

Introduction to Density Functional Theory

Eric CANCES

Ecole des Ponts ParisTech and Inria Paris, France

SIAM Linear Algebra, Paris, May 13-17, 2024



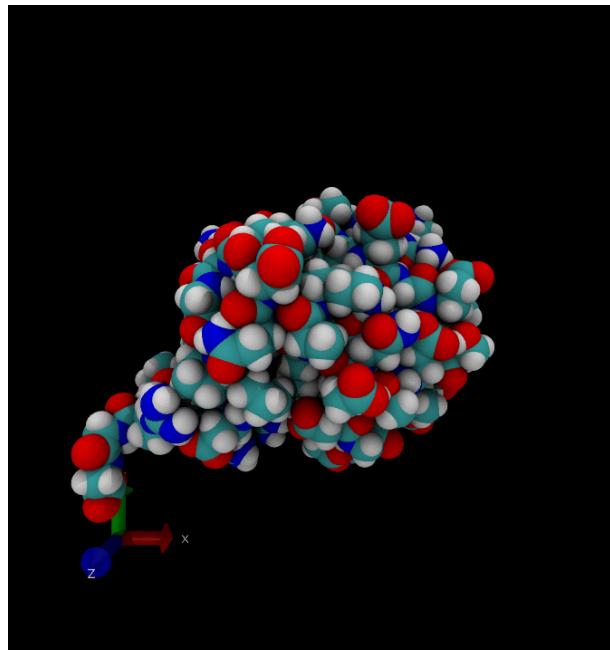
- 1. First-principle molecular simulation in a nutshell**
- 2. Density Functional Theory (DFT) for molecules (quantum chemistry)**
- 3. DFT for materials (condensed matter physics/materials science)**

Number of hits (May 2024)

# of hits (March 2024)	Web of Science
"fluid dynamics"	118,056
"machine learning"	419,607
"Density Functional Theory"	257,400

1 - First-principle molecular simulation in a nutshell

- one of the major application fields of scientific computing
(1998 and 2013 Nobel prizes in Chemistry)
- an inexhaustible source of problems for interdisciplinary research
- many linear algebra (sub)problems: large-scale linear systems, linear and nonlinear eigenvalue problems, matrix exponentials...



Ubiquitin (Filippo Lipparini, Pisa)

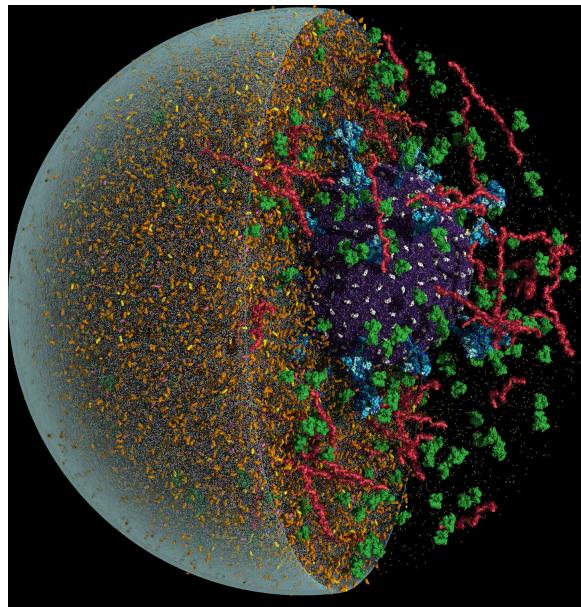
Study of physical or biological phenomena



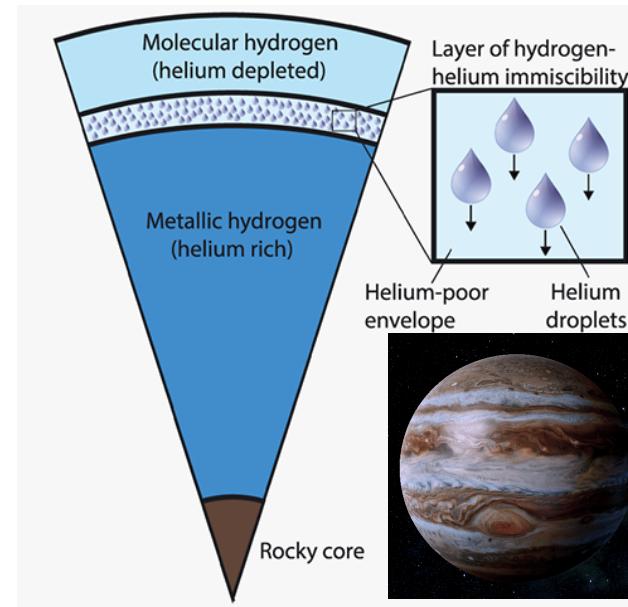
Condensed-matter physics



Materials science/mechanical engineering



Biology

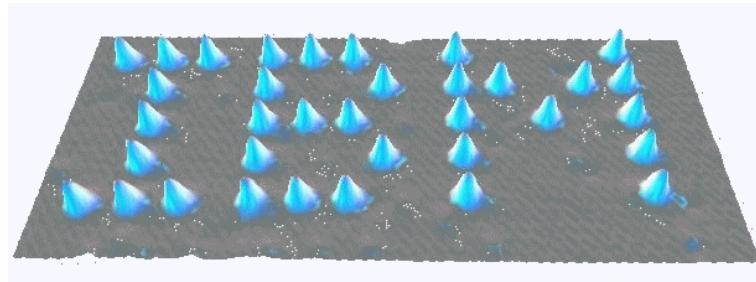


Astrophysics

Study of physical or biological phenomena

Computer-aided design of

- new materials (e.g. **energy production and storage**)
- new drugs
- nano-objects: **nano-electronics, nano-robots**
- ...



Xe atoms on Ni surface

STM image - IBM (1989)

<http://www.thenanoage.com>

STM: Scanning Tunneling Microscope, 1986 Nobel Prize in Physics (Binning & Rohrer, IBM Zürich)

First-principle molecular simulation

- Any molecular system can be seen as an assembly of atomic nuclei and electrons in Coulomb interactions
- Such a system can be described by the laws of quantum mechanics (many-body Schrödinger equation) and statistical physics
- The only parameters of these models are
 - a few fundamental constants of physics (atomic units)
 $\hbar = 1, \quad m_e = 1, \quad e = 1, \quad \varepsilon_0 = (4\pi)^{-1},$
 $c \simeq 137.0359996287515\dots, \quad k_B = 3.16681537\dots \times 10^{-6}$
 - the charges z_k and masses m_k of the atomic nuclei
e.g.: $z_{\text{H}} = 1, \quad m_{\text{H}} = 1836.152701\dots, \quad z_{\text{O}} = 8, \quad m_{^{16}\text{O}} = 29156.944123\dots$

In principle, it is therefore possible to predict all the properties of any molecular system from its chemical formula

However, these “exact” models are too difficult to handle: approximations are required

First-principle molecular simulation

- Any molecular system can be seen as an assembly of atomic nuclei and electrons in Coulomb interactions
- Such a system can be described by the laws of quantum mechanics (many-body Schrödinger equation) and statistical physics
- The only parameters of these models are
 - a few fundamental constants of physics (atomic units)
 $\hbar = 1$, $m_e = 1$, $e = 1$, $\varepsilon_0 = (4\pi)^{-1}$,
 $c \simeq 137.0359996287515\dots$, $k_B = 3.16681537\dots \times 10^{-6}$
 - the charges z_k and masses m_k of the atomic nuclei
e.g.: $z_H = 1$, $m_H = 1836.152701\dots$, $z_O = 8$, $m_{^{16}O} = 29156.944123\dots$

Born-Oppenheimer approximation (used in 99% of the simulations)

- nuclei behave as classical point-like particles
- the (quantum) state of the electrons adapts instantly to the positions $R_1(t), \dots, R_M(t)$ of the nuclei \rightarrow it is fully determined by $(z_k, R_k(t))_{1 \leq k \leq M}$

Molecular dynamics within the Born-Oppenheimer approximation

- state of the system at time t : positions et momenta of the M atomic nuclei

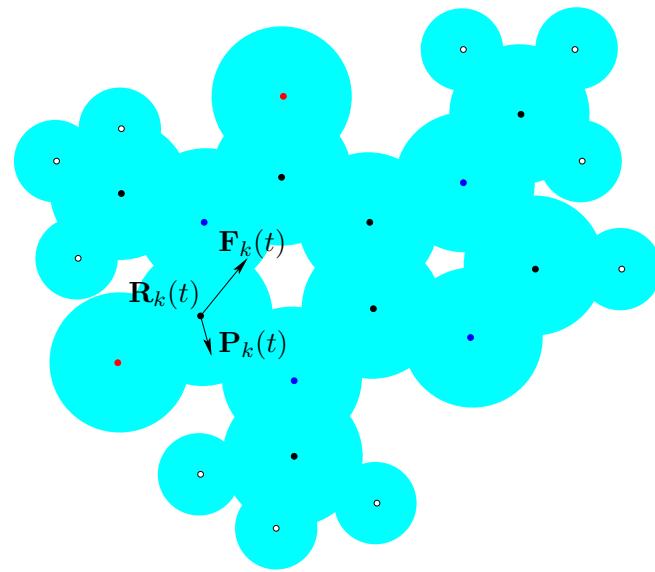
$$(\mathbf{R}_1(t), \dots, \mathbf{R}_M(t), \mathbf{P}_1(t), \dots, \mathbf{P}_M(t))$$

- Newton's laws of classical mechanics (simulation at constant energy)

$$\frac{d\mathbf{R}_k(t)}{dt} = \frac{1}{m_k} \mathbf{P}_k(t), \quad \frac{d\mathbf{P}_k(t)}{dt} = \mathbf{F}_k(t)$$

- Schrödinger-Dirac-Born-Oppenheimer model

$$\mathbf{F}_k(t) = - \sum_{j \neq k} z_j z_k e^2 \frac{\mathbf{R}_j(t) - \mathbf{R}_k(t)}{4\pi\varepsilon_0 |\mathbf{R}_j(t) - \mathbf{R}_k(t)|^3} + z_k e^2 \int_{\mathbb{R}^3} \underbrace{\rho_{(\mathbf{R}_1(t), \dots, \mathbf{R}_M(t))}(\mathbf{x})}_{\text{ground state electronic density when nuclei are in configuration } (\mathbf{R}_1(t), \dots, \mathbf{R}_M(t))} \frac{\mathbf{x} - \mathbf{R}_k(t)}{4\pi\varepsilon_0 |\mathbf{x} - \mathbf{R}_k(t)|^3} d\mathbf{x}$$



**ground state electronic density
when nuclei are in configuration
 $(\mathbf{R}_1(t), \dots, \mathbf{R}_M(t))$**

$$\rho_{(\mathbf{R}_1(t), \dots, \mathbf{R}_M(t))}(\mathbf{x}) \geq 0$$

$$\int_{\mathbb{R}^3} \rho_{(\mathbf{R}_1(t), \dots, \mathbf{R}_M(t))}(\mathbf{x}) d\mathbf{x} = N$$

Direct computation of $\rho_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x})$ doomed by the curse of dimensionality

$$\rho_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x}) = N \int_{\mathbb{R}^{3(N-1)}} \underbrace{|\Psi_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2}_{\text{solution to a } 3N \text{ dimensional PDE}} d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

solution to a $3N$ dimensional PDE (N : number of electrons)

Electronic Schrödinger equation

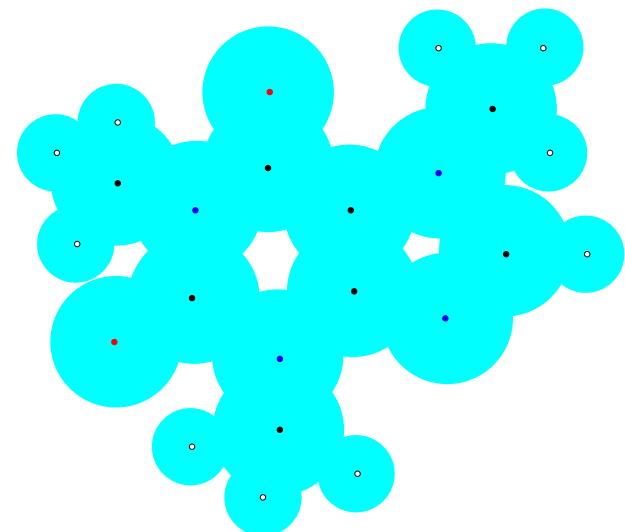
$$\left(-\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{x}_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|\mathbf{x}_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \right) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = E \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$$

$$\|\Psi\|_{L^2} = 1, \quad \Psi \in \bigwedge^N L^2(\mathbb{R}^3; \mathbb{C}^2)$$

Atomic units:

$$m_e = 1, e = 1, \hbar = 1, 4\pi\varepsilon_0 = 1$$

**E : lowest eigenvalue (ground-state energy)
in 99% of the cases**



Direct computation of $\rho_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x})$ doomed by the curse of dimensionality

$$\rho_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x}) = N \int_{\mathbb{R}^{3(N-1)}} \underbrace{|\Psi_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2}_{\text{solution to a } 3N \text{ dimensional PDE}} d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

solution to a $3N$ dimensional PDE (N : number of electrons)

The special case of the hydrogen atom ($M = 1, z_1 = 1, N = 1$)

$$-\frac{1}{2}\Delta\Psi(\mathbf{x}) - \frac{1}{|\mathbf{x} - \mathbf{R}|}\Psi(\mathbf{x}) = E\Psi(\mathbf{x}), \quad \Psi \in L^2(\mathbb{R}^3; \mathbb{C}^2), \quad \|\Psi\|_{L^2} = 1$$

The ground state has an explicit expression

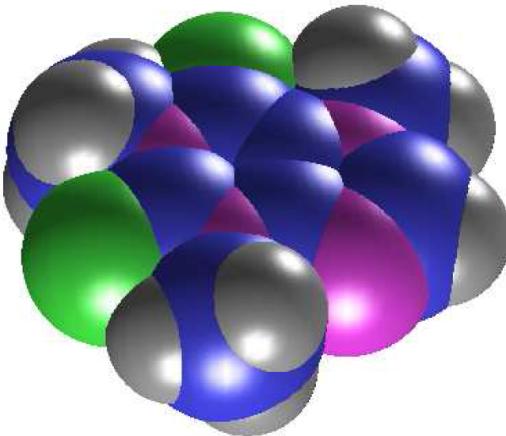
$$E = -\frac{1}{2}, \quad \Psi(\mathbf{x}) = \frac{e^{-|\mathbf{x}-\mathbf{R}|}}{\sqrt{\pi}} \begin{pmatrix} \alpha_{\uparrow} \\ \alpha_{\downarrow} \end{pmatrix}, \quad \alpha_{\uparrow}, \alpha_{\downarrow} \in \mathbb{C}, \quad |\alpha_{\uparrow}|^2 + |\alpha_{\downarrow}|^2 = 1$$

$$\rho_{\mathbf{R}}(\mathbf{x}) = \frac{e^{-2|\mathbf{x}-\mathbf{R}|}}{\pi}$$

Direct computation of $\rho_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x})$ doomed by the curse of dimensionality

$$\rho_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x}) = N \int_{\mathbb{R}^{3(N-1)}} \underbrace{|\Psi_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2}_{d\mathbf{x}_2 \cdots d\mathbf{x}_N}$$

solution to a **3N** dimensional PDE (N : number of electrons)



Caffein molecule $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$

- 24 atomic nuclei
- 102 electrons

→ **306-dimensional PDE**
72 real parameters

Direct computation of $\rho_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x})$ doomed by the curse of dimensionality

$$\rho_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x}) = N \int_{\mathbb{R}^{3(N-1)}} \underbrace{|\Psi_{(\mathbf{R}_1, \dots, \mathbf{R}_M)}(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2}_{\text{solution to a } 3N \text{ dimensional PDE}} d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

(N : number of electrons)

Approximate, accurate electronic structure models (quantum chemistry)

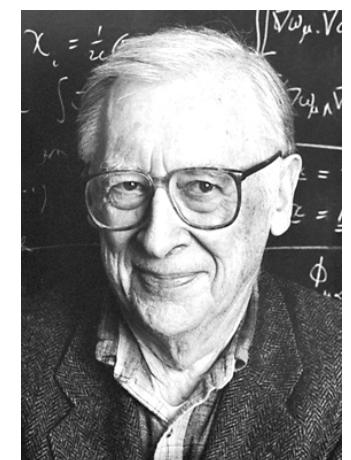
- wavefunction methods (e.g. Hartree-Fock, coupled-clusters, DMRG...)
- Density Functional Theory (DFT)
- Quantum Monte Carlo (QMC)



1998 Nobel Prize in Chemistry



Walter Kohn



John Pople

2 - DFT for molecules (quantum chemistry)

For simplicity, we consider closed-shell systems with N_{el} electron pairs (stable molecules), but the Kohn-Sham model also works for open-shell systems (radicals)

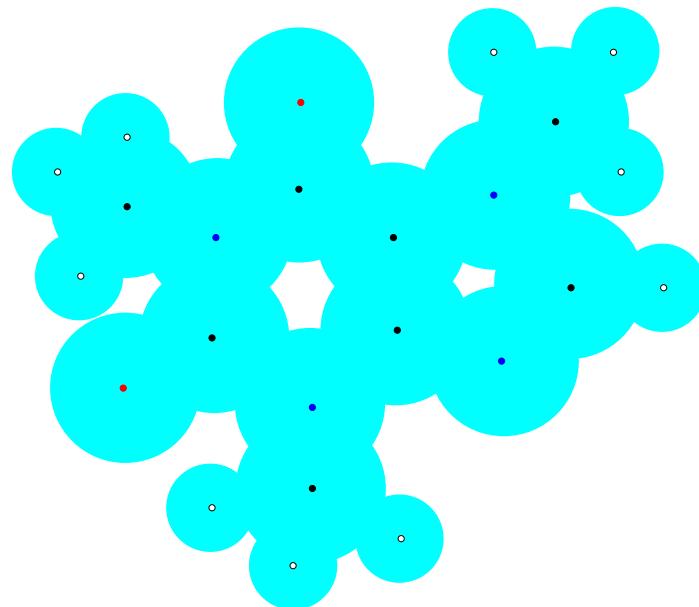
From now on, we use atomic units

$$\hbar = 1, \quad m_e = 1, \quad e = 1, \quad \varepsilon_0 = \frac{1}{4\pi} \quad (\text{definition of atomic units})$$

The KS model provides an approximate ground state electronic density $\rho(\mathbf{x})$ for a set of $2N_{\text{el}}$ electrons for a nuclear configuration $(z_k, \mathbf{R}_k)_{1 \leq k \leq M} \in (\mathbb{N}^* \times \mathbb{R}^3)^M$

→ allows to compute forces for Born-Oppenheimer molecular dynamics

$$\mathbf{F}_k = - \sum_{j \neq k} z_j z_k \frac{\mathbf{R}_j - \mathbf{R}_k}{|\mathbf{R}_j - \mathbf{R}_k|^3} + z_k \int_{\mathbb{R}^3} \rho(\mathbf{x}) \frac{\mathbf{x} - \mathbf{R}_k}{|\mathbf{x} - \mathbf{R}_k|^3} d\mathbf{x}$$



The KS model provides an approximate ground state electronic density $\rho(\mathbf{x})$ for a set of $2N_{\text{el}}$ electrons for a nuclear configuration $(z_k, \mathbf{R}_k)_{1 \leq k \leq M} \in (\mathbb{N}^* \times \mathbb{R}^3)^M$

Kohn-Sham model: a nonlinear elliptic eigenvalue problem

$$\left\{ \begin{array}{l} \rho(\mathbf{x}) = 2 \sum_{n=1}^{N_{\text{el}}} |\phi_n(\mathbf{x})|^2 \\ \\ -\frac{1}{2}\Delta\phi_n + (V_{\text{nucl}} + V_{\text{Hxc}}[\rho]) \phi_n = \lambda_n \phi_n \quad \text{on } \mathbb{R}^3, \quad \int_{\mathbb{R}^3} \phi_m \phi_n = \delta_{mn} \\ \\ \lambda_1 \leq \lambda_2 \leq \dots \leq \lambda_{N_{\text{el}}} \text{ lowest } N_{\text{el}} \text{ eigenvalues of } H_\rho = -\frac{1}{2}\Delta + V_{\text{nucl}} + V_{\text{Hxc}}[\rho] \text{ on } L^2(\mathbb{R}^3) \\ \\ V_{\text{Hxc}}[\rho] = \rho \star \frac{1}{|\mathbf{x}|} + V_{\text{xc}}[\rho] \end{array} \right.$$

The KS model provides an approximate ground state electronic density $\rho(\mathbf{x})$ for a set of $2N_{\text{el}}$ electrons for a nuclear configuration $(z_k, \mathbf{R}_k)_{1 \leq k \leq M} \in (\mathbb{N}^* \times \mathbb{R}^3)^M$

Kohn-Sham model: a constrained optimization problem

Variational formulation of the Kohn-Sham problem:

$$\rho(\mathbf{x}) = 2 \sum_{n=1}^{N_{\text{el}}} |\phi_{n,0}(\mathbf{x})|^2$$

where $\Phi_0 = (\phi_{1,0}, \dots, \phi_{N_{\text{el}},0})$ is a minimizer of

$$\inf \left\{ E_{\text{KS}}(\Phi), \Phi = (\phi_1, \dots, \phi_{N_{\text{el}}}) \in (H^1(\mathbb{R}^3))^{N_{\text{el}}}, \int_{\mathbb{R}^3} \phi_m \phi_n = \delta_{mn} \right\}$$

$$E_{\text{KS}}(\Phi) = \sum_{n=1}^{N_{\text{el}}} \int_{\mathbb{R}^3} |\nabla \phi_n|^2 + \int_{\mathbb{R}^3} \rho_\Phi V_{\text{nucl}} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_\Phi(\mathbf{x}) \rho_\Phi(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x} d\mathbf{x}' + E_{\text{xc}}(\rho_\Phi)$$

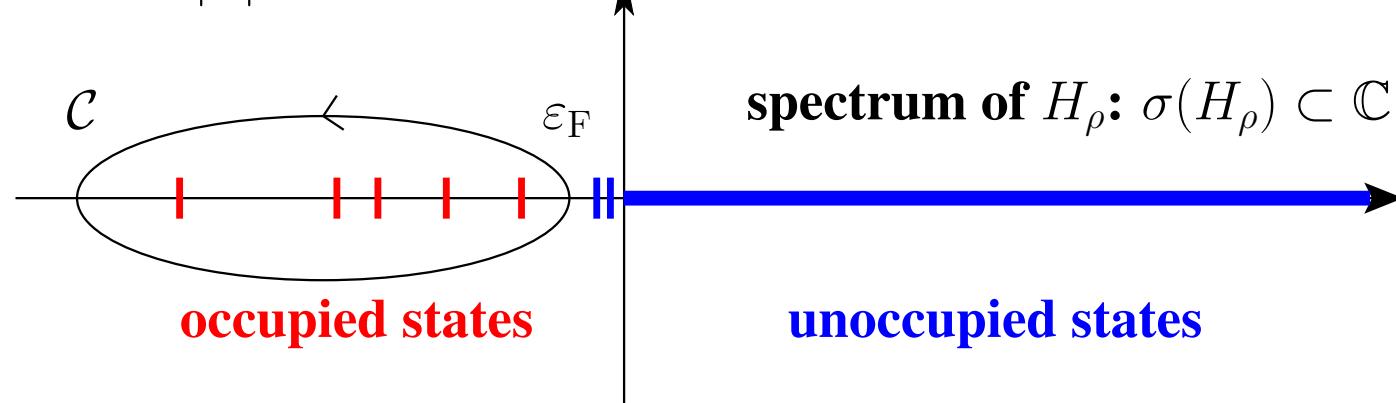
$$\rho_\Phi(\mathbf{x}) = 2 \sum_{n=1}^{N_{\text{el}}} |\phi_n(\mathbf{x})|^2, \quad E_{\text{xc}}^{\text{X}\alpha}(\rho) = -C_{\text{X}} \int_{\mathbb{R}^3} \rho(\mathbf{x})^{4/3} d\mathbf{x}$$

The KS model provides an approximate ground state electronic density $\rho(\mathbf{x})$ for a set of $2N_{\text{el}}$ electrons for a nuclear configuration $(z_k, \mathbf{R}_k)_{1 \leq k \leq M} \in (\mathbb{N}^* \times \mathbb{R}^3)^M$

Kohn-Sham model: operator formulation

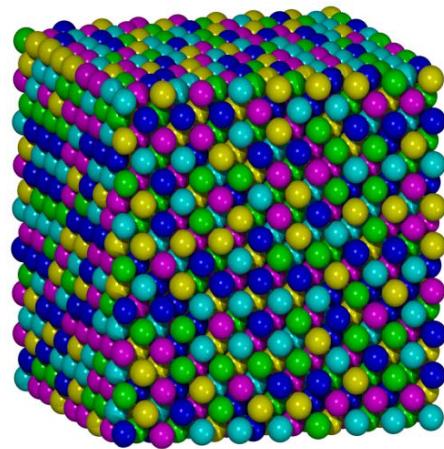
$$\left\{ \begin{array}{l} \rho(\mathbf{x}) = 2\gamma(\mathbf{x}, \mathbf{x}), \quad \gamma(\mathbf{x}, \mathbf{x}') = \sum_{n=1}^{N_{\text{el}}} \phi_n(\mathbf{x})\phi_n(\mathbf{x}') \text{ integral kernel of the operator} \\ \gamma = \mathbb{1}_{(-\infty, \varepsilon_F]}(H_\rho) = \frac{1}{2\pi} \oint_{\mathcal{C}} (z - H_\rho)^{-1} dz \quad \text{(orthogonal projector)} \\ H_\rho = -\frac{1}{2}\Delta + V_{\text{nucl}} + V_{\text{Hxc}}[\rho] \quad \text{self-adjoint operator on } L^2(\mathbb{R}^3) \end{array} \right.$$

$$V_{\text{Hxc}}[\rho] = \rho \star \frac{1}{|\mathbf{x}|} + V_{\text{xc}}[\rho] \quad \text{on } \mathbb{R}^3$$

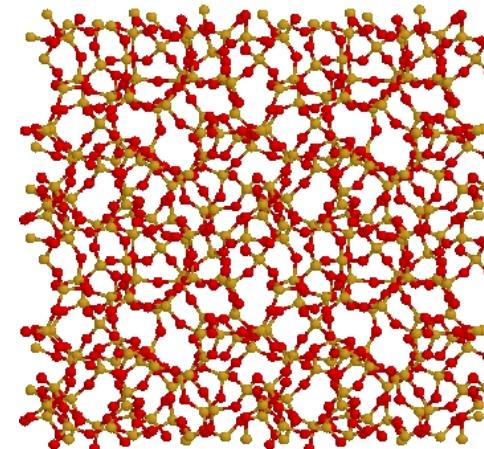


3 - DFT for materials (condensed matter physics/materials science

Periodic simulation cell $\Omega = [0, L)^3$, periodic lattice $= L\mathbb{Z}^3$

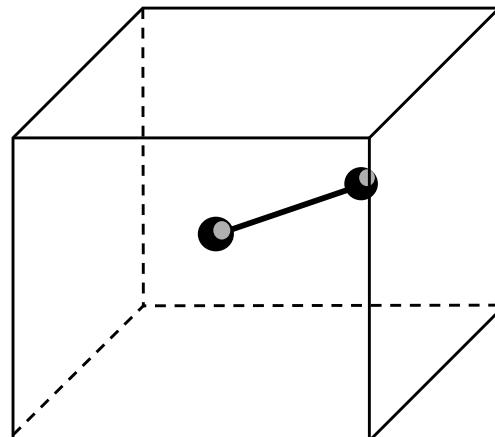


High entropy alloy

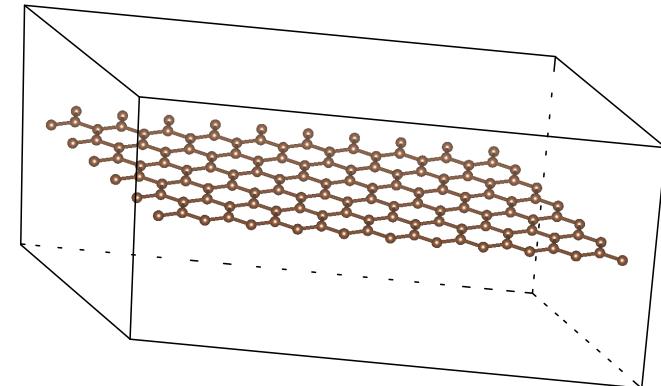


Amorphous system

but also...



Isolated molecule



2D material

Periodic simulation cell $\Omega = [0, L)^3$, periodic lattice $\mathbb{L} = L\mathbb{Z}^3$

Spin-unpolarized system with M ionic cores and N valence electron pairs

Kohn-Sham equations on the periodic simulation cell (PSC-KS)

$$\left\{ \begin{array}{l} \rho(\mathbf{x}) = 2 \sum_{n=1}^N |\psi_n^0(\mathbf{r})|^2 \\ \\ \left(-\frac{1}{2}\Delta + V_{\text{ion}} + V_{\text{Hxc}}[\rho] \right) \psi_n = \lambda_n \psi_n \quad \psi_n \text{ } \mathbb{L}\text{-periodic}, \quad \int_{\Omega} \psi_m^* \psi_n = \delta_{mn} \end{array} \right.$$

Remarks:

- **ionic core:** nucleus + core electrons, described by a nonlocal linear potential
- **Aufbau principle:** for most systems, $\lambda_1 \leq \dots \leq \lambda_N$ lowest N eigenvalues of H_ρ
- the system must be **electrically neutral**. Otherwise, uniform charge background implicitly taken into account:

$$-\Delta V_H^{\text{tot}} = 4\pi (\rho - \rho_{\text{ion}}) \text{ with PBC} \implies \widehat{(V_H^{\text{tot}})}_{\mathbf{G}} = 4\pi \frac{(\widehat{\rho} - \widehat{\rho}_{\text{ion}})_{\mathbf{G}}}{|\mathbf{G}|^2} \delta_{\mathbf{G} \neq 0}$$