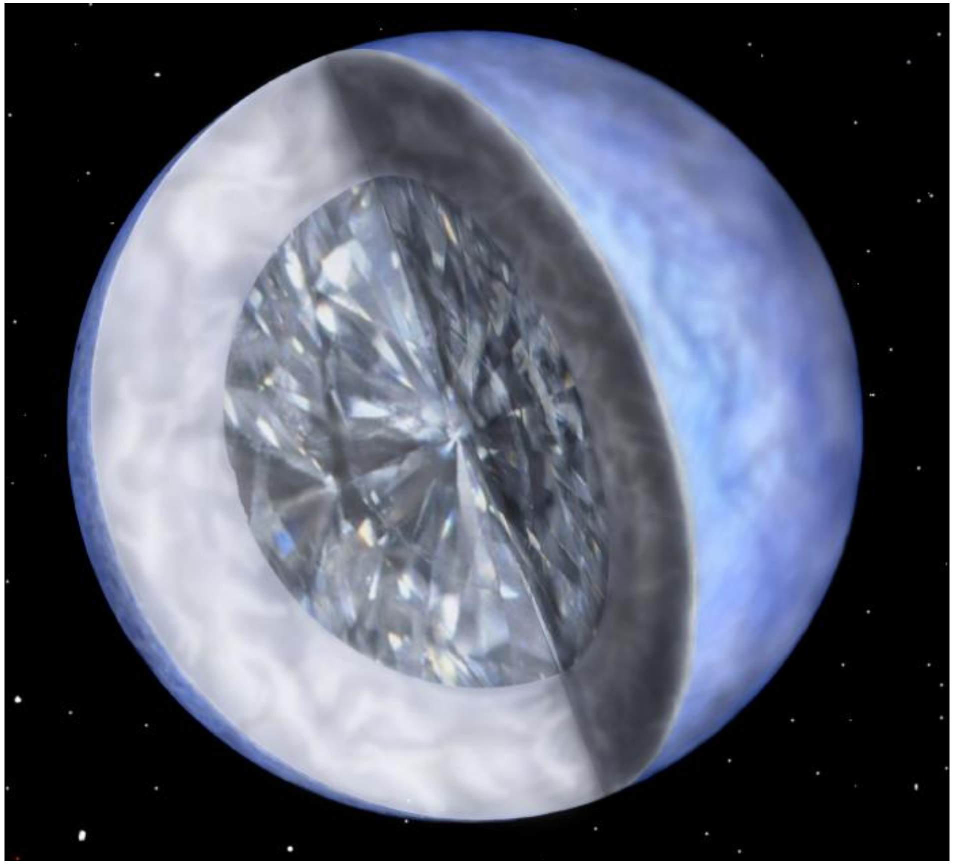
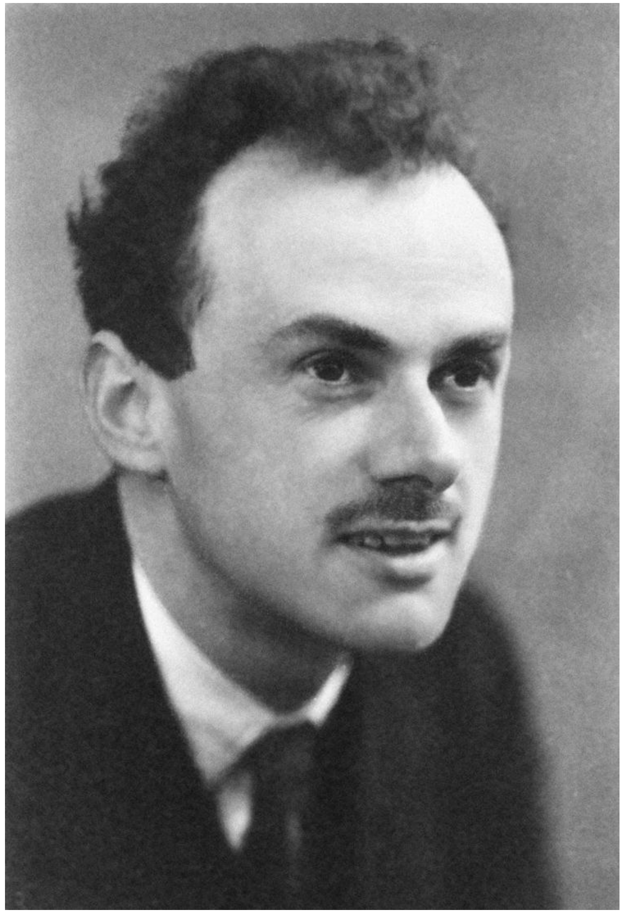


Lucy

Just electrons and nuclei

The underlying physical laws necessary for the mathematical theory of . . . the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

Paul Dirac, 1929

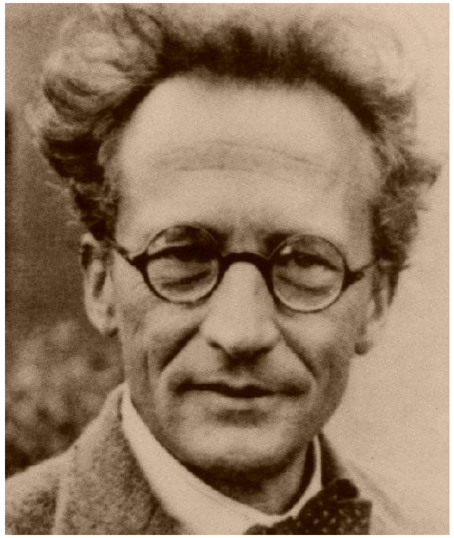


Just electrons and nuclei?

Dirac's statement just after quantum revolution

Quantum mechanics

of Heisenberg (1925) and Schrödinger (1926)



Schrödinger equation:

$$\hat{H}\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = E\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$

This is the fundamental equation to be solved for most systems of electrons and nuclei.

A function defined in a space of

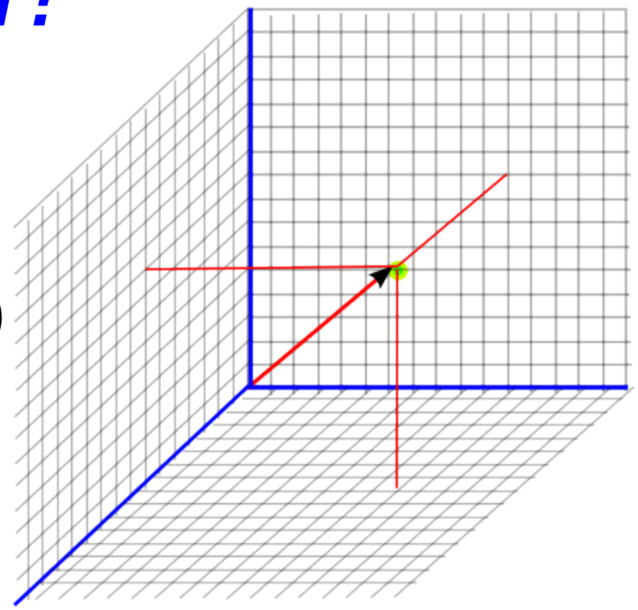
3N dimensions

(N = number of particles) (most = non-relativistic)

Just electrons and nuclei?

Exponential **Complexity**

$$\hat{H}\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = E\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$



Solving in a computer:

e.g. discretising space

A 3D grid in 100 points per side => 100^3 points

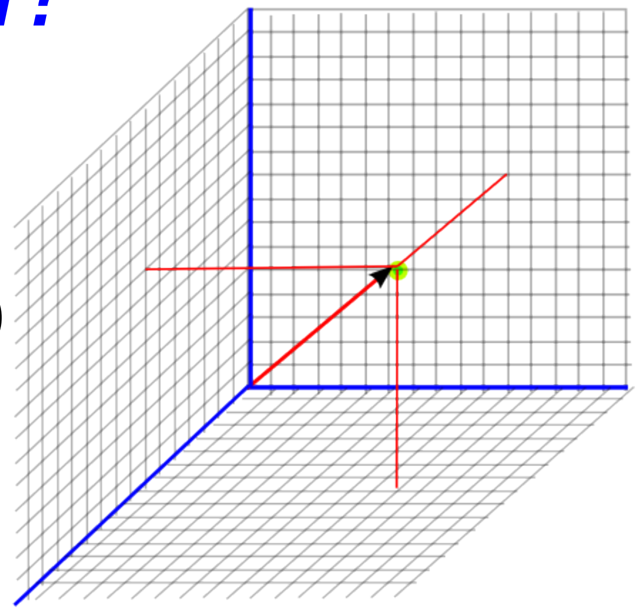
Similar grid in 3N space => 100^{3N} points

Computational costs (CPU & memory)

scales ***~exp(N)***

Just electrons and nuclei?

Exponential **Complexity**



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Computational costs (CPU & memory) scales ***~exp(N)***

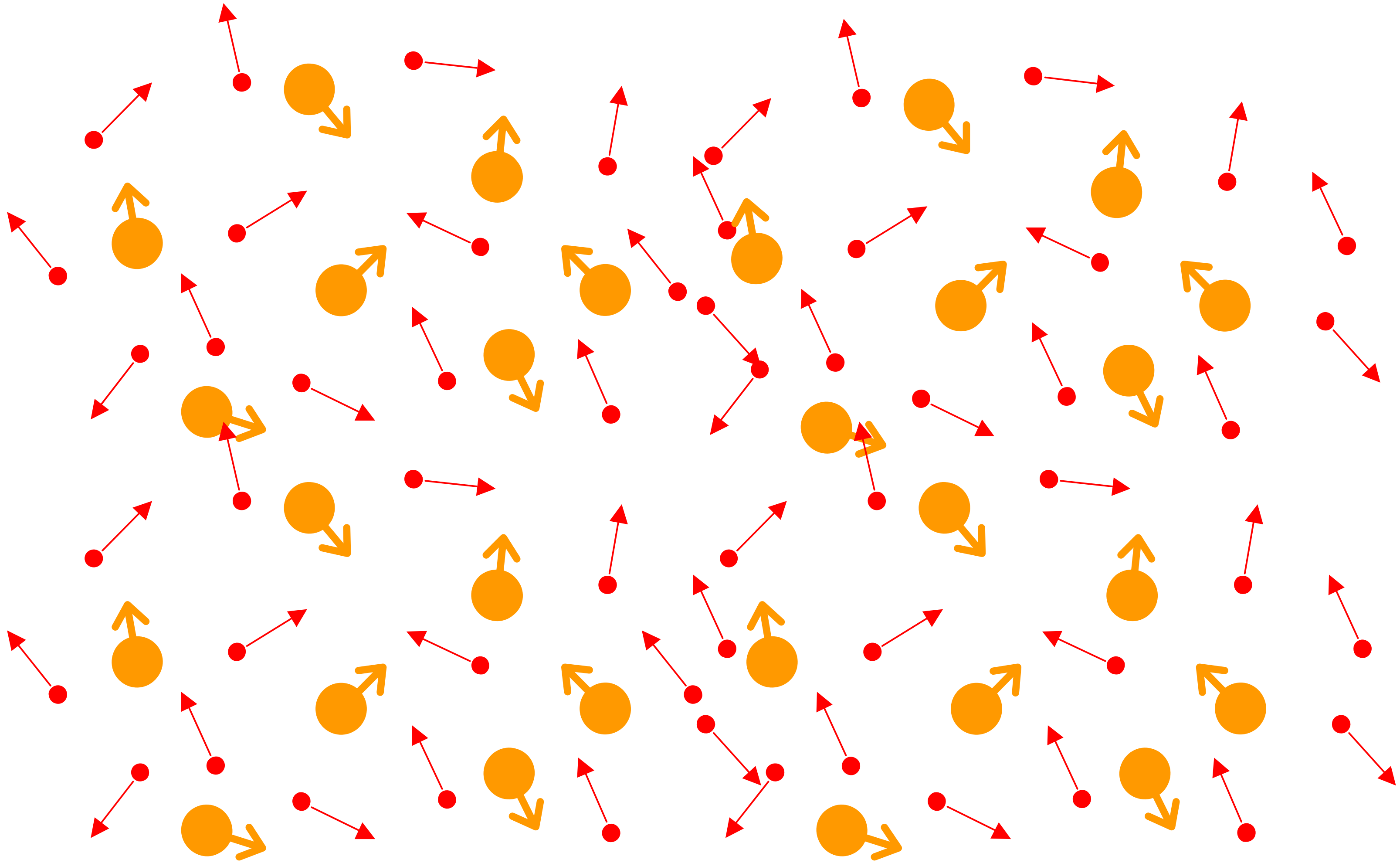
Walter Kohn, in Nobel Lecture 1998,

First-principles calculations to simulate the behaviour of matter

- *Fundamental laws of physics*
- *Set of "accepted" approximations*
  to solve the corresponding equations on a computer
- *No empirical input*

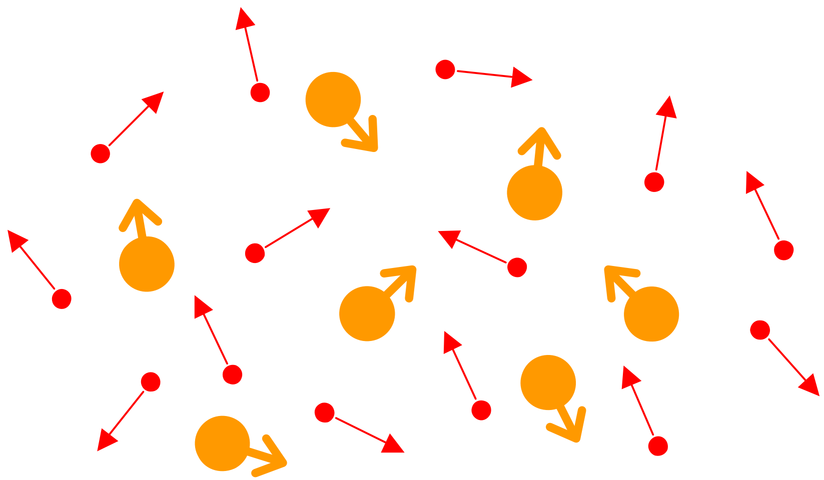
PREDICTIVE POWER

(as opposed to empirical atomistic simulations)



Problem faced: dynamics of electrons & nuclei

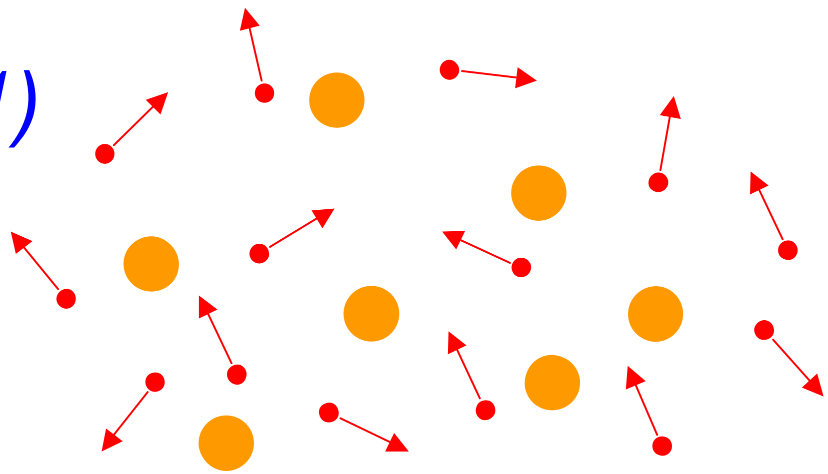
Adiabatic decoupling



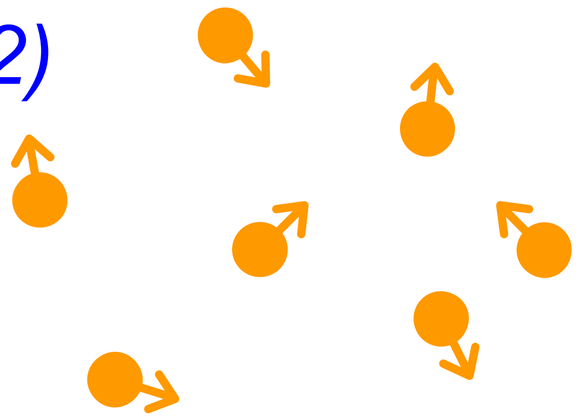
$$\frac{m_n}{m_e} >> 1$$

$\Rightarrow$ *Nuclei are much slower than electrons*

(1)



(2)



Quantum mechanics Many electron problem:

F = m a, *evolution in (discretised) time:*

Quantum mechanics for many particles

Schroedinger's equation

$$\hat{H}\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = E\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$

is exactly solvable for

- Two particles (analytically)

- Very few particles (numerically)

The number of electrons and nuclei

in a pebble is ~10^{23}

=> APPROXIMATIONS

Many-electron problem

Old and extremely hard problem!

Different approaches

- *Quantum Chemistry (Hartree-Fock, CI…)*
- *Quantum Monte Carlo*
- *Perturbation theory (propagators)*
- *Density Functional Theory (DFT)*

Very efficient and general
BUT implementations are approximate
and hard to improve
(no systematic improvement)

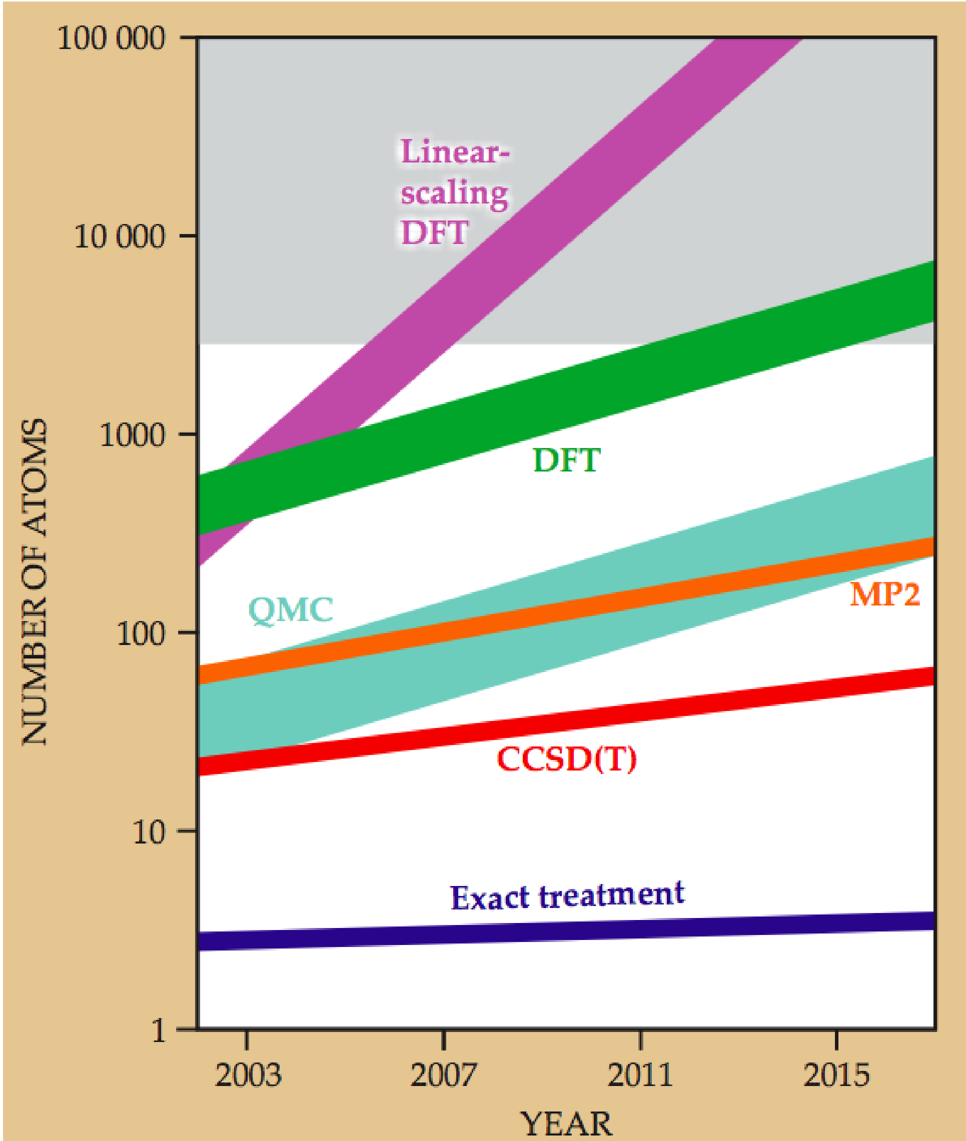
(… actually running out of ideas …)

Many-electron problem

Lots of physics behind first-principles methods
(90 years of quentum many-particle physics)

DFT
best compromise efficiency/accuracy

From laptops to huge supercomputers (10^5 cores)



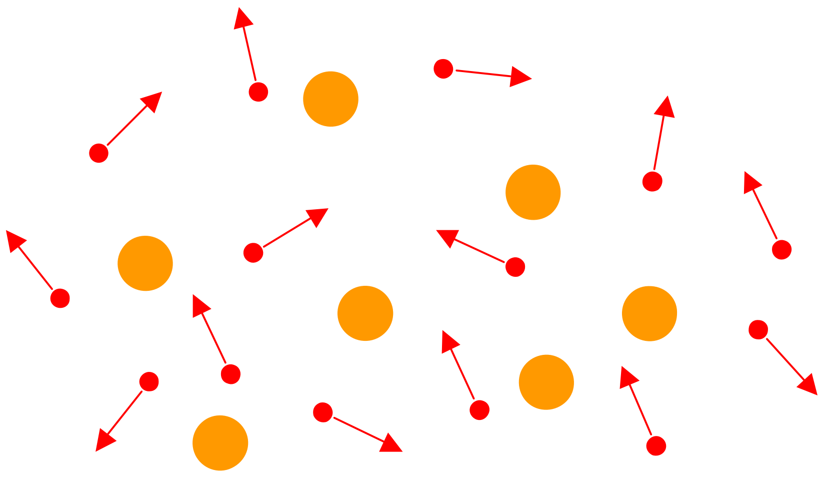
M. Head-Gordon and E. Artacho

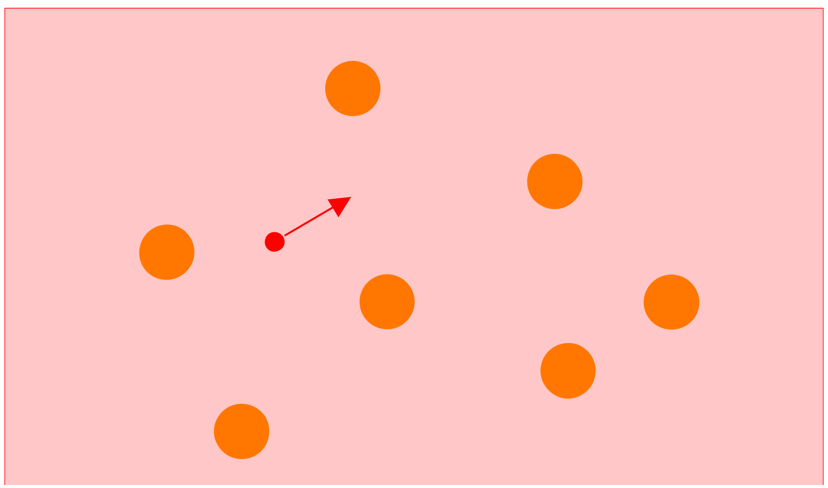
Many-electron problem

Density-Functional Theory

1. $\min E[\Psi(\{\vec{r}_i\})] \rightarrow \min E[\rho(\vec{r})]$

2. *As if non-interacting electrons in an effective (self-consistent) potential*





Hohenberg - Kohn

$$\Psi(\{\vec{r}_i\}) \longrightarrow n(\vec{r})$$

For our many-electron problem $\hat{H} = T + V_{ee} + \sum_{i=1}^{N} V_{ext}(\vec{r}_i)$

1. $E[n(\vec{r})] \equiv \int d^3\vec{r}\, V_{ext}(\vec{r})n(\vec{r}) + F[n(\vec{r})] \quad \geq E_{GS}$

(depends on nuclear positions) (universal functional)

2. $E[n_{GS}(\vec{r})] = E_{GS}$

PROBLEM:
Functional unknown!

Kohn - Sham

Independent particles in an effective potential

They rewrote the functional as:

$$E[\rho] = T_0[\rho] + \int d^3\vec{r}\,\rho(\vec{r})[V_{ext}(\vec{r}) + \tfrac{1}{2}\Phi(\vec{r})] + E_{xc}[\rho]$$

Kinetic energy for system with no e-e interactions ($T_0[\rho]$)

Hartree potential ($\tfrac{1}{2}\Phi(\vec{r})$)

The rest: exchange correlation ($E_{xc}[\rho]$)

Equivalent to independent particles under the potential

$$V(\vec{r}) = V_{ext}(\vec{r}) + \Phi(\vec{r}) + \frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}$$

E_{xc} & V_{xc}

$$V_{xc} \equiv \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

Local Density Approximation (LDA)

$$V_{xc}[n](\mathbf{r}) \approx V_{xc}(n(\mathbf{r}))$$

(function parameterised for the homogeneous electron liquid as obtained from QMC)

Generalised Gradient Approximation (GGA)

$$V_{xc}[n](\mathbf{r}) \approx V_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

(new terms parameterised for heterogeneous electron systems (atoms) as obtained from QC)

E_{xc} & V_{xc}

$$V_{xc} \equiv \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

Local Density Approximation (LDA)

$$E_{xc}^{LDA}[n] = \int d^3\mathbf{r}\; n(\mathbf{r})\, \varepsilon_{xc}(n)$$

In terms of the energy density

$$E_{x}^{LDA}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/2} \int d^3\mathbf{r}\; n(\mathbf{r})^{4/3}$$

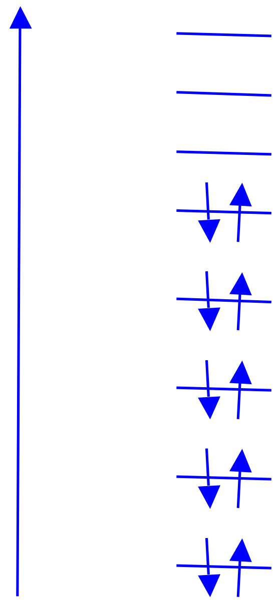
Exact result for the homogeneous electron liquid (from solving HF equations)
Dirac expressed it like this (Slater)

Independent particles

$$\hat{h} = -\frac{1}{2}\nabla^2 + V(\vec{r})$$

$$\hat{h}\psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r})$$

ε_n



$$\rho(\vec{r}) = \sum_{n}^{occ} \left|\psi_n(\vec{r})\right|^2$$

CAREFUL

Density Functionals

LDA (PZ)

GGAs: - Chemistry: BLYP, …

- Physics: PBE, RPBE, WC

MetaGGAs (kinetic energy density)

….

Hybrids: exchange: 75% GGA + 25% HF

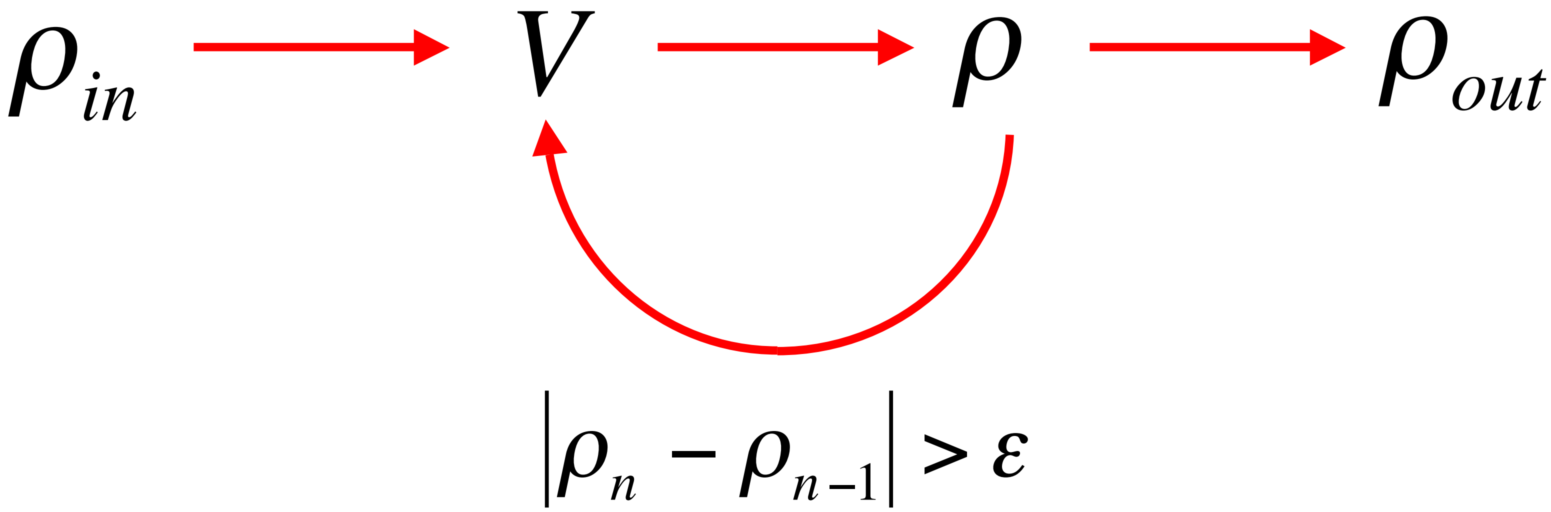
(not strictly DFT, non-local potential: costly)

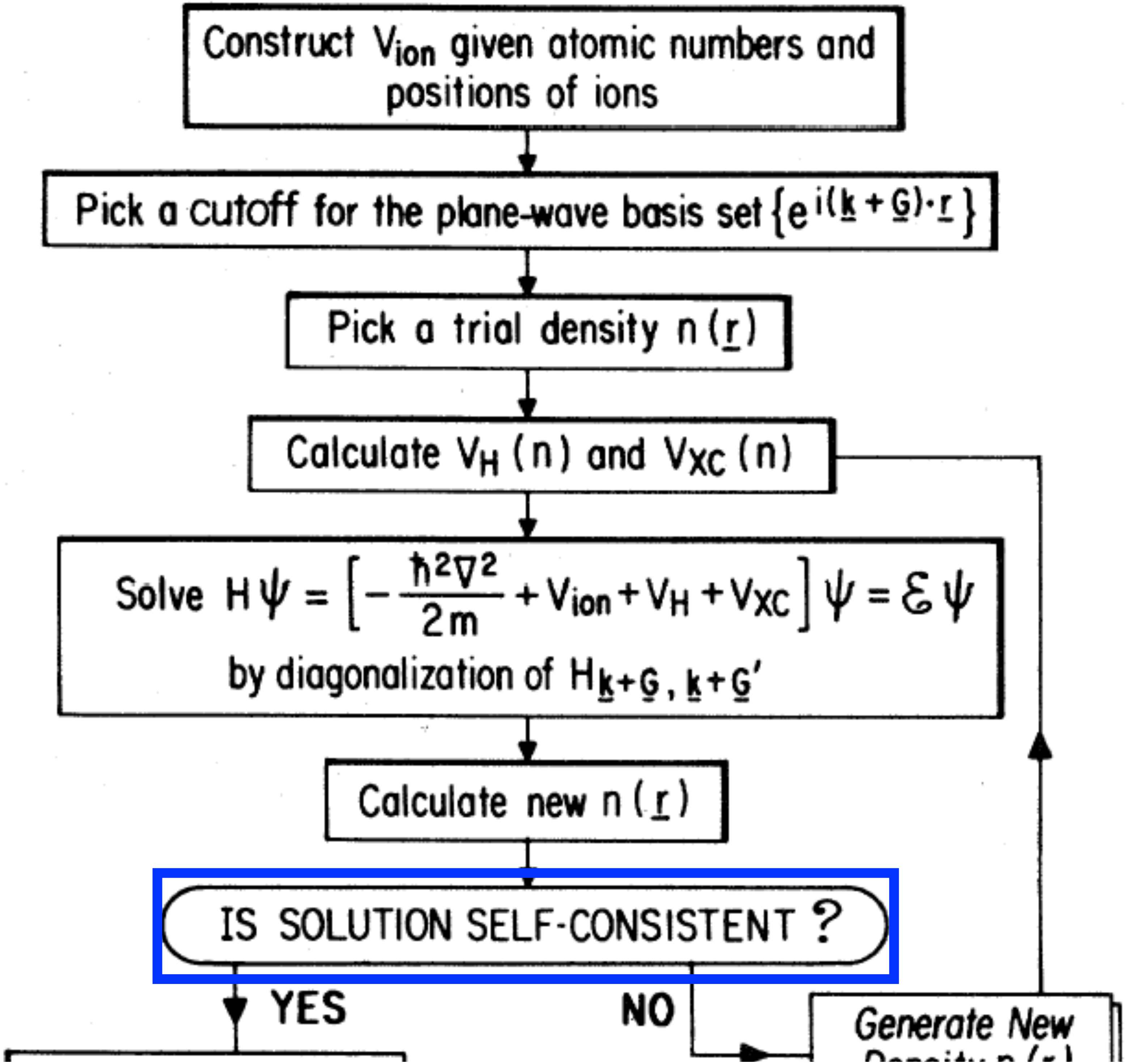
B3LYP, PBE0, etc

Practical aspects

Self-consistency

PROBLEM: The potential (input) depends on the density (output)




Construct V_{ion} given atomic numbers and positions of ions
Pick a cutoff for the plane-wave basis set $\{e^{i(\underline{k}+\underline{G})\cdot\underline{r}}\}$
Pick a trial density $n(\underline{r})$
Calculate $V_H(n)$ and $V_{XC}(n)$
Solve $H\psi = \left[-\frac{\hbar^2\nabla^2}{2m} + V_{ion} + V_H + V_{XC}\right]\psi = \mathcal{E}\psi$
by diagonalization of $H_{\underline{k}+\underline{G},\,\underline{k}+\underline{G}'}$
Calculate new $n(\underline{r})$
IS SOLUTION SELF-CONSISTENT ?
YES
NO
Generate New

k-point sampling

Electronic quantum states in a periodic solid labelled by:

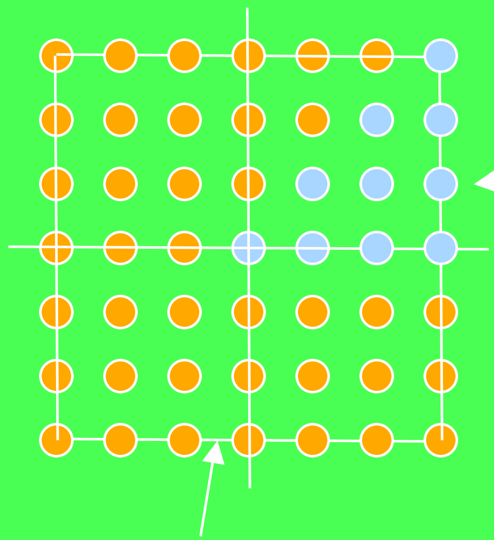
- *Band index*
- *k-vector: vector in reciprocal space within the first Brillouin zone (Wigner-Seitz cell in reciprocal space)*
- *Other symmetries (spin, point-group representation…)*

$$\rho(\mathbf{r}) = \sum_{n}^{occ} \left|\psi_n(\mathbf{r})\right|^2 \Rightarrow \sum_{n}^{occ} \int_{\mathbf{k}\in B.Z.} \mathrm{d}^3\mathbf{k} \left|\psi_{n,\mathbf{k}}(\mathbf{r})\right|^2$$

Approximated by sums over selected k-points

K-point sampling

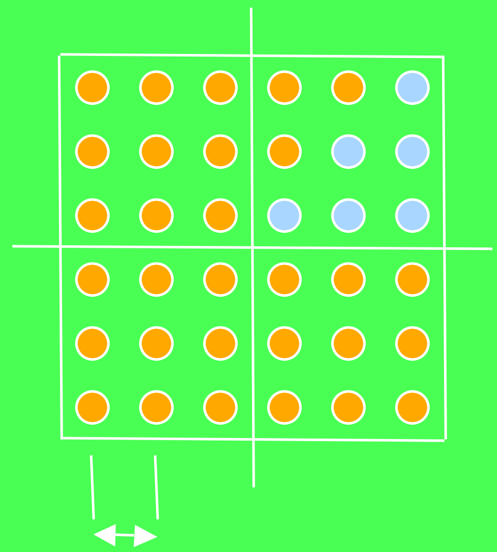
Regular k-grid



Inequivalent points

First Brillouin Zone

Monkhorst-Pack



$\Delta k \Rightarrow l_c = \pi / \Delta k$

6x6

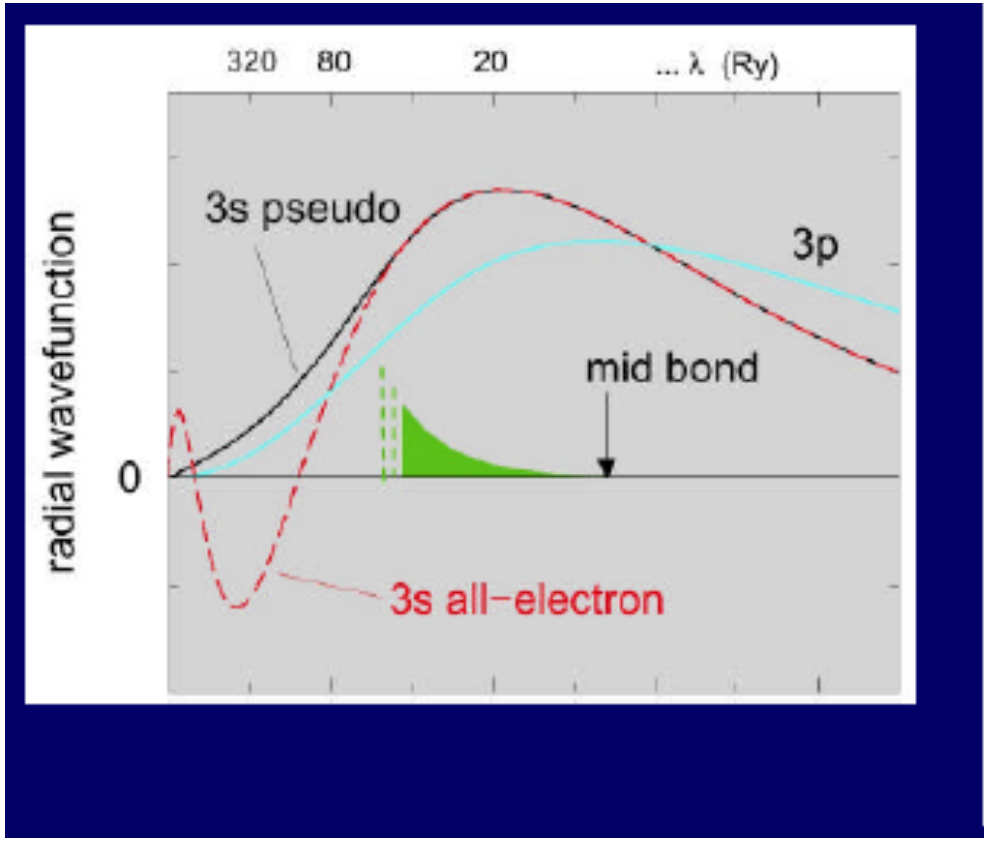
6x6 shifted

Pseudopotentials

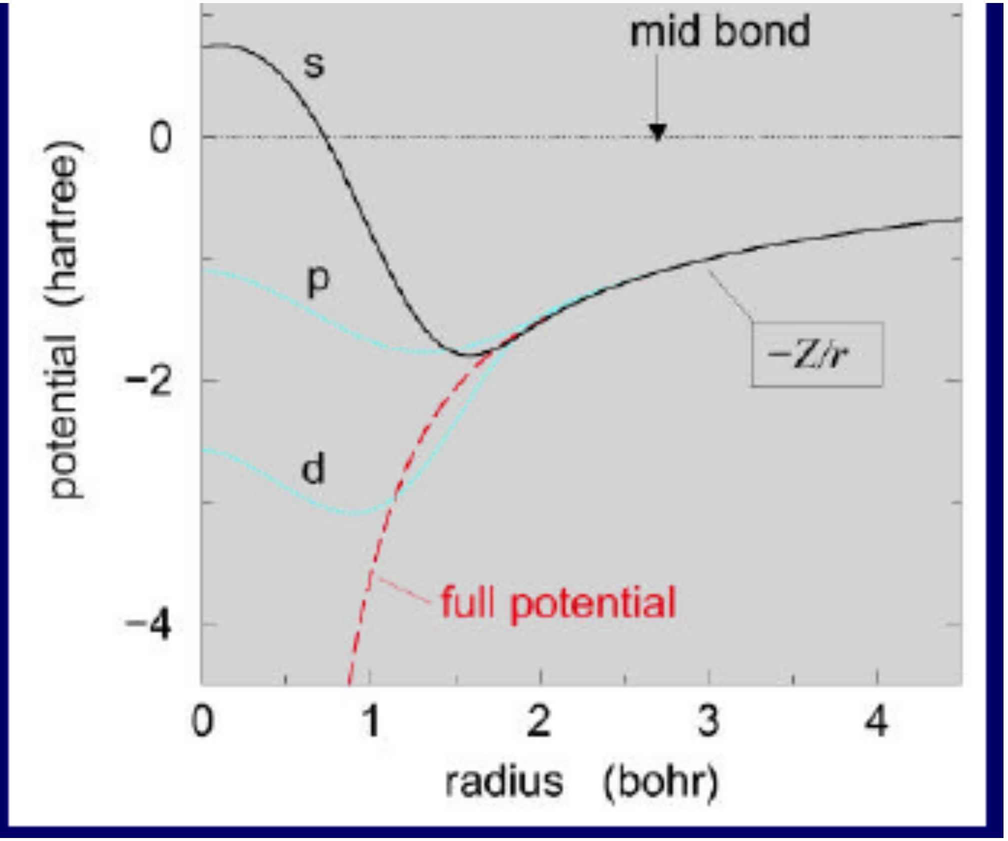
valence-core interactions

net effect of core electrons

Pseudo wave-function



pseudopotential



Solving: Basis set

Expand in terms of a finite set of basis functions $\left\{\phi_\mu(\mathbf{r})\right\}$: $\psi_n(\mathbf{r}) \approx \sum_\mu \phi_\mu(\mathbf{r})\, c_{\mu,n}$

unknown

$$\hat{h}\psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r}) \quad \Rightarrow \quad \sum_\mu \left[\hat{h}\,\phi_\mu(\mathbf{r})\right] c_{\mu,n} = \varepsilon_n \sum_\mu \phi_\mu(\mathbf{r})\, c_{\mu,n} \quad \Rightarrow$$

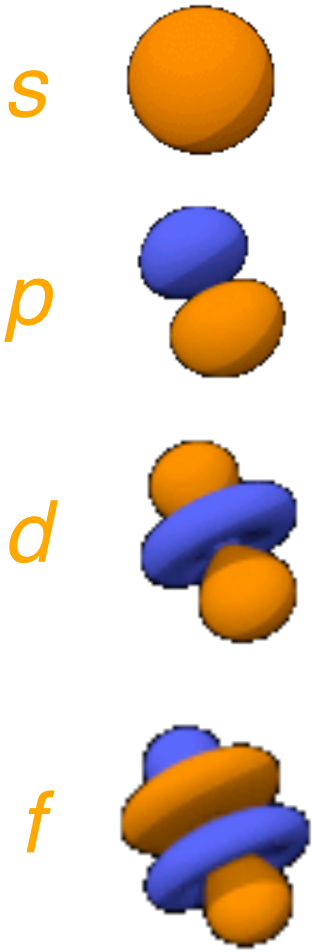
$$\sum_\mu h_{\nu\mu} c_{\mu,n} = \varepsilon_n \sum_\mu S_{\nu\mu} c_{\mu,n}$$

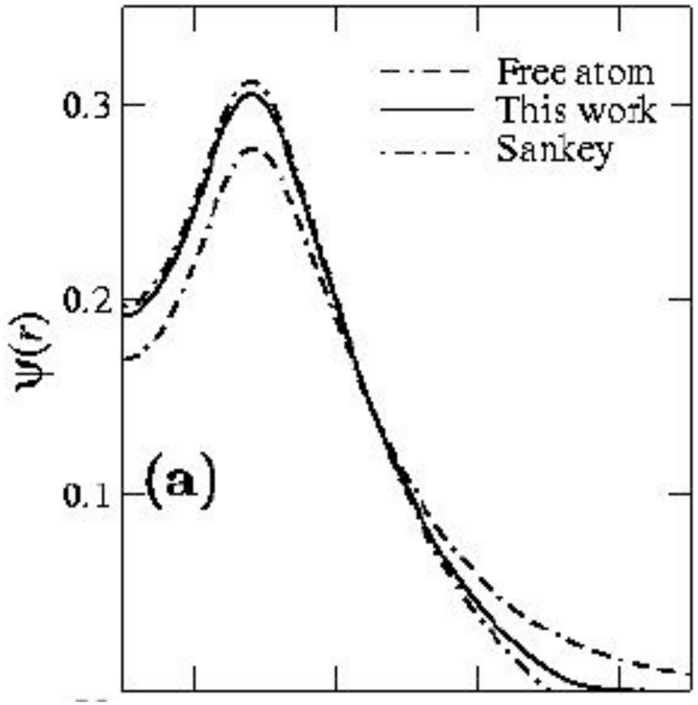
where

$$h_{\nu\mu} \equiv \int \mathrm{d}^3\mathbf{r}\ \phi_\nu^*(\mathbf{r})\ \hat{h}\phi_\mu(\mathbf{r})$$

$$S_{\nu\mu} \equiv \int \mathrm{d}^3\mathbf{r}\ \phi_\nu^*(\mathbf{r})\ \phi_\mu(\mathbf{r})$$

Basis set: Atomic orbitals





SIESTA: Strictly localized
(zero beyond cut-off radius)

[redacted]