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Centre Européen de Calcul Atomique et Moléculaire

Density Functional Theory
and the siesta code

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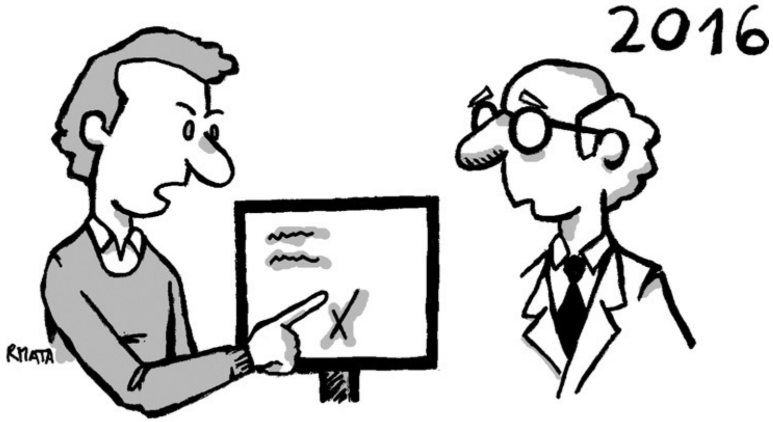
Program

1. Density Functional Theory

- Introduction to Simulation in Materials
- Solving the quantum mechanical problem: approximations
- Density Functional Theory – The basics
- Density Functional Theory – In practice
    - Functionals
    - Numerical Methods
    - Codes

"There must be something wrong with your calculations."



"There must be something wrong with your experiments."

Computational Materials Science

R. Mata and M. A. Suhm, Angew. Chem. Int. Ed. 2017, 56, 11011 – 11018

Why Computer Simulation?

The advantages of Simulations (the "virtual lab")

- Basic understanding
- Focus on specific details
- Systems and conditions not feasible in experiments
- Specify external conditions

These give us:

- Predictive power
- Aid in the interpretation of experiments

Further advantages:

- Solve complex (i.e., realistic) models without approximations
- Scales up with the available computer power
- Developing simulation methods allows us to understand the physics

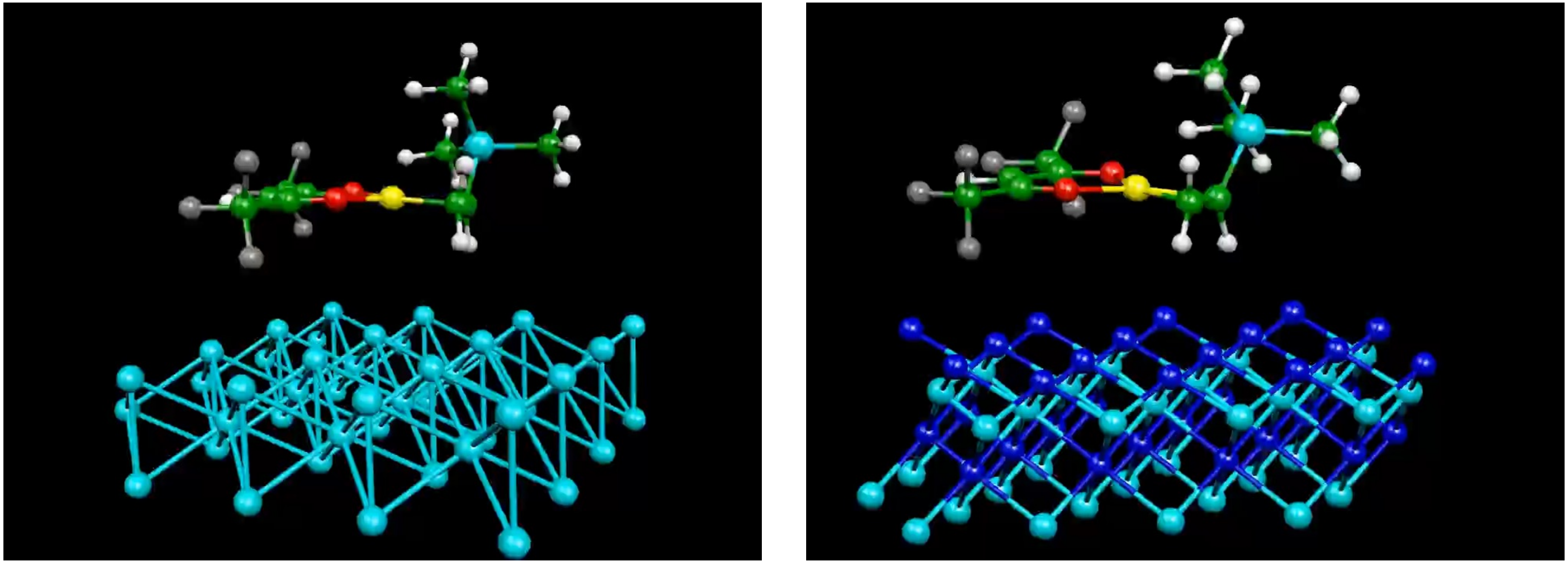
Materials Simulations

An example of industrial interest:

CupraSelect®

Chemicals for the CVD deposition of Cu for electrodes in microelectronic circuits

Problems of adhesion when deposited over Ta films



Industrial project with Air Products

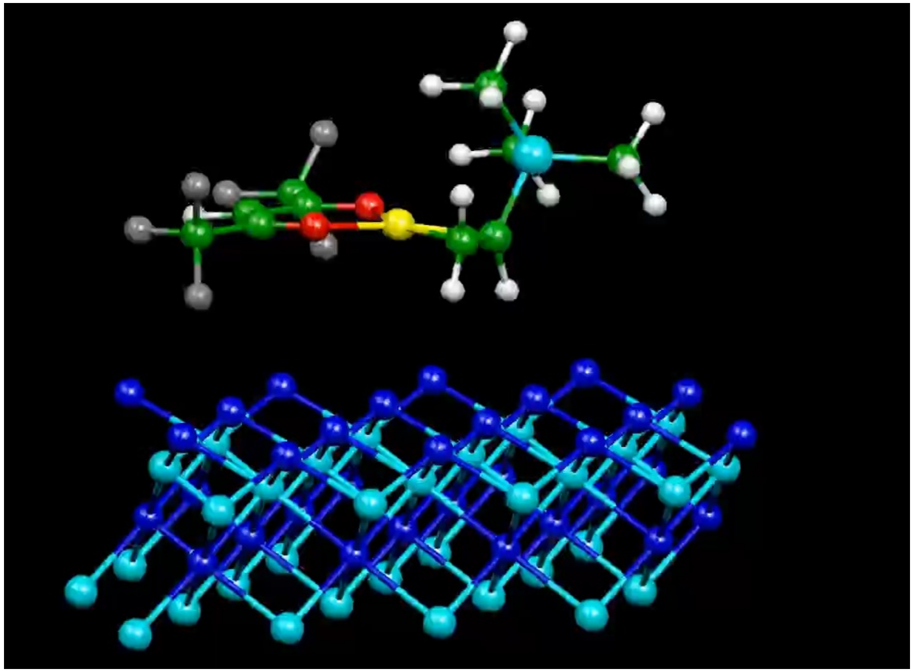
Machado, Kaczmarski, Ordejón, Garg, Norman and Cheng, Langmuir **21**, 7608 (2005)

US Patent 7985449

Materials Simulations

Ingredients of a Simulation

Simulation in materials: Study the way in which the “blocks” that build the material interact with one another and with the environment, and determine the internal structure, the dynamic processes and the response to external factors (pressure, temperature, radiation, etc…).



1. A **<u>model of the interactions</u>** between the “blocks” that build the material.

   Here: atomistic models.

2. A **<u>simulation algorithm</u>**: the numerical solution to the equations that describe the model.

3. A set of **<u>tools for the analysis</u>** of the results of the simulation.

The "model of the interactions" and the "equations of motion": Going to First Principles (or ab-initio)

- What are materials made of?

  Nuclei and electrons

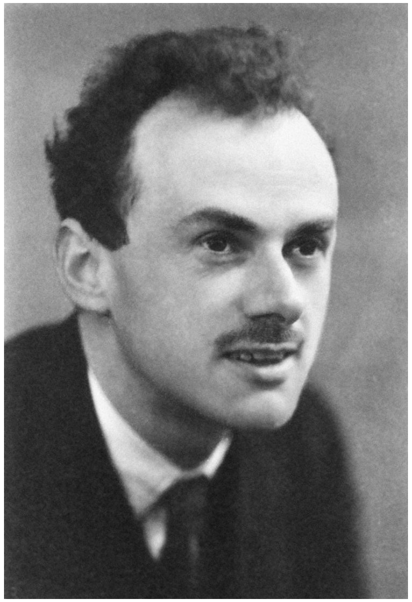
- Which are the fundamental laws that describe the behaviour of nuclei and electrons in materials?

  Electromagnetic forces
  Quantum Mechanics
  Special Relativity

Going to First Principles (or ab-initio)

"The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and 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, Proc. Roy. Soc. (London) A123, 714 (1929).



"It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

Why care about electrons and Quantum Mechanics?

Let's just consider atoms as classical objects, model their interactions using classical potentials and use Newton's classical laws to describe their motion

Empirical potentials

Force Fields

Classical Molecular Dynamics

....

Extremely easy equations (Newton)

Easy to implement in computer codes

Low computational cost

System-dependent

Limited generality

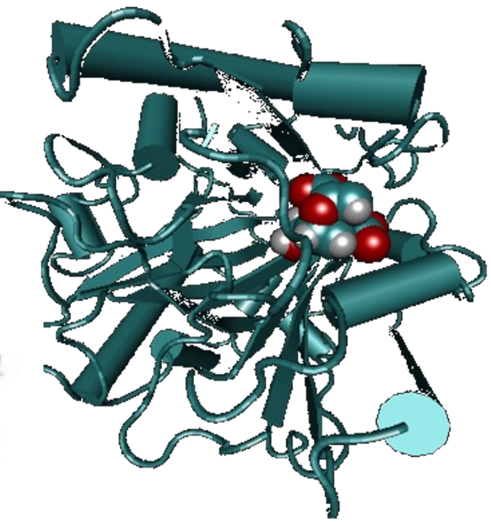
Need fitting to data from experimental or higher-level theory

Overfitting – extrapolating

Limited flexibility of predefined functional forms

Example: The AMBER Force Field

A classical, empirical Force Field very popular in biology



$$U = \sum \tfrac{1}{2} K_b (b - b_0)^2 + \sum \tfrac{1}{2} K_\theta (\theta - \theta_0)^2$$

All Bonds

All Angles

$$+ \sum K_\phi [1 - \cos(n\phi + \delta)]$$

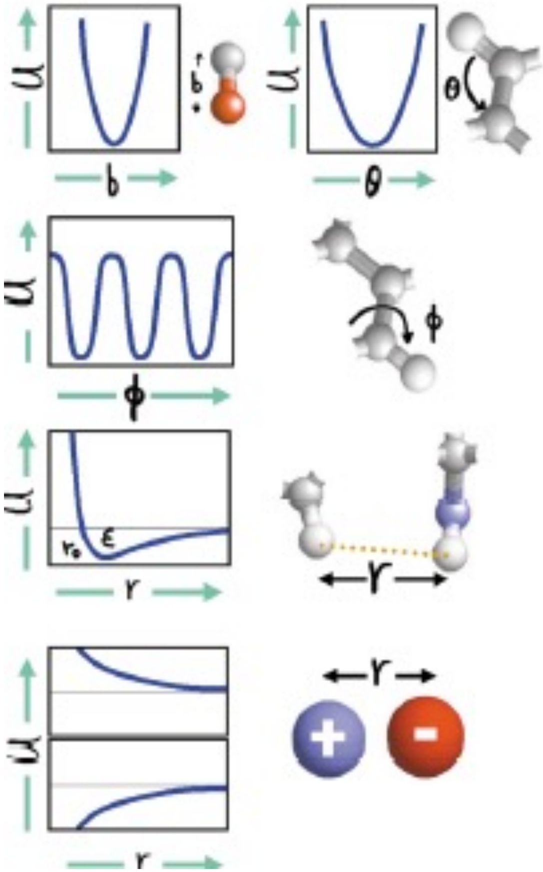
All Torsion Angles

$$+ \sum \epsilon \left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6} \right]$$

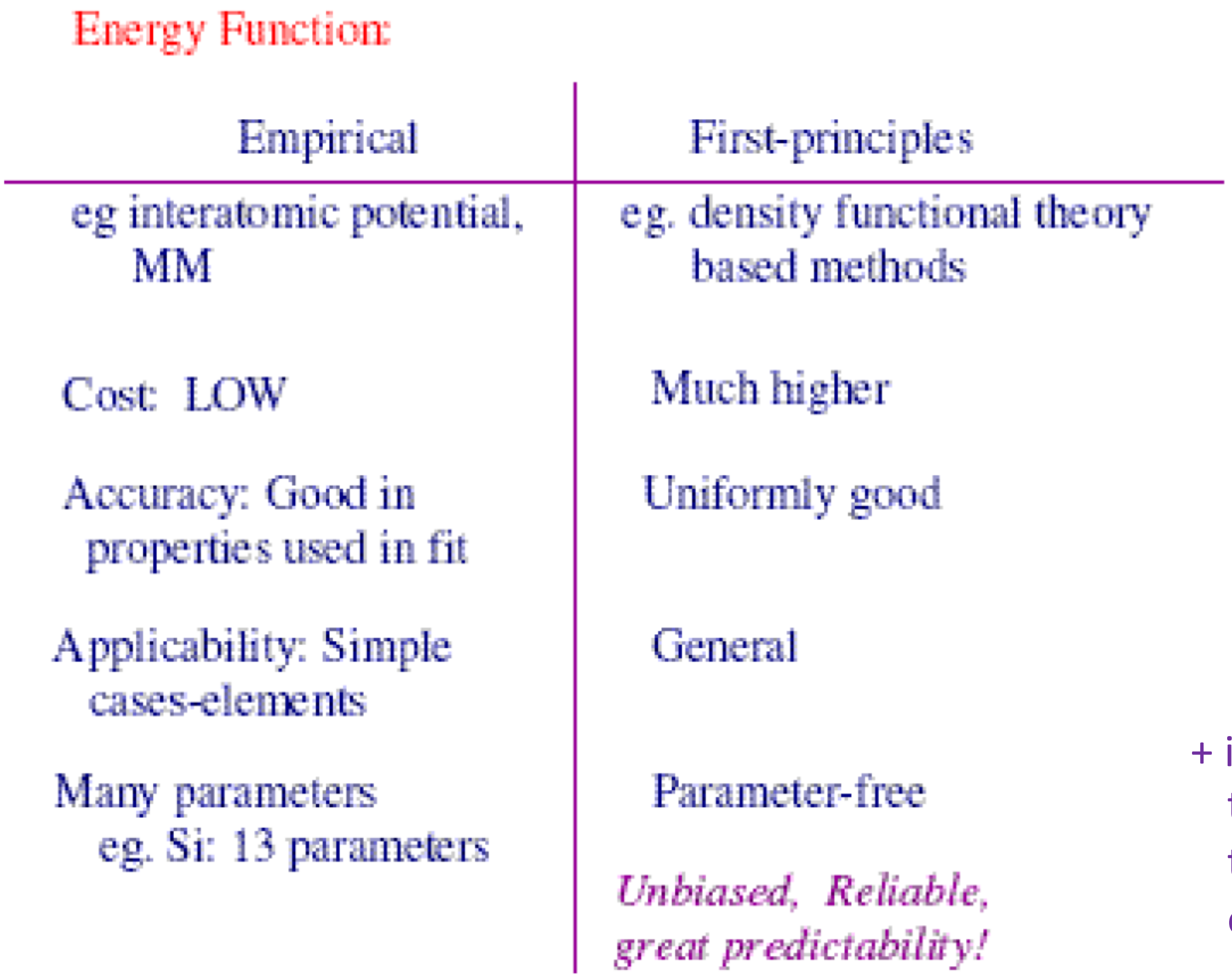
All nonbonded pairs

$$+ \sum 332 q_i q_j / r$$

All partial charges



Why take that extra work?



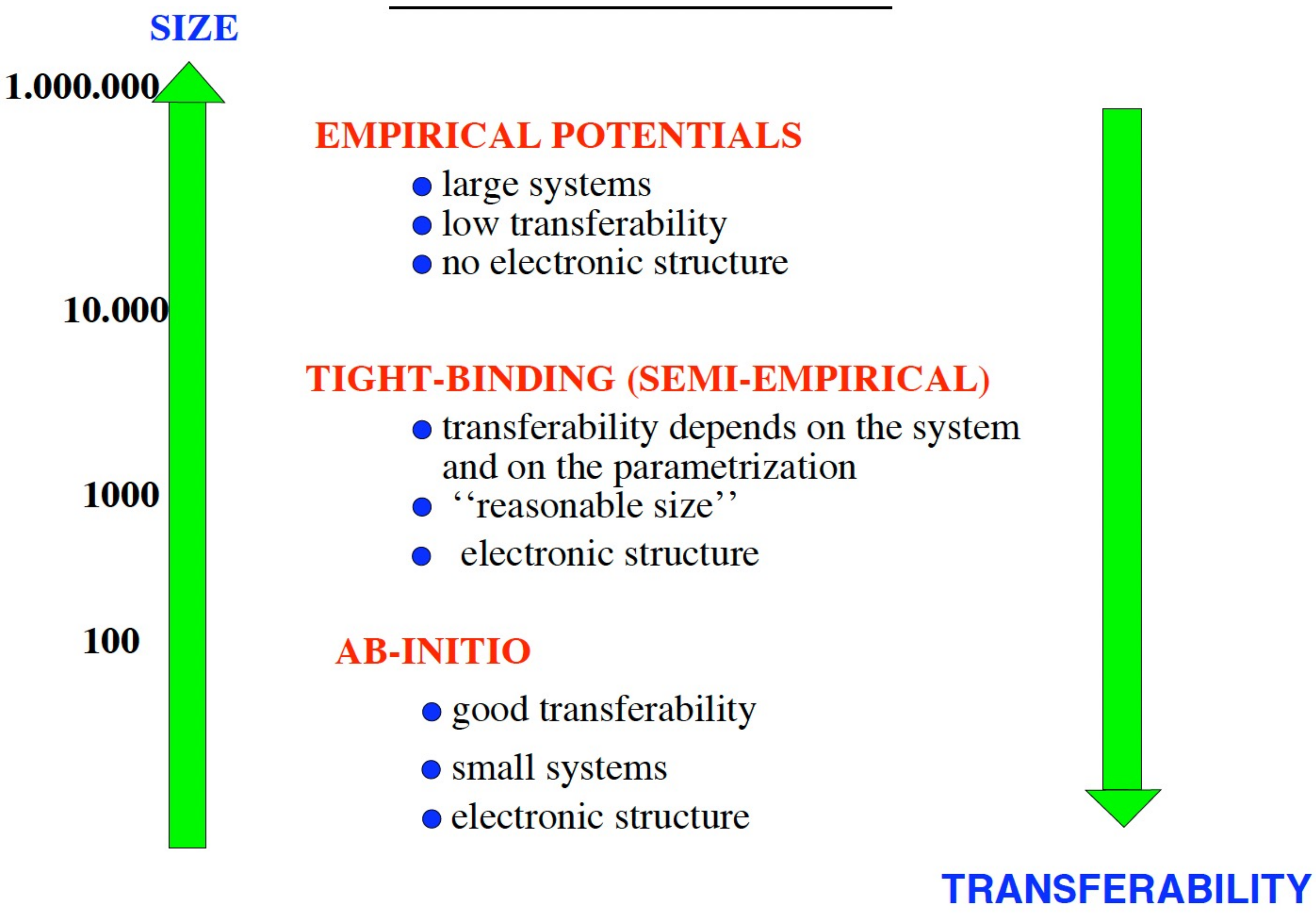
Energy Function:

Empirical	First-principles
eg interatomic potential, MM	eg. density functional theory based methods
Cost: LOW	Much higher
Accuracy: Good in properties used in fit	Uniformly good
Applicability: Simple cases-elements	General
Many parameters eg. Si: 13 parameters	Parameter-free
	Unbiased, Reliable, great predictability!

+ information about
the electrons,
their dynamics,
excitations, etc

Fron Umesh Waghmare; http://nanohub.org/resources/9683/supportingdocs

But... computational cost!



EMPIRICAL POTENTIALS

- large systems
- low transferability
- no electronic structure

TIGHT-BINDING (SEMI-EMPIRICAL)

- transferability depends on the system and on the parametrization
- ''reasonable size''
- electronic structure

AB-INITIO

- good transferability
- small systems
- electronic structure

(Warning!!: Old slide!! Now sizes affordable are significantly larger ... x10 at least)

But... computational cost!

Scaling or "complexity" of a simulation method:

The relation between computing time T (CPU ... of degrees of freedom N (number of atomic coordinat ... gth...)

$T \propto O(N)$ in the best ... (linear scaling)
empi ... ut not always)

$T \propto O(N^3$ ... ar methods
... diagonalisation and inversion) (Some schemes towards O(N))

some models and systems
(Quantum chemistry; multiple minima problems, etc)

AI – driven Interatomic Potentials!!

Critics of computer simulation

* *Calculation without Classic Standards is Dangerous.*
A Computer is Incapable of Setting its own Standards.

* *By its Emphasis on Application of the Already Known, Computing can Delay Basic Discovery and thus Reduce the Field of Applications in the Future.*

* *Classic Theories used Inductive and Deductive Models.*
Computing Encourages Floating Models.

(Headings from the essay: "The Computer: Ruin of Science and Threat to Mankind", by Clifford Truesdell, in "An Idiot's Fugitive Guide to Science", Springer, 1984)

A simple model can shed more light on Nature's workings than a series of "ab-initio" calculations of individual cases, which, even if correct, are so detailed that they hide reality instead of revealing it. ...A perfect computation simply reproduces Nature, it does not explain it.

(P.W. Anderson)

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The ab-initio approach

- The problem: To obtain the energies and forces on the atomic nuclei by solving the **quantum mechanical** problem.

- Mathematically: Solve Schrödinger’s eq.:

$$i\hbar \frac{d\Psi(\{\mathbf{r}_i,\mathbf{R}_I\};t)}{dt} = \hat{H}\Psi(\{\mathbf{r}_i,\mathbf{R}_I\};t)$$

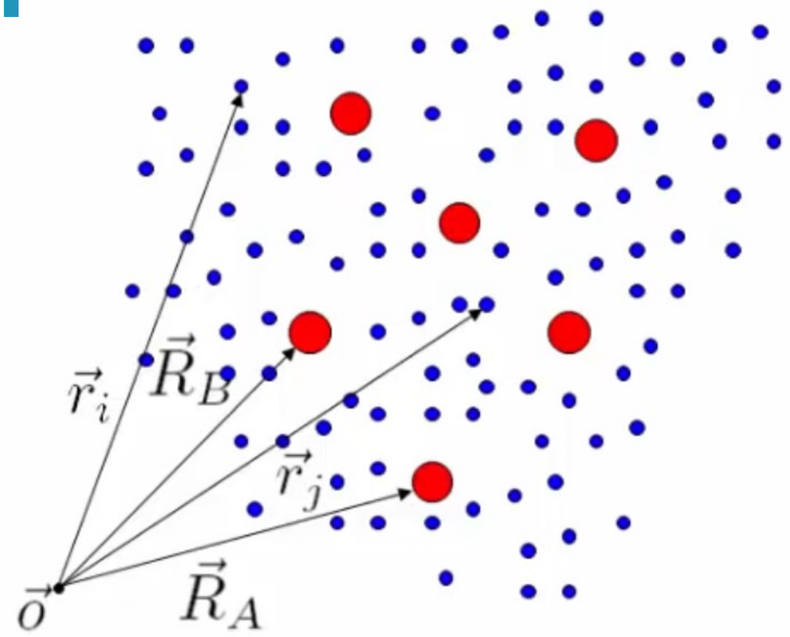
$$\hat{H}\Psi(\{\mathbf{r}_i,\mathbf{R}_I\}) = E\Psi(\{\mathbf{r}_i,\mathbf{R}_I\})$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \boxed{V(\{\mathbf{r}_i,\mathbf{R}_I\})}$$

Coulomb interactions

The ab-initio approach

$$\hat{H}\Psi(\{\mathbf{r}_i,\mathbf{R}_I\}) = E\Psi(\{\mathbf{r}_i,\mathbf{R}_I\})$$



$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},$$

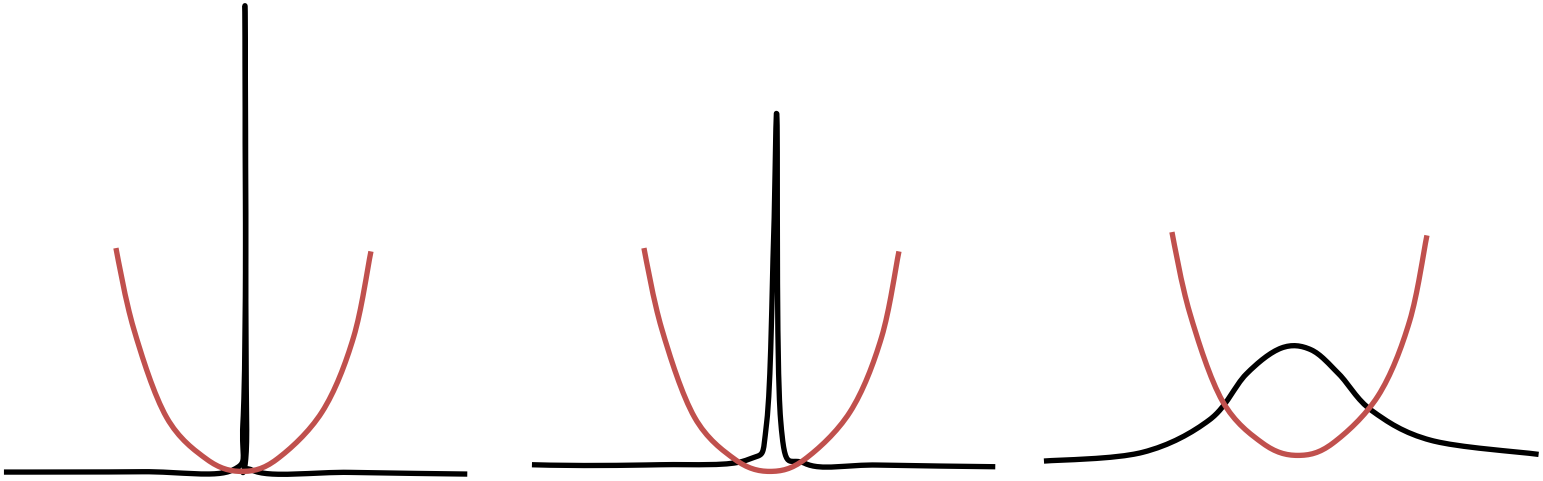
How do we simplify to make computations feasible? (remember Dirac’s comment)

The Kinetic Energy

$$\hat{H} = \hat{T} + V_{ext}(r) \qquad \hat{T}_i = -\frac{\hbar^2}{2m_i}\nabla_i^{\,2}$$

The smaller the mass, the larger the quantum delocalization effect:

A quantum particle in a parabolic well in its ground state



$m_1 \rightarrow \infty \quad >>>> \quad m_2 \quad > \quad m_3$

(Classical limit)

The Born-Oppenheimer Approx.

Saparating the Electronic and Ionic degrees of freedom:

- ***Born-Oppenheimer approximation***: decouple the ionic and electronic degrees of freedom

$$\Psi(\{\mathbf{r}_i,\mathbf{R}_I\}) \approx \psi_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right) * \chi\left(\{\mathbf{R}_I\}\right)$$

- Retains the quantum description of both electrons and ions. Assumes that mass of ions is much larger than mass of electrons

$$\hat{H}_e \psi_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right) = E(\{\mathbf{R}_I\})\, \psi_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right) \qquad \hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + V(\{\mathbf{r}_i,\mathbf{R}_I\})$$

- ***Classical ions approximation:*** Ions are treated classically, because of their large mass; electrons are treated quantum mechanically.

- Ionic dynamics – Atomic forces and Newton's law

$$\vec{\mathbf{F}}_I = M_I \vec{\mathbf{a}}_I = -\frac{\partial E(\{\mathbf{R}_I\})}{\partial \mathbf{R}_I}$$

The (electronic) Many Body Problem

$$\hat{H}_e \psi_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right) = E(\{\mathbf{R}_I\})\, \psi_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right)$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + V(\{\mathbf{r}_i, \mathbf{R}_I\})$$

$$\hat{H}_\mathrm{e} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2}_{\hat{T}} \underbrace{-\sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}}_{\boxed{\hat{V}_{ext}}} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{V}_{\mathrm{int}}} + \underbrace{\frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}}_{E_{II}},$$

$V_{ext}(r)$ may include also other external potentials (electric fields, etc)

The (electronic) Many Body Problem

$$\hat{H}_e \psi_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right) = E(\{\mathbf{R}_I\})\,\psi_{\{\mathbf{R}_I\}}\left(\{\mathbf{r}_i\}\right)$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + V(\{\mathbf{r}_i,\mathbf{R}_I\})$$

Numerical Solutions of the Electronic ‘Many-Body’ Problem:

- Quantum Monte Carlo (stochastic solutions)

TurboRVB
Quantum Monte Carlo Package SISSA

- Quantum Chemistry Methods (approximations on the wave function that can be systematically improved)
- Density Functional Theory (approximations to the exact Exchange-Correlation potential) - The one that provides highest computational speed, whereas retaining a very good accuracy in general.

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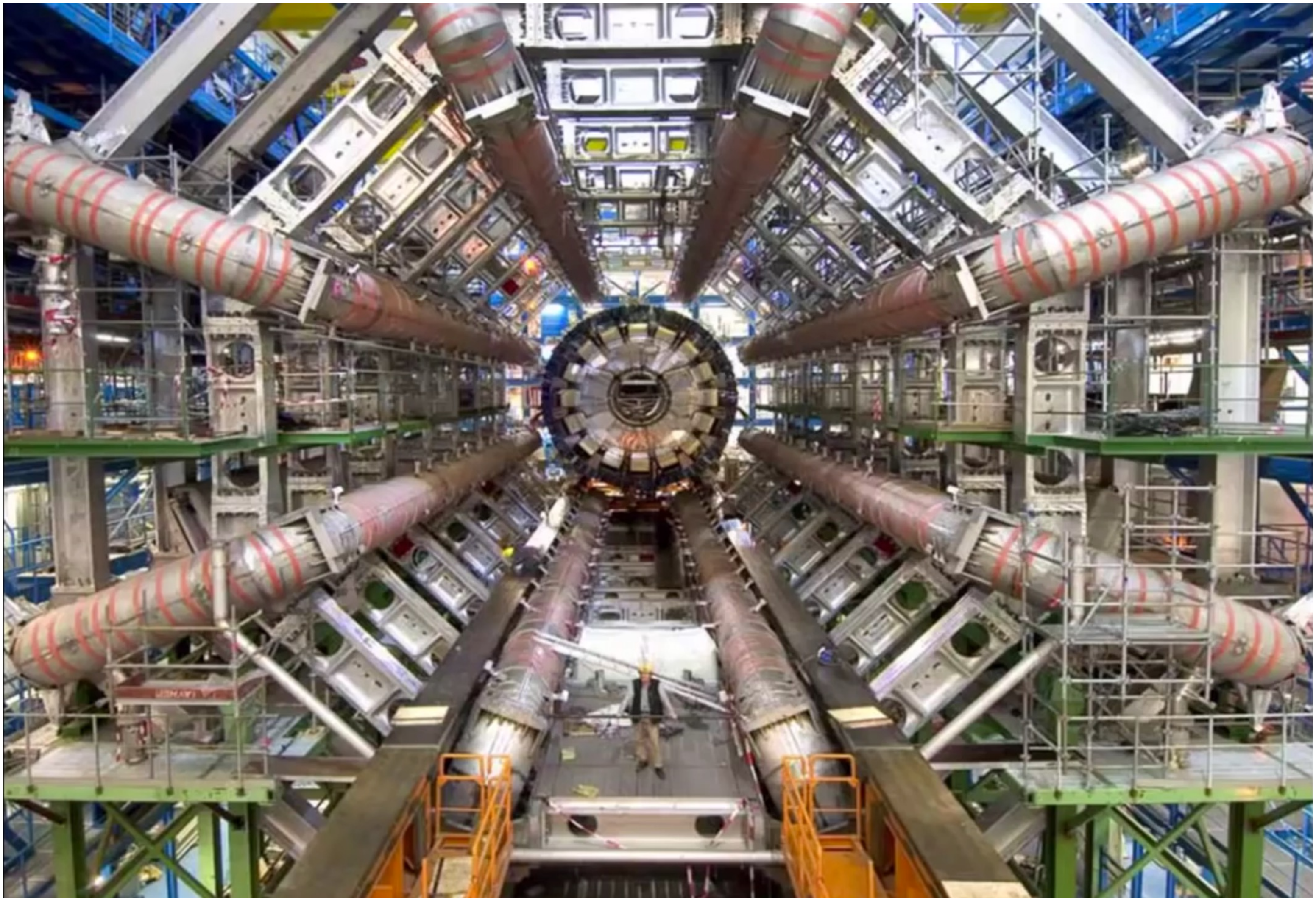
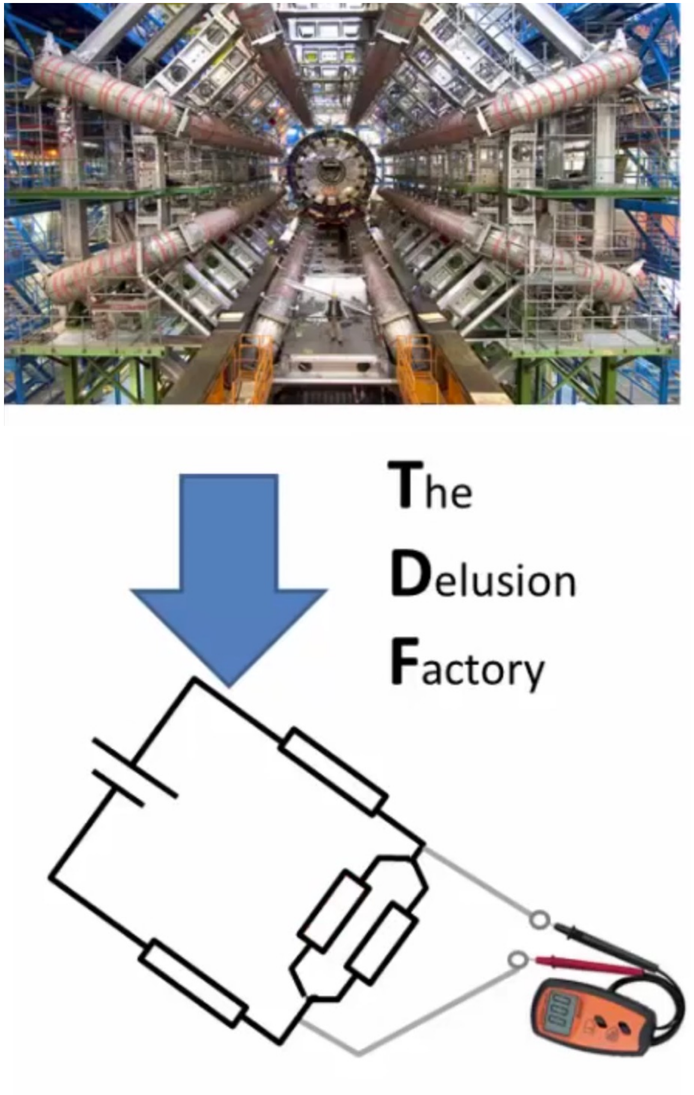
What is Density Functional Theory?



Taken fron Stefaan Cottenier; https://www.youtube.com/watch?v=jZi2EOrCrpY

What is Density Functional Theory?



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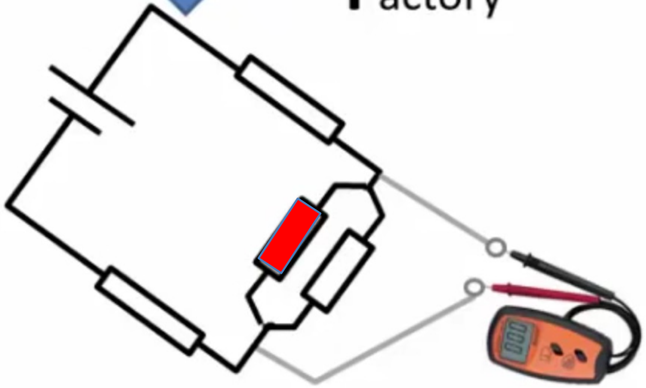
What is Density Functional Theory?

The

Delusion

Factory



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

many-body Schrödinger equation

$$\Psi\left(\vec{r}_1,\ldots,\vec{r}_N\right)$$

many—body wavefunction

Density

Functional

Theory

XC?

$\rho(\vec{r})$ - charge density

$$\hat{\mathcal{H}}_{KS}\,\phi(\vec{r}) = E\,\phi(\vec{r})$$

single-particle Kohn-Sham equations

Adapted fron Stefaan Cottenier; https://www.youtube.com/watch?v=jZi2EOrCrpY

[The Electron Density: n(r)]

1 electron wave function:

$$\psi(r) \longrightarrow n(r) = |\psi(r)|^2$$

N electron wave function:

$$\psi(r_1, r_2, \ldots, r_N) \longrightarrow n(r) = N \int |\psi(r, r_2, \ldots, r_N)|^2 dr_2 \ldots dr_N$$

See the difference in the complexity of wf and n

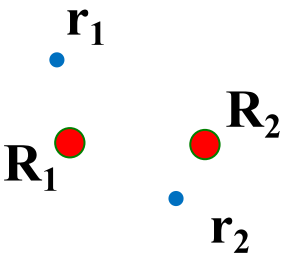
ψ is a function of 3N variables
n is a function of 3 variables

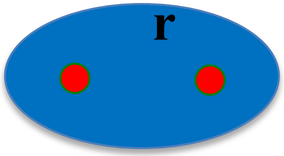
Wave functions and Density

$$\hat{H}_e \psi(\{\mathbf{r}_i\}) = E(\{\mathbf{R}_I\})\, \psi(\{\mathbf{r}_i\})$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + V(\{\mathbf{r}_i, \mathbf{R}_I\}) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + E_{II}$$

$$H_e = \quad T \quad + \quad V_{ext} \quad + \quad V_{int} \quad + \quad E_{II}$$





$$V_{ext} \longrightarrow \psi_0(\mathbf{r}_1, \mathbf{r}_2) \longrightarrow n_0(\mathbf{r})$$

Ground state wf

Ground state electron density

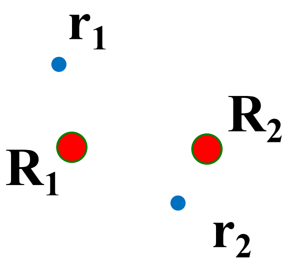
Wave functions and Density

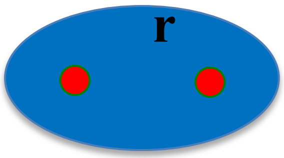
Total Energy (for a given ψ):

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{\mathrm{int}} \rangle + \int \mathrm{d}^3 r \, V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{II}$$

The Ground State Energy:

$$E_G = \min_{\psi} E = \min_{\psi} \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$





$$V_{ext} \longrightarrow \psi_o(\mathbf{r}_1, \mathbf{r}_2) \longrightarrow n_o(\mathbf{r})$$

Ground state wf

Ground state electron density

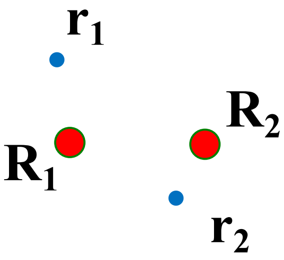
Wave functions and Density

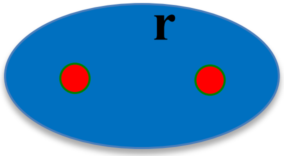
Total Energy (for a given ψ):

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{\mathrm{int}} \rangle + \int \mathrm{d}^3 r \, V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{II}$$

Forces: Hellmann-Feynman Theorem

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\int \mathrm{d}^3 r \, n(\mathbf{r}) \frac{\partial V_{\mathrm{ext}}(\mathbf{r})}{\partial \mathbf{R}_I} - \frac{\partial E_{II}}{\partial \mathbf{R}_I}$$





$$V_{ext} \longrightarrow \psi_o(\mathbf{r}_1, \mathbf{r}_2) \longrightarrow n_o(\mathbf{r})$$

Ground state wf

Ground state electron density

Hohenberg – Kohn Theorems (PRB, 1964)

Theorem 1: For any system of electrons in an external potential $V_{ext}(r)$, that potential is determined uniquely (within an additive constant) by the ground state density n(r)

As a result, ***the full many body wave function and derived properties are also determined uniquely by n(r).*** *But we don't know how to compute it, but trough the MB Wave Function!*

Theorem 2: A universal functional of the density F[n(r)] can be defined for all electronic systems. The global minumum of E[n] = $\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ for a given external potential $v(\mathbf{r})$ = V_{ext} gives the exact ground state energy and density

$$\langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle$$

$$\begin{tikzcd}
V_{ext} \arrow[r] & \psi_o(\mathbf{r}_1, \mathbf{r}_2) \arrow[r] & n_o(\mathbf{r}) \arrow[ll, bend left]
\end{tikzcd}$$

[Functionals]

A **function** maps numbers into numbers

$$f : \mathbb{R} \to \mathbb{R} : x \mapsto f(x)$$

$$f(x) = \sin(x)$$

Wave functions: Function $\mathbb{R}^{3N} \longmapsto \mathbb{C}$

$$\psi(\vec{r_1}, \vec{r_2}, \dots, \vec{r_N})$$

A **functional** maps functions into numbers

$$F : \mathcal{F} \to \mathbb{C} : f \mapsto \mathcal{F}[f]$$

$$F[f] = f(0)$$

$$F[f] = \int_{-\infty}^{\infty} f(x)\,dx$$

Energy: Functional $\mathcal{F} \longmapsto \mathbb{R}$

$$F\,[n(\vec{r})]$$

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The EXACT form of the functional F[n] is unknown and must be very complicated

F[n] can give only the ground state; excited states require more work… but the information is there!

$$\begin{tikzcd}
V_{ext} \arrow[r, shift left] & \psi(\mathbf{r}_1,\mathbf{r}_2) \arrow[l, shift left] \arrow[r, shift left] & n(\mathbf{r}) \arrow[l, shift left]
\end{tikzcd}$$

Kohn – Sham formulation
(PRB, 1965)

1. KS Ansatz: The exact ground state density of the interacting system can be represented by the ground state density of an auxiliary system of non-interacting particles.

$$n(r) = \sum_{i}^{occ} \left|\psi_i(r)\right|^2$$

2. The non-interacting system is chosen to have the usual 1e kinetic energy operator, plus an effective *local* potential $V_{eff}(\mathbf{r})$ acting on an electron at point $\mathbf{r}$

$$H_{eff} = -\frac{1}{2}\nabla^2 + V_{eff}(r)$$

(See later for the connection of V_{eff} with the functional E[n])

Kohn – Sham formulation (PRB, 1965)

$$n(r) = \sum_i^{occ} |\psi_i(r)|^2$$

The effective potential

$$H_{eff} = -\frac{1}{2}\nabla^2 + V_{eff}(r) =$$

$$= -\frac{1}{2}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)$$

Hartree potential

$$V_H(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

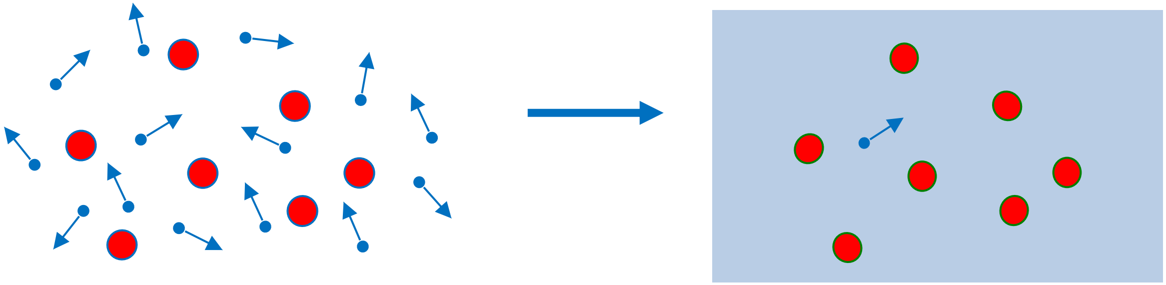
Exchange-Correlation potential

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

(See later)

Kohn – Sham formulation (PRB, 1965)

Interacting electrons: As if *non-interacting* electrons in an *effective potential* (Kohn-Sham Ansatz)

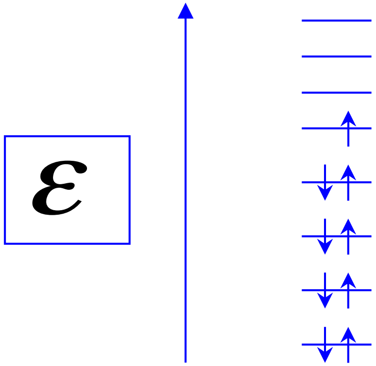


$$\hat{h}\psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r})$$

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

$$H_{eff} = -\frac{1}{2}\nabla^2 + \boxed{V_{eff}(r)} =$$

$$= -\frac{1}{2}\nabla^2 + V_{ext}(r) + V_H(r) + \boxed{V_{xc}(r)}$$



Kohn – Sham formulation (PRB, 1965)

Self-consistency

PROBLEM: The potential (input)

depends on the density (output)

$$\begin{tikzcd}
n_{in} \arrow[r] & V \arrow[r] & n \arrow[r] \arrow[l, bend left=90, "|n_n - n_{n-1}| > \varepsilon"] & n_{out}
\end{tikzcd}$$

Kohn – Sham formulation (PRB, 1965)

The Energy Functional: $E_{KS}[n]$

$$E_{\mathrm{KS}} = T_s[n] + \int \mathrm{d}\mathbf{r}\, V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\mathrm{Hartree}}[n] + E_{II} + E_{\mathrm{xc}}[n].$$

The effective potential: $V_{eff}(r)$

$$\begin{aligned} V_{\mathrm{KS}}^{\sigma}(\mathbf{r}) &= V_{\mathrm{ext}}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hartree}}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r},\sigma)} \\ &= V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{Hartree}}(\mathbf{r}) + V_{\mathrm{xc}}^{\sigma}(\mathbf{r}). \end{aligned}$$

What can be computed with DFT?

- The GS density n(r)
- The Ground State energy $E_G = E_{KS}$

- Equations of state (both for T=0 and finite T)
- Deviation from equilibrium: harmonic and anharmonic → phonon; thermal conductivity, …
- Forces → Equilibrium geometries and energies
- Molecular dynamics: How do the atoms move in different external conditions → chemical reactions, ...
- And many others...

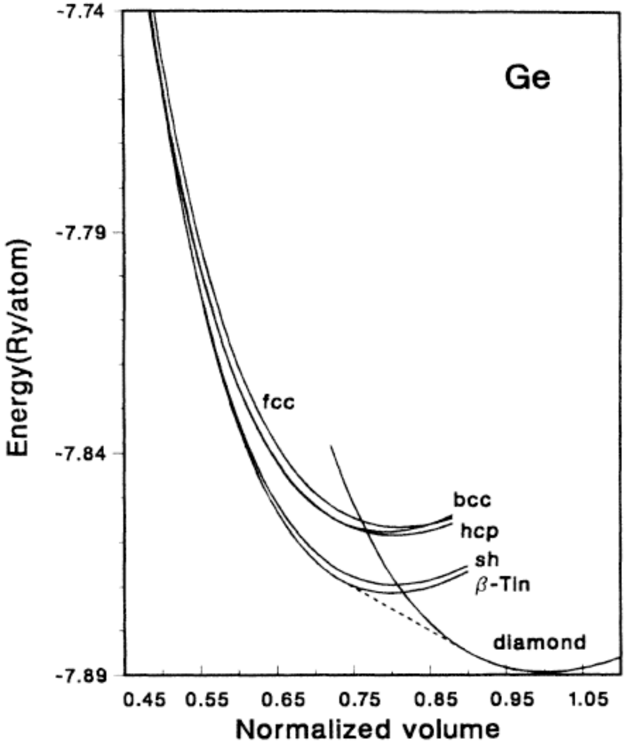


FIG. 1. Crystal energies versus volume normalized by the calculated equilibrium volume of 22.5616 Å^3 for the cubic diamond phase in Ge.

What can be computed with DFT? Perturbation Theory

$$V_{ext} \rightarrow V_{ext}^{(0)} + \lambda V_{ext}^{(1)} + \lambda^2 V_{ext}^{(2)} + \ldots$$

$2n+1$ Theorem(Gonze and Vigneron, 89)

Knowledge of Kohn-Sham wavefunctions up to order *n* is adequate to yield Kohn-Sham energy up to order *(2 n + 1)*.

$$\psi_i \rightarrow \psi_i^{(0)} + \lambda \psi_i^{(1)} + \lambda^2 \psi_i^{(2)} + \ldots$$
$$E_G \rightarrow E_G^{(0)} + \lambda E_G^{(1)} + \lambda^2 E_G^{(2)} + \ldots$$
$$\{ \psi_i^{(1,..n)} \} \Rightarrow E_G^{(2n+1)}$$

E.g: unperturbed wf $(\psi_i^{(0)})$ allow us to compute forces $(\frac{dE}{dx})$

E.g: first order wf $(\psi_i^{(1)})$ allow us to compute phonons and beyond $(\frac{d^2E}{dx^2}, \frac{d^3E}{dx^3})$

Adapted fron Umesh Waghmare; http://nanohub.org/resources/9683/supportingdocs

What can be computed with DFT? Perturbation Theory

n=0: Ground state Kohn-Sham solution

2 n +1 = 1: All first derivatives of EG can be obtained from the ground state ψ's.

Example:
1. Hellman-Feynman forces on atoms (deriv. wrt atomic position)
2. Stress on the crystal (deriv. wrt strain)
3. Magnetization (deriv. wrt magnetic field)
4. Electric polarization (deriv. wrt electric field)

n=1: Kohn-Sham DFT Linear Response

2 n +1 = 3: All second and third derivatives can be obtained from the first order (linear response) ψ's.

Examples:
1. Force constant matrices
2. Elastic constants
3. Dielectric constant
4. All the mixed second derivatives like piezoelectric const.

5. Raman tensor (third deriv. wrt atomic position, E, E).

$$(H_{KS}^{0}-\varepsilon_i^{0})\,\psi_i^{1} = (H_{KS}^{1}-\varepsilon_i^{1})\,\psi_i^{0}$$

Taken fron Umesh Waghmare; http://nanohub.org/resources/9683/supportingdocs

What can be computed with DFT?

Second derivative of E_{tot} or F wrt	**Physical property**
d_j, d_i (atomic displacement)	Force spring const: phonons
E, E (E-field)	Dielectric constant
ε, ε (strain)	Elastic constant
E, ε	Piezo-electric constant
E, d_i	Born Dynamical charge
ε, d_i	Strain-phonon coupling
H, H (magnetic field)	Magnetic susceptibility
E, H	Magneto-electric constant
H, ε	Piezo-magnetic constant

$T \neq 0$: E_{total} → tools of statistical mechanics → free energy F

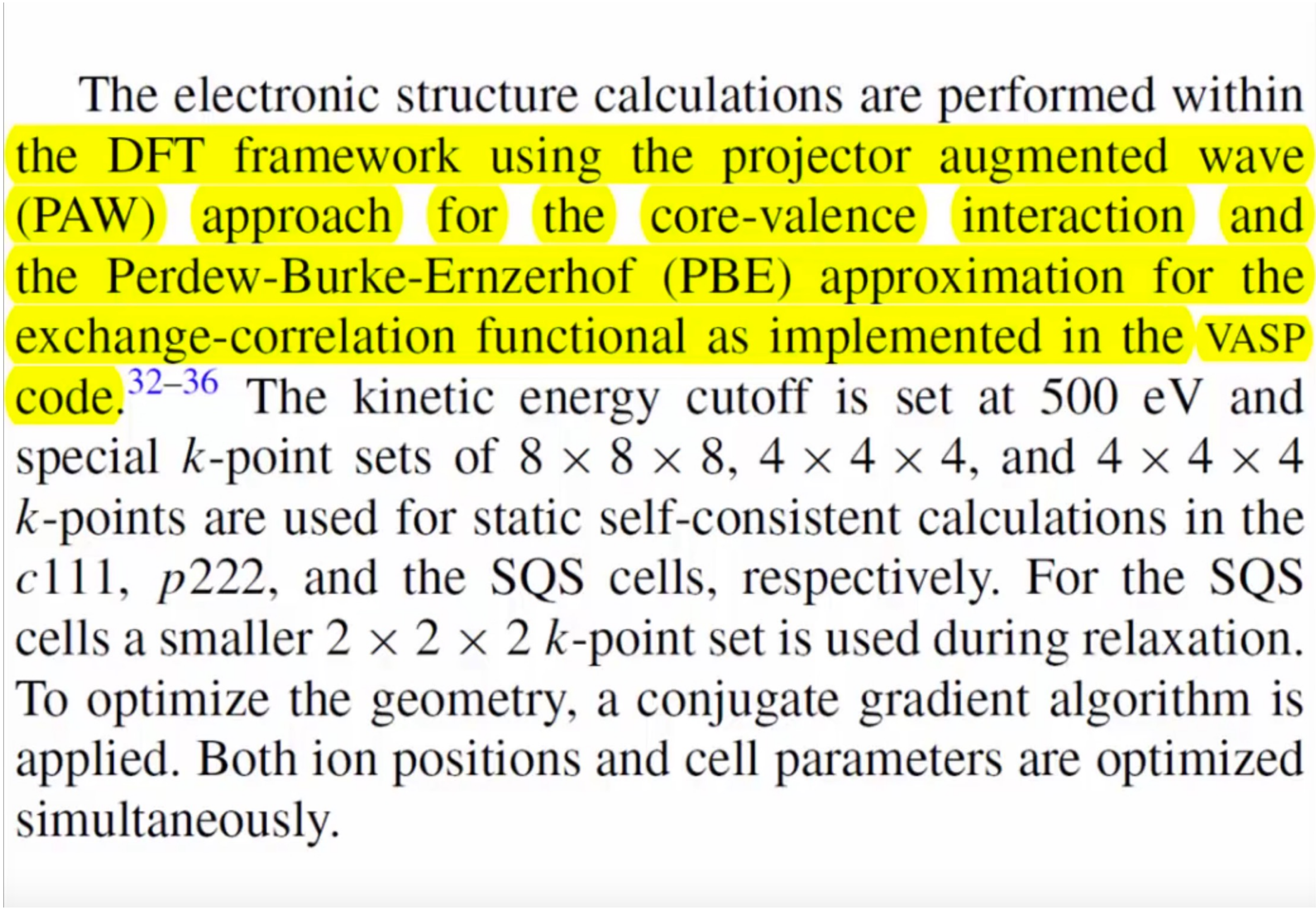
Taken fron Umesh Waghmare; http://nanohub.org/resources/9683/supportingdocs

Program

1. Density Functional Theory

- Introduction to Simulation in Materials
- Solving the quantum mechanical problem: approximations
- Density Functional Theory – The basics
- Density Functional Theory – In practice
    - Functionals
    - Numerical Methods
    - Codes

DFT in practice – overcoming the jargon



The electronic structure calculations are performed within the DFT framework using the projector augmented wave (PAW) approach for the core-valence interaction and the Perdew-Burke-Ernzerhof (PBE) approximation for the exchange-correlation functional as implemented in the VASP code.[32–36] The kinetic energy cutoff is set at 500 eV and special k-point sets of $8 \times 8 \times 8$, $4 \times 4 \times 4$, and $4 \times 4 \times 4$ k-points are used for static self-consistent calculations in the $c111$, $p222$, and the SQS cells, respectively. For the SQS cells a smaller $2 \times 2 \times 2$ k-point set is used during relaxation. To optimize the geometry, a conjugate gradient algorithm is applied. Both ion positions and cell parameters are optimized simultaneously.

Taken fron Stefaan Cottenier; https://www.youtube.com/watch?v=jZi2EOrCrpY

A short guide to understand DFT

1. Which is the XC Functional?

2. What are the numerical methods used to solve the one-electron Kohn-Sham equations?

3. What code has been used?

1. Which XC Functional?

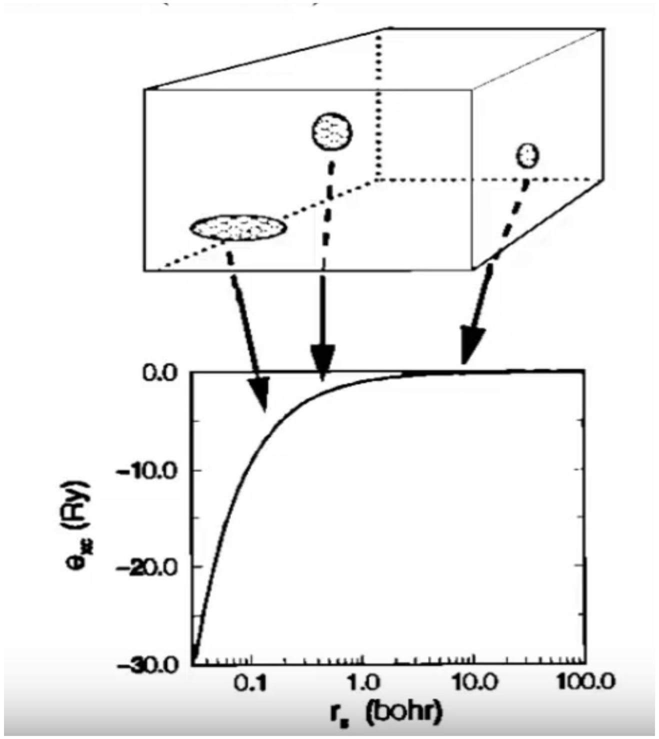
The Local Density Approximation - LDA

Already proposed by Kohn-Sham

Assume that $E_{xc}[n]$ is a sum of contributions from each point in real space, depending only on the density of that point, independent of the others

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

$$v_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r}) = \frac{\delta E^{\mathrm{LDA}}}{\delta \rho(\mathbf{r})} = \epsilon_{\mathrm{xc}}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{\partial \epsilon_{\mathrm{xc}}(\rho(\mathbf{r}))}{\partial \rho(\mathbf{r})}$$



Taken from the homogeneous electron gas (exact results available from Monte Carlo and analytic Many Body calculations)

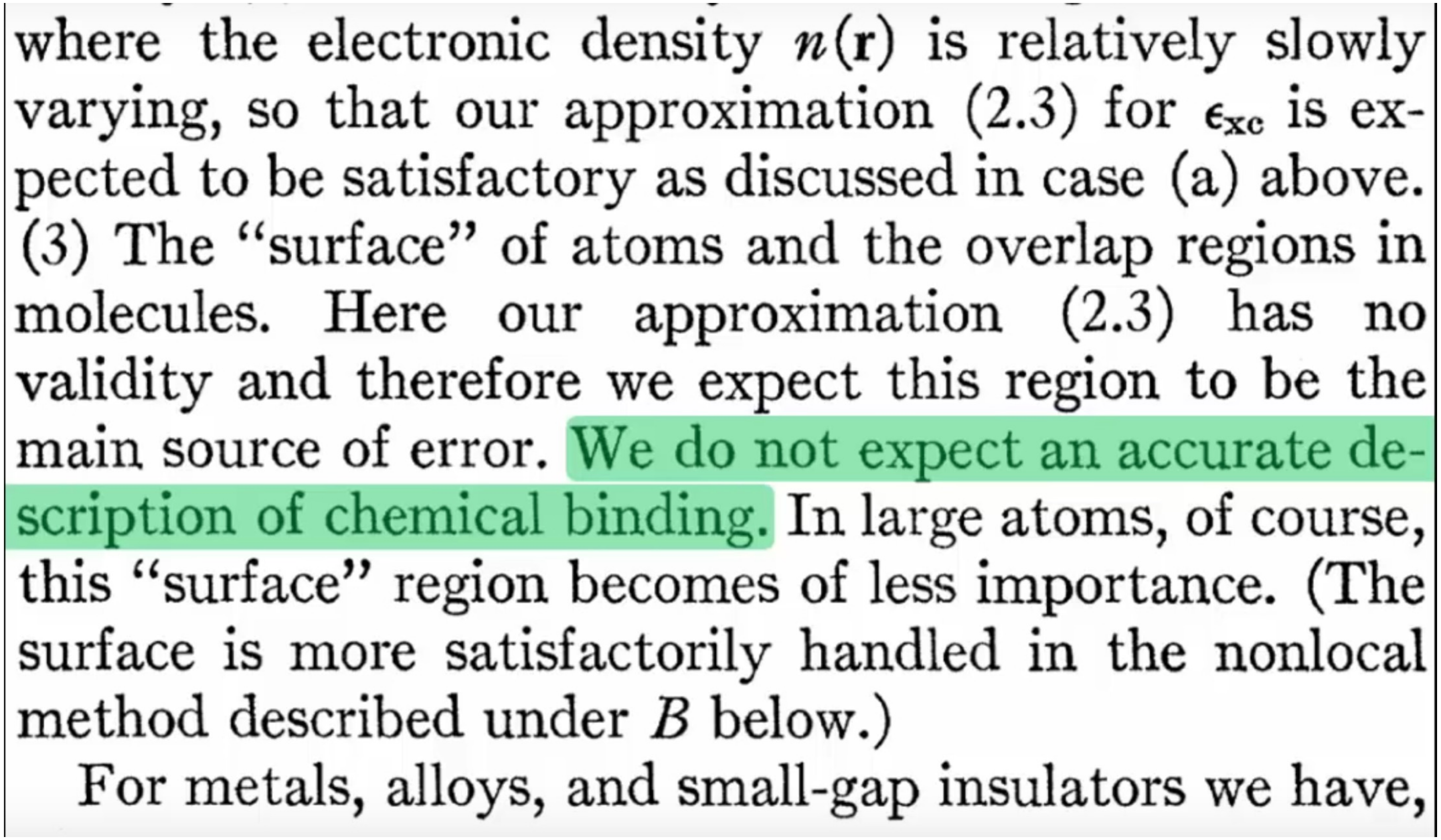
D. M. Ceperley and B. J. Alder (Phys. Rev. Lett. 1980)

LDA functional:

J. Perdew and A. Zunger (Phys. Rev. B, 1981)

1. Which XC Functional?

The Local Density Approximation - LDA



where the electronic density $n(\mathbf{r})$ is relatively slowly varying, so that our approximation (2.3) for ϵ_{xc} is expected to be satisfactory as discussed in case (a) above. (3) The "surface" of atoms and the overlap regions in molecules. Here our approximation (2.3) has no validity and therefore we expect this region to be the main source of error. We do not expect an accurate description of chemical binding. In large atoms, of course, this "surface" region becomes of less importance. (The surface is more satisfactorily handled in the nonlocal method described under *B* below.)

For metals, alloys, and small-gap insulators we have,

Kohn – Sham, Phys. Rev. 1965

1. Which XC Functional?

The Generalized Gradients Approximation - GGA

Assume that $E_{xc}[n]$ is a sum of contributions from each point in real space, depending only on the density *and its gradients* at that point, independend of the others

$$E_{xc}[n] = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

Many GGA functionals (PW91, PBE, BLYP, PB86, PBEsol…)

J. P. Perdew, K. Burke, M. Ernzerhof, "Generalized Gradient Approximation Made Simple," Phys. Rev. Lett. **77**, 3865-3868 (1996).

Better cohesion and dissociation energies than LDA, to the point that the errors are acceptable for many purposes in Chemistry and Materials Science

1. Which XC Functional?

	LDA	GGA
Lattice Constants	-1% , -3%	+1%
Bulk Modulus	+10, +40%	-20%, +10%
Cohesive Energy	+15%	-5%
E_{gap}	-50%	-50%

LDA: crude approximation but sometimes is accurate enough (structural properties, …).

GGA: Better cohesion energies; usually tends to overcompensate LDA results, not always better than LDA.

1. Which XC Functional?

Usual problems with the common functionals (LDA, GGA):

- Problems describing weak interactions (Van der Waals)

  (solution: new non-local functionals)

- Problems describing strongly correlated systems

  (solution: methods to include better exchange and correlations)

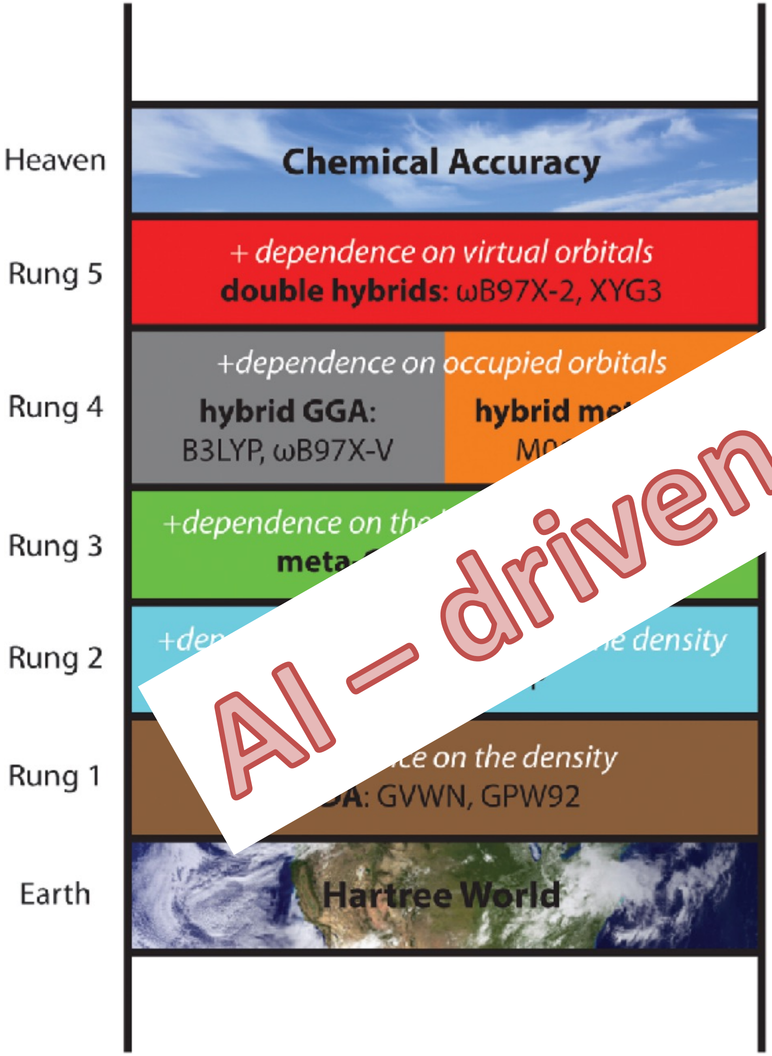
- Excited electronic states: DFT is a ground state technique

  solution: methods beyond DFT to compute electronic excitations

  Many Body Perturbation Diagrammatic techniques: 'GW' for quasiparticles; Bethe-Salpeter for optical excitations, ...

1. Which XC Functional?

Beyond LDA & GGA - "Jacob's Ladder"



AI – driven XC Functionals!!

Mardirossian & Hea
Phys. Chem. Ch
, 9904

DFT functionals for van der Waals interactions (depend on density **at two points**)

DFT becomes widely used (much more than Quantum Chemistry methods)

W. Kohn gets the Nobel prize in Chemistry (1998)

1. Which XC Functional? - A word of caution

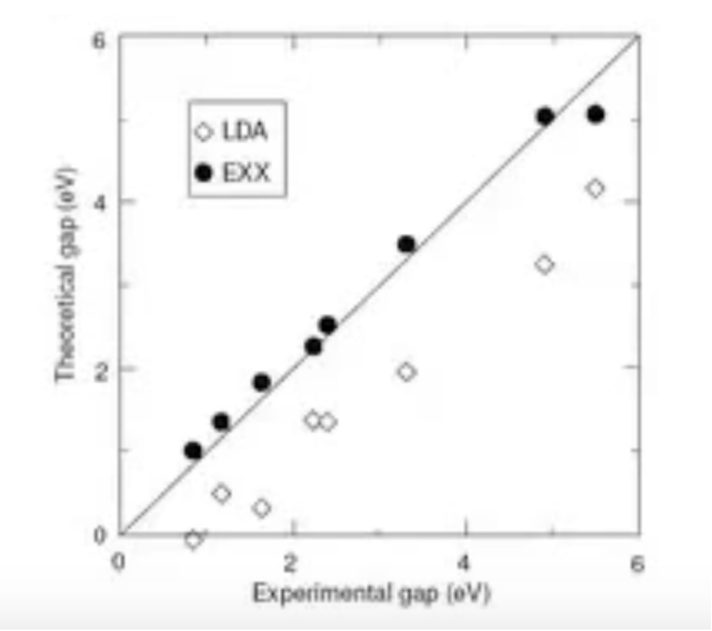
DFT provides the right ground state density and energy, nothing else.

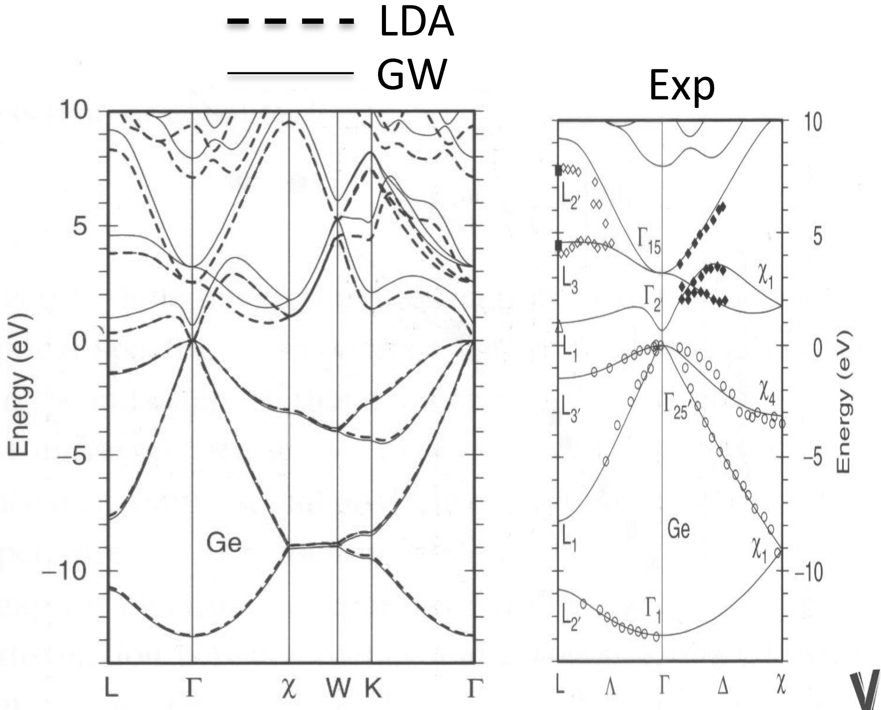
The one-electron eigenvalues and eigenvectors have no physical meaning; they are just a mathematical step to construct the density.

They should not be interpreted as physically sound quantities! **(Beware!! – very often they are…)**

1. Which XC Functional? - A word of caution

- Eigenvalues ε_i do not have a rigourous physical meaning. They are ***not*** the excitation (quasiparticle) energies (although there are some theorems
- In practice, ε_i are good approximantions to the excitation energies, but band gaps are too small





A short guide to understand DFT

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2. What are the numerical methods used to solve the one-electron Kohn-Sham equations?
3. What code has been used?

2. The Numerical Methods

$$\begin{tikzcd}
n(\vec{r}) = \sum_{n}^{occ} \left|\psi_n(\vec{r})\right|^2 \arrow[rr, bend left] & & \hat{h} = -\frac{1}{2}\nabla^2 + \boxed{V_{eff}[n]} \arrow[dl, bend left] \\
& \hat{h}\psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r}) \arrow[ul, bend left] &
\end{tikzcd}$$

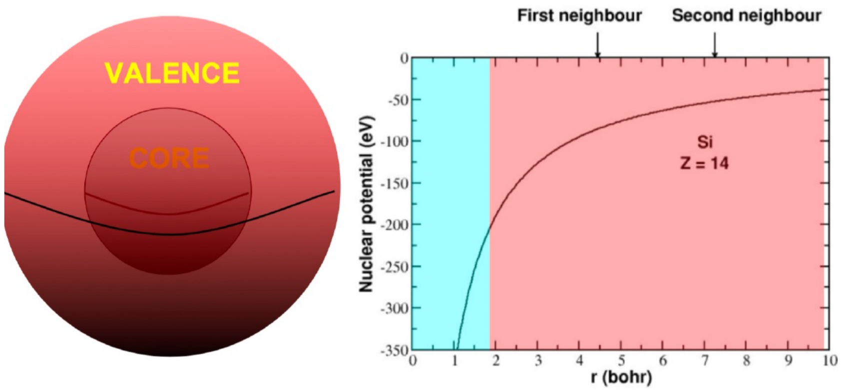
N second order differential equations

Non-linear

Orthogonality condition on ψ

2. The Numerical Methods

1. How many electros do we consider?



Courtesy of E. Artacho

- All electrons in the atoms present

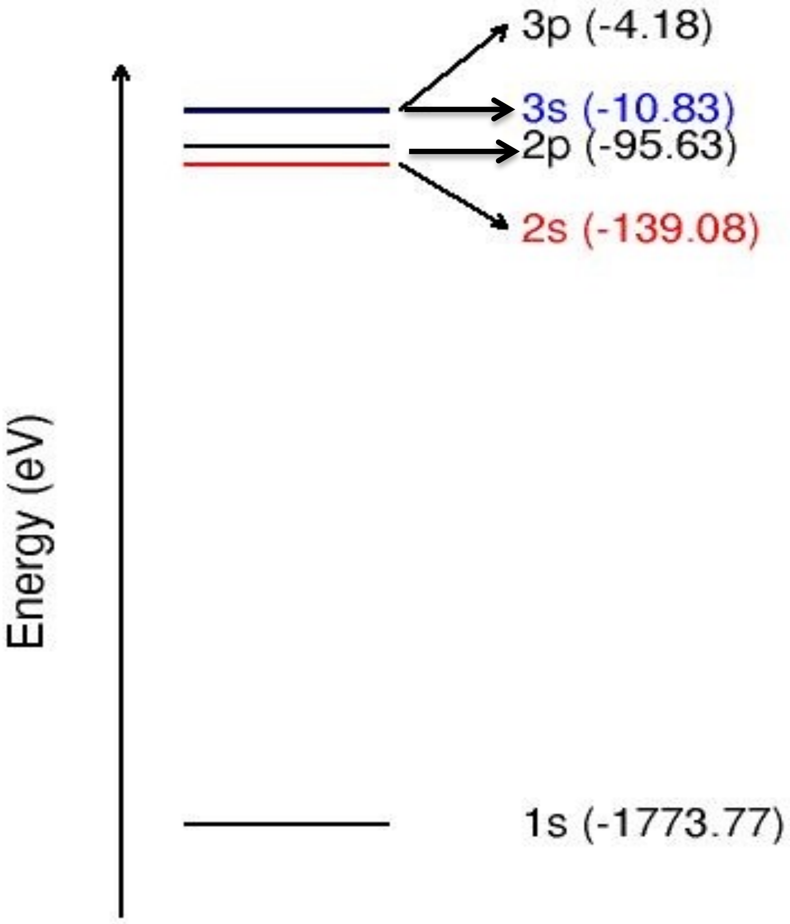
  Si: 14 electrons $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^2$

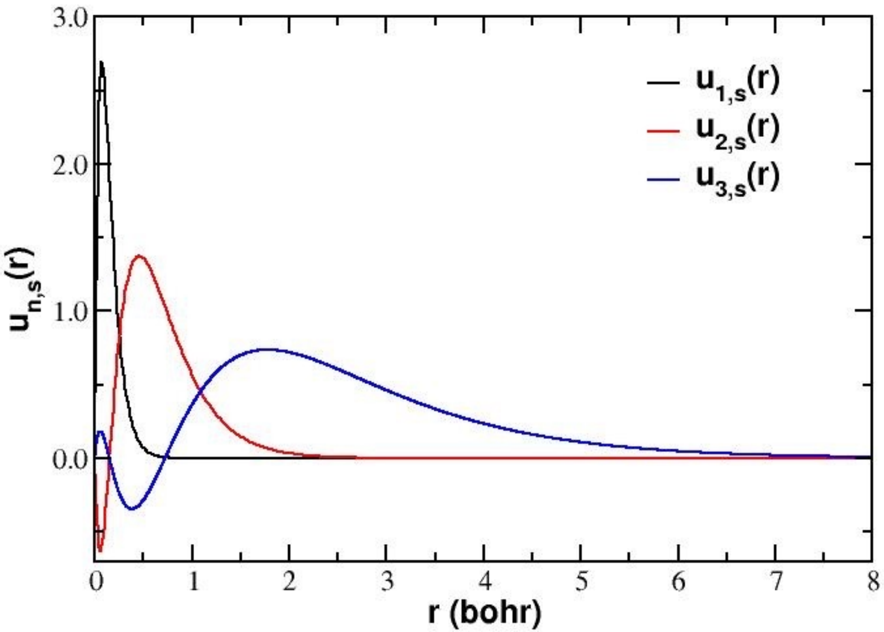
- Only the valence electrons

  Si: 4 electrons: $3s^2$, $3p^2$

2. The Numerical Methods

1. How many electros do we consider?





Core electrons…

highly localized

very deep energy

… are chemically inert

2. The Numerical Methods

1. How many electros do we consider?

- All electron calculations (APW, LMTO...)

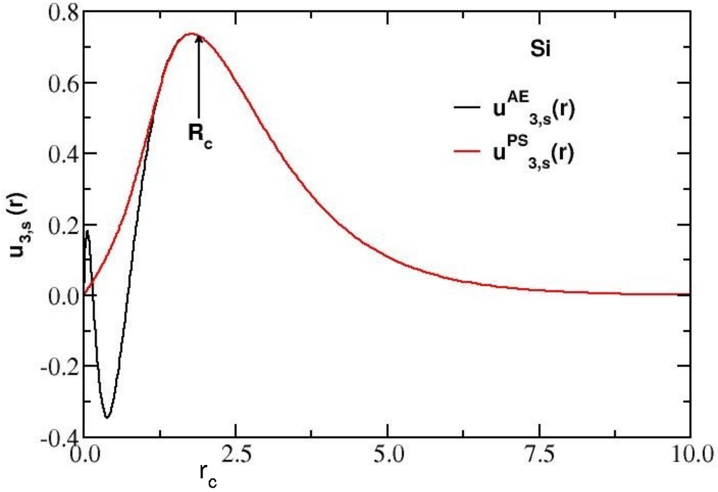
- Pseudopotentials calculations
  (and related, like PAW)

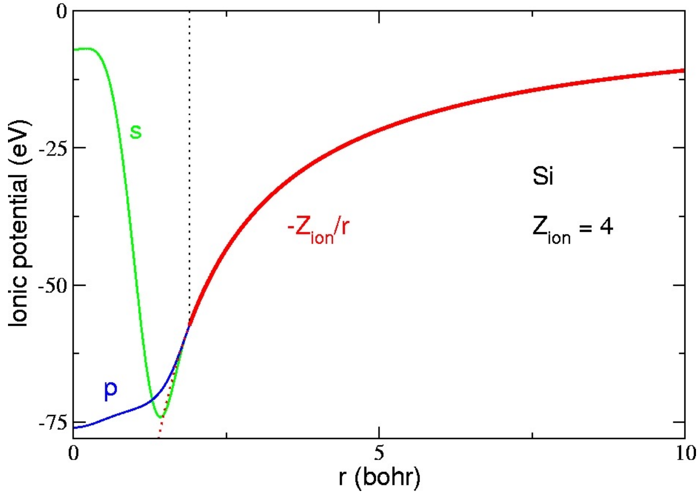
2. The Numerical Methods

1. How many electros do we consider?

Pseudopotentials:

- Substitute the all-electron potential and the nuclear attraction by an effective (l-dependent) dependent potential potential, inside r_c
- Impose that ψ is unchanged beyond r_c
- Impose that ε for the valence electrons does not change





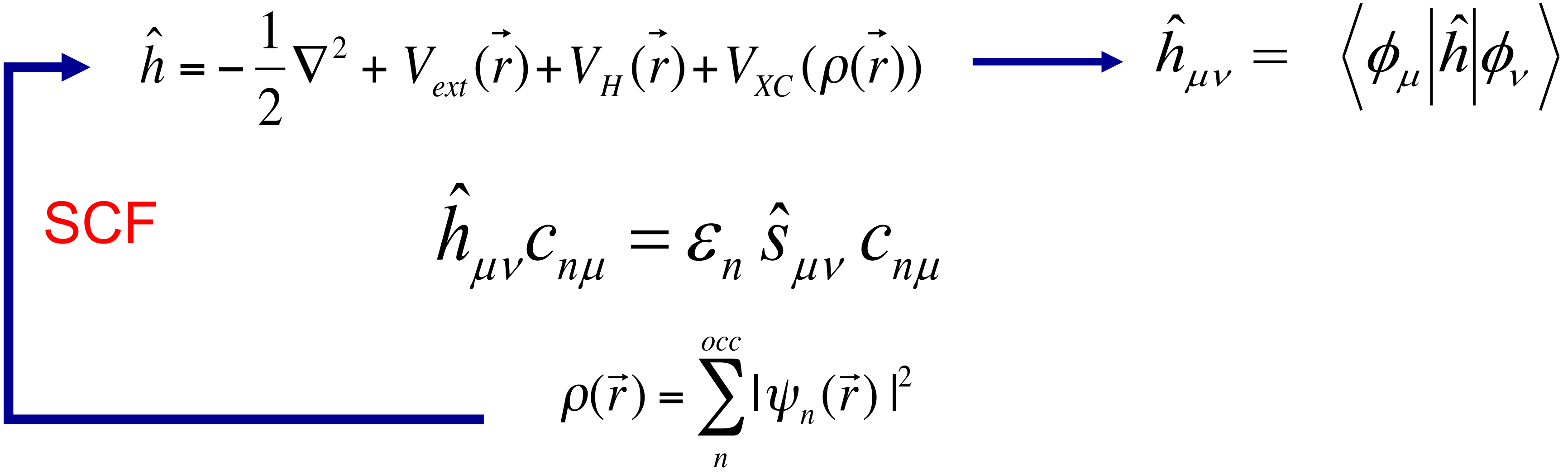
2. The Numerical Methods

2. Discretizing the problem: What basis set?

We discretize the differential equation problem by expanding the wave functions in a basis set:

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

Solve the ***SELF-CONSISTENT*** one electron problem: Building H and obtaining the eigenstates ***by linear algebra***:



$$\hat{h} = -\frac{1}{2}\nabla^2 + V_{ext}(\vec{r})+V_H(\vec{r})+V_{XC}(\rho(\vec{r})) \longrightarrow \hat{h}_{\mu\nu} = \left\langle \phi_\mu \middle| \hat{h} \middle| \phi_\nu \right\rangle$$

SCF

$$\hat{h}_{\mu\nu}c_{n\mu} = \varepsilon_n \hat{s}_{\mu\nu} c_{n\mu}$$

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

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3. The Codes

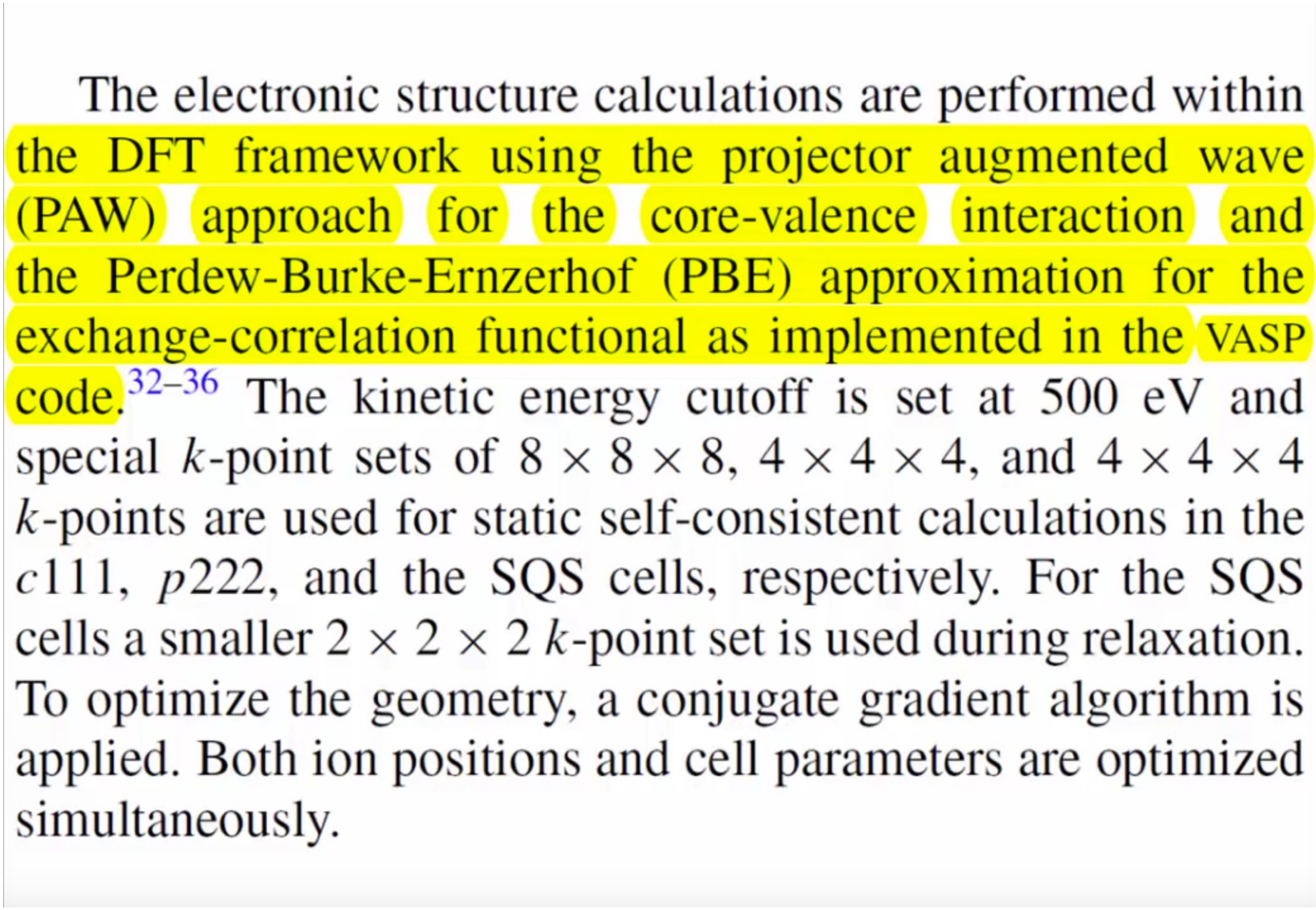
2. What basis set do is used?
3. What code to use?

The choice of functions φ will determine what method/code we will be using (each code is tied to a specific choice of basis set!):

- Gaussian type orbitals (GTOs): Gaussian, Gamess, …
- Atomic-like orbitals: LCAO – SIESTA
- Molecular orbitals: LCMO
- Plane waves: Quantum Espresso, VASP, Abinit
- Augmented plane waves: FLEUR, WIEN2k
- Wavelets: BigDFT

Some Open-source, free codes

A bit clearer now??



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Thank you!

Questions? pablo.ordejon@icn2.cat