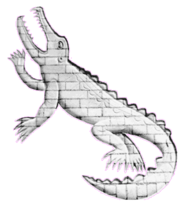
Density Functional Theory and General Notions of First-Principles Codes

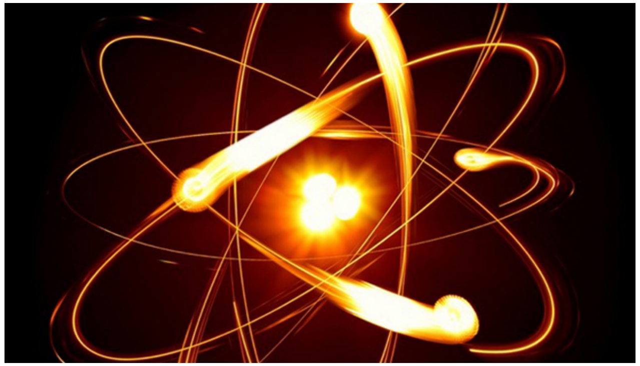
Emilio Artacho

Nanogune, Ikerbasque & DIPC, San Sebastian, Spain
Cavendish Laboratory, University of Cambridge



The physics of low-energy matter

Made of electrons & nuclei
(interacting with photons)



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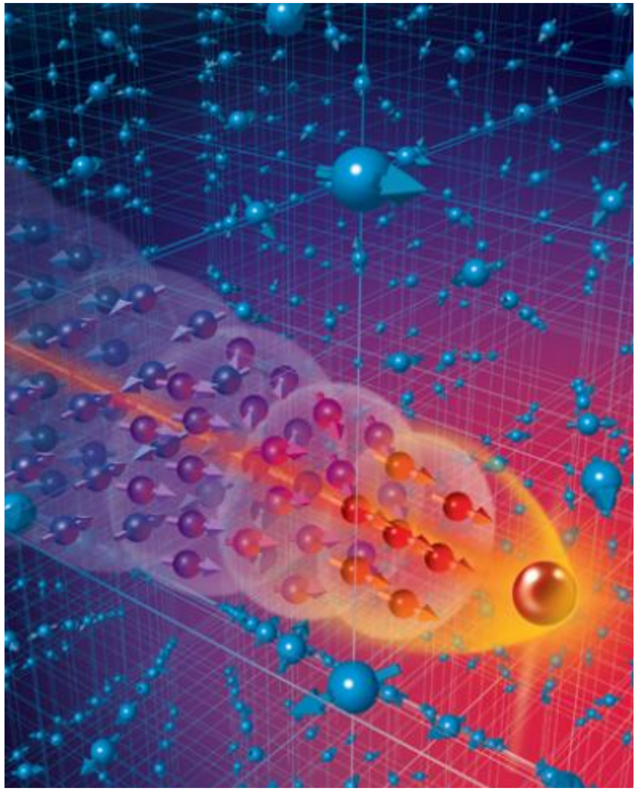
matter at T up to several millon K

(except for nuclear fission and radioactive decay)

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

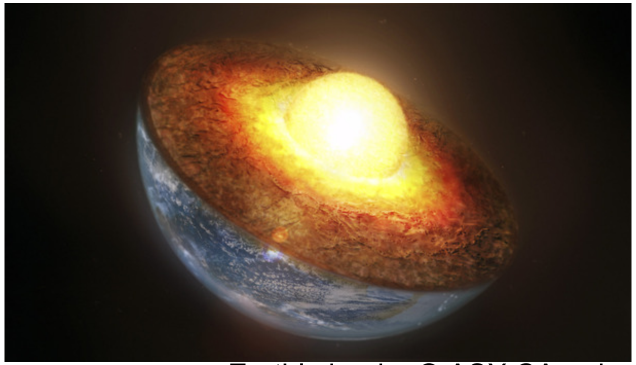


Low energy in the sense of
not probing inner structure of nuclei

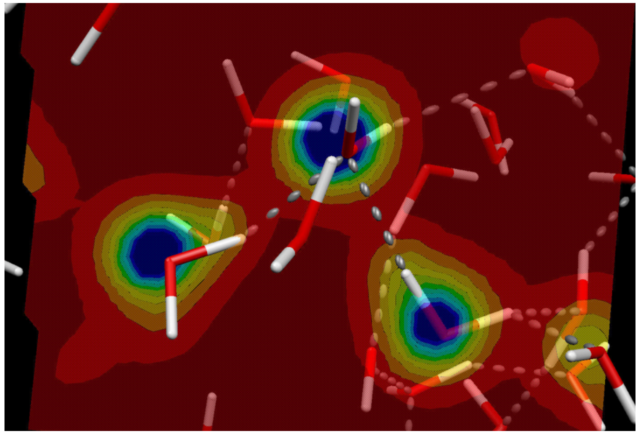
The physics of low-energy matter

Behind properties and processes in

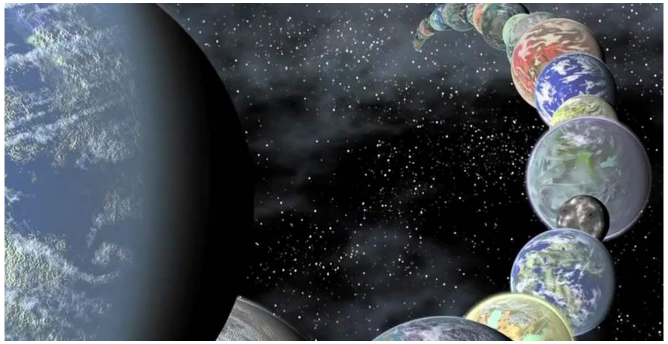
- *Chemistry*
- *Biomedicine (biochem, biophys, molecular bio)*
- *Geo (geophyiscs, geochemistry)*
- *Lots of astrophysics (planets, exoplanets)*
- *Engineering (materials, electronics …)*
- *Energy research*
- *Nanoscience and technlogy*

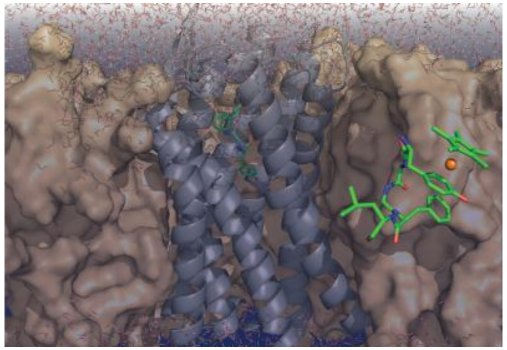


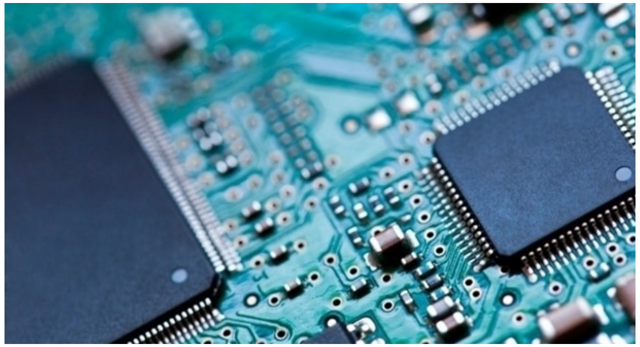
Earth's inerior © ASX CAnada



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)

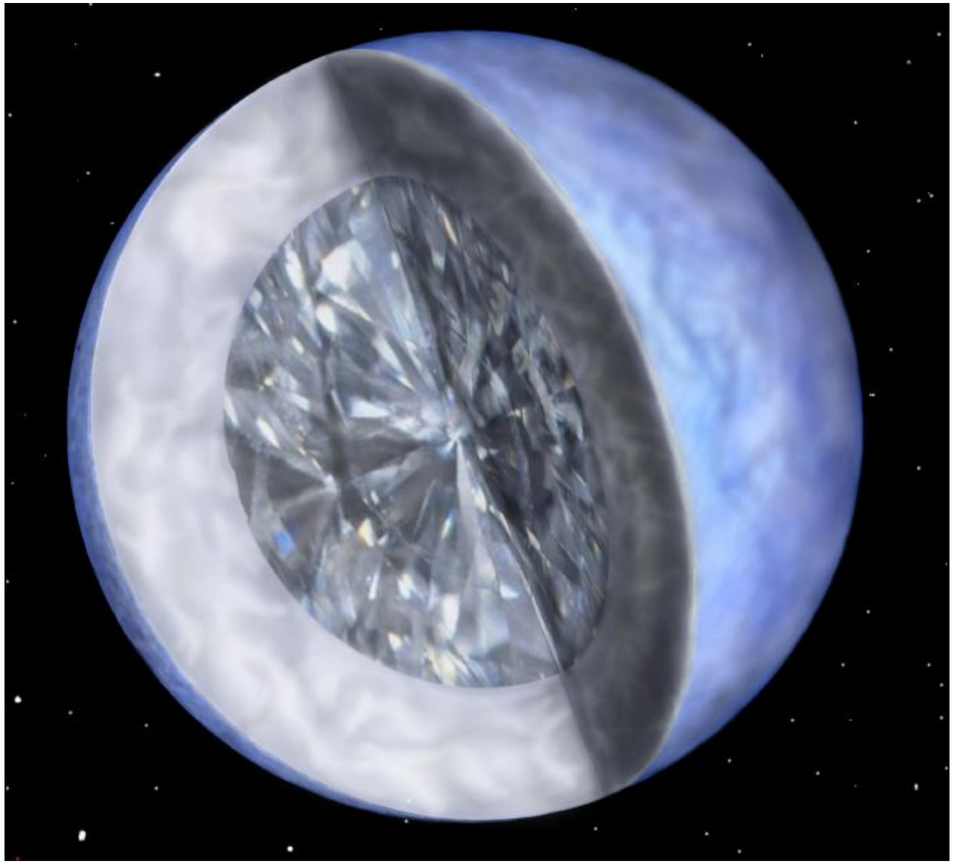
White dwarf (dead star) in Centaur (50 light-years away)

$R = 2000$ Km (< Earth)

$M = 300{,}000 \times M_{Earth}$

$T = 2$ million K

Density = 10^6 gr/cc

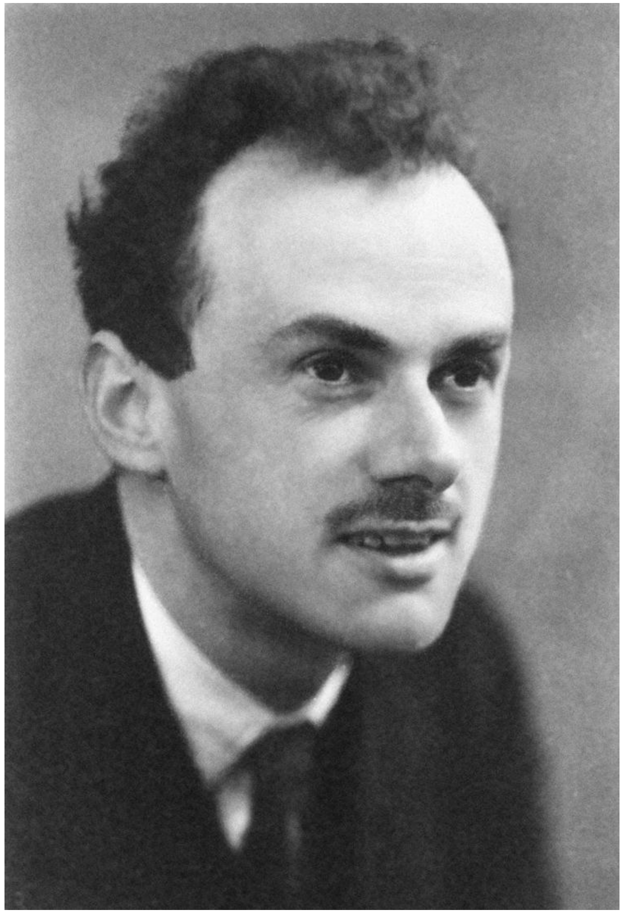


Lucy

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:

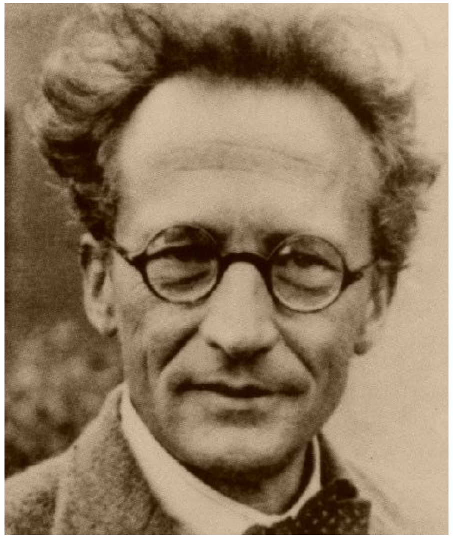
$$\hat{H}\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = E\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$

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

A function defined in a space of

3N dimensions

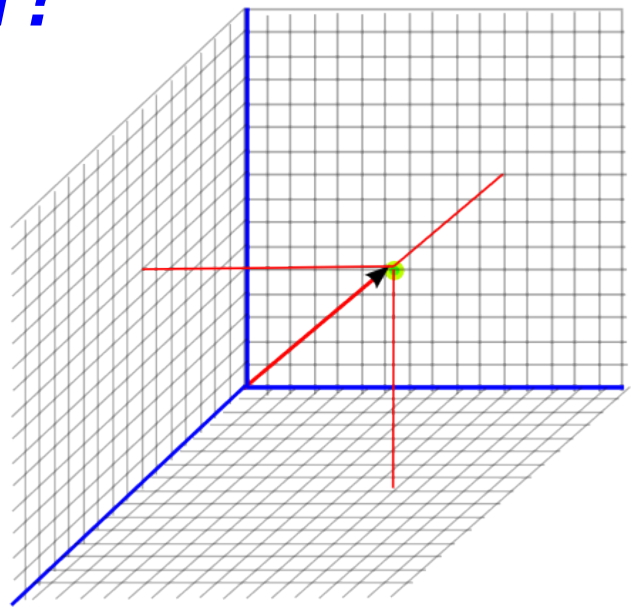
(N = number of particles) (most = non-relativistic)



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

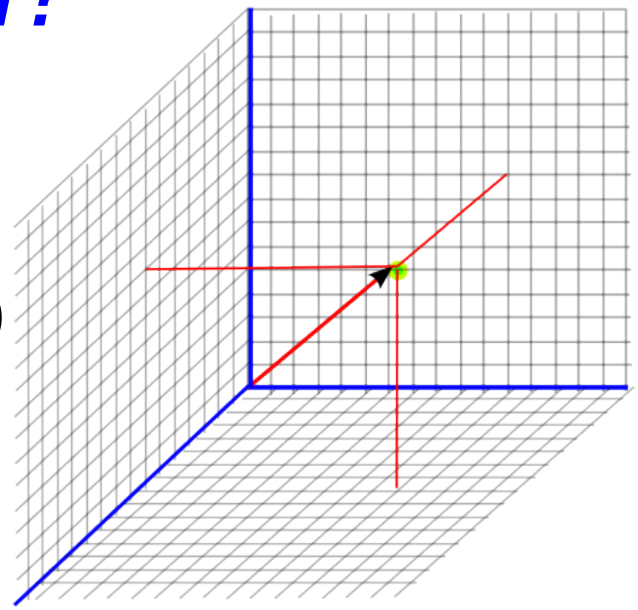
Similar grid in 3N space => 100^{3N} points

Computational costs (CPU & memory)

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

Just electrons and nuclei?

Exponential **Complexity**



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

Solving in a computer:

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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)***

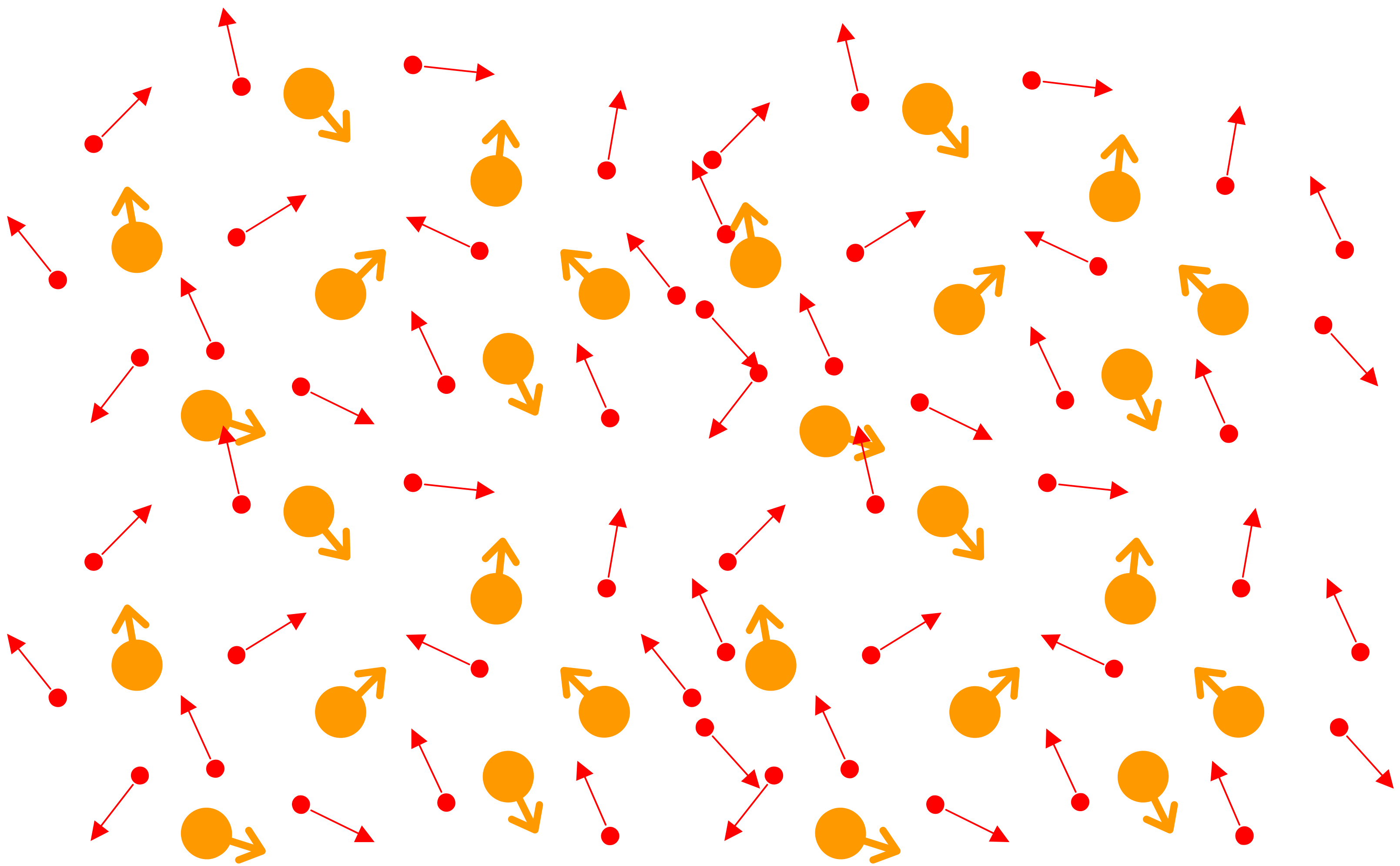
Walter Kohn, in Nobel Lecture 1998,

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*

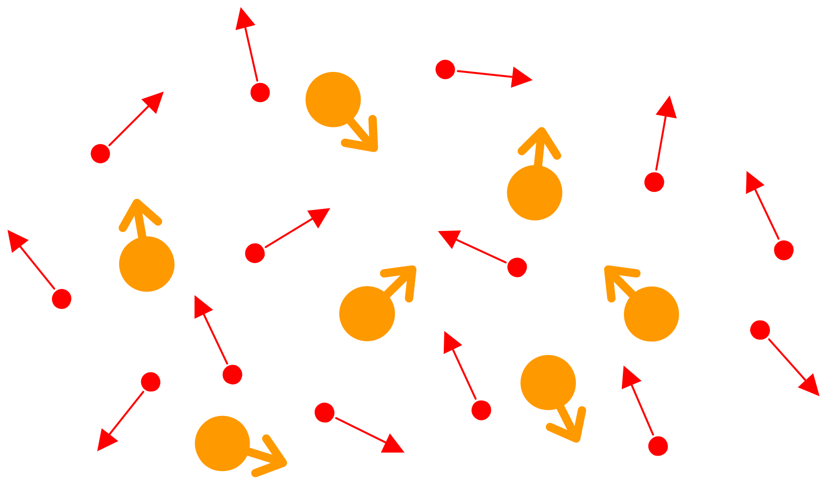
PREDICTIVE POWER

(as opposed to empirical atomistic simulations)



Problem faced: dynamics of electrons & nuclei

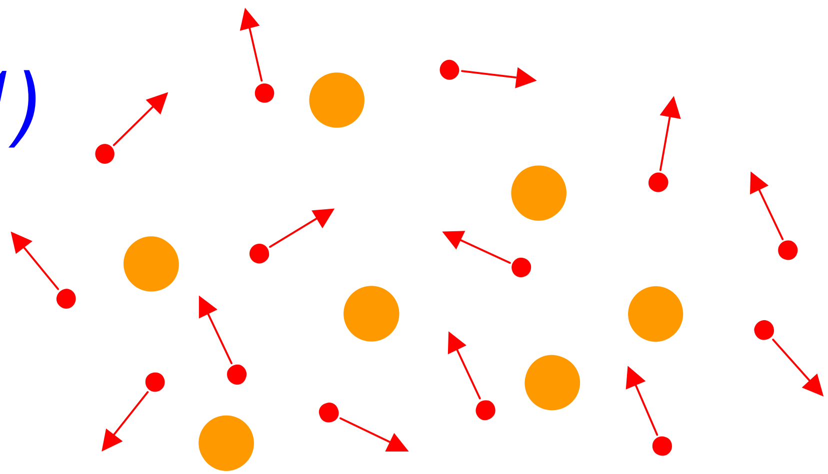
Adiabatic decoupling



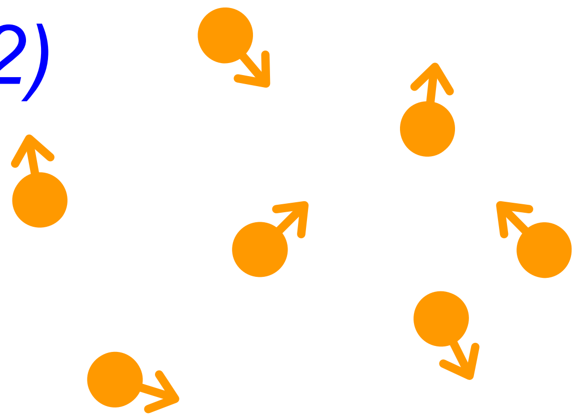
$$\frac{m_n}{m_e} >> 1$$

$\Rightarrow$ *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

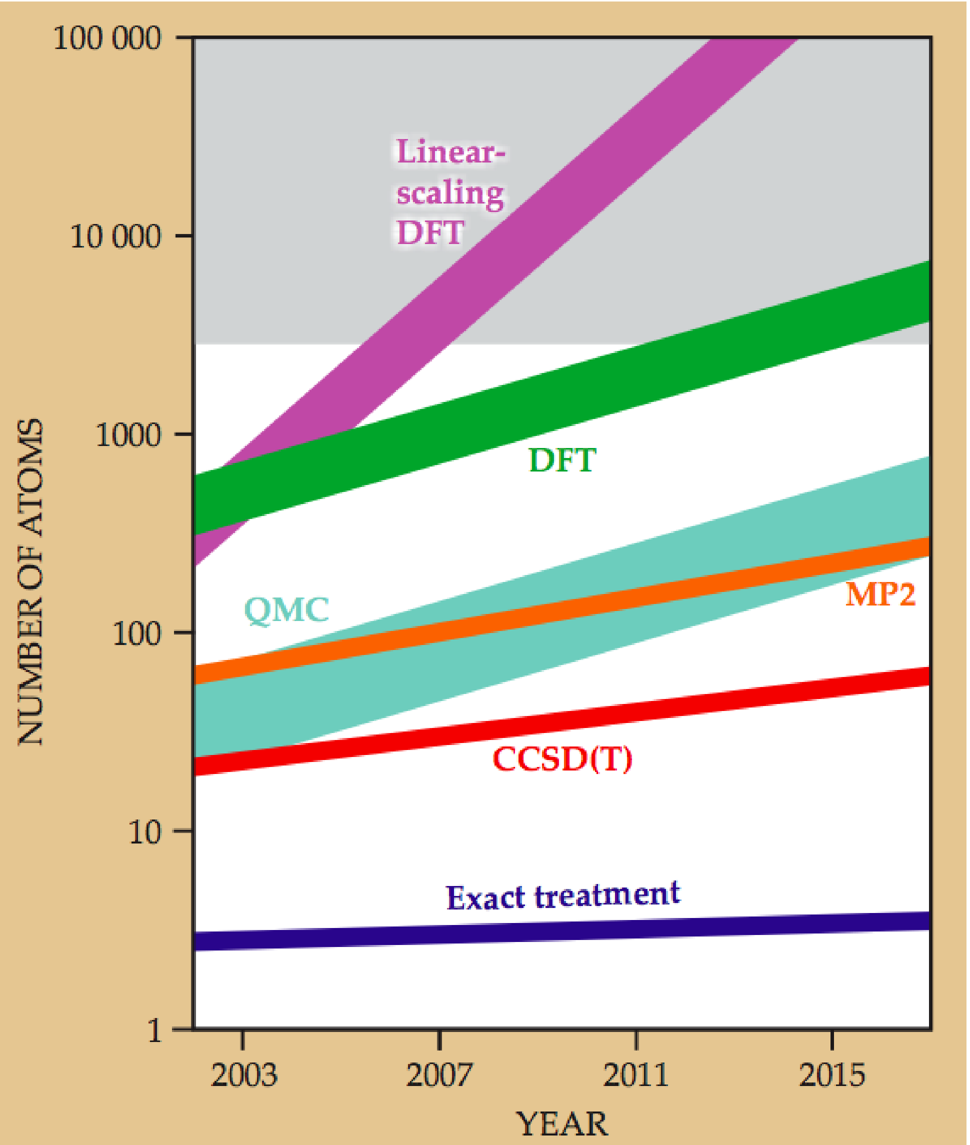
Lots of physics behind first-principles methods

(90 years of quentum many-particle physics)

DFT

best compromise efficiency/accuracy

From laptops to huge supercomputers (10^5 cores)



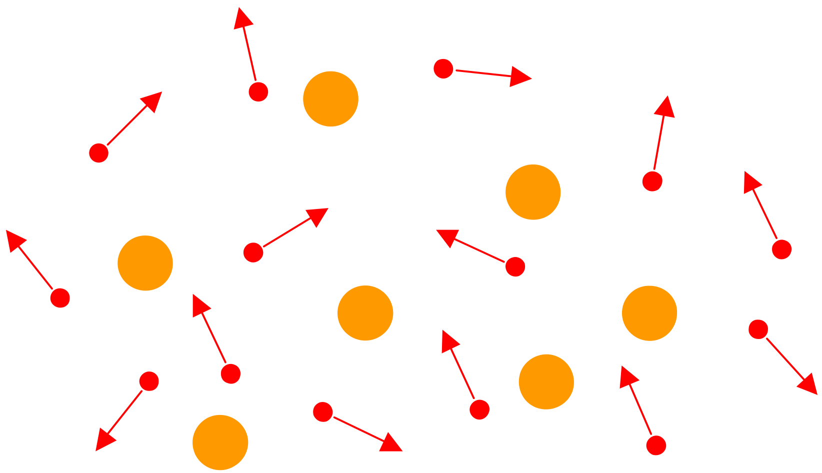
M. Head-Gordon and E. Artacho

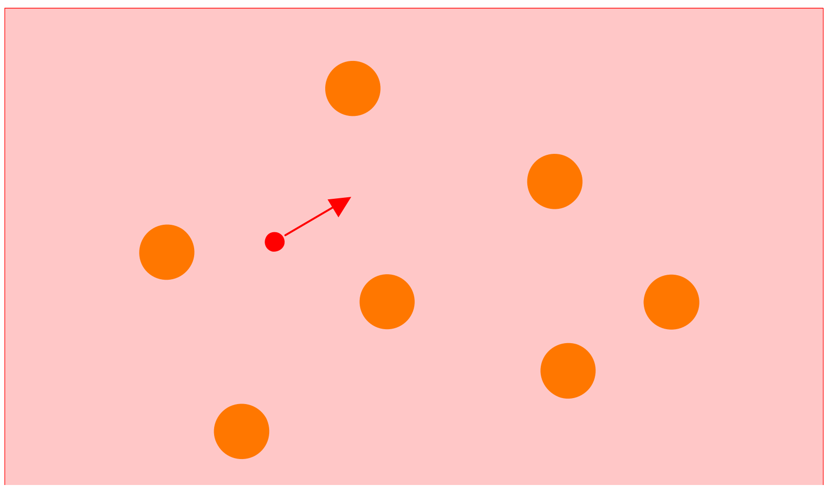
Many-electron problem

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

Hartree potential

The rest: exchange correlation

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)

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

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

Generalised Gradient Approximation (GGA)

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

(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

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

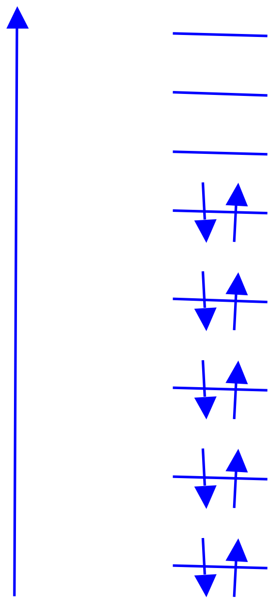
Exact result for the homogeneous electron liquid (from solving HF equations)
Dirac expressed it like this (Slater)

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)

….

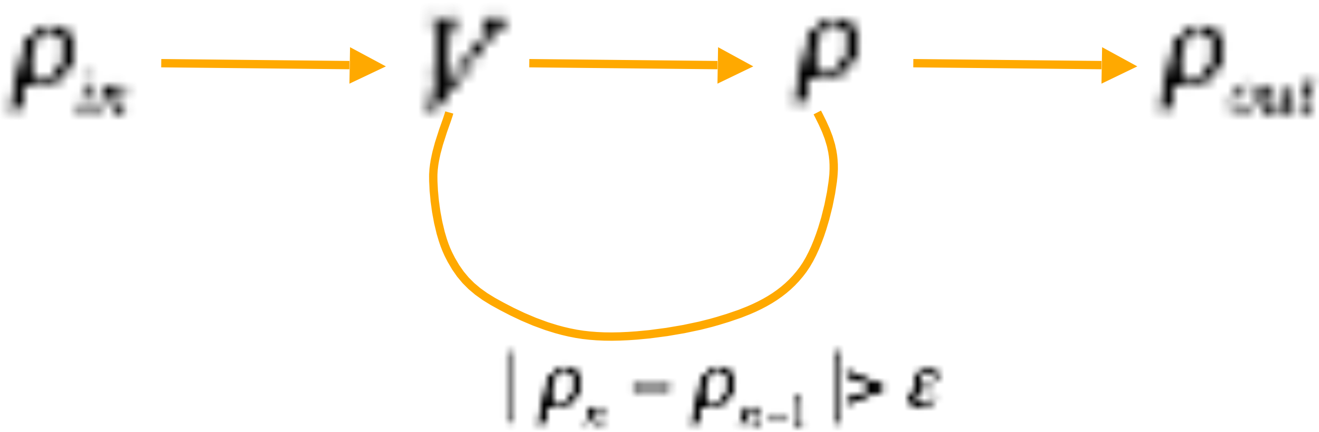
Hybrids: exchange: 75% GGA + 25% HF

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

B3LYP, PBE0, etc

Self-consistency

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



Practical Implementations

Solving: 1. Basis set

$$\psi_n(\vec{r}) = \sum_{\mu} c_{\mu n} \phi_\mu(\vec{r})$$

unknown

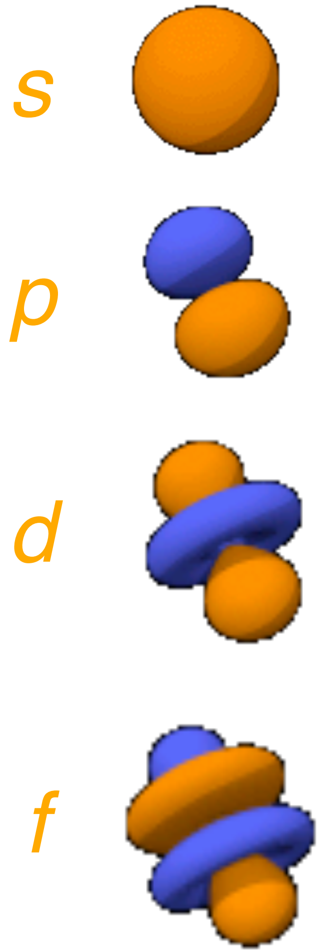
Expand in terms of a finite set of basis functions $\phi_\mu(\vec{r})$

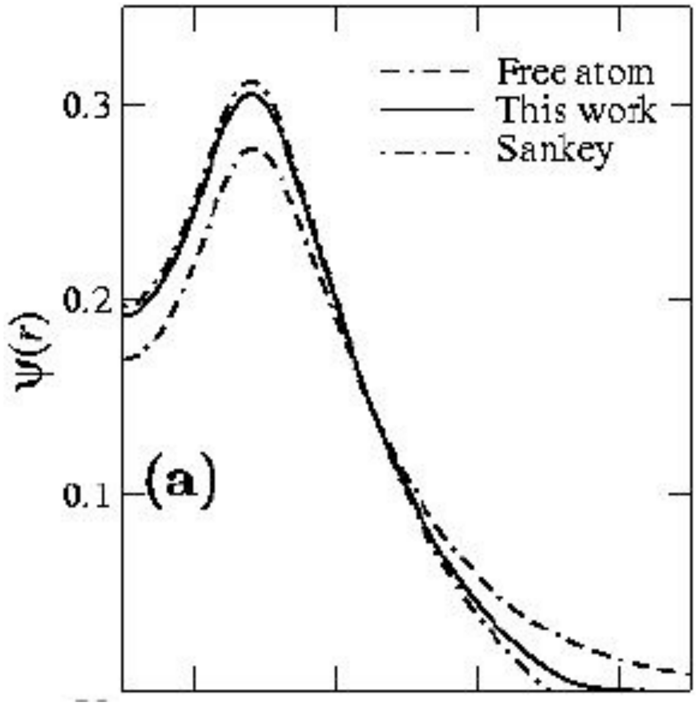
$$\hat{h}\psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r}) \rightarrow \sum_{\mu} c_{\mu n} \hat{h}\phi_\mu(\vec{r}) = \varepsilon_n \sum_{\mu} c_{\mu n} \phi_\mu(\vec{r})$$

$$h_{\nu\mu} = \int \phi_\nu^*(\vec{r}) \hat{h} \phi_\mu(\vec{r}) d^3\vec{r} \qquad S_{\nu\mu} = \int \phi_\nu^*(\vec{r}) \phi_\mu(\vec{r}) d^3\vec{r}$$

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

Basis set: Atomic orbitals





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

ADVANTAGES OF ATOMIC ORBITALS:

- Very efficient in terms of number of orbitals per electron (solution is close to the atomic one)
- Chemical information (charge population, etc) can be easily extracted. Very well suited to describe localization.
- No need for periodicity
- Vacuum does not have any cost

DISADVANTAGES OF ATOMIC ORBITALS:

- Lack of systematics in the convergence. How to improve the basis in terms of number of orbitals and their shape??
- They are biased, since they are optimal for an atomic problem. Basis set superposition error
- Orbitals move with atoms, which brings extra terms (cumbersome to calculate) in the forces
- Calculation of the Hamiltonian matrix elements is quite complicated and expensive

Kohn-Sham eqns in a Plane Wave Basis (1)

Bloch's Theorem (k in 1st BZ) ⇒ $\phi_{i,\bar{k}}(\bar{r}) = e^{i\bar{k}\bar{r}} u_i(\bar{r})$

$u_i(r)$ periodic ⇒ expanded in reciprocal lattice vectors {G} (Fourier Transform)

$$\phi_{i,\bar{\mathbf{k}}}(\mathbf{r}) = \sum_{\bar{\mathbf{G}},\frac{\hbar^2}{2m}|\bar{\mathbf{G}}+\mathbf{k}|^2\leq E_{\rm cut}} c_{i,\bar{\mathbf{G}}+\bar{\mathbf{k}}}\, e^{i(\bar{\mathbf{G}}+\bar{\mathbf{k}})\cdot\mathbf{r}}$$

Uniform convergence with E_{cut} !!!

Kohn-Sham equations

$$\begin{aligned}\varepsilon_i c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}} &= \left(\frac{\hbar^2}{2m}|\mathbf{G}+\bar{\mathbf{k}}|^2\right) c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}} + \sum_{\bar{\mathbf{G}}'} V_{\rm H}(\bar{\mathbf{G}}-\bar{\mathbf{G}}')c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}'} \\ &+ \sum_{\bar{\mathbf{G}}'}\left[V_{\rm XC}(\bar{\mathbf{G}}-\bar{\mathbf{G}}') + V_{e-ion}(\bar{\mathbf{k}}+\bar{\mathbf{G}},\bar{\mathbf{k}}+\bar{\mathbf{G}}')\right] c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}'}\end{aligned}$$

$$V_H = \frac{4\pi}{\Omega_c}\frac{n(\bar{\mathbf{G}})}{|\bar{\mathbf{G}}|^2}$$

$$n(\bar{\mathbf{G}}) = \sum_{i,\bar{\mathbf{k}},\bar{\mathbf{G}}'} c^*_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}}\, c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}+\bar{\mathbf{G}}'}$$

V_H easy to calculate in reciprocal space

Ω_c = unit cell volume

(we need twice the number of PWs to describe n(r) than $\phi_{i,k}(r)$)

Kohn-Sham eqns in a Plane Wave Basis (2)

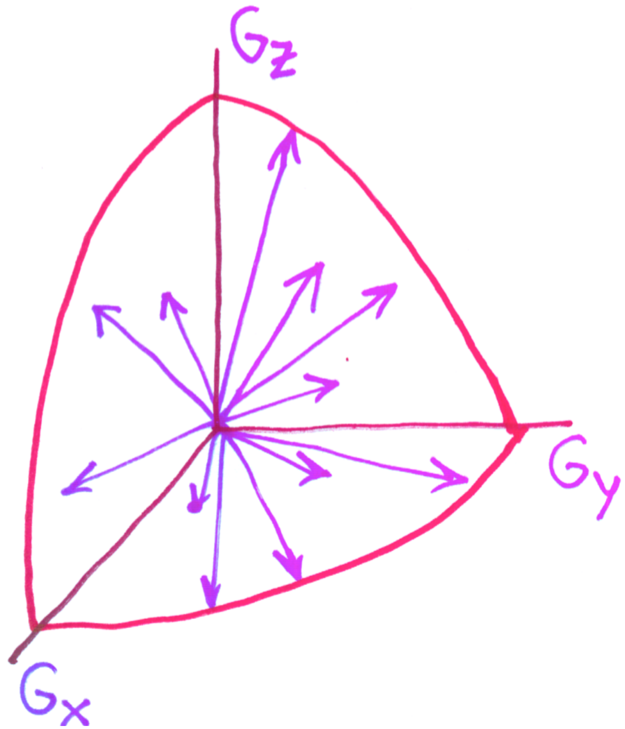
$$\varepsilon_i c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}} = \left(\frac{\hbar^2}{2m}|\mathbf{G}+\bar{\mathbf{k}}|^2\right) c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}} + \sum_{\bar{\mathbf{G}}'} V_{\mathrm{H}}(\bar{\mathbf{G}}-\bar{\mathbf{G}}')c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}'} + \sum_{\bar{\mathbf{G}}'}\left[V_{\mathrm{XC}}(\bar{\mathbf{G}}-\bar{\mathbf{G}}') + V_{e-ion}(\bar{\mathbf{k}}+\bar{\mathbf{G}},\bar{\mathbf{k}}+\bar{\mathbf{G}}')\right] c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}'}$$

$$T_S = \Omega_c \sum_{i,\bar{\mathbf{k}},\bar{\mathbf{G}}} |c_{i,\bar{\mathbf{k}}+\bar{\mathbf{G}}}|^2 \frac{\hbar^2}{2m}|\bar{\mathbf{k}}+\bar{\mathbf{G}}|^2$$

$$E_H = \frac{1}{2}\Omega_c \sum_{\bar{\mathbf{G}}} V_H(\bar{\mathbf{G}})n^*(\bar{\mathbf{G}})$$

$$E_{XC} = \Omega_c \sum_{\bar{\mathbf{G}}} \epsilon_{XC}(\bar{\mathbf{G}})n^*(\bar{\mathbf{G}})$$

V_{ion}: Structure factor + Atomic Pseudopotentials



$$V_{e-ion}(\bar{k}+\bar{G},\bar{k}+\bar{G}') = \sum_j S_j(\bar{G}-\bar{G}')\phi(\bar{k}+\bar{G},\bar{k}+\bar{G}')$$

ADVANTAGES OF PWs:

- Systematic basis set: G_{max} (or $E_{cut} = |G_{max}|^2/2$) determines the quality of the calculation
- It is unbiased: no assumption on the system under study, and treats all space equally
- The calculation is variational, and the potentials can also be expressed in terms of plane waves (keeping the variational properties)
- Expressions of H and Hψ are simple and very fast to compute
- They are orthogonal, and Hellmann-Feynman theorem applies to them (even if the calculation is not converged in terms of the number of PWs)

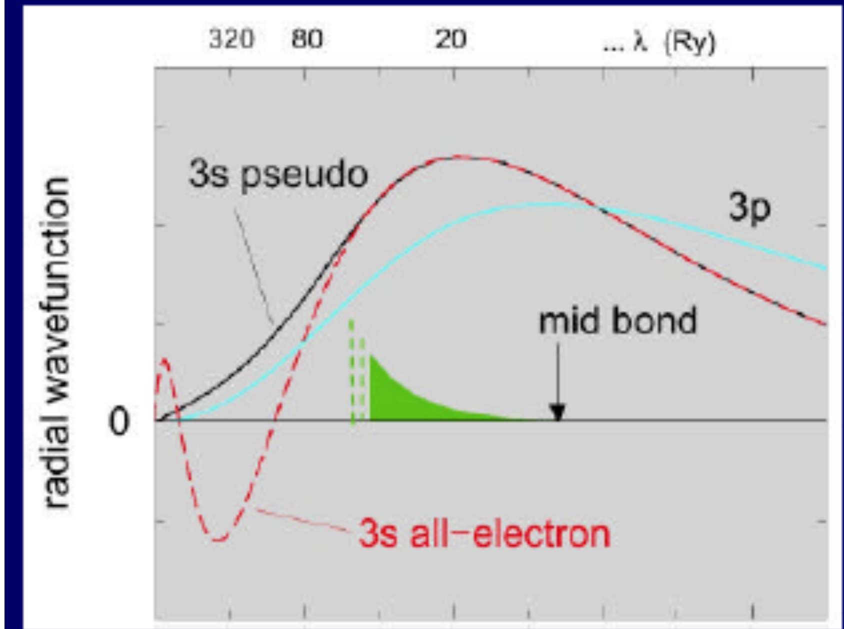
DISADVANTAGES OF PWs:

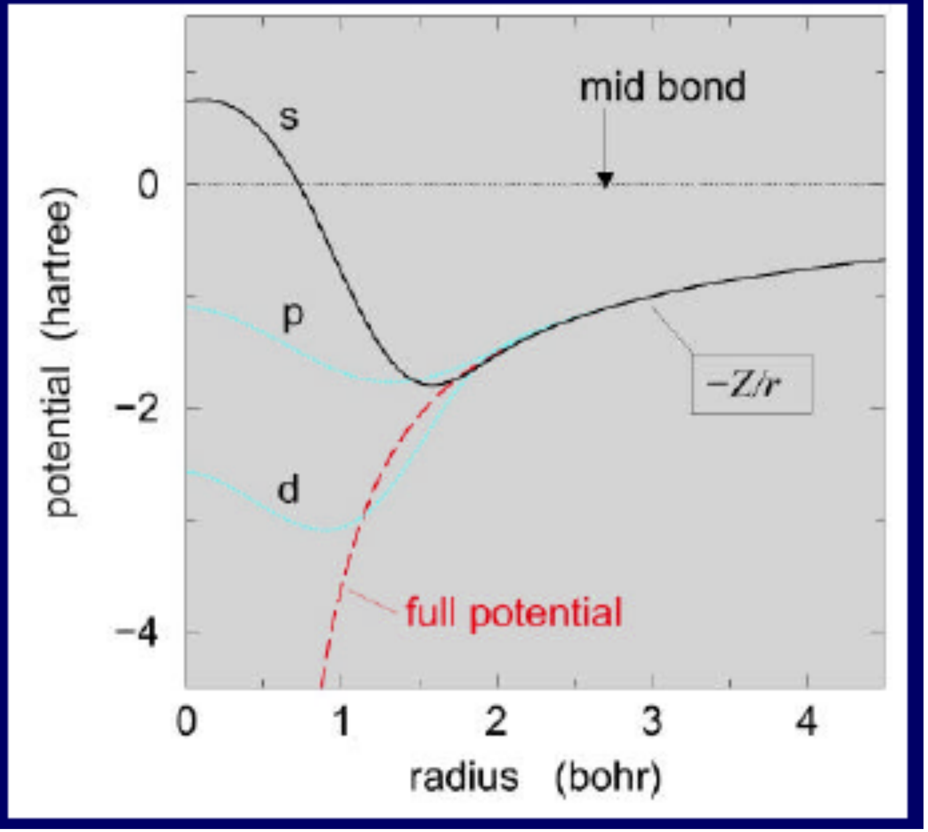
- The number of PWs per electron is very large (typically 100xN). Larger for more compact orbitals
- Vacuum is as costly as matter!
- Compact orbitals (transition metals) are very expensive, because they require larger cutoffs

  (Note that UltraSoft Pseudopotentials remove this problem to a large extent).
- Localization ideas are not easily implemented in a PW basis.

Pseudopotential is a semilocal operator

(different for each angular component of the wfn)





k-point sampling

Electronic quantum states in a periodic solid labelled by:

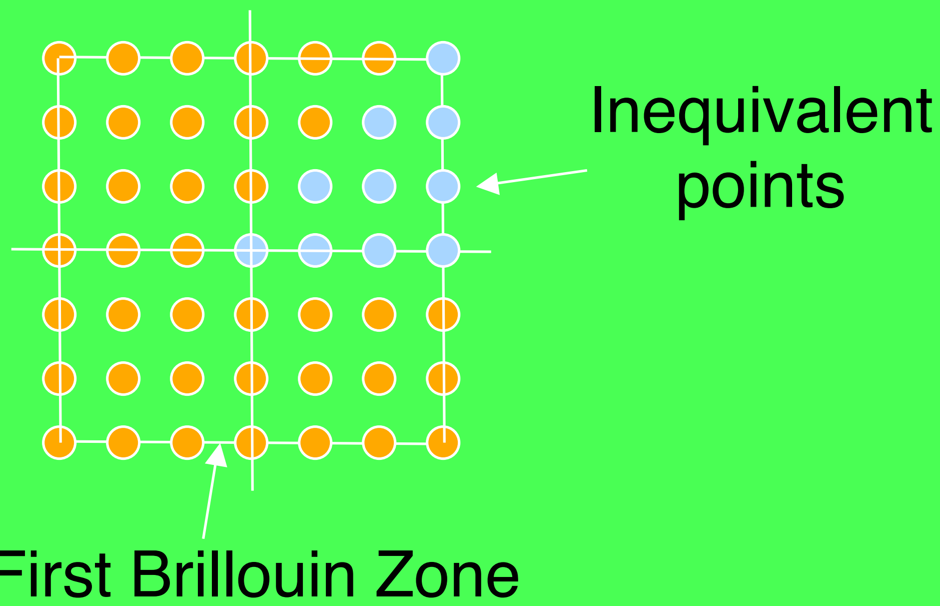
- *Band index*
- *k-vector:* *vector in reciprocal space within the first Brillouin zone (Wigner-Seitz cell in reciprocal space)*
- *Other symmetries (spin, point-group representation…)*

$$\rho(\vec{r}) = \sum_{n}^{occ} |\psi_n(\vec{r})|^2 \Rightarrow \int_{\vec{k}\in BZ} d^3\vec{k}$$

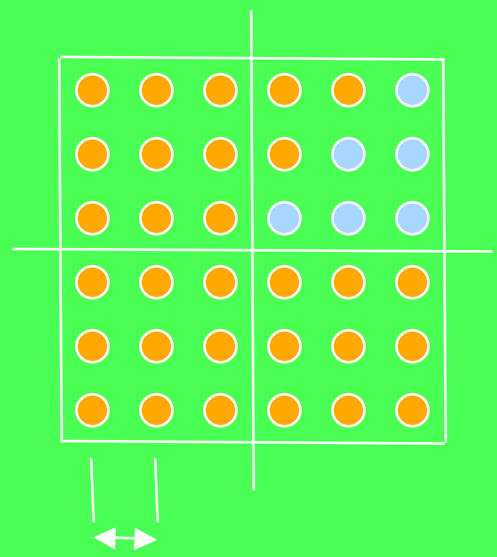
Approximated by sums over selected k-points

K-point sampling

Regular k-grid



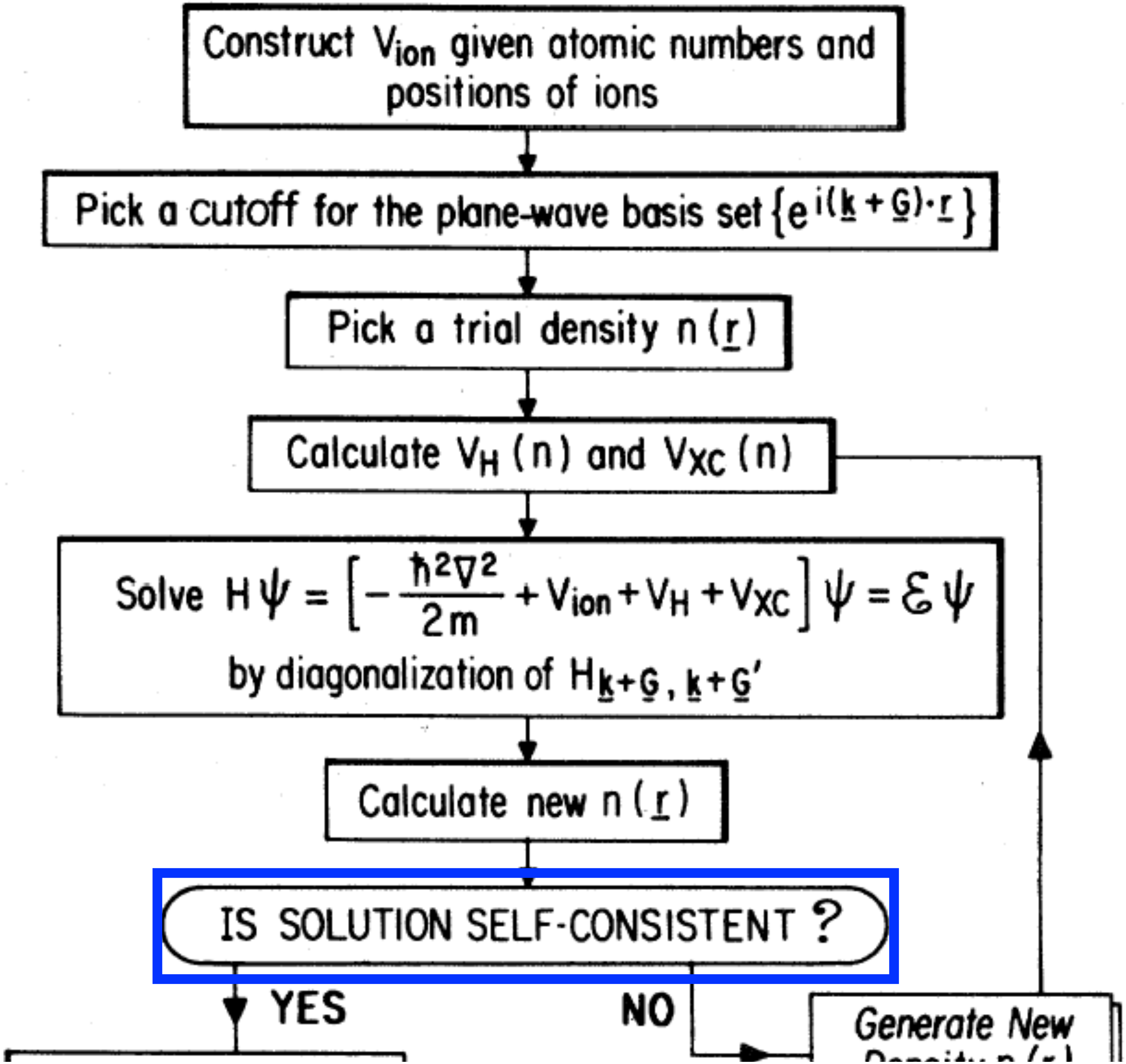
Monkhorst-Pack



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

6x6

6x6 shifted


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