

# WORKSHOP ON QUANTUM ESPRESSO

**Day 01**

Theories + Documentation  
Linux operating system  
software setup

**Day 02**

Program Simulation  
Visualization  
QNA



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MSc on going KUET

**Free Registration**

IEEE KUET SB, March 17, 2023

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Acknowledgement: All the slides are collected from online resources (see references). All credits to the three slides attached in the end section.

**Presented By: Md. Rayid Hasan Mojumder, Jikrul Sayeed, and Md. Sakib Hassan**



**INSTRUCTOR:**

# Workshop on First Principles Density Functional Theorem (FP-DFT) for Materials Simulation in Quantum Espresso

## Part-1: Fundamental theorem and principles





Ab initio materials modelling

Quantum Mechanics

First-principles calculations: approximations

Born-Oppenheimer approximation

Density Functional Theory

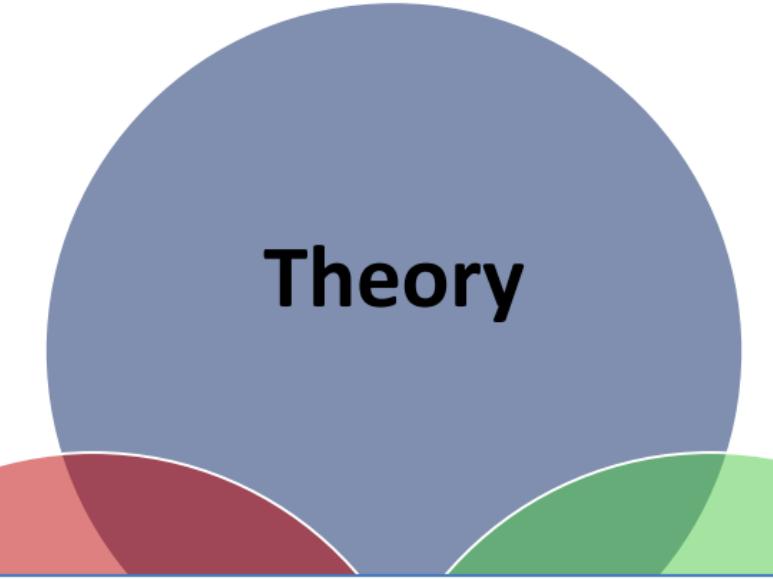
Bloch's theorem – periodic system

Electron-ion interaction (pseudopotential)

DFT : Practical considerations

References

# Ab initio materials modelling

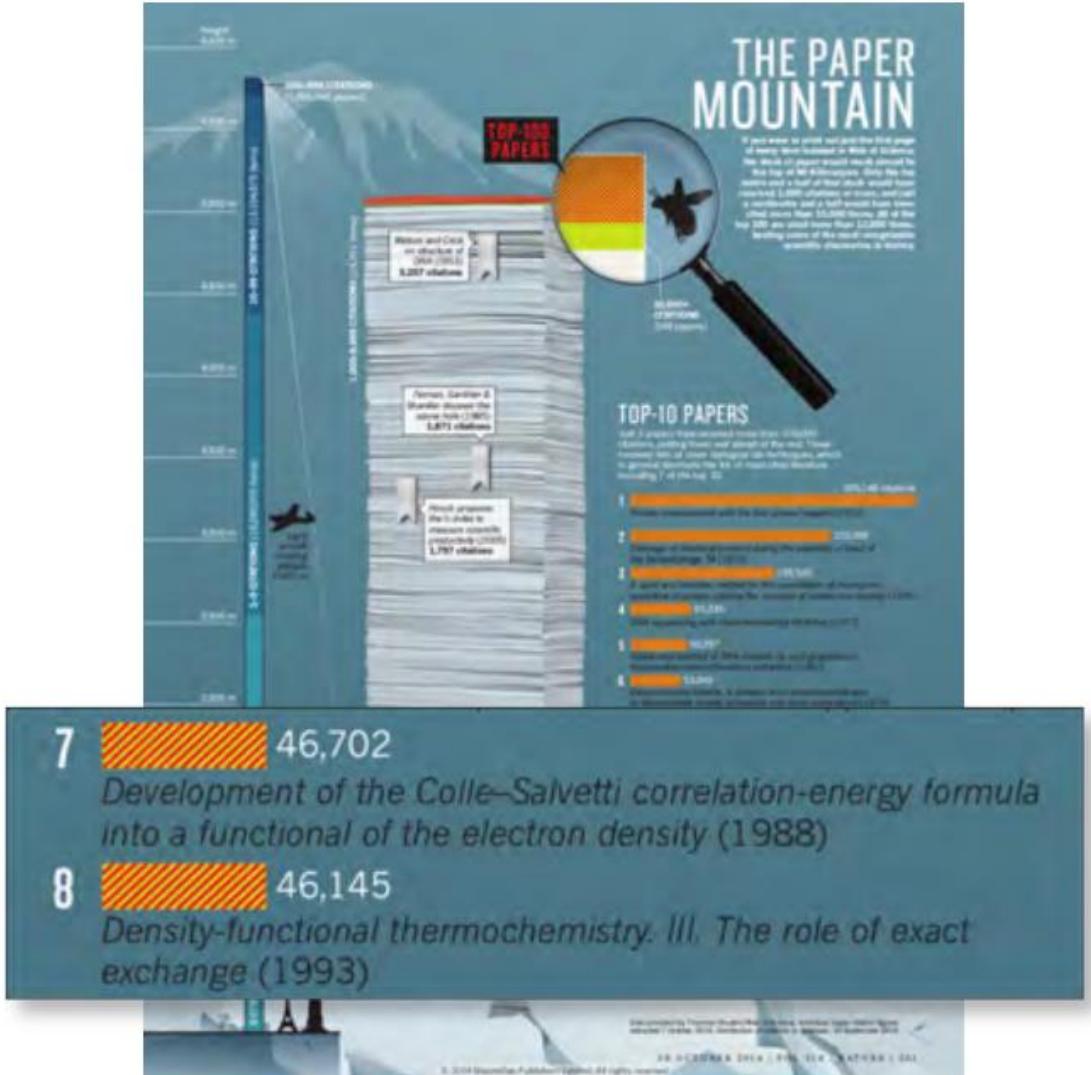


“Computer modeling & simulation” has emerged as an indispensable method for scientific research of materials in parallel to experiment and theory.

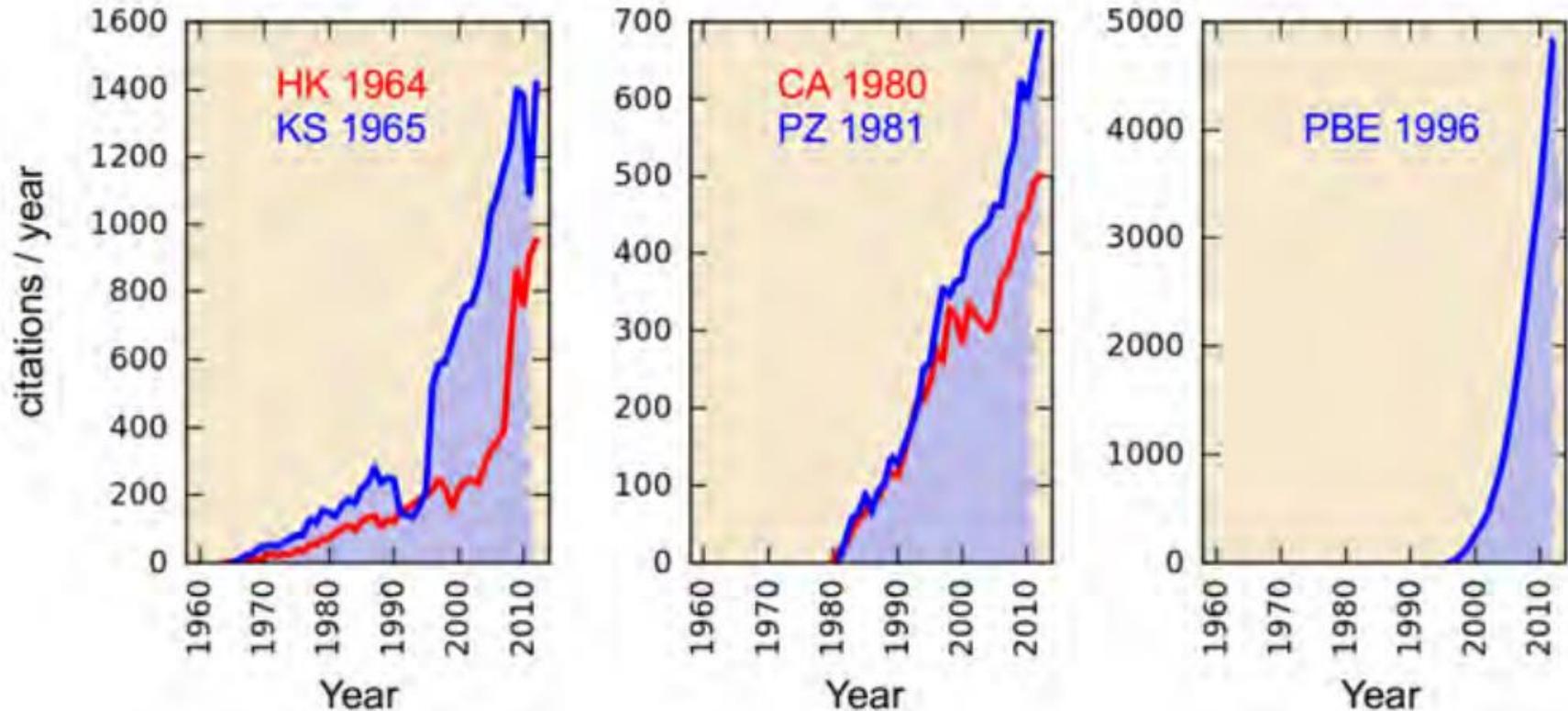
# Impact of DFT

# THE TOP 100 PAPERS

Interview by R. Van Norden  
Nature 514, 550 (2014)



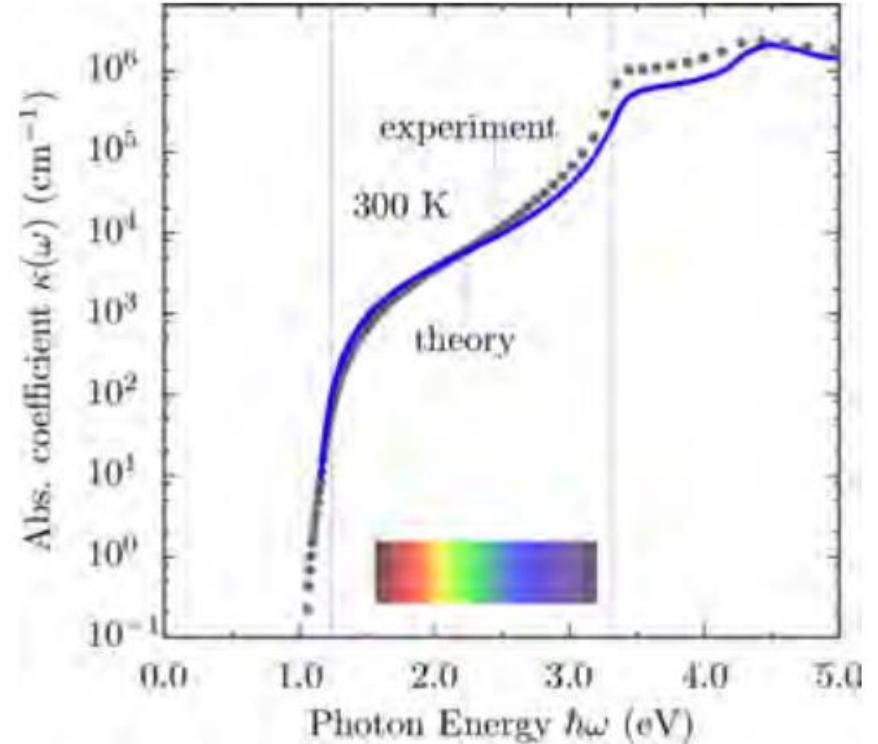
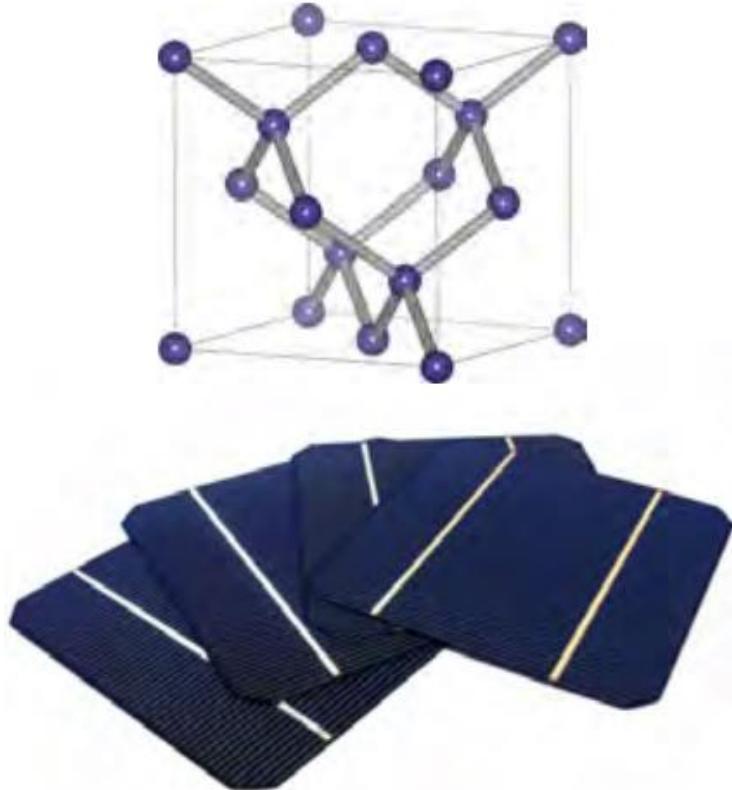
# Impact of DFT



- HK 1964 Hohenberg, Kohn, Phys. Rev. 136, B864 (1964)  
KS 1965 Kohn, Sham, Phys. Rev. 140, A1133 (1965)  
CA 1980 Ceperley, Alder, Phys. Rev. Lett. 45, 566 (1980)  
PZ 1981 Perdew, Zunger, Phys. Rev. B 23, 5048 (1981)  
PBE 1996 Perdew, Burke, Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)  
Feliciano Giustino, QS3 School, Cornell, June 2018

# Examples of calculations based on DFT

## Predictive calculations of optical properties



Zacharias, Patrick, and FG, Phys. Rev. Lett. 115, 177401 (2015)

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# Examples of calculations based on DFT

8



## Predictive calculations of transport properties

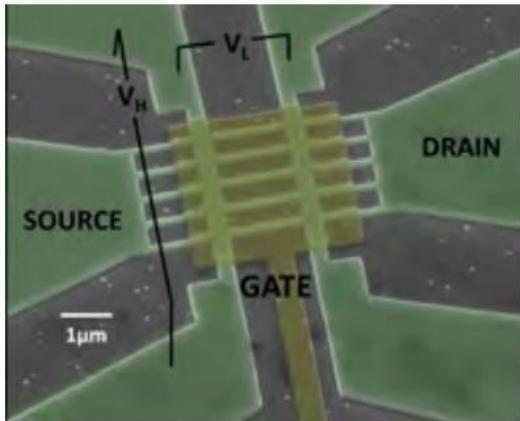
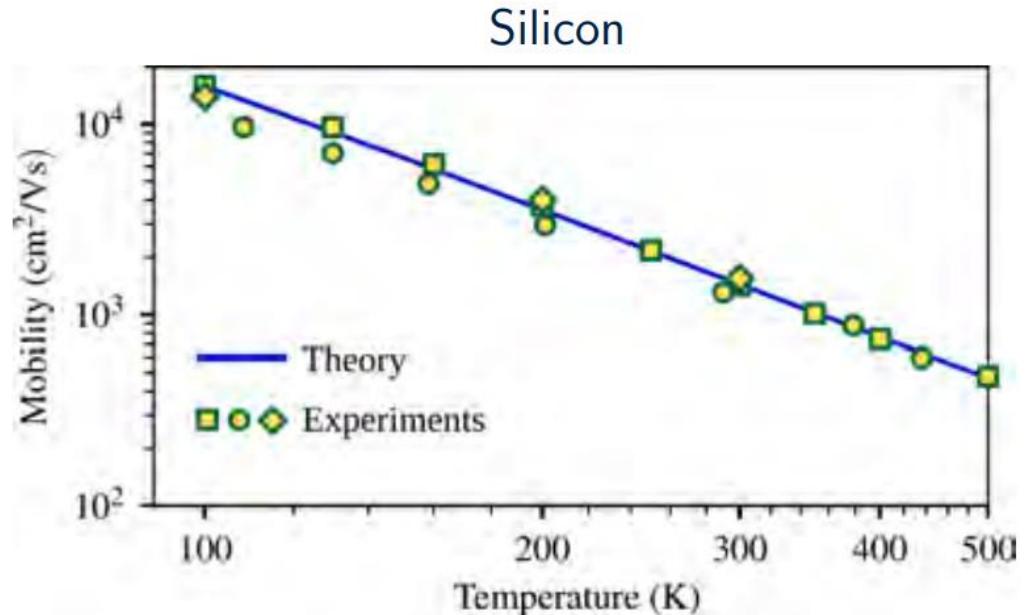


Image from Thathachary et al,  
Nano Lett. 14, 626 (2014)

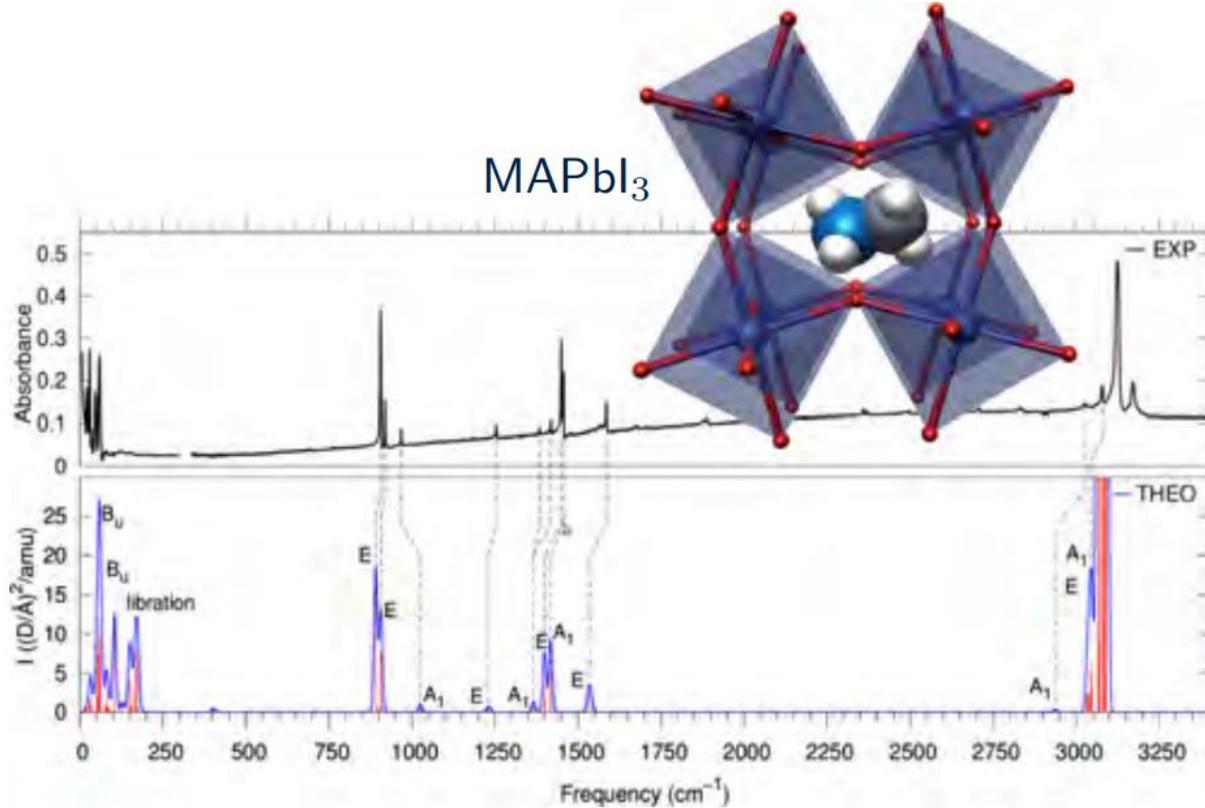


Poncé, Margine, and FG, Phys. Rev. B(R) 97, 121201 (2018)

Feliciano Giustino, QS3 School, Cornell, June 2018

# Examples of calculations based on DFT

Materials characterization via vibrational spectroscopy



Perez-Osorio, Milot, Filip, Patel, Herz, Johnston, and FG, J. Phys. Chem. C 119, 25703 (2015)

Feliciano Giustino, QS3 School, Cornell, June 2018

# Examples of calculations based on DFT

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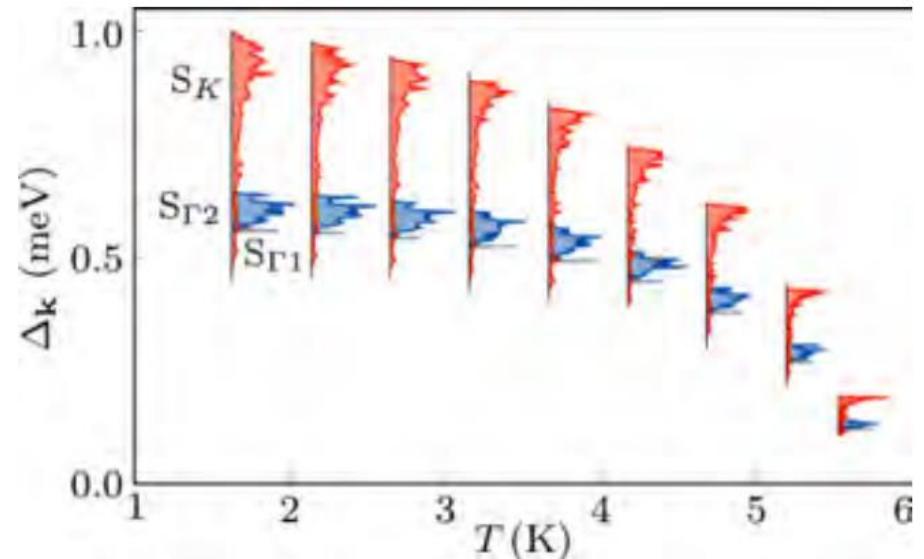
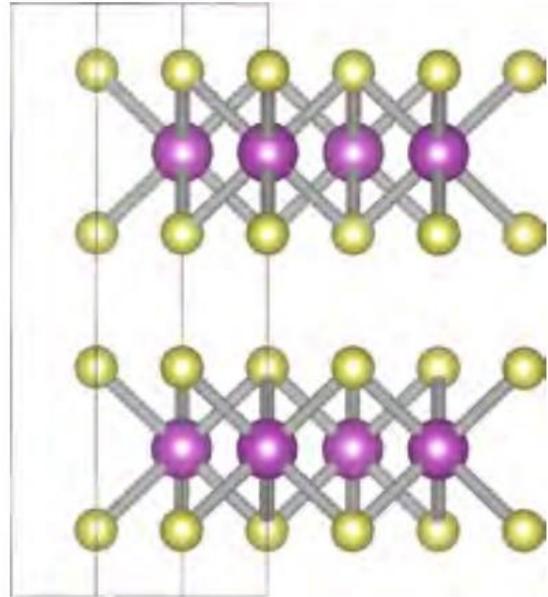
# Computational materials discovery

/olonakis, Filip, Haghaghirad, Sakai, Wenger, Snaith, and FG, J. Phys. Chem. Lett. 7, 1254 (2016)

# Examples of calculations based on DFT

Predictive calculations of the superconducting critical temperature

$\text{NbS}_2$



Heil, Poncé, Lambert, Schlipf, Margine, and FG, Phys. Rev. Lett., 119, 087003 (2017)

Feliciano Giustino, QS3 School, Cornell, June 2018

# Why is DFT so popular?

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- **Transferability**

We can use the same codes/methods for very different materials

- **Simplicity**

The Kohn-Sham equations are conceptually very similar to the Schrödinger equation for a single electron in an external potential

- **Reliability**

Often we can predict materials properties with high accuracy, sometimes even before experiments

- **Software sharing**

The development of DFT has become a global enterprise, e.g. open source and collaborative software development

- **Robust platform**

Often the shortcomings of DFT can be cured by using more sophisticated approaches, which still use DFT as their starting point



# Quantum Mechanics

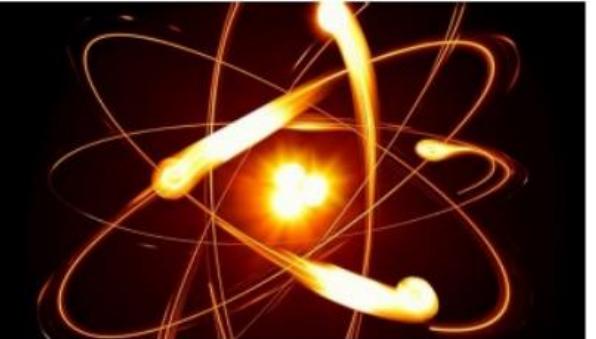
# The physics of low-energy matter

Made of **electrons and nuclei**  
(interacting with photons)

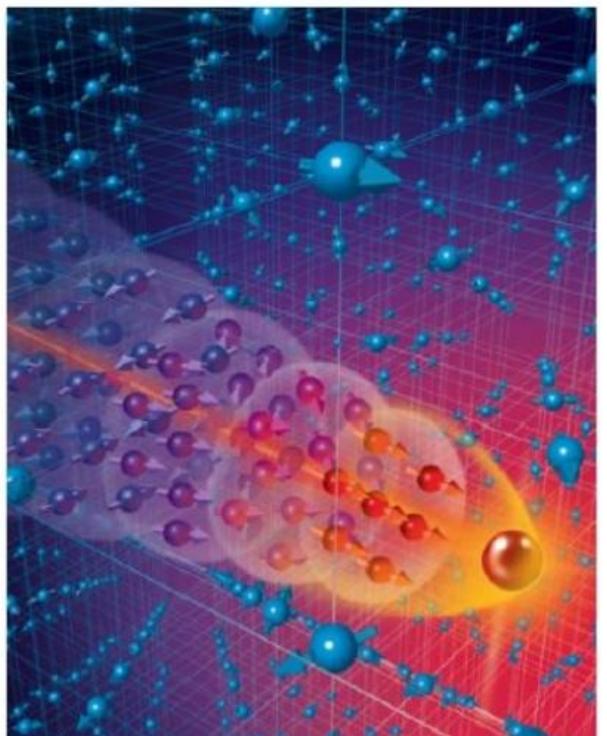
Matter at T up to several million K  
(except for nuclear fission and radioactive decay)

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

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



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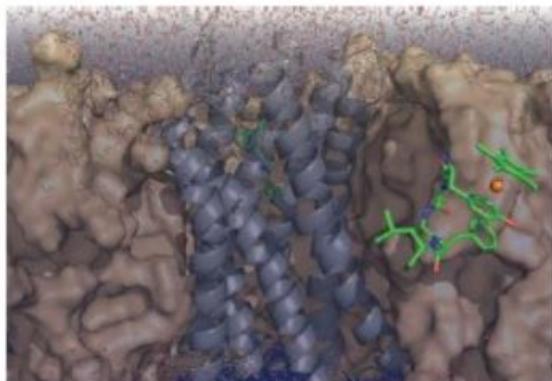


# The physics of low-energy matter

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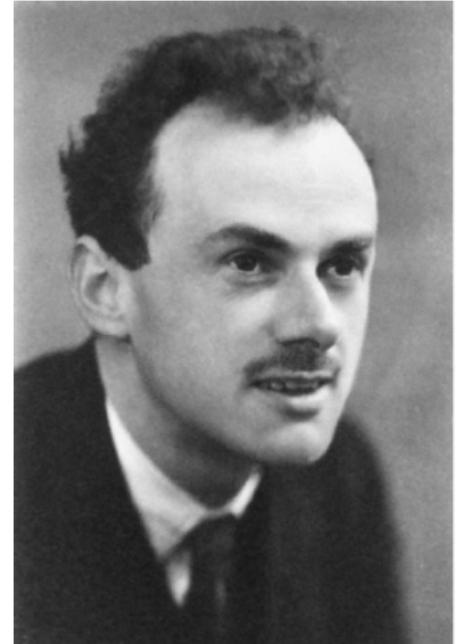
Electrons and nuclei are behind properties and processes in

- Chemistry
- Material science
- Biomedicine (biochem, biophys, molecular bio)
- Geo (geophysics, geochemistry)
- Electronics
- Energy research
- Nanoscience and nanotechnology





*“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. 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.”*



Paul Dirac (1929)



## 1) Electromagnetism

## 2) Quantum Mechanics: Schrödinger equation

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

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)



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

Schrödinger's equation is exactly solvable for

- Two particles (analytically)
- Very few particles (numerically)

The number of electrons and nuclei in a pebble is  $\sim 10^{23}$

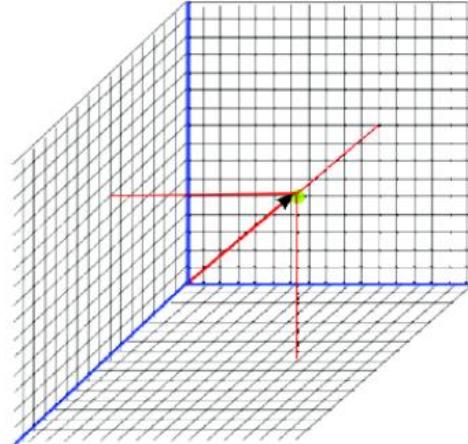
# Quantum mechanics for many particles

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

Solving in a computer e.g. discretizing space

A 3D grid in 100 points per side  $\rightarrow 100^3$  points

Similar grid in  $3N$  space  $\rightarrow 100^{3N}$  points



Computational costs (CPU and memory) scales  $\sim \exp(N)$



*Exponential Complexity*

$\rightarrow$  We need **approximations!**



Walter Kohn, in Nobel Lecture (1998)

# Many-body Schrodinger equation

- Many-body wavefunction (keep it simple: only 3 electrons)

$$\psi(\mathbf{r}) \rightarrow \Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

- Probability of finding electron #1 at the point  $\mathbf{r}$

$$\text{prob}(\mathbf{r}_1 = \mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)|^2 d\mathbf{r}_2 d\mathbf{r}_3$$

- Electron density at the point  $\mathbf{r}$

$$n(\mathbf{r}) = \text{prob}(\mathbf{r}_1 = \mathbf{r}) + \text{prob}(\mathbf{r}_2 = \mathbf{r}) + \text{prob}(\mathbf{r}_3 = \mathbf{r})$$

- Electrons are indistinguishable

$$n(\mathbf{r}) = 3 \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)|^2 d\mathbf{r}_2 d\mathbf{r}_3$$

# First-principles calculations

- Fundamental laws of physics
  - Chemical composition
- First-principles calculation → Properties

Set of “accepted” approximations  
to solve the corresponding equations on a computer

No empirical input or model

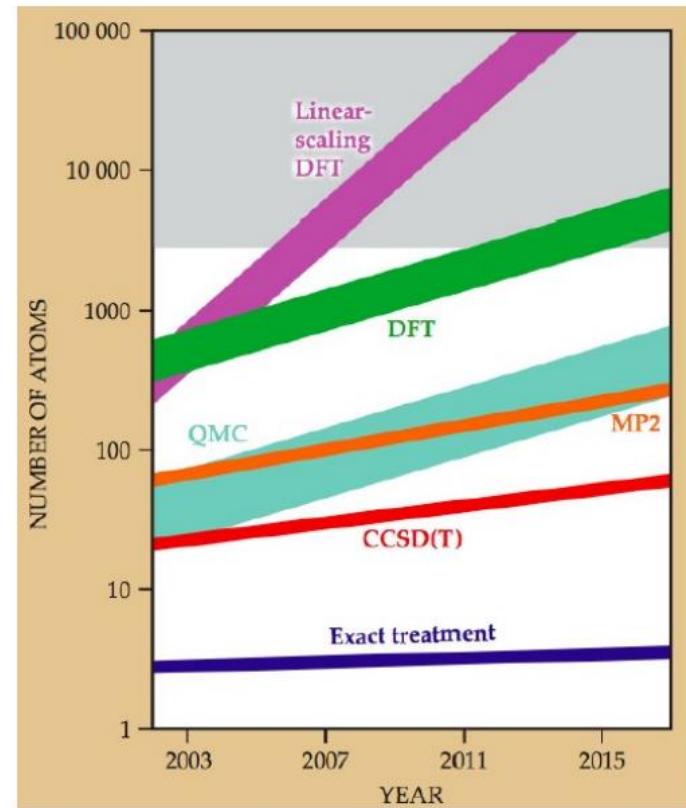
Predictive power!



Many-electron problem: old and extremely hard problem

Many different approaches:

- Quantum Chemistry: CI, CCSD(T), MP2...
- Quantum Monte Carlo (QMC)
- **Density Functional Theory (DFT)**
  - Very efficient and general
  - Best compromise efficiency/accuracy
  - BUT implementations are approximate and hard to improve (no systematic improvement)



M. Head-Gordon and E. Artacho

# Total Energy Calculation: First-principles method



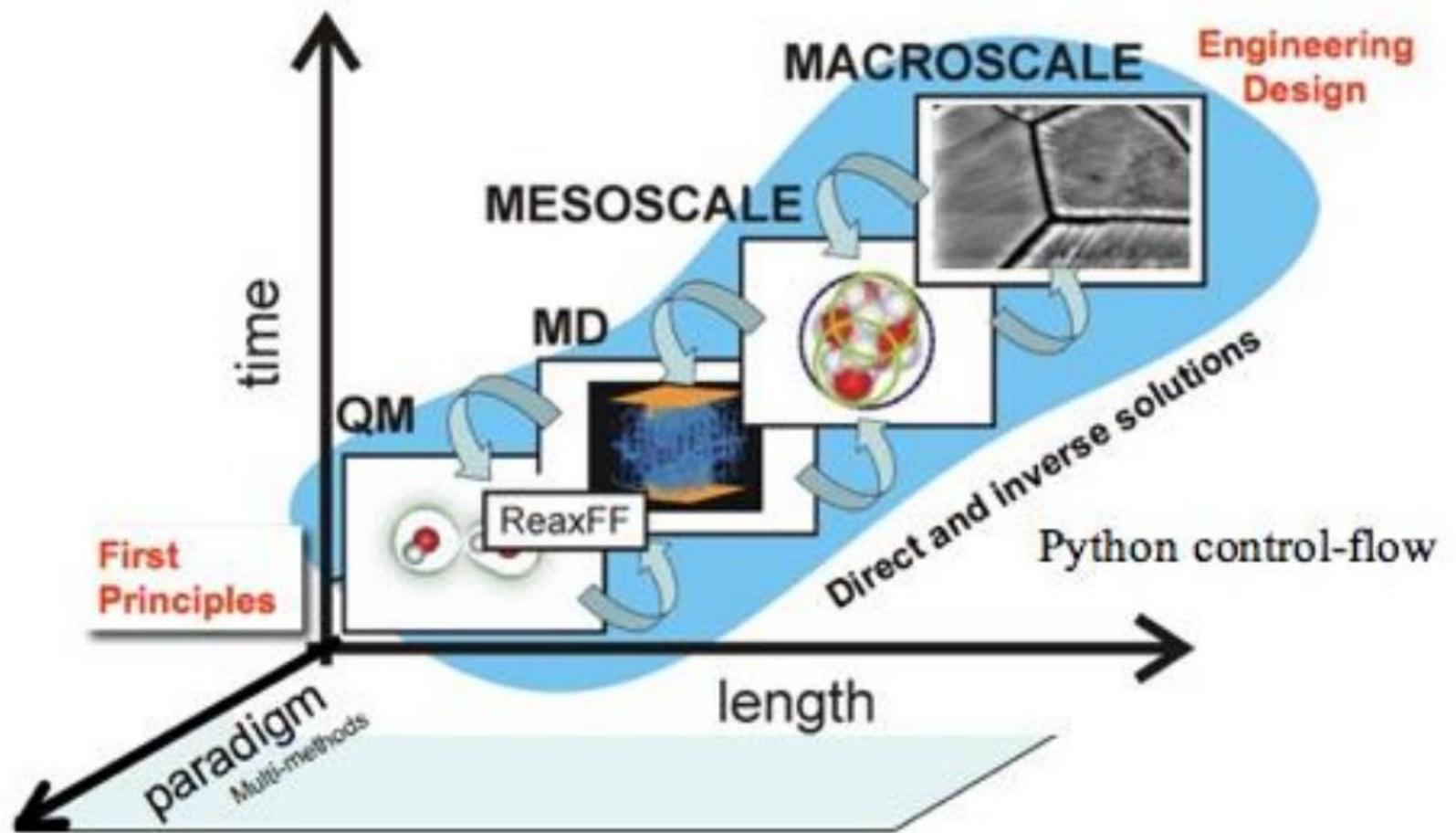
## Origin: the first mover

- ✓ Newton's first law: an object either remains at rest or continues to move at a constant velocity, unless acted upon by a net force.
- ✓ If all the objects were at rest at the start of the universe, yet they moved later. What is the origin of their movement?
- ✓ Newton believes this is moved by the God, "the first mover".
- ✓ The first mover should base on one principle, called "first principle"

## Quantum mechanics theory – first principle

- ✓ quantum mechanics reflects structure of atom & molecule and thus the properties of matter, such theory approximates the principle that reflects nature of the universe.

# First-principles method





Solve quantum mechanic Schrodinger equation to obtain Eigen value and Eigen function, and thus the electronic structure.

- The charm: only atomic number and crystal structure as input, which can determine precisely the structure and the properties of the real materials.
- **first principles** - physics, materials
  - Density functional theory
- ***ab initio*** -quantum chemistry
  - Hartree-Fork self-consistent field

# First-principles

According to the interaction between nucleus and electrons based on quantum mechanics principles, first principles method finds the solution to the Schrodinger equation through series of approximations and simplifications.

## 1D Schrodinger equation

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi(x, t)}{\partial x^2} + U(x, t) \psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t}$$

## 3D Schrodinger equation

$$-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U(x, y, z) \psi = i\hbar \frac{\partial \psi}{\partial t}$$

## Stationary Schrodinger equation

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi + U \psi = E \psi$$

Wave function



Eigen value, Eigen function



Energy, electron density



**Nearly all physical properties are related to total energies or to differences between total energies.**

- Equilibrium lattice constant: energy minimum
- surfaces, interfaces and defects, nanostucture: structure that minimize the total energy
- force: derivative of energy with respect to a position
- stress: derivative of energy with respect to a strain
- elastic constant: second derivative of energy

**If total energies can be calculated, any physical properties that can be related to a total energy or a difference between total energies can be determined computationally.**



## First-principles methods

- compute the total energy of a system of electrons and nuclei
- a subsequent minimization of the energy with respect to the electronic and nuclear coordinates.

## Technique: constructing a Hamiltonian

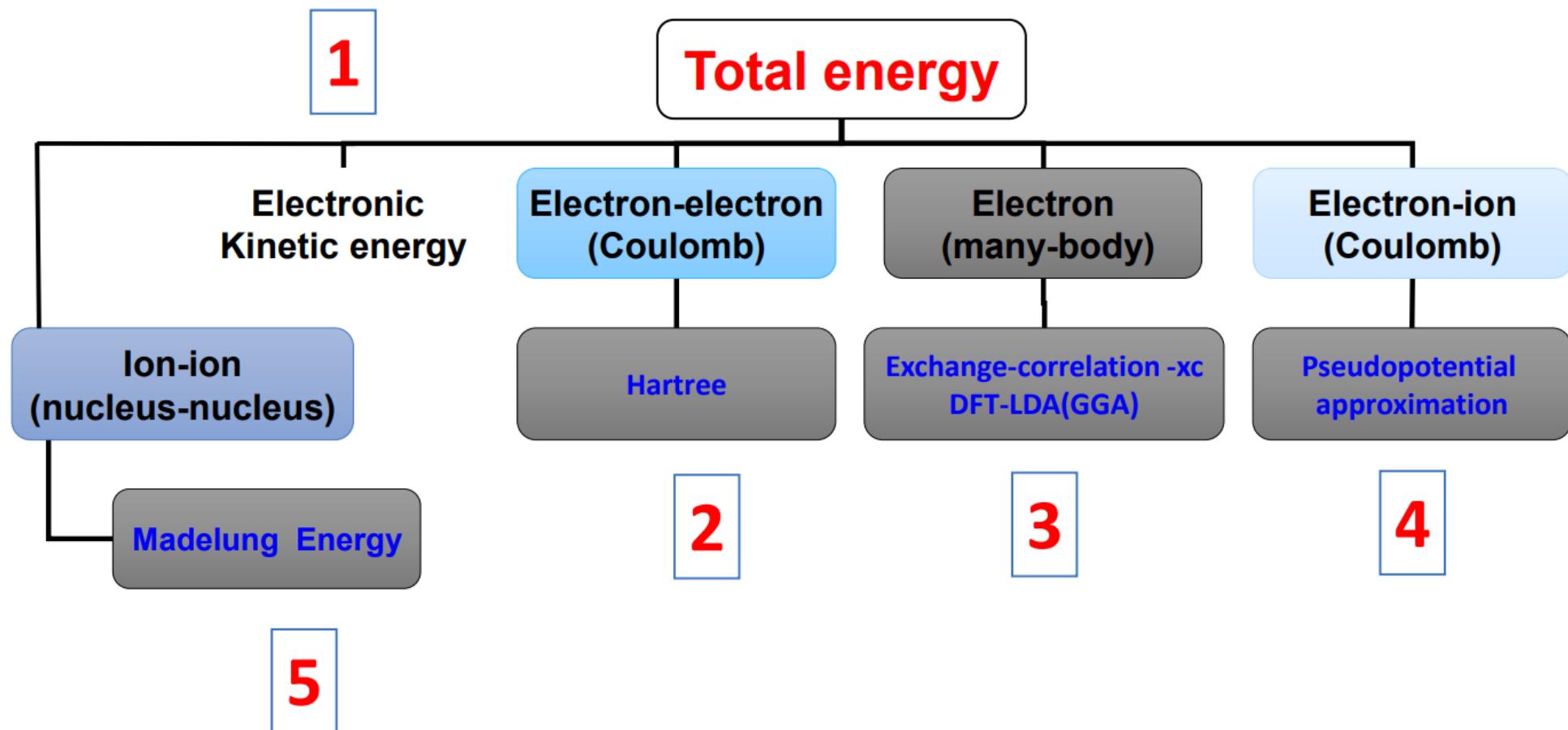
- kinetic energy of particles
- Coulomb interactions between all the particles

## Total-energy calculations: simplifications and approximations needed

- many-body system: nuclei and electrons
- computation: formidable



- Five parts consist of total energy





$$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{\alpha} -\frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,\alpha} \frac{Z_{\alpha} e^2}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} - \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}$$

**Kinetic energy operator for the electrons**

**Kinetic energy operator for the nuclei**

**Electron-electron interaction**

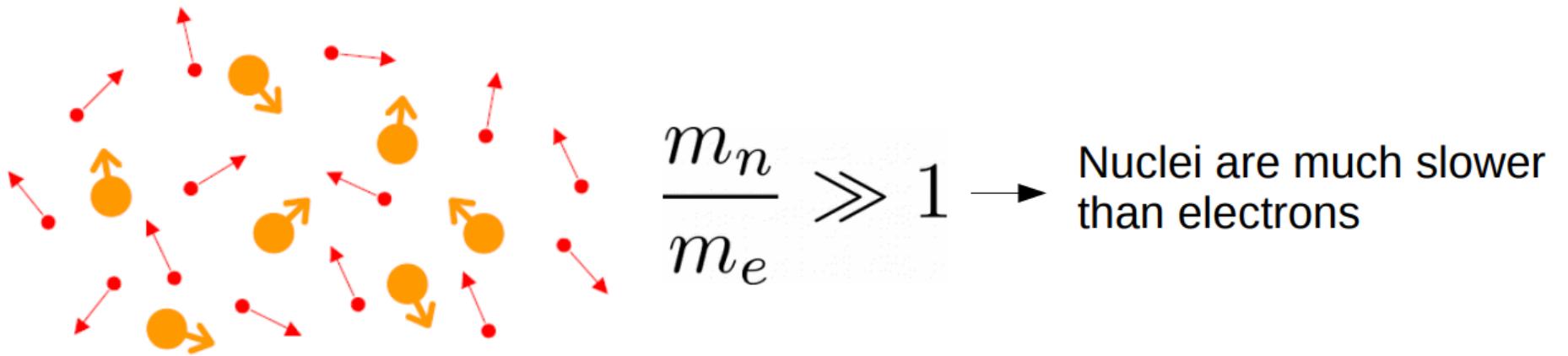
**Potential acting on the electrons due to the nuclei**

**Nucleus-nucleus interaction**

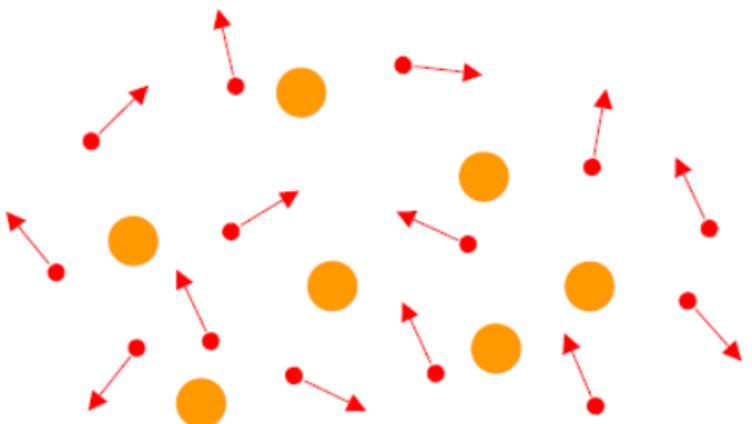
# First-principles calculations: approximations

## 1. Separation of electron and nucleus: Born-Oppenheimer approximation

# Adiabatic or Born-Oppenheimer approximation



(1) Solve the many-electron problem with fixed positions for the nuclei



(2) Move the nuclei in the potential generated by the electrons



# Adiabatic or Born-Oppenheimer approximation

$$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \cancel{\sum_{\alpha} -\frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i, \alpha} \frac{Z_{\alpha} e^2}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} - \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_{\alpha} Z_{\beta} e^2}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}$$

Fixed potential  
“external” to  $e^-$

Constant

**Electrons**

For a fixed set of  $\{\mathbf{R}_{\alpha}\}$

$$\left\{ \begin{array}{l} \hat{H}_{\{\mathbf{R}_{\alpha}\}}^{\text{el}} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + V_{\text{ext}, \{\mathbf{R}_{\alpha}\}}(\{\mathbf{r}_i\}) \\ \hat{H}_{\{\mathbf{R}_{\alpha}\}}^{\text{el}} \Psi_{n, \{\mathbf{R}_{\alpha}\}}^{\text{el}}(\{\mathbf{r}\}) = E_{n, \{\mathbf{R}_{\alpha}\}}^{\text{el}} \Psi_{n, \{\mathbf{R}_{\alpha}\}}^{\text{el}}(\{\mathbf{r}_i\}) \end{array} \right.$$

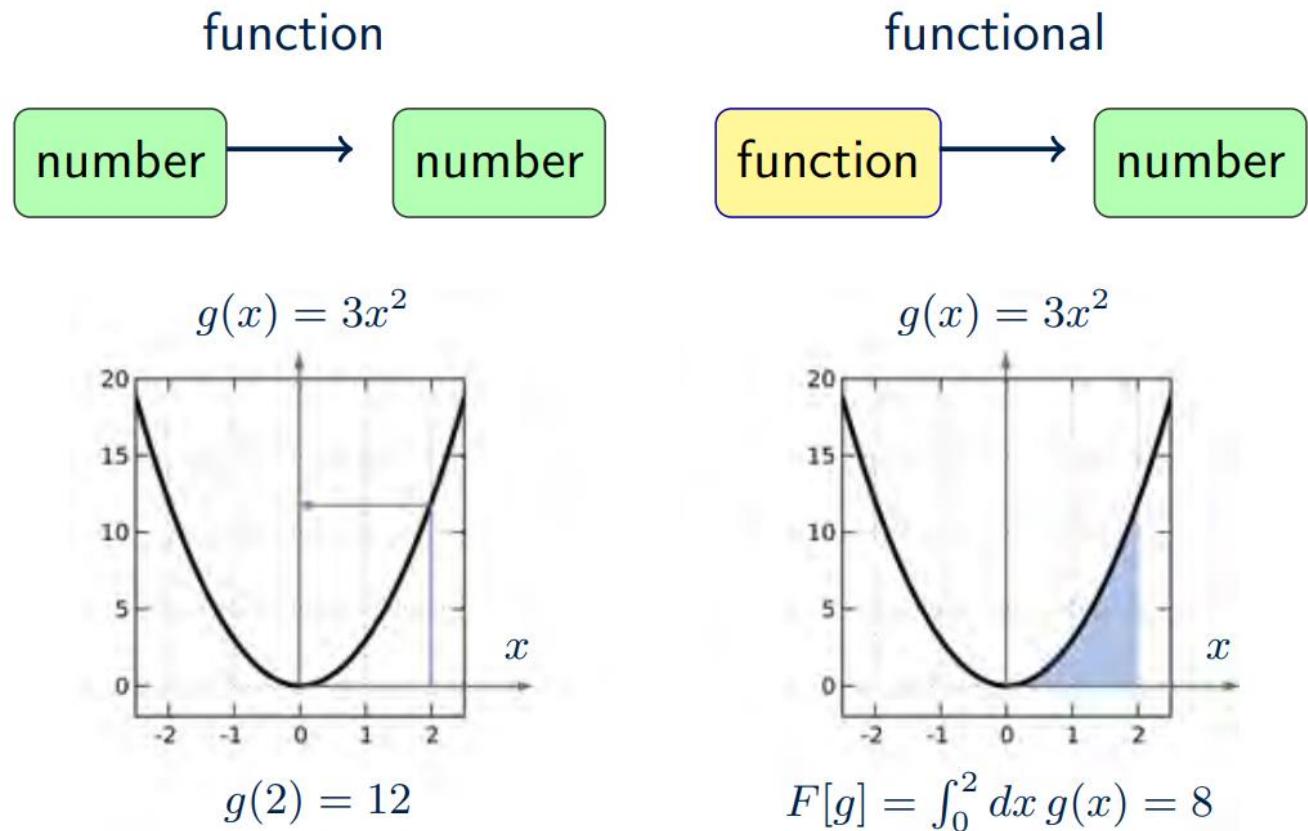
**Nuclei**

$$\left\{ \begin{array}{l} \hat{H} = \sum_{\alpha} -\frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 + E_{n, \{\mathbf{R}_{\alpha}\}}^{\text{el}} \\ \text{Classical dynamics} \rightarrow \mathbf{F}_{\beta} = -\frac{\delta E_{0, \{\mathbf{R}_{\alpha}\}}^{\text{el}}}{\delta \mathbf{R}_{\beta}} \end{array} \right.$$

## 2. Electron-electron interaction: Density Functional Theorem

# Density functional theory

**Density Functional Theory** = theory about the **energy** of electrons being a **functional** of their **density**



# Density functional theory

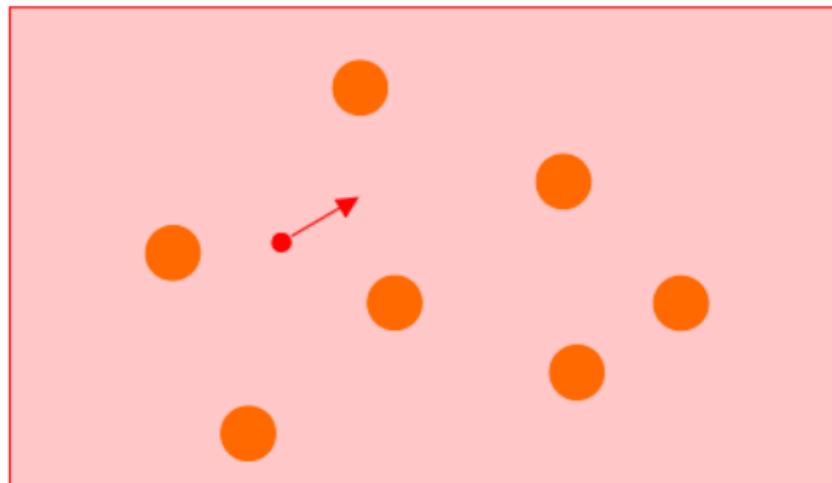
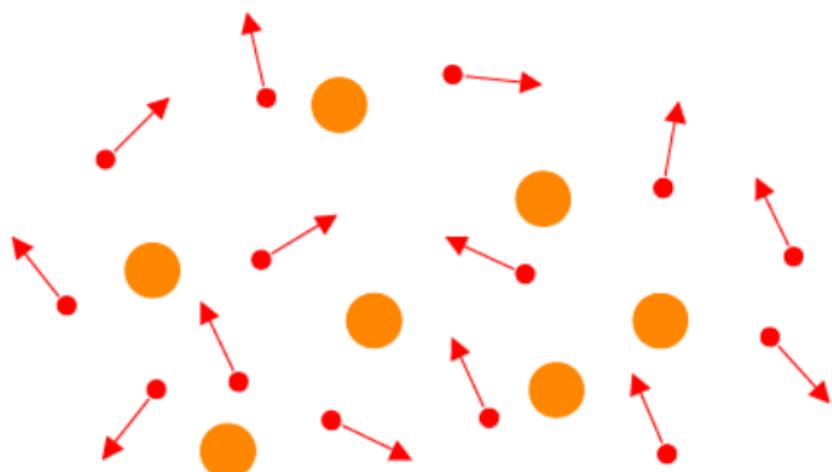
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Many electron wave-function  $\rightarrow$  one electron density

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

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





## Exchange-correlation

- exchange: energy reduction due to a spatial separation between the electrons with the same spin
- correlation: energy reduction due to a spatial separation between the electrons with the opposite spin

## Density Functional Theory (DFT)

- strongly interacting electron gas → a single particle moving in an effective potential
- (one-electron or mean-field approximation)
- Hohenberg and Kohn (1964), Kohn and Sham (1965)



## **Total energy: a unique functional of electron density**

The minimum value of the total energy functional is the **ground-state energy** of the system, and the density that yields this minimum value is the exact single-particle ground-state density.

**(Hohenberg and Kohn, 1964)**

How to replace the many-electron problem by an exactly equivalent set of **self-consistent one-electron** equations.

**(Kohn and Sham, 1965)**

# Density functional theory

## Hohenberg-Kohn theorems

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{ext}(\mathbf{r}_i) = T + V_{ee} + \sum_i V_{ext}(\mathbf{r}_i)$$

$$E_{HK}[n] = \underbrace{T[n] + E_{int}[n]}_{\downarrow} + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{II}$$

$$1. E_{HK}[n] \equiv F_{HK}[n] + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{II} \geq E_{GS}$$

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

If  $F_{HK}[n]$  was known, by minimizing  $E_{HK}$  with respect to variations in  $n(\mathbf{r})$ , one would find the exact ground state density and energy.

**PROBLEM:** Functional  $F_{HK}[n]$  is unknown

# Density functional theory

The total energy is a **functional** of the **wavefunction**

$$\hat{H} \Psi = E \Psi \longrightarrow E = \int d\mathbf{r}_1 \dots d\mathbf{r}_N \Psi^* \hat{H} \Psi$$

So for a generic quantum state we have

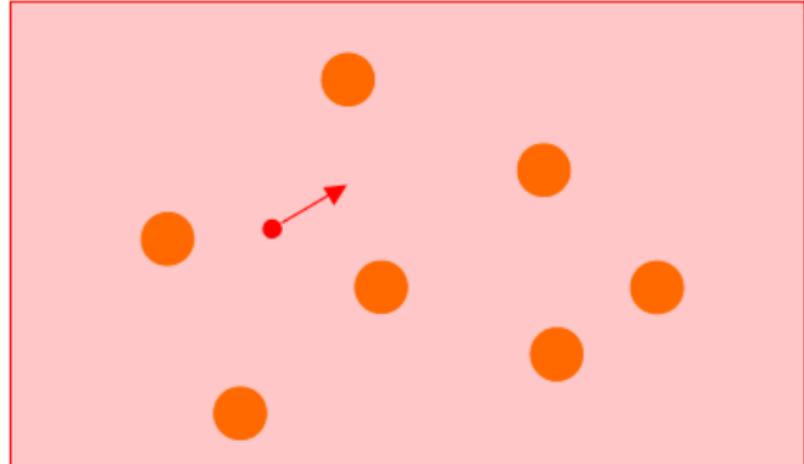
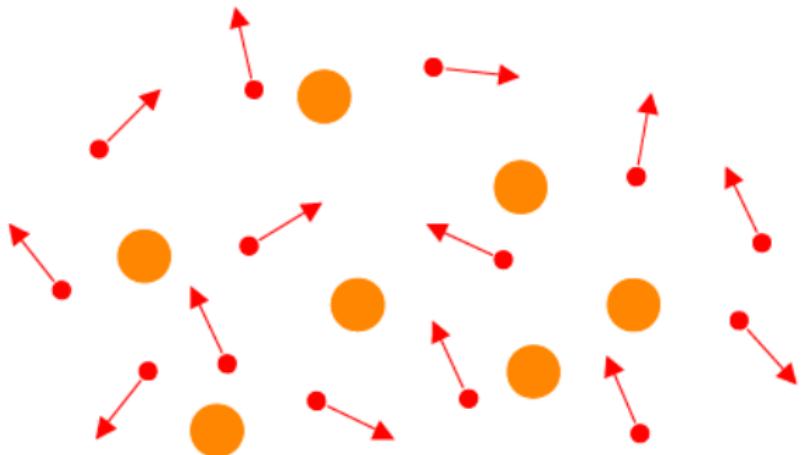
$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \longrightarrow E \qquad E = E[\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)]$$

In 1964 Hohenberg and Kohn noted that, for the lowest-energy state, the total energy is a **functional** of the **density**

$$n(\mathbf{r}) \longrightarrow E \qquad E = E[n(\mathbf{r})]$$

## Kohn-Sham ansatz

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



Actual calculations are performed on the auxiliary independent-particle system defined by the auxiliary Hamiltonian:

$$\hat{H}_{\text{aux}}^{\sigma} = -\frac{1}{2}\nabla^2 + V_{\text{eff}}^{\sigma}(\mathbf{r})$$



## Hohenberg-Kohn theorems

**Theorem I:** For any system of interacting particles in an external potential  $V_{\text{ext}}(\mathbf{r})$ , the potential  $V_{\text{ext}}(\mathbf{r})$  is determined uniquely, except for a constant, by the ground state particle density  $n_{\text{GS}}(\mathbf{r})$ .

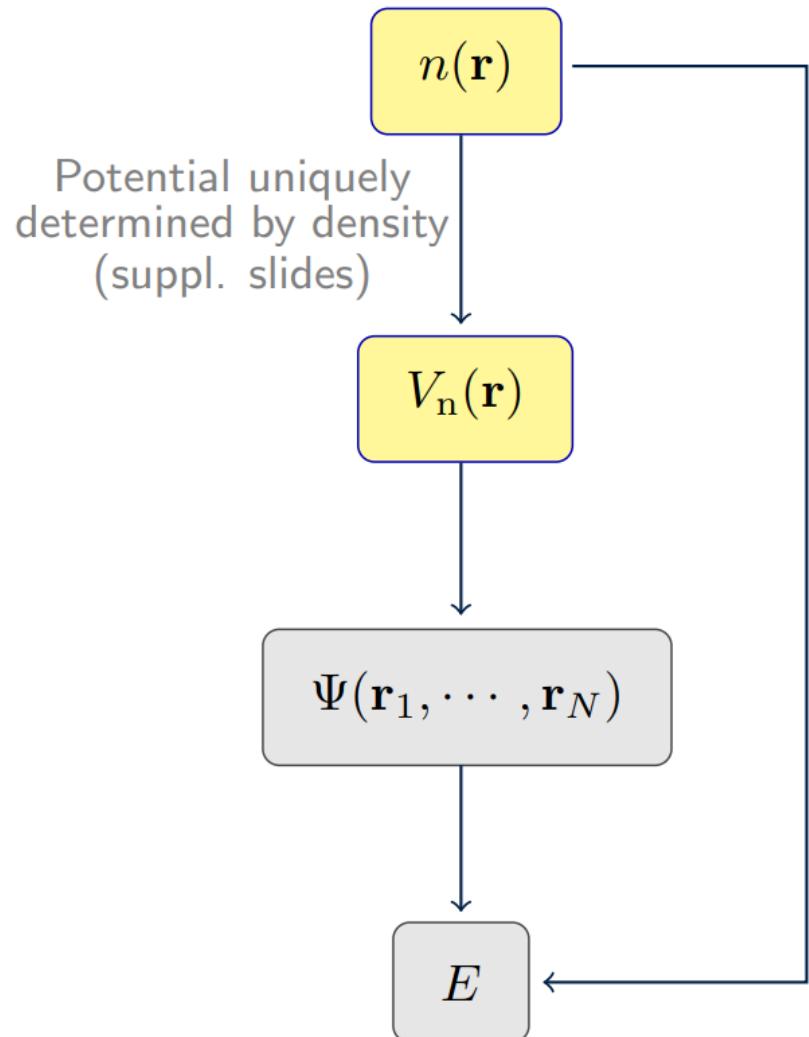
→ All properties of the system are completely determined given only  $n_{\text{GS}}(\mathbf{r})$ .

**Theorem II:** A universal functional for the energy  $E[n]$  in terms of the density  $n(\mathbf{r})$  can be defined, valid for any external potential  $V_{\text{ext}}(\mathbf{r})$ . For any particular  $V_{\text{ext}}(\mathbf{r})$ , the exact ground state energy of the system is the global minimum value of this functional, and the density  $n(\mathbf{r})$  that minimizes the functional is the exact ground state density  $n_{\text{GS}}(\mathbf{r})$ .

→ The functional  $E[n]$  alone is sufficient to determine the exact ground state energy and density. Excited states must be determined by other means.

# Density functional theory

## Hohenberg-Kohn theorems



### HK theorem

In the ground-state the electron density  $n_0(\mathbf{r})$  uniquely determines the total energy  $E_0$

### HK variational principle

Any  $n(\mathbf{r}) \neq n_0(\mathbf{r})$  yields  $E > E_0$ .

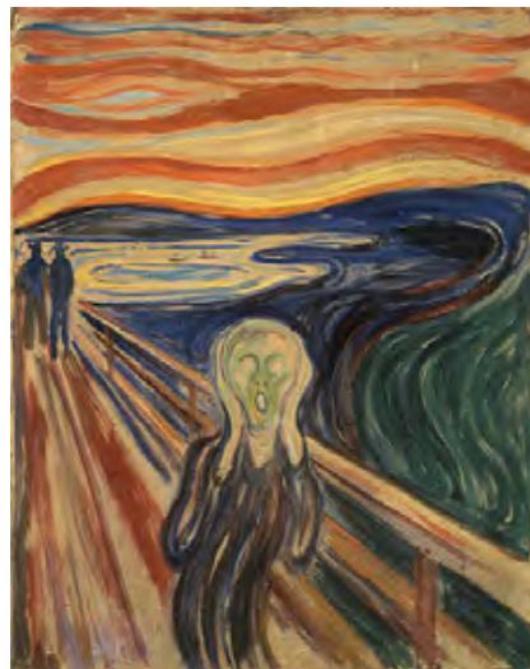


## Hohenberg-Kohn theorems

The HK theorem states that, in the ground state, the total energy of many electrons is a functional of their density,  $E = E[n(\mathbf{r})]$ .

What is this functional?

The energy functional is unknown



*The scream* by E. Munch (1910)  
Feliciano Giustino, QS3 School, Cornell, June 2018

# Density functional theory

## Hohenberg-Kohn theorems

$$E[n] = \underbrace{\int d\mathbf{r} n(\mathbf{r}) V_n(\mathbf{r})}_{\text{External potential}} + \underbrace{\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{\text{Hartree energy}} + \text{Everything Else}$$

Kohn and Sham (1965) proposed to

- (1) Express the electron density **as if** we had a system of independent electrons

$$n(\mathbf{r}) = \sum_{i \in \text{occ}} |\phi_i(\mathbf{r})|^2$$

- (2) Take out the kinetic energy of these electrons from the “everything else”

$$\text{Everything Else} = - \sum_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) + \text{Unknown Terms}$$



## Kohn-Sham ansatz

Finally they rewrote the functional as:

$$E_{KS}[n] = T_0[n] + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\text{Hartree}}[n] + E_{\text{II}} + E_{\text{xc}}[n]$$

Kinetic energy of the system  
of independent particles

$$\frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

All the rest:  
exchange-correlation

Equivalent to independent particles under the potential:

$$V_{KS}^\sigma = V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}^\sigma(\mathbf{r})$$

The problem is now to determine the exchange-correlation functional



- **Kohn-Sham equation** (Redberg a.u.)

$$[-\nabla^2 + V_{eff}(r)] \psi_i(r) = \varepsilon_i \psi_i(r)$$

$$V_{eff}(r) = V_{ion}(r) + V_H(r) + \mu_{xc}(r)$$

$$V_H(r) = \int \frac{2n(r')}{|r - r'|} dr' \quad (\text{Hartree potential})$$

$$\mu_{xc}(r) = \frac{\delta E_{xc}(n)}{\delta n} \quad (\text{exchange - correlation potential})$$

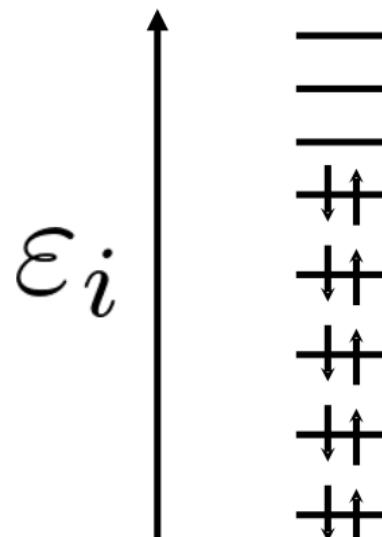
$$n(r) = \sum_i^{occ} |\psi_i(r)|^2 \quad (\text{electron density})$$



## Kohn-Sham ansatz

$$\hat{h}_{\text{KS}} = -\frac{1}{2}\nabla^2 + V_{\text{KS}}(\mathbf{r})$$

$$\hat{h}_{\text{KS}}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

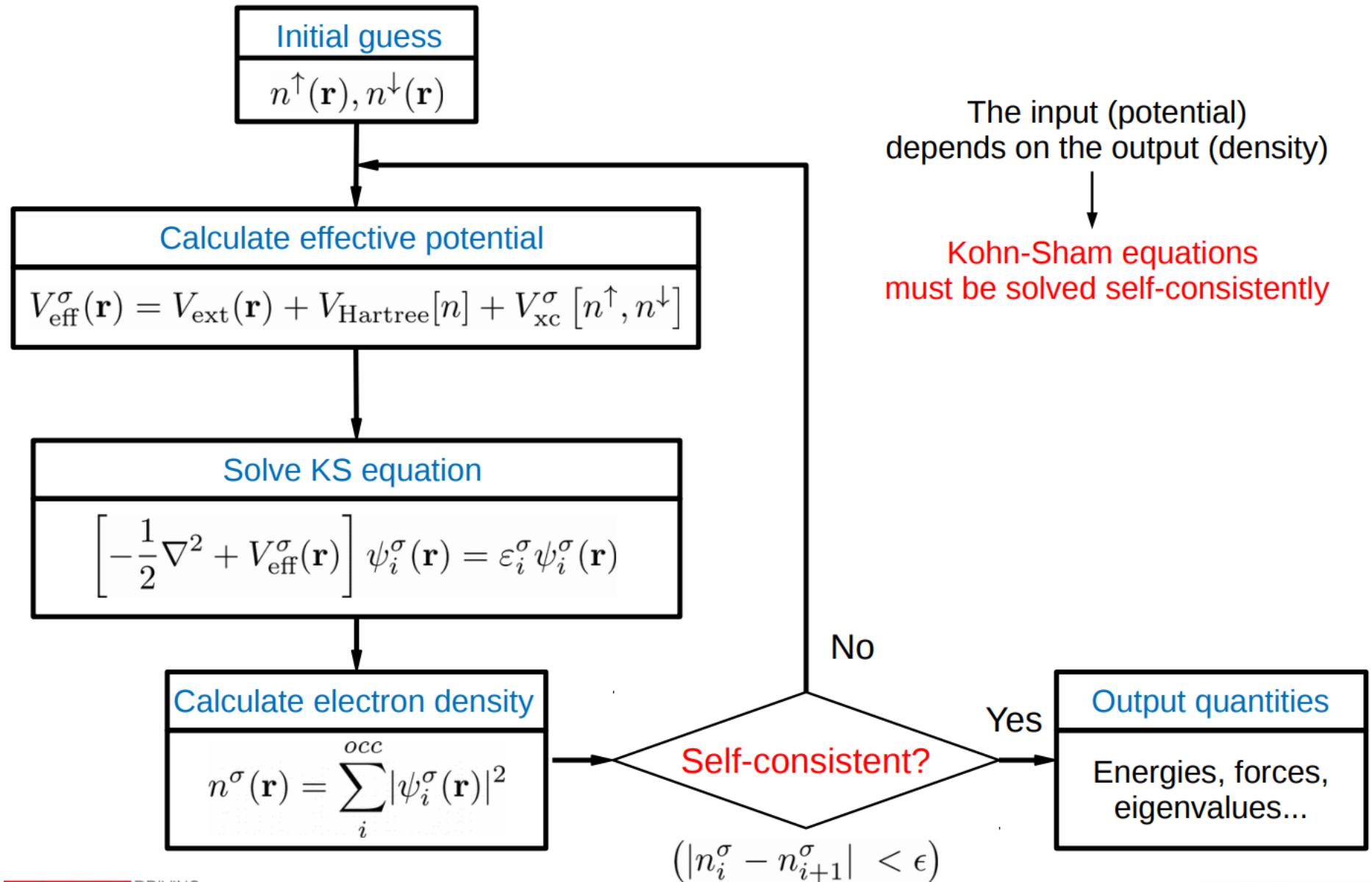


The one-particle eigenstates are filled from lower to higher energies

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

**Careful:** Kohn-Sham eigenvalues correspond to “Kohn-Sham electrons”, not to the real electrons from the interacting many-body system.

# Density functional theory



# Density functional theory

## Exchange and correlation functionals

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

## Local density approximation (LDA)

Solids can be often be considered as close to the limit of the homogeneous electron gas.  
In this limit the effects of exchange and correlation are *local* in character.

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

Exchange-correlation energy of the homogeneous electron gas  
as a function of a given density

### Exchange

$$E_x^{\text{LDA}}[n] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int n(\mathbf{r})^{\frac{4}{3}} d^3\mathbf{r}$$

### Correlation

$E_c$  calculated from Quantum Monte Carlo



## Local density approximation (LDA)

- **Exchange-correlation energy:** exchange-correlation energy per electron in a homogeneous electron gas with the same density as the electron gas at point r.

$$\varepsilon_{xc}(r) = \varepsilon_{xc}^{\text{hom}}[n(r)]$$

$$E_{xc}(n) = \int \varepsilon_{xc}(r)n(r)dr^3$$

$$\mu_{xc}(r) = \varepsilon_{xc}(r) + n(r) \frac{\delta \varepsilon_{xc}}{\delta n}$$



## DFT: Many-body → an effective single-particle interaction

### Computation: *a formidable task*

- *infinite* number of noninteracting electrons in a static potential of an *infinite* number of nuclei or ions.

### Two difficulties

- a wave function must be calculated for each of the *infinite* number of electrons in the system
- since each electronic wave function extends over the entire solid, the basis set required to expand each wave function is *infinite*.



$$\begin{aligned}
 E_{total} &= T(n) + \int V_{ion}(r)n(r)dr^3 + \frac{1}{2} \int V_H(r)n(r)dr^3 + E_{xc}(n) + E_{i-i} \\
 &= \sum_i^{occ} \int \psi_i^*(r) \left( -\nabla^2 \right) \psi_i(r) dr^3 + \int V_{ion}(r)n(r)dr^3 \\
 &\quad + \frac{1}{2} \int \int \frac{2n(r)n(r')}{|r - r'|} dr^3 dr'^3 + \int \epsilon_{xc}(r)n(r)dr^3 + E_{i-i}
 \end{aligned}$$

# Bloch's theorem – periodic system

# Bloch's theorem

**Bloch's theorem:** in a periodic solid, each electronic wave function can be written as the product of a cell-periodic part and a wavelike part

$$\psi(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) u(\vec{r})$$

$$\psi(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R}) \psi(\vec{r})$$

Real space, reciprocal space

$$a_i \cdot b_j = 2\pi\delta_{ij} = \begin{cases} 2\pi & i=j \\ 0 & i \neq j \end{cases}$$

Wave function can be calculated only in a **primitive cell**

**Bloch theorem:**

wave vector  $k$  can be calculated only in the *first Brillouin zone*

However, still  
*Infinite number of  $k$  points are needed.*

The electronic wave functions at  $k$  points that are very close together will be almost identical, hence it is possible to represent the electronic wave functions over a region of  $k$  space by the wave functions at a single  $k$  point.

-- **Monkhorst-Pack sampling method:**  
uniform sampling



$$\psi(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) u(\vec{r})$$

Fourier expansion

$$u(r) = C_{i,G} \exp[iG \cdot r]$$



$$\psi(r) = C_{i,k+G} \exp[i(k + G) \cdot r]$$



- In principle, an *infinite* plane-wave basis sets are required to expand the electronic wave functions.

- The coefficients for the PW with small kinetic energy are typically important than those with large kinetic energy.

$$\text{kinetic energy} = \frac{\hbar^2}{2m} |k + G|^2$$

- **Kinetic energy cutoff:** PW basis set can be truncated to include only plane waves that have kinetic energies less than some particular cutoff energy.

# Plane-wave representation of KS equation

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Secular equation

$$\sum_{G'} \left[ \frac{\hbar^2}{2m} |k + G|^2 \delta_{G,G'} + V_{ion}(G - G') + V_H(G - G') + V_{xc}(G - G') \right] C_{i,k+G'} = \varepsilon_i C_{i,k+G}$$

Kinetic energy, potential: *Fourier transforms*

$$H_{k+G,k+G'}$$

Solution: *diagonalization of a Hamiltonian matrix*

# Now system computationally tractable?

No.

- Matrix size is still intractably large for systems that contain both valence and core electrons.

A severe problem, but can be overcome by use of *the pseudopotential approximation.*

# Electron-ion interaction (pseudopotential)

# Separation of valence and core electrons

Most physical properties of solids are dependent on the **valence electrons** to a much greater extent than on the core electrons.

**Core region:** large number of PWs needed.

- Tightly bound core orbital and the rapid WF oscillations of the valence electrons in the core region.

**Electron (core+valence) - nucleus system**

**→ valence electron-ion (nucleus+core) system**

- Only valence electrons are taken into account
- **Pseudopotential approximation**

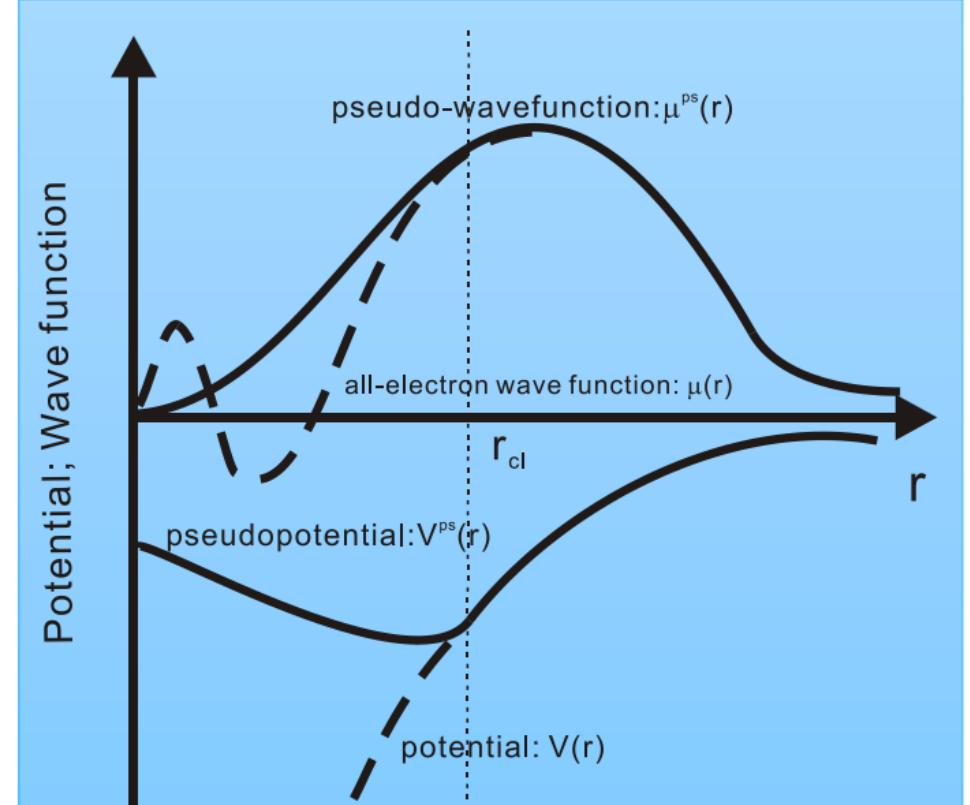
# Pseudopotential approximation

Phillips (1958); Heine and Cohen (1970); Yin and Cohen (1982)

- Nucleus-electron → ion-valence electron

## PP approximation

- Strong ionic potential → weak pseudopotential
- True valence wave functions (with radial nodes) → pseudo wave function (without nodes)



# Norm-conserved pseudopotential

- outside the core region:  $u_l^{PS}(r) = u_l^{AE}(r)$
- pseudo wave functions and real wave functions should be **identical** (both spatial dependences and absolute magnitudes) so that the two wave functions generate identical charge densities.
- inside the core region:  $\int_0^{r_d} |u_l^{PS}(r)|^2 dr = \int_0^{r_d} |u_l^{AE}(r)|^2 dr$ 
  - integral the squared amplitudes of real and pseudo wave function are identical.
- The same eigen value:  $\varepsilon^{PS} = \varepsilon^{AE}$



## Large energy cutoff for PW basis set

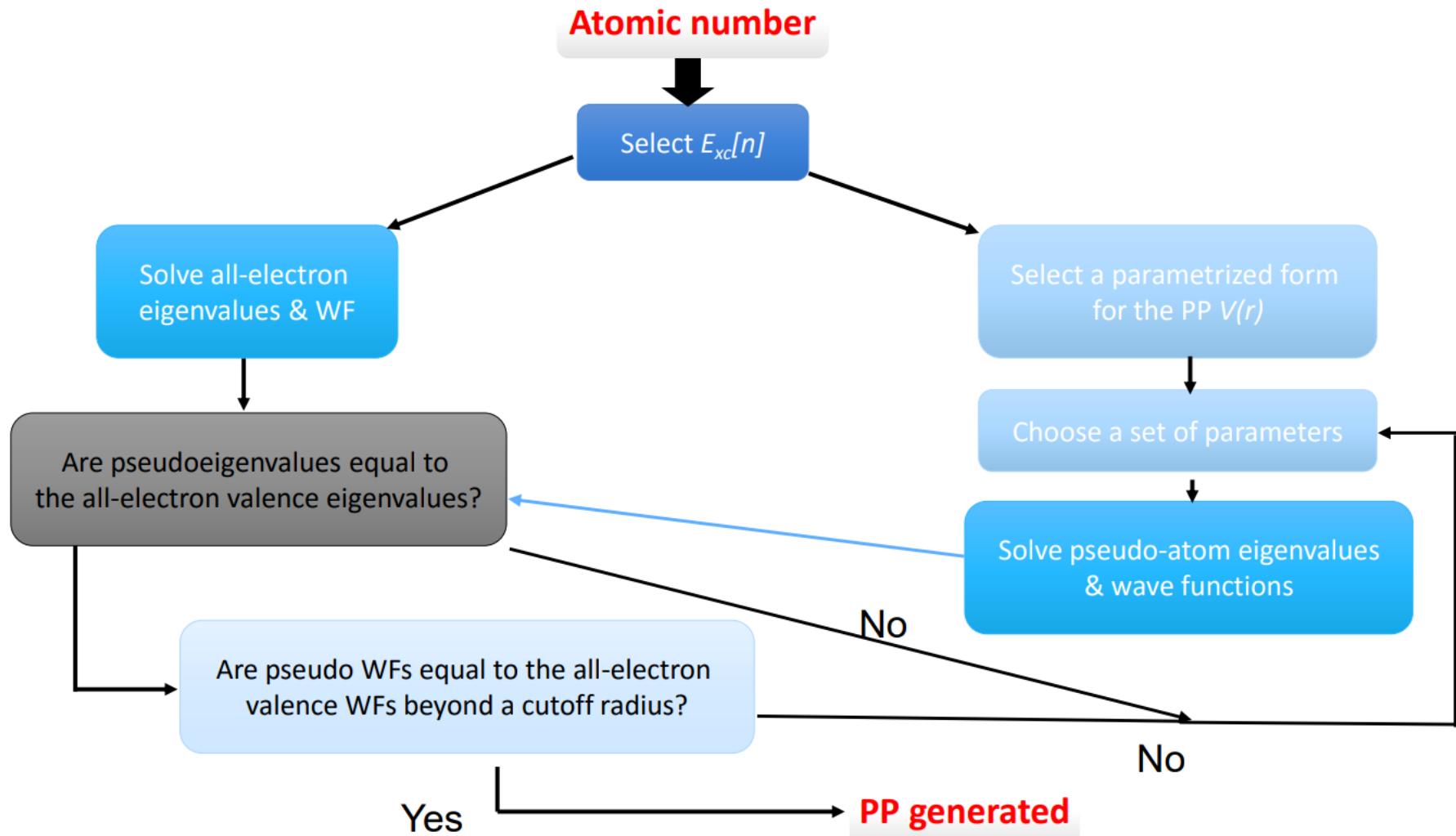
- first-row elements and TM (tightly bound orbital)

**Vanderbilt (1990):** Relaxing the norm conservation of the pseudopotential.

**Wave function:** expanded using a much smaller PW basis set.

**Charge deficiency:** modification needed

# Construct a pseudopotential (isolated atom)



# Advantages of Pseudopotential Method



- Much fewer plane waves basis states
- Removal of the core electrons: fewer electronic WFs
- Total energy: a thousand times smaller than that of all-electron system. Accuracy increases!

✓ Only total energy differences  
are meaningful!

# Nonperiodic systems: supercell approximation

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Bloch  
theorem:  
periodic  
system only

Defect or  
surface etc:  
not  
applicable

**Supercell  
approximation:**  
containing an array of  
defects, rather than a  
single defect.

Independence  
of defects:  
supercell  
volume



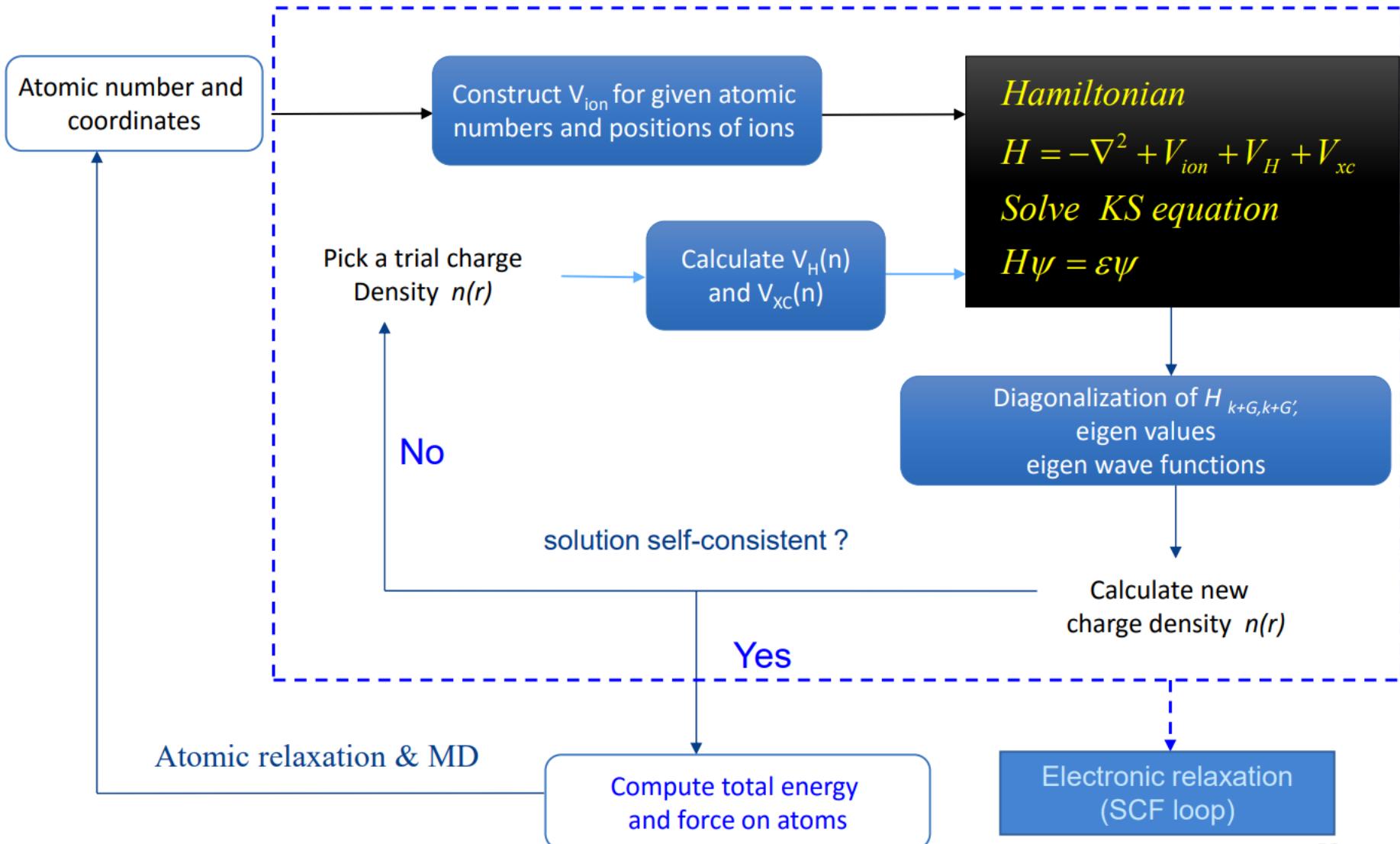
Answer is still **No.**

Conventional matrix diagonalization technique vs.  
alternative methods

Efficient computational **algorithms** minimizing  
Kohn-Sham energy functional needed

- Car-Parrinello Molecular Dynamics (CPMD)
- Steepest decent (SD)
- Conjugate-gradient (CG)
- RMM-DIIS (Residual Minimization - Direct Inversion in the Iterative Subspace)

# Computational procedure of FP-PP method



# DFT

## Practical considerations



## Density functional theory

Exchange and correlation functionals

*John Perdew's Jacob's ladder*



<b>Ingredients</b>	<b>XC families</b>	<b>Examples</b>
unoccupied $\{\phi_i\}$	generalized RPA	<i>so far not practical</i>
$n, \nabla n, (\tau, ) \varepsilon_x$	hyper-GGA	B3LYP, B3PW91, PBE0...
$n, \nabla n, \tau$ and/or $\nabla^2 n$	meta-GGA	TPSS, M06L, tHCTH...
$n, \nabla n$	GGA	PBE, PW91, AM05, BLYP...
$n$	LDA	PW, CA(PZ), VWN...

Increased accuracy ↑

In addition, dispersion corrected (vdW) functionals (Dion, Langreth...), LDA+U



- **Basis sets:** how we expand the wave-function?
- **Pseudopotentials:** do we treat all electrons on an equal footing?
- **Boundary conditions:** are we considering periodic or non-periodic systems?
- **Other issues:** numerical algorithms, license...

Different choices lead to different implementations:

Many different codes



## Richard Martin's classification

### 1) Plane waves and grids:

- Pros:** Expansion in plane waves is conceptually simple and easy to implement  
Systematic way of improving the calculation, no dependence on atomic positions
- Cons:** Large number of plane waves → memory requirements  
Vacuum as expensive as matter
- Codes:** [Quantum Espresso](#), VASP, Abinit, CASTEP...

### 2) Localized atomic-like orbitals: gaussians, slater type, numerical atomic orbitals...

- Pros:** Very efficient, straightforward physical interpretation, no cost for vacuum
- Cons:** Harder to reach convergence, greater care in the election of the basis, Pulay terms
- Codes:** [SIESTA](#), Gaussian, CRYSTAL, OpenMX, ADF...

### 3) Atomic sphere methods: FP-LAPW, LMTO, KKR...

Atomic-like features near the nucleus, smooth functions between atoms

- Pros:** Very precise, best of both worlds
- Cons:** Computationally expensive, more difficult to implement
- Codes:** [FLEUR](#), Wien2k, Elk, RSPt...

If applied carefully, all of them agree after convergence



Do we treat all electrons on an equal footing?

- **YES:** all-electron methods

No approximation, but more expensive. Difficult for plane-waves basis sets.

**CODES:** **FLEUR**, Wien2k, RSPT, FHI-AIMS, CRYSTAL, Gaussian...

- **NO:** pseudopotentials (ECP's)

The core electrons are substituted by an effective ionic potential acting on the valence e<sup>-</sup>

More efficient

**CODES:** **SIESTA**, **Quantum Espresso**, VASP, Abinit, Gaussian...

**PAW:** “all-electron frozen core”, between both worlds

**CODES:** **Quantum Espresso**, VASP, Abinit...



- **Periodic boundary conditions:** 3D periodic objects, crystals  
A unit cell is repeated filling all the space  
Makes use of Bloch theorem  
Surfaces, molecules can be treated by the inclusion of vacuum (supercells)  
**CODES:** **SIESTA, Quantum Espresso, FLEUR...**
- **Open boundary conditions:** atoms, molecules, clusters  
**CODES:** Gaussian, NRMOL, deMon, TURBOMOLE...
- **Mixed boundary conditions:** 1D and 2D periodic objects (chains, slabs)  
**CODES:** **FLEUR, KKR-GF...**

# References

# Major software for first-principles calculations

## Periodic, DFT, Plane-wave basis set

- VASP: [cms.mpi.univie.ac.at/vasp](http://cms.mpi.univie.ac.at/vasp)
- CASTEP: [www.accelrys.com](http://www.accelrys.com)
- WIEN2K: [www.wien2k.at](http://www.wien2k.at)
- ABINIT: [www.abinit.org](http://www.abinit.org)
- PWSCF: [www.pwscf.org](http://www.pwscf.org)
- CPMD: [www.cpmd.org](http://www.cpmd.org)



## Periodic/molecule, DFT(and/or Hartree-Fock), atomic basis set

- DMol: [www.accelrys.com](http://www.accelrys.com)
- ADF: [www.scm.com](http://www.scm.com)
- Crystal03: [www.crystal.unito.it](http://www.crystal.unito.it)
- Siesta: [www.uam.es/departamentos/ciencias/fismateriac/siesta](http://www.uam.es/departamentos/ciencias/fismateriac/siesta)

## Molecule, DFT (and/or Hartree-Fock), All-electron, atomic basis set

- Gaussian03: [www.gaussian.com](http://www.gaussian.com)
- GAMESS: [www.msg.ameslab.gov/GAMESS](http://www.msg.ameslab.gov/GAMESS)

# Major software for DFT: Researchers

## Computing

- [ABINIT](#)
- [ATAT](#) (Alloy Theoretical Automated Toolkit)
- [ASE](#) (Atomic Simulation Environment)
- [CALYPSO](#) (Crystal structure AnaLYsis by Particle Swarm Optimization)
- [DFTB+](#) (Density Functional Based Tight Binding)
- [GAMESS](#) (The General Atomic and Molecular Electronic Structure System)
- [LAMMPS](#) (Large-Scale Atomic Molecular Massively Parallel Simulator)
- [LIGGGHTS](#) (LAMMPS Improved for General Granular and Granular Heat Transfer Simulations)
- [MCCCS Towhee](#) (The Monte Carlo for Chemical Systems)
- [Mathematica](#)
- [PHON](#)
- [Quantum ESPRESSO](#)
- [Quantum Wise](#)
- [SIESTA](#)
- [SPPARKS](#) (Stochastic Parallel Particle Kinetic Simulati
- [TINKER](#)
- [VASP](#) (Vienna Ab initio Simulation Package)
- [WHAM](#) (Weighted Histogram Analysis Method)

## Databases

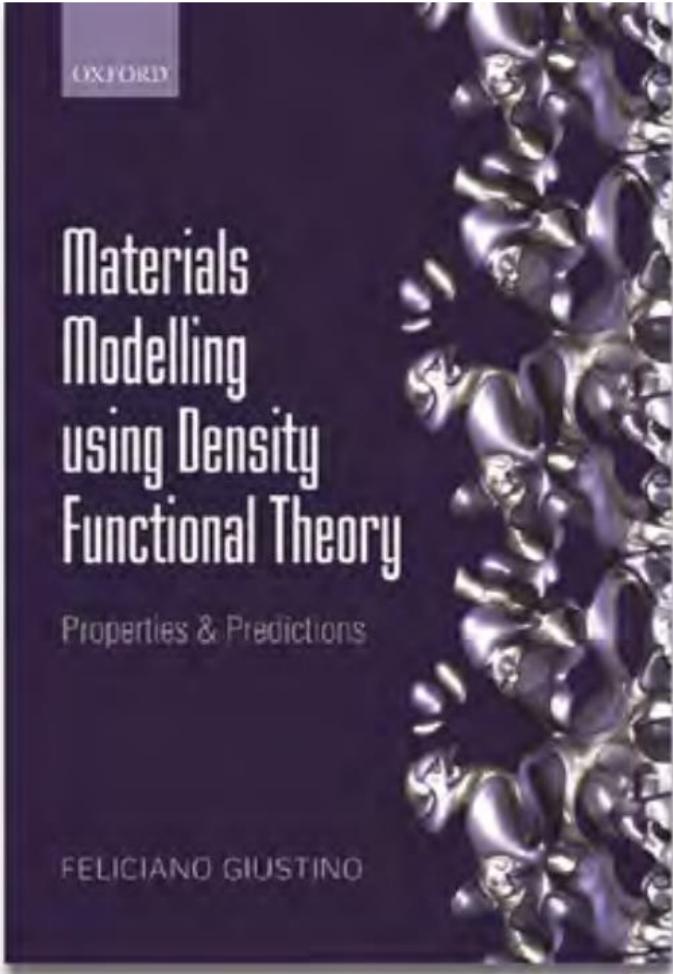
- [AFLOW](#) (Automatic – FLOW for Materials Discovery)
- [AiiDA](#) (Automated Interactive Infrastructure and Database for Computational Science)
- [aNANt](#) (Functional Materials Database)
- [C2DB](#) (Computational 2D Materials Database)
- [CSD](#) (Cambridge Structural Database)
- [ICSD](#) (Inorganic Crystal Structure Database)
- [Materials Project](#)
- [OQMD](#) (Open Quantum Materials Database)
- [2DMatPedia](#) (2D Materials Encyclopedia)

## Visualization & Tools

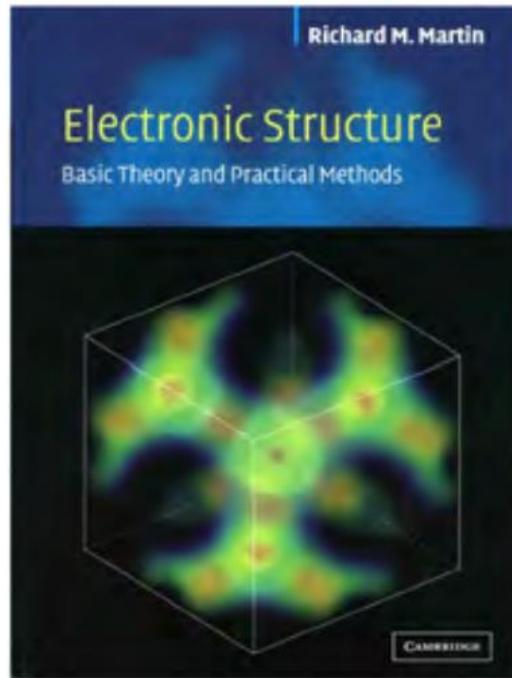
- [AVOGADRO](#)
- [CaGe](#) (The Chemical & abstract Graph environment)
- [Gnuplot](#)
- [Jmol](#)
- [OVITO](#) (The Open Visualization TOol)
- [QSTEM](#) (Quantitative TEM/STEM Simulations)
- [VMD](#) (Visual Molecular Dynamics)
- [Visit](#)
- [VESTA](#)
- [XCrySDen](#) (X-window Crystalline Structures and Densities)
- [YASARA](#) (Yet Another Scientific Artificial Reality Application)

# Reference Books

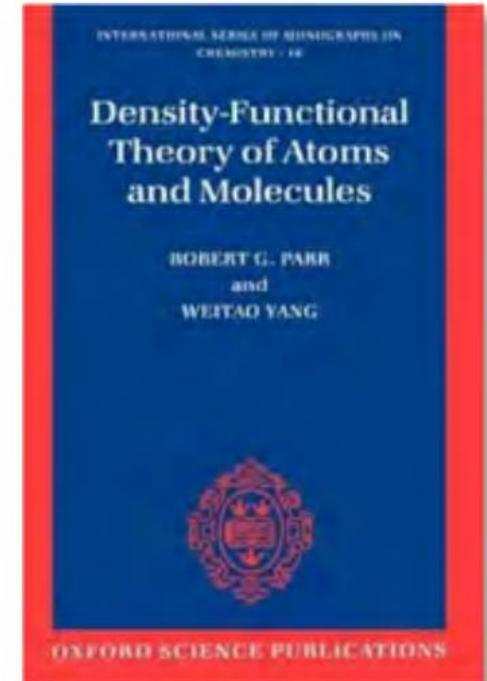
MSc and 1st year PhD level



Advanced PhD level



Theoretical foundations



# Slide Credits

## 1. Introduction to First-Principles Method - Guang-Hong LU, Beihang University

[Joint ICTP/CAS/IAEA School & Workshop on Plasma-Materials Interaction in Fusion Devices, July 18-22, 2016, Hefei]



Joint ICTP/CAS/IAEA School & Workshop on Plasma-Materials Interaction in  
Fusion Devices, July 18-22, 2016, Hefei

## Introduction to First-Principles Method

by Guang-Hong LU (吕广宏)  
Beihang University



## 2. Density Functional Theory and General Notions about First-Principles Codes - Roberto Robles [ICN2, Barcelona, Spain]

The title slide features a light blue background with a wavy pattern. At the top left is the MAX logo with the text "DRIVING THE EXASCALE TRANSITION". In the center is the siesta logo with a yellow circle containing the word "siesta". At the top right is the ICN2 logo with the text "EXCELENCIA SEVERO OCHOA" and "Institut Català de Nanociència i Nanotecnologia". The main title "Density Functional Theory and General Notions about First-Principles Codes" is centered in a large, bold, dark blue font. Below it, the author's name "Roberto Robles" and location "ICN2, Barcelona, Spain" are listed. A "Thanks to Emilio Artacho, Javier Junquera" message is at the bottom. Logos for CERCA, Generalitat de Catalunya, CSIC, and UAB are at the bottom right.

**Density Functional Theory and  
General Notions about First-Principles Codes**

Roberto Robles

ICN2, Barcelona, Spain

Thanks to Emilio Artacho, Javier Junquera

Patrons:

CERCA  
Generalitat de Catalunya  
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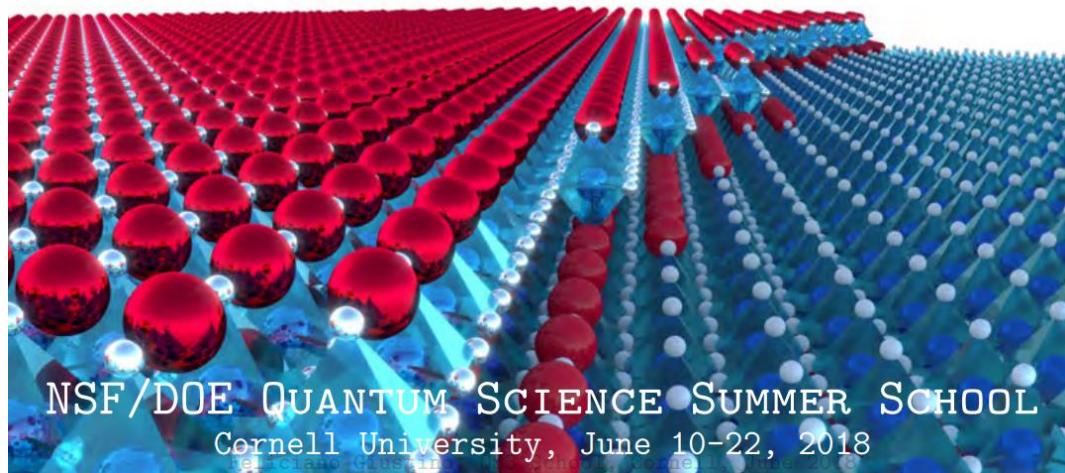


3. Introduction to density functional theory - Feliciano Giustino, Department of Materials, University of Oxford, Department of Materials Science and Engineering, Cornell University  
[NSF/DOE Quantum Science Summer School Cornell University, June 10-22, 2018]

## Introduction to density functional theory

Feliciano Giustino

Department of Materials, University of Oxford  
Department of Materials Science and Engineering, Cornell University



NSF/DOE QUANTUM SCIENCE SUMMER SCHOOL  
Cornell University, June 10-22, 2018