

HighNESS International School on Thermal Neutron Scattering Kernel Generation

Atomistic Simulation of Materials

Davide Campi,

University of Milano-Bicocca

davide.campi@unimib.it

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What do we need?

Cold neutrons wavelengths have the same order of magnitude as the atomic distances



Atomic positions

Cold neutrons energies are in the same range as dynamical excitations



Dynamical properties

What do we need?

Cold neutrons wavelengths have the same order of magnitude as the atomic distances



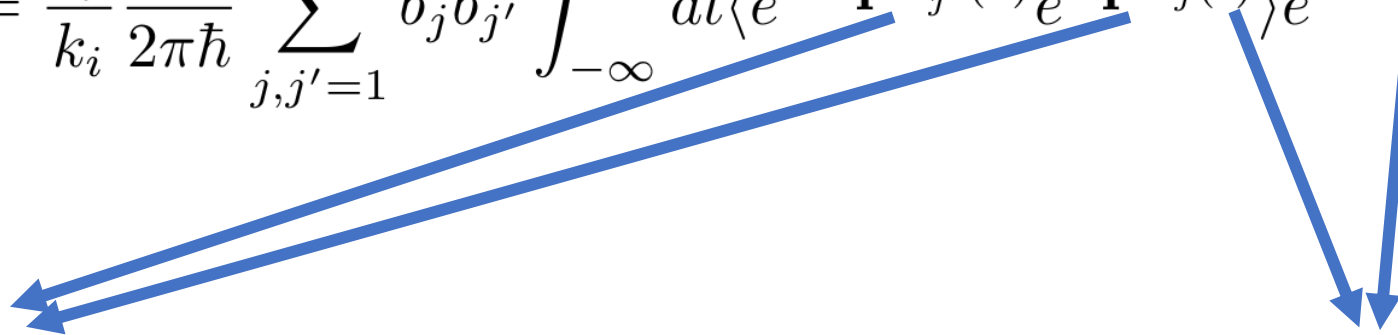
Atomic positions

Cold neutrons energies are in the same range as dynamical excitations



Dynamical properties

$$\frac{d^2\sigma}{d\Omega_f dE_f} = \frac{k_f}{k_i} \frac{1}{2\pi\hbar} \sum_{j,j'=1}^N b_j b_{j'} \int_{-\infty}^{\infty} dt \langle e^{-i\mathbf{q}\mathbf{R}_{j'}(0)} e^{i\mathbf{q}\mathbf{R}_j(t)} \rangle e^{-i\omega t}$$



Where are the atoms

How they move

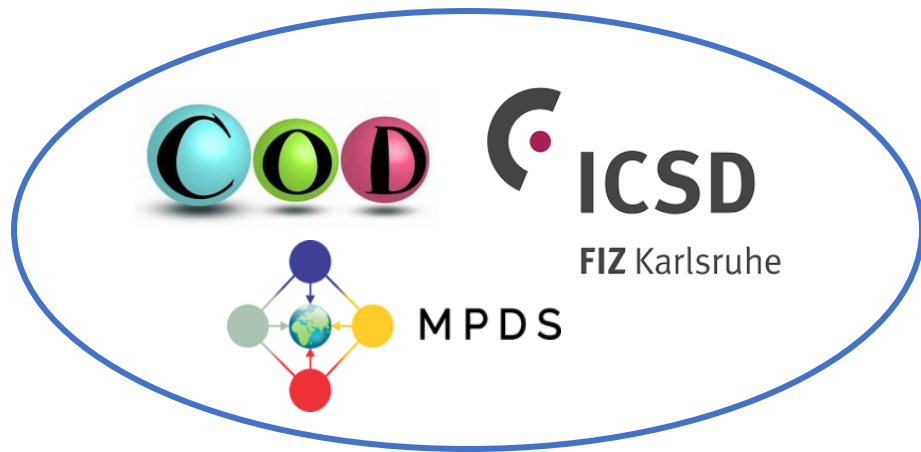
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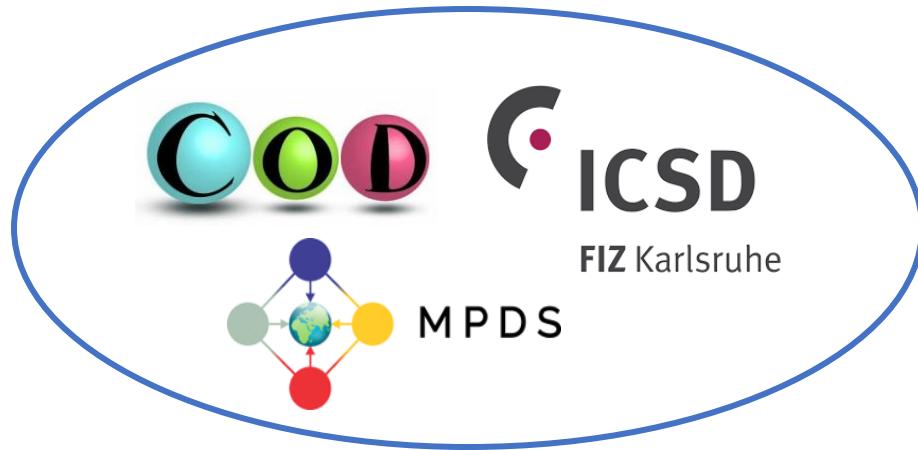
Inorganics



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Organic, MOFs, COFs



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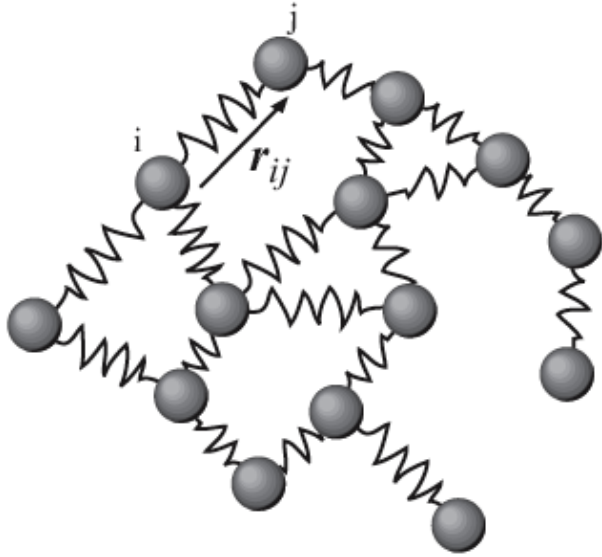


But not always the material has been characterized or all the atoms are included (for example if the characterization was done with X-rays H atoms might be missing), or you want to engineer a material or model the effect of defects



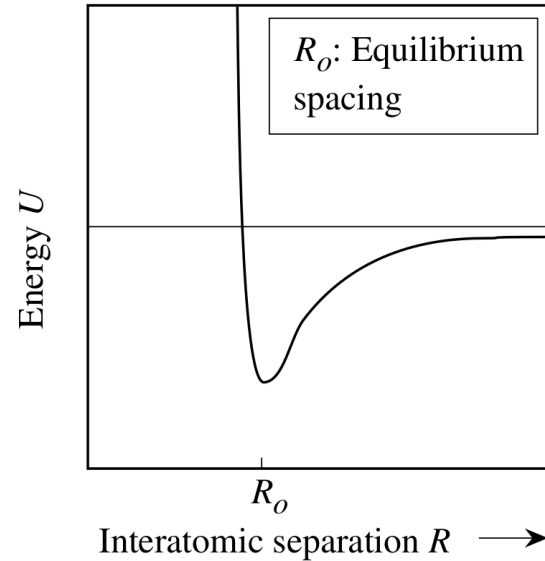
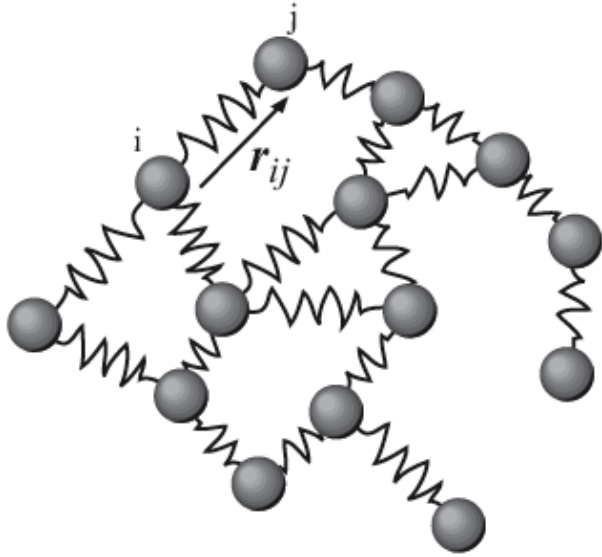
We need a way to predict the positions of all the atoms for every material of our interest!

How they move



In a very simplistic picture we can imagine a material as a number of masses connected by springs representing the atomic bonds

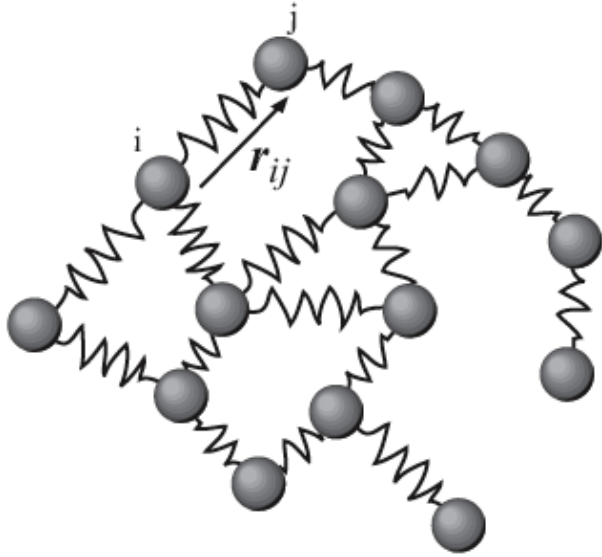
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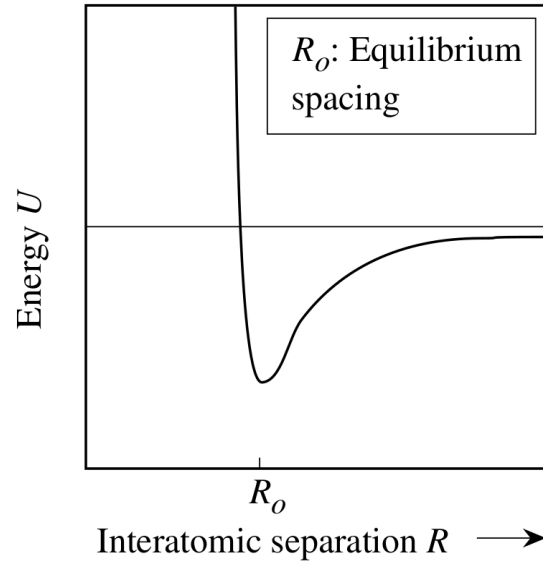
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Each atom will sit on average at the bottom of a potential well

How they move



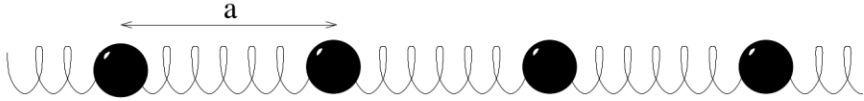
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Each atom will sit on average at the bottom of a potential well

Even if just a single atom is set in motion by an incident neutron, in a fully connected systems all the atoms will start to move and they will do it according to the **normal modes** of the systems

Ideal 1D chain



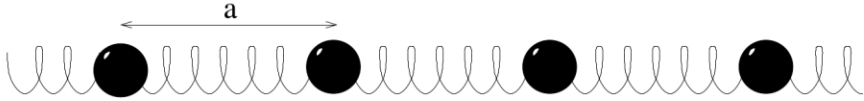
$$F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n)$$

$$M \frac{d^2 u_n}{dt^2} = C(u_{n+1} + u_{n-1} - 2u_n)$$

$$u_n = u e^{inQa} e^{-i\omega t}$$

$$\omega = (4C/M)^{1/2} \left| \sin \frac{1}{2} Qa \right|$$

Ideal 1D chain

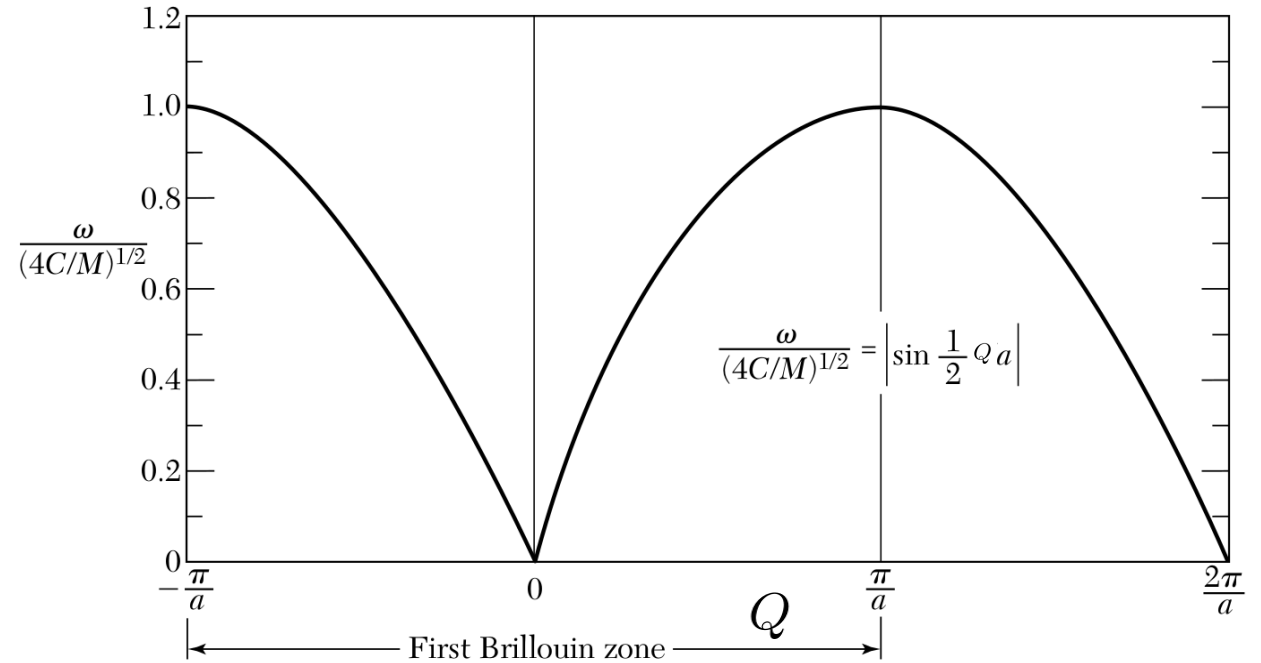


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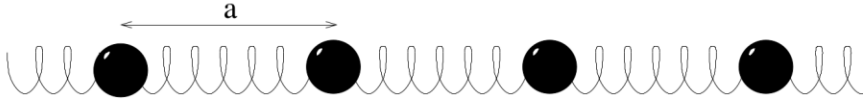
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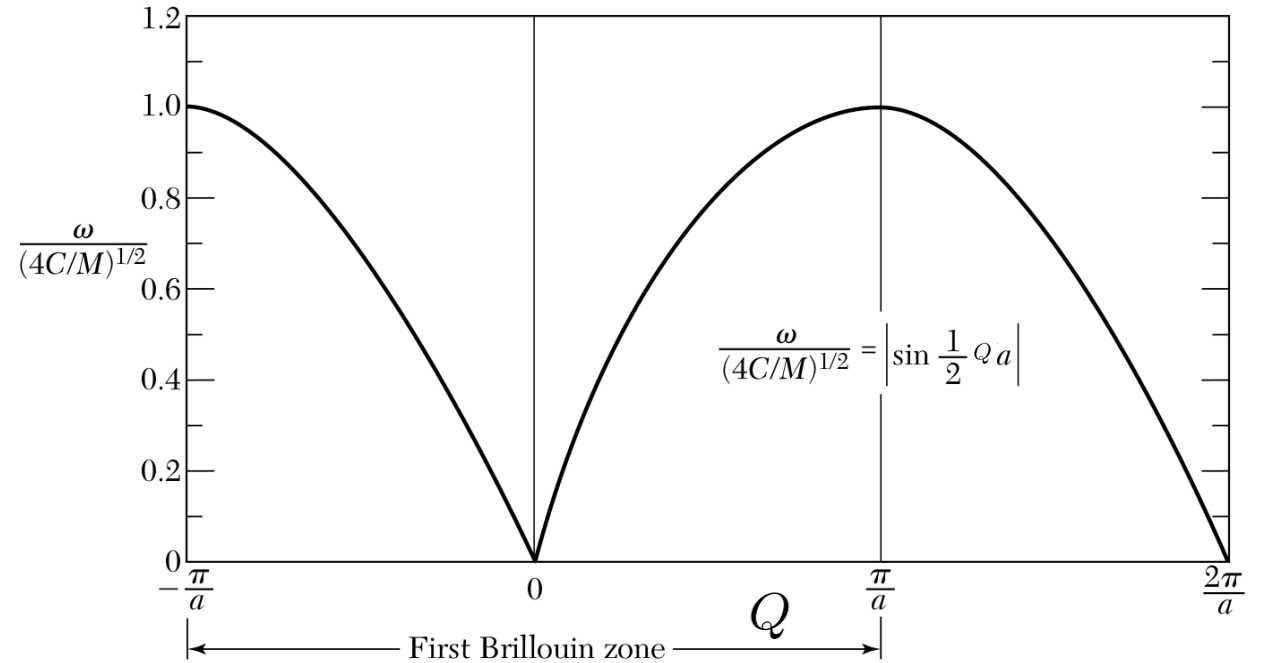


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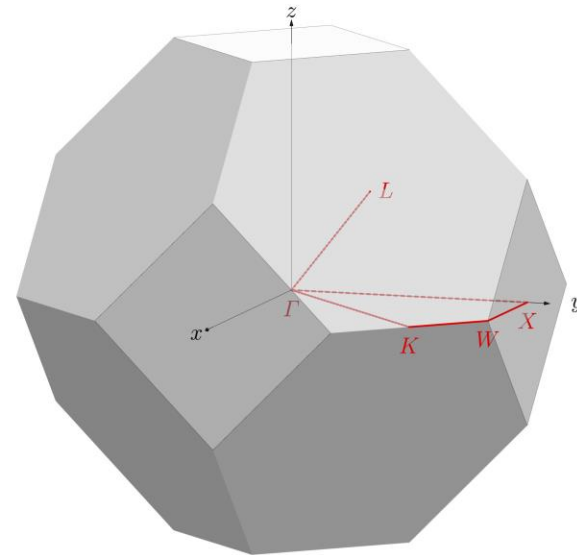
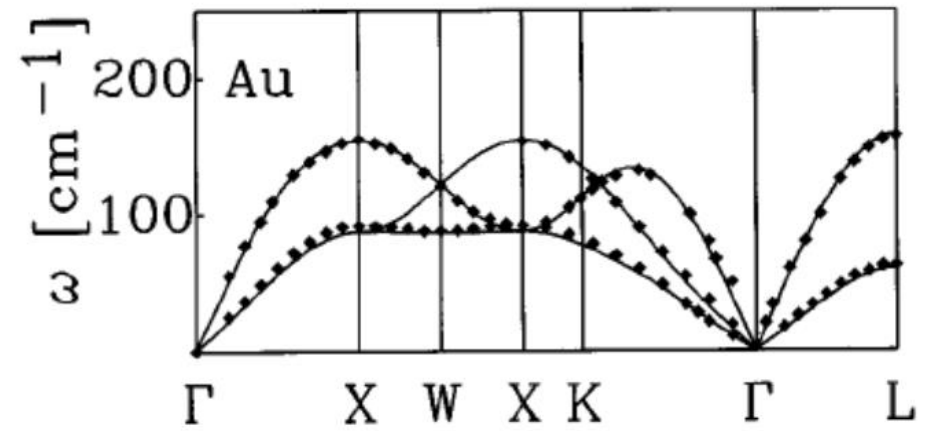
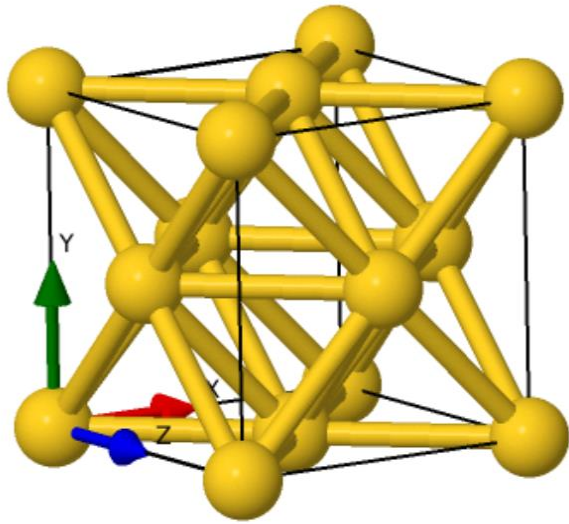
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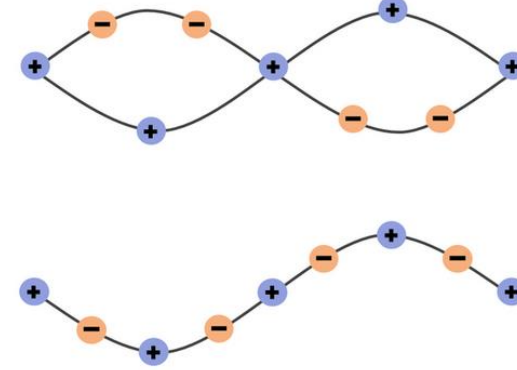
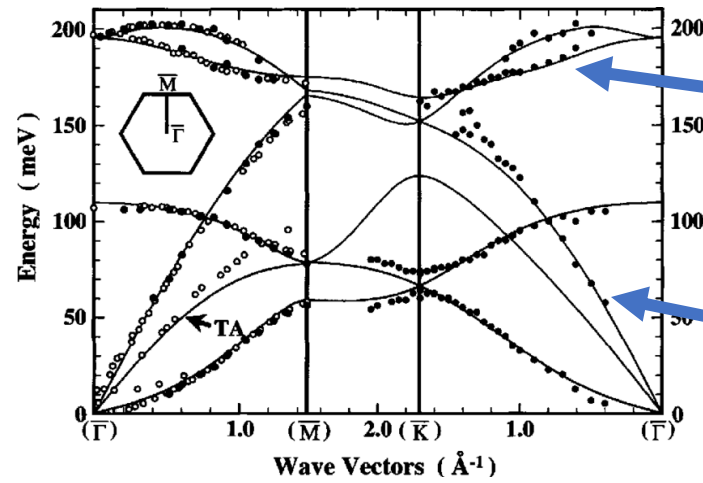


Normal modes a.k.a Phonons!

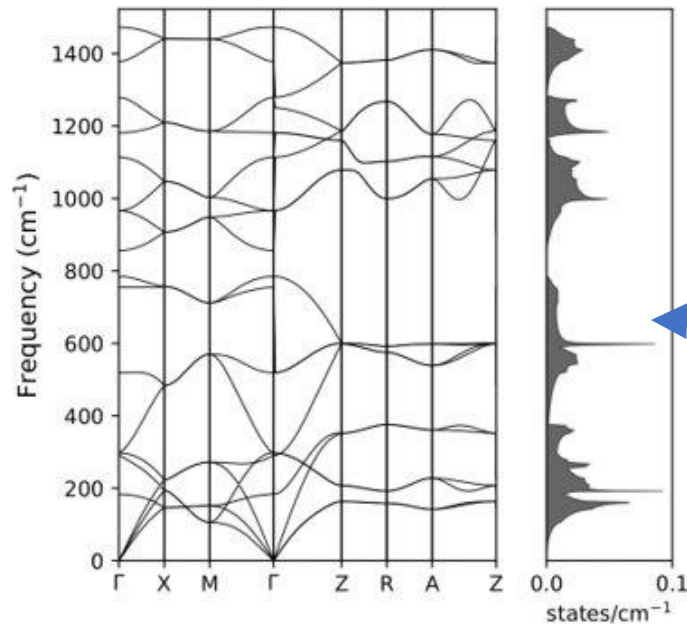
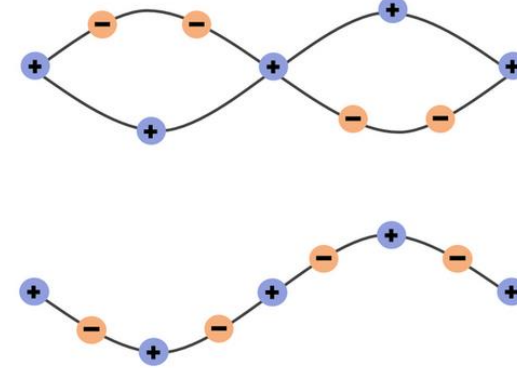
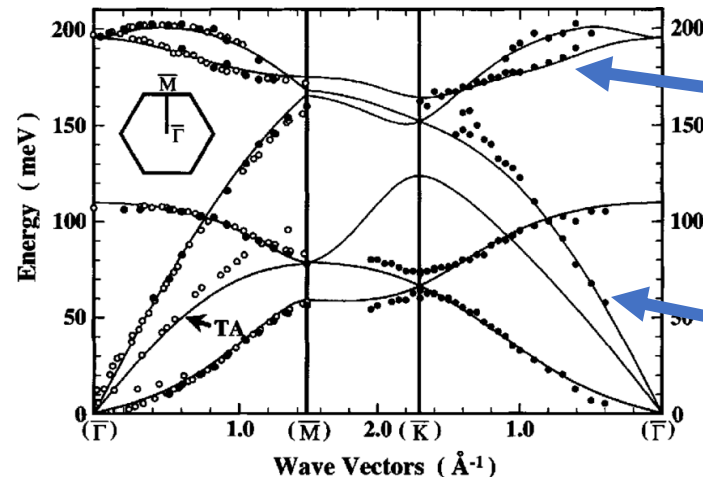
A simple 3D crystal



More complicated 3D crystals



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Phonon density of states, i.e. sum on the entire Brillouin Zone

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We need to predict the energies and the forces for each atom in the system

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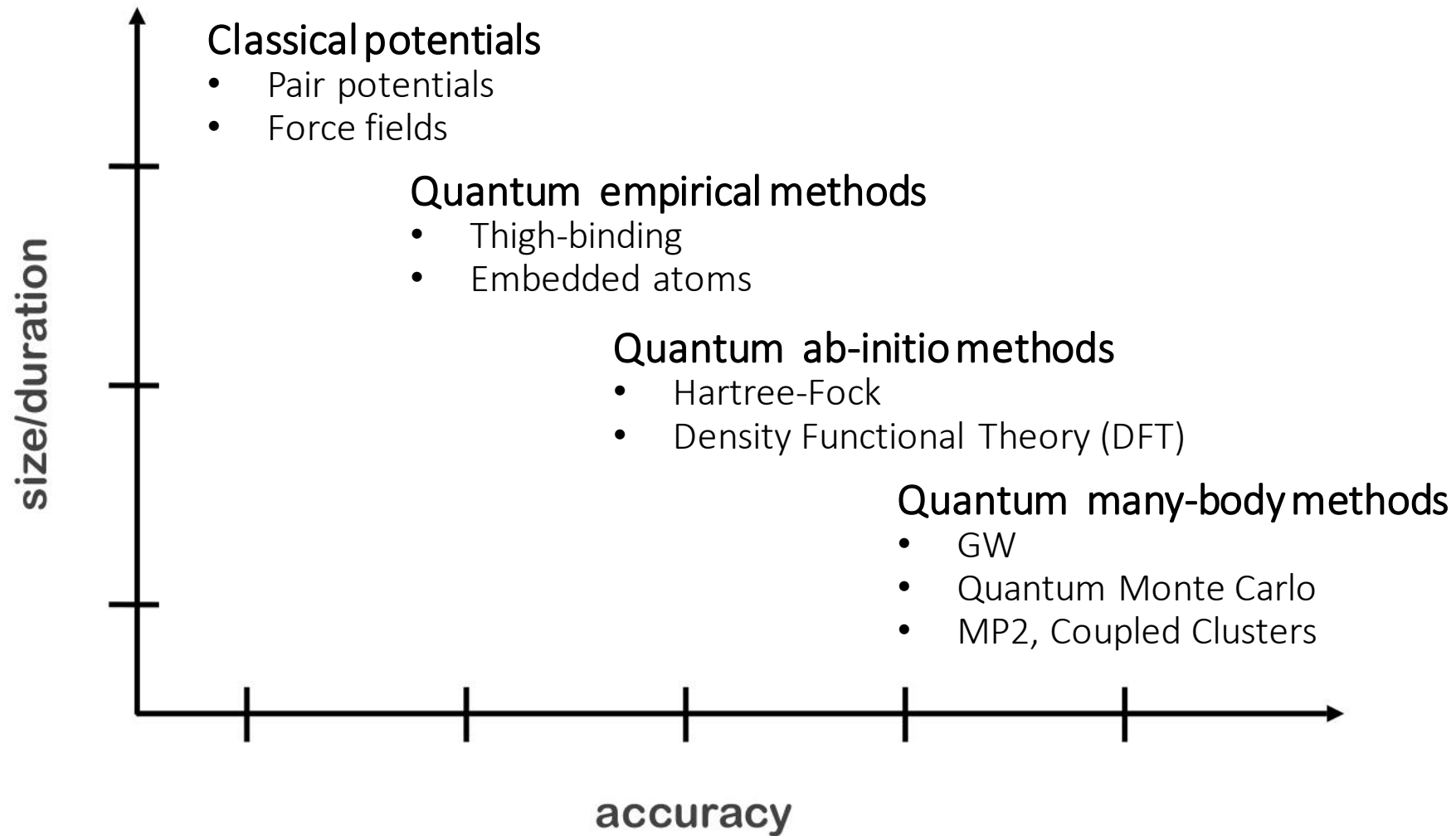
With that we can:

Find the equilibrium geometry and thus all the positions in our system

The phonons, i.e. the harmonic dynamic of the system

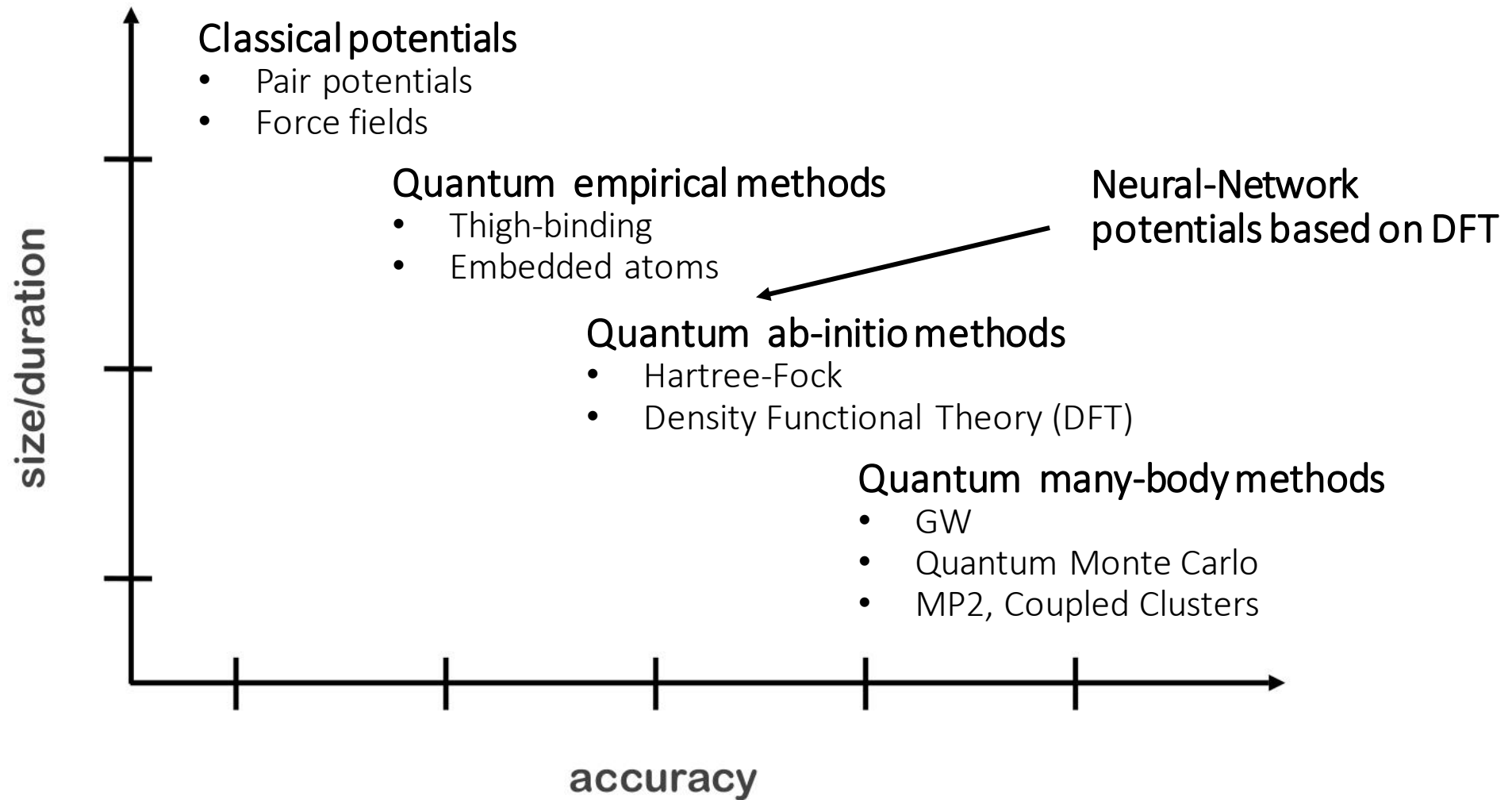
Tools and techniques for atomistic simulations

Tools and approaches for atomistic simulations



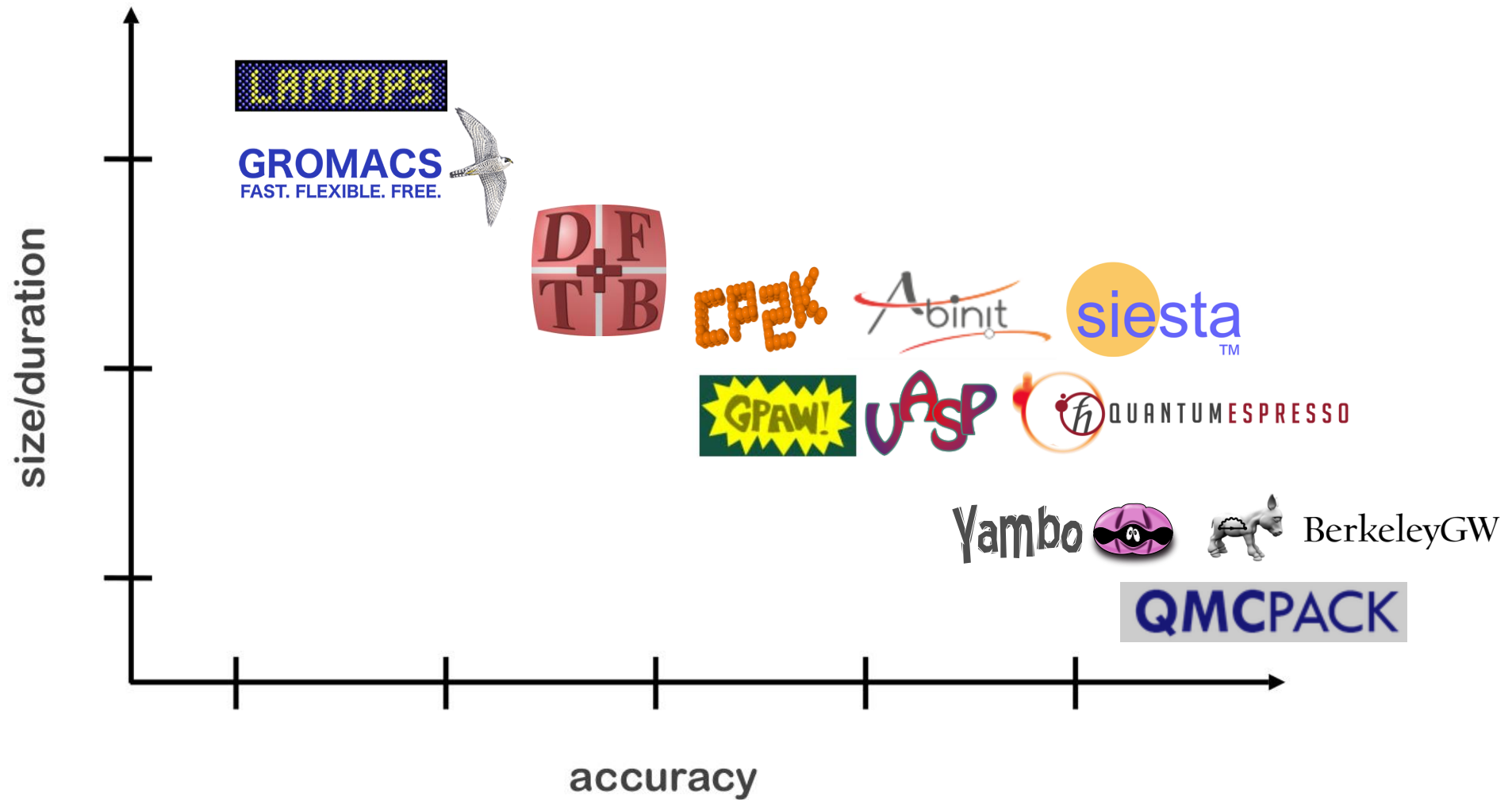
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- Different methods suits different problems

Tools and approaches for atomistic simulations

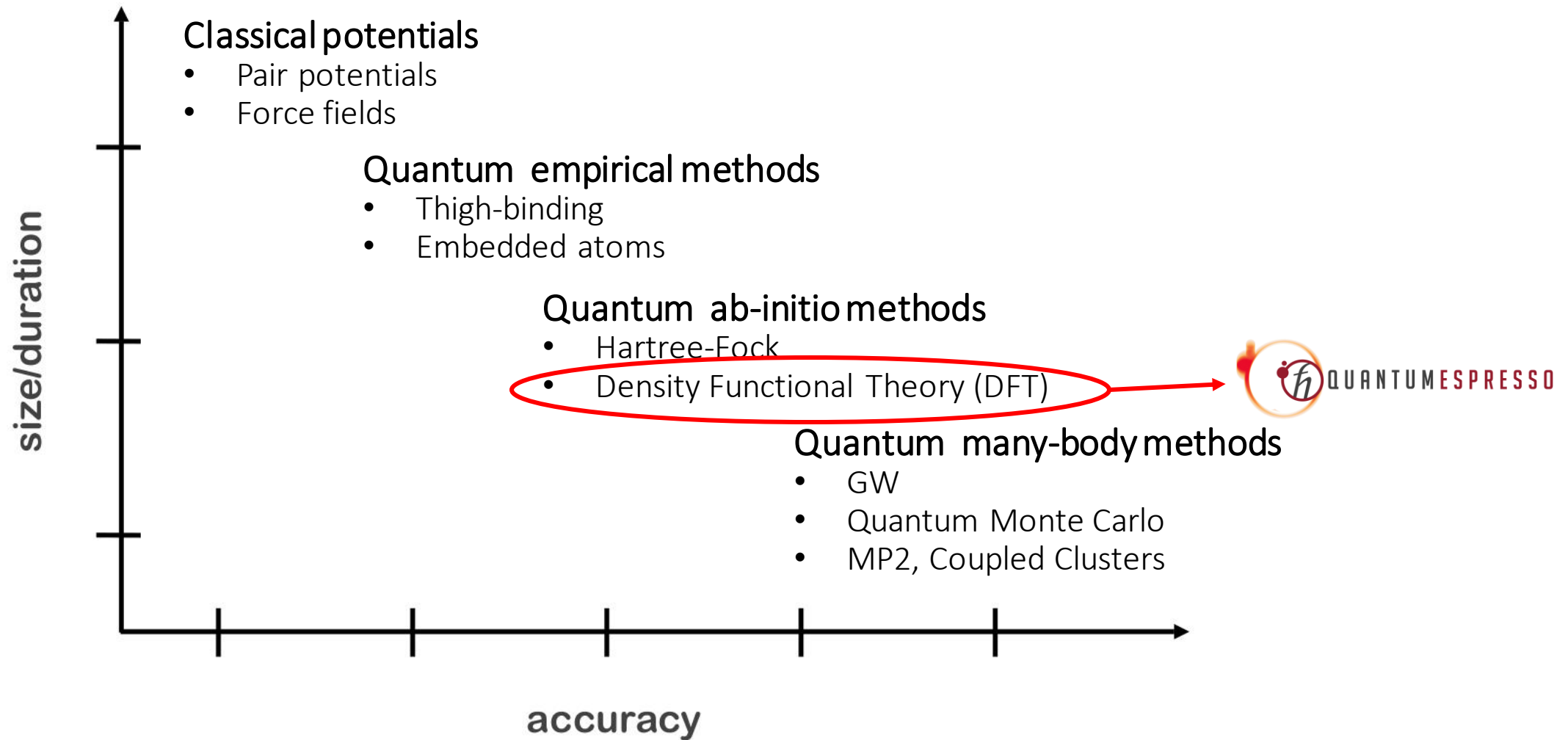


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Tools and approaches for atomistic simulations



Tools and approaches for atomistic simulations



Theoretical foundations of DFT calculations

Ab-initio simulations

$$\hat{H}\Psi = E\Psi$$

In the simplest case we need to solve the static (time-independent) Schrödinger equation

Ab-initio simulations

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$

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kinetic energy of
electrons

kinetic energy of
nuclei

electron-nuclei
interaction

electron-electron
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nuclei-nuclei
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NOTE: we are using Hartree atomic units

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Born-Oppenheimer Approximation

$$\hat{H}_{B.O.} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - 0 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} + Const.$$

Ab-initio simulations

$$\hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}}$$

$$\hat{H}_{elec} \Psi_{elec}(r_1, \dots, r_N) = E_{elec} \Psi_{elec}(r_1, \dots, r_N)$$

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$$\hat{H}_{elec} \Psi_{elec}(r_1, \dots, r_N) = E_{elec} \Psi_{elec}(r_1, \dots, r_N)$$

This is still a massive 3N-dimensional problem!

For systems with more than few electrons this is a monumental task and no supercomputer can handle it in a reasonable amount of time

We need to express the problem in an alternative form!

Hohenberg-Kohn theorems

In the ground state, the electron density uniquely determines the external potential

Thus, the total energy can be written as a functional of the electronic density and the ground state energy can be determined through a variational approach

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$$E = E[n(r)]$$

$$E_0 = \min(E[n(r)])$$

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$$n(r) \leftrightarrow V_{ext}(r) \longrightarrow \Psi \longrightarrow E$$

$$F[f(x)] = \int_{-1}^1 f(x) dx$$

$$f(x) = x^2 + 1$$

$$E = E[n(r)]$$

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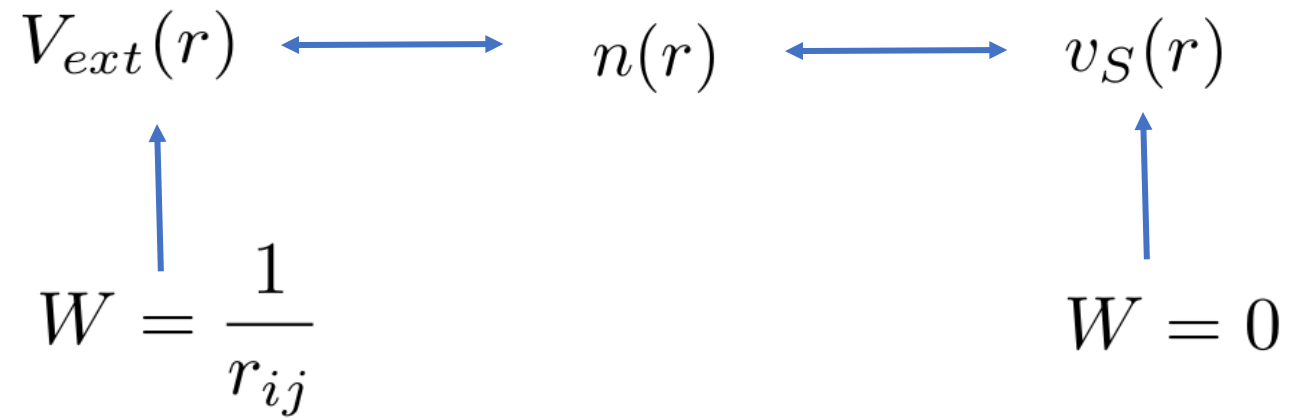
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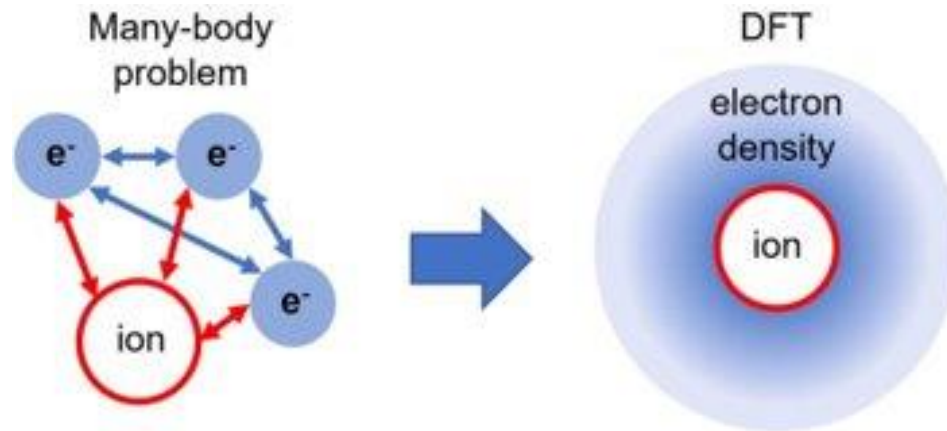
The only problem is that $E[n(r)]$ is unknown!

Kohn-Sham approach



Kohn-Sham approach

$$\begin{array}{ccccc} V_{ext}(r) & \longleftrightarrow & n(r) & \longleftrightarrow & v_S(r) \\ \uparrow & & & & \uparrow \\ W = \frac{1}{r_{ij}} & & & & W = 0 \end{array}$$



Kohn-Sham approach

$$\hat{H}_{KS} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N v_S(r_i)$$

$$\Psi_{elec}(r_1, \dots, r_N) \rightarrow \phi_1(r_1)\phi_2(r_2)\dots\phi_N(r_N)$$

$$n(r) = \sum_i \phi_i^*(r)\phi_i(r)$$

Kohn-Sham approach

$$E^{DFT}[n] = T_s[\{\phi_i\}] + E_{ext}[n] + E_{Har}[n] + E_{xc}[n]$$

$$T_s[\{\phi_i\}] = \sum_i^N \int dr \phi_i^*(r) \nabla^2 \phi_i(r)$$

$$E_{ext}[n] = \int dr n(r) V_{ext}(r)$$

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All the unknowns i.e. the complex many body behavior that should appear in the kinetic term and the interaction term are now in here!

Approximations

The simplest one is the Local Density Approximation (LDA).

Here we consider a homogenous electron gas for which the exchange potential can be computed analytically, and we compute our potential point by point as it was the one of a homogeneous gas at the same density

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$$E_x^{HEG} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n^{\frac{4}{3}} V$$

$$E_x^{LDA} = \int_V \frac{E_x^{HEG}[n(r)]}{V} dr$$

Kohn-Sham approach

$$\hat{H}^{KS} \phi_i(r) = (-\nabla^2 + V_{ext}(r) + V_{Har}(r) + V_{xc}(r)) \phi_i(r) = \epsilon_i(r) \phi_i(r)$$

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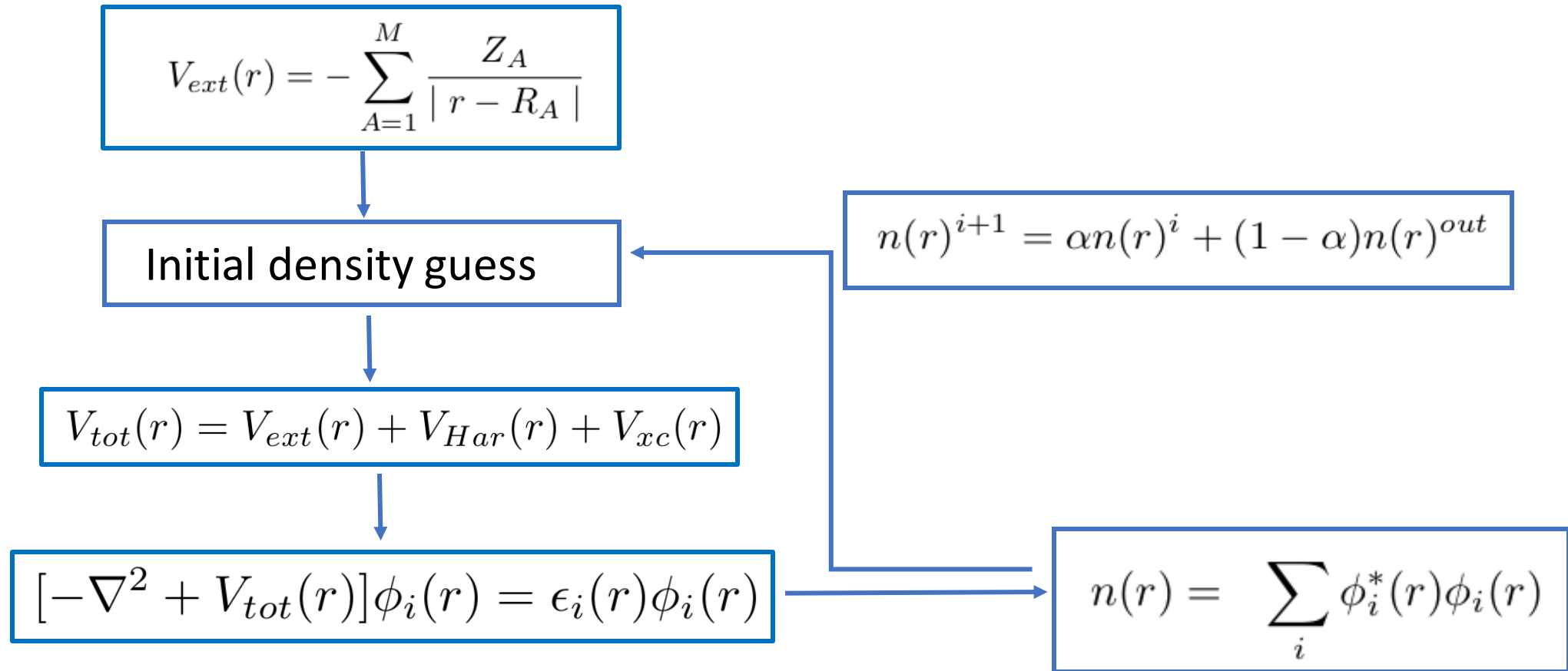
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Structural Optimization

Forces

$$\hat{H} = -\frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} + E(R_1, \dots, R_N)$$

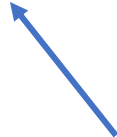
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$$U(R_1, \dots, R_N) = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} + E(R_1, \dots, R_N)$$



Coulomb repulsion



"Glue" from the negative charge of the electrons

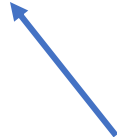
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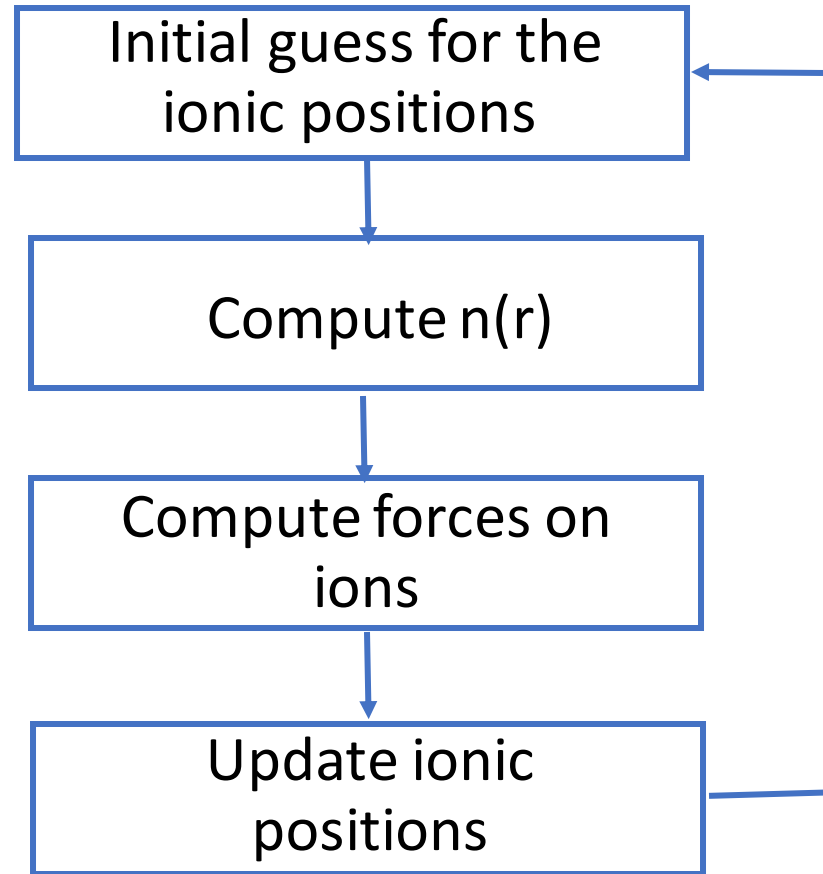
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$$M_A \frac{d^2 \mathbf{R}_A}{dt^2} = \mathbf{F}_A = -\frac{\partial U}{\partial \mathbf{R}_A}$$

Structural Optimization



Calculation of Phonons

Methods

- Density Functional Perturbation Theory (DFPT)
- Finite differences
- Autocorrelation

Phonons

$$U(R_1, \dots, R_N) = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} + E(R_1, \dots, R_N)$$

$$\sum_{A,\beta} \left(C_{B,A}^{\alpha\beta}(R) - M_A \omega^2 \delta_{A,B} \delta_{\alpha,\beta} \right) U_A^\beta = 0$$

$$C_{B,A}^{\alpha\beta} = \frac{\partial^2 U(R_1, \dots, R_N)}{\partial R_A^\alpha \partial R_B^\beta}$$

Density Functional Perturbation Theory

$$\tilde{C}_{s,t}^{\alpha\beta}(q) = \sum_R e^{-iqR} C_{B,A}^{\alpha\beta}(R) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^\alpha(q) \partial u_t^\beta(q)}$$

$$\frac{\partial n(r)}{\partial u_s^\alpha(q)}$$

Thanks to the **Hellmann-Feynman** theorem this quantity only depends on the first order charge density derivative

This quantity can be directly obtained through a self-consistent cycle similar to the one used for the charge density!

DFPT allows to directly compute the phonons at an arbitrary q-point

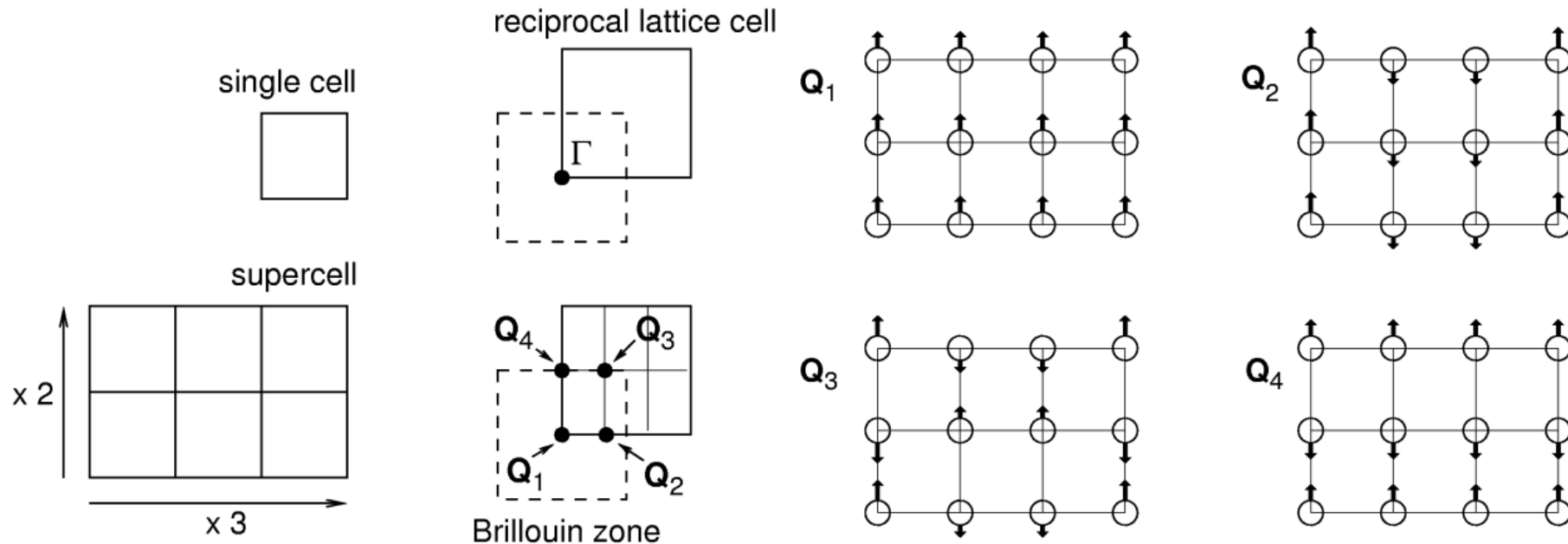
Finite differences

With finite differences you displace an atom and compute the forces on all the other atoms

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To access q points outside of Gamma you need to build supercells



Autocorrelation

$$D(\omega) = \frac{1}{3Nk_B T} \int_0^\infty \frac{\langle v(0)v(t) \rangle}{\langle v(0)v(0) \rangle} e^{i\omega t} dt$$

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Through velocity-velocity autocorrelation you don't have direct access to the dynamical matrices

You need to run long simulations, usually expensive for DFT but very common with classical methods for systems in which the diagonalization of the dynamical matrix becomes problematic

You automatically include temperature, thus anharmonicity and free rotors

Pros and Cons of DFT

DFT can give, without the need of any parametrization, results in good agreement with experiments for:

- Structural relaxation and phase stability
- Energy differences (thermodynamics, kinetics..)
- Phonon dispersions (dynamical stability)
- Electronic properties (with limitations!)

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Doesn't work for:

- Band Gaps
- Optical properties
- Strongly correlated materials

Pros and Cons of DFT



Note that what we discussed is valid only for the simplest cases, extension of theory are needed for:

- Magnetic materials
- Heavy atoms (spin-orbit and relativist effects)
- Localized orbitals

Practical aspects of DFT calculations in periodic systems

Boundary conditions

DFT calculations require the numerical solutions of the KS equations:

$$[-\nabla^2 + V_{tot}(r)]\phi_i(r) = \epsilon_i(r)\phi_i(r)$$

2nd order partial differential equations.

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$$\phi_i(x + a, y, z) = \phi_i(x, y, z)$$

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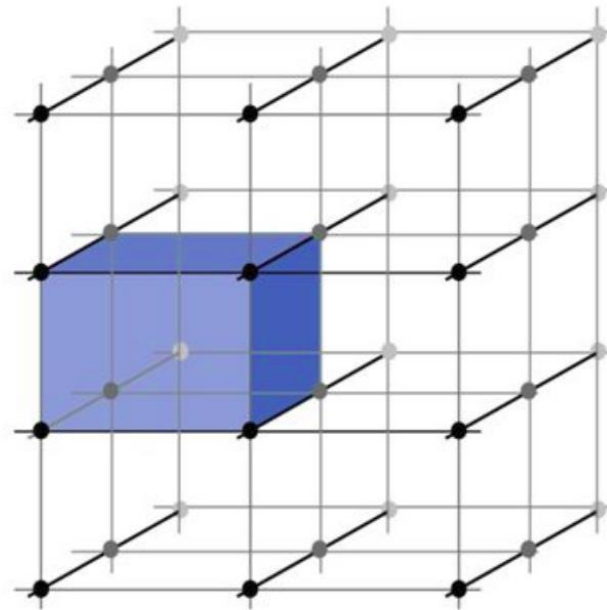
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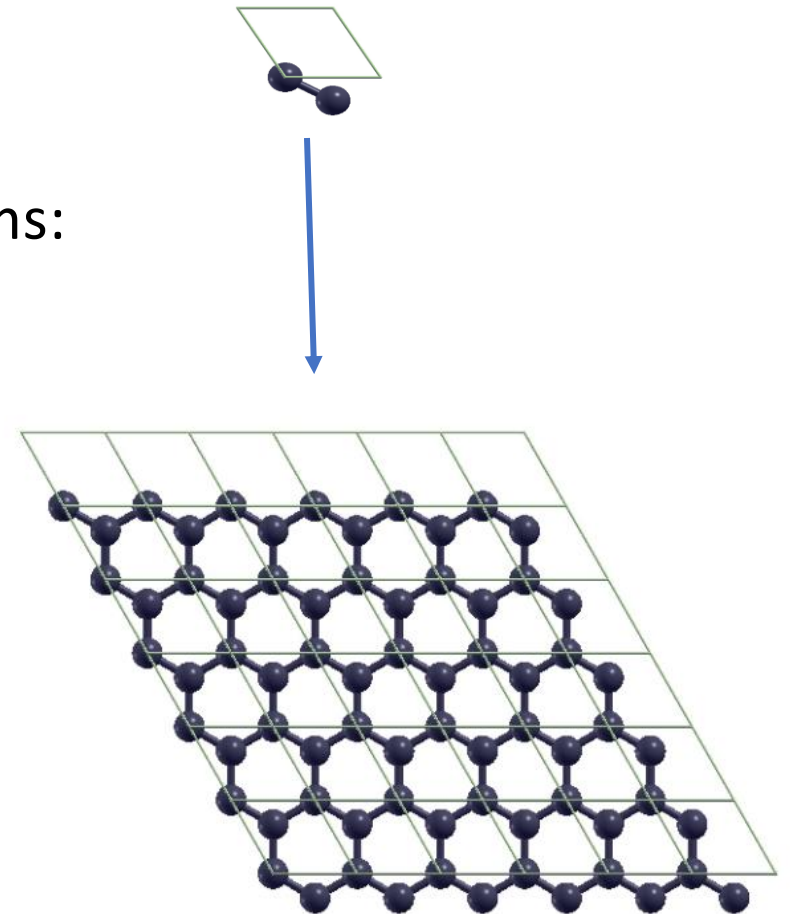
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Basis set

A convenient way of handling the KS states is to expand them in a basis of **planewaves**

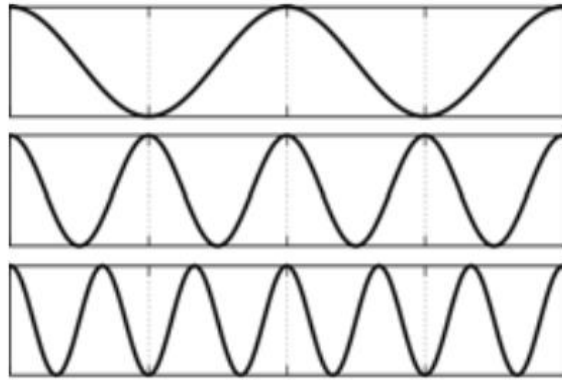
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$$

$$\phi_i(r) = \sum_{\mathbf{G}} c_i(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}$$

$$\frac{|\mathbf{G}|^2}{2} c_i(\mathbf{G}) + \sum_{\mathbf{G}'} V_{tot}(\mathbf{G} - \mathbf{G}') c_i(\mathbf{G}') = \epsilon_i c_i(\mathbf{G})$$

Basis set

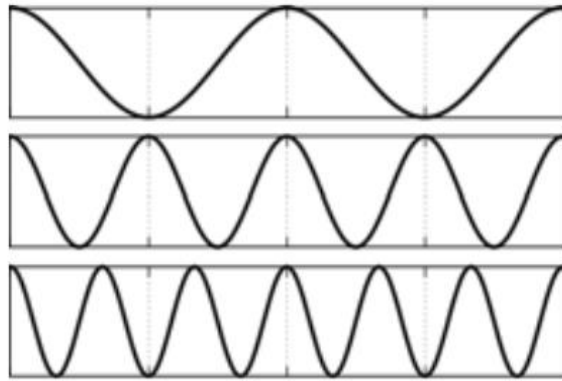


$$|\mathbf{G}| = 2\pi/a$$

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Basis set



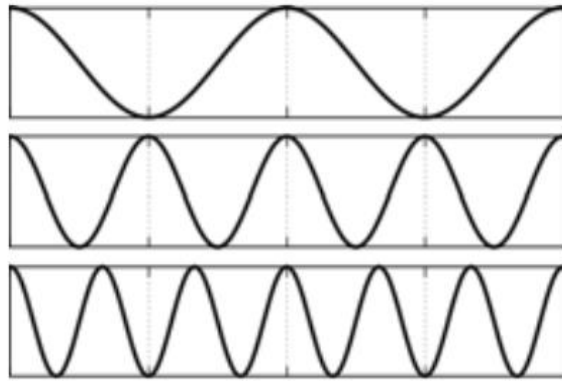
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Basis set



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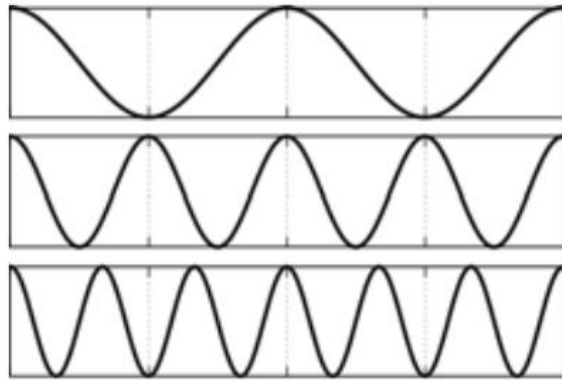
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- Orthonormality
- Built-in PBCs
- Basis set independent of nuclear positions
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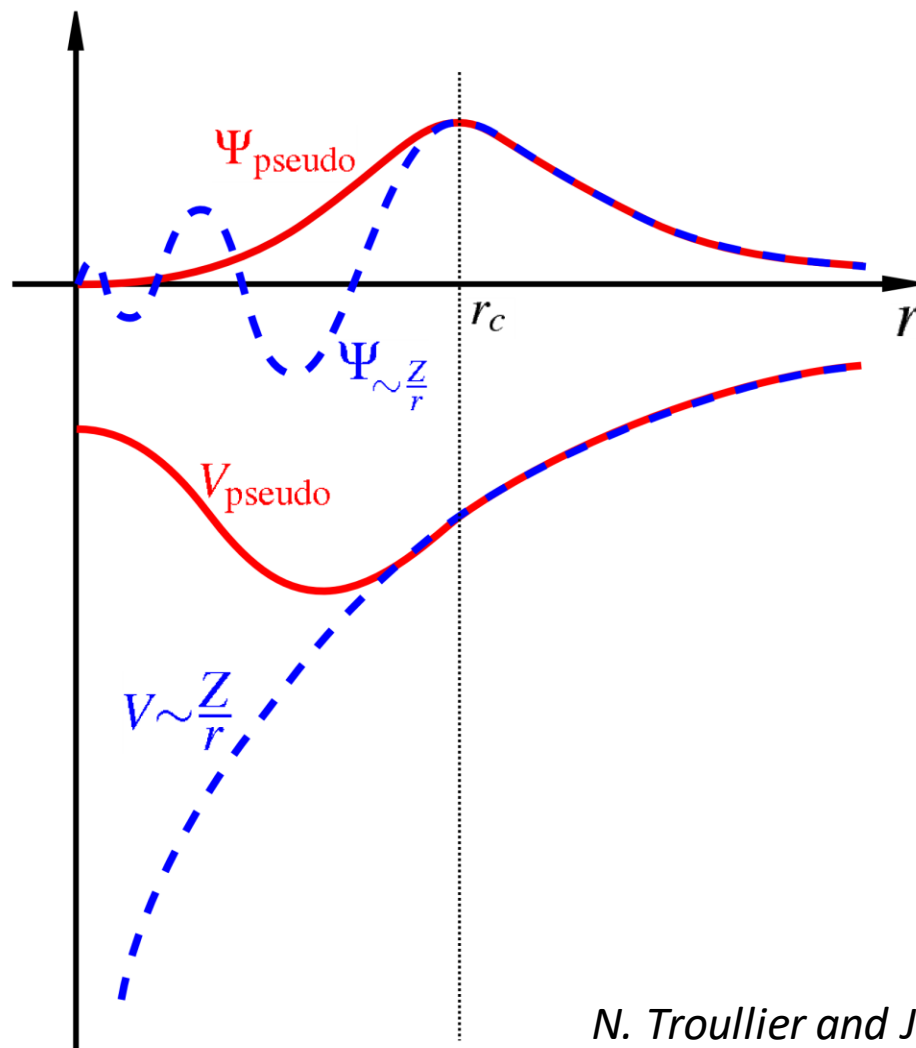
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But needs a larger basis set than other methods!

Pseudopotentials



N. Troullier and José Luís Martins Phys. Rev. B **43**, (1993).
D.Vanderbilt Phys. Rev. B **15** 41:7892-7895 (1990).
G. Kresse and D. Joubert Phys. Rev. B **59**, 1758 (1999).

Bloch's Theorem

For wavefunctions of non-interacting electrons in an external potential that has the periodicity of the lattice

$$V_{tot}(r + R) = V_{tot}(r)$$

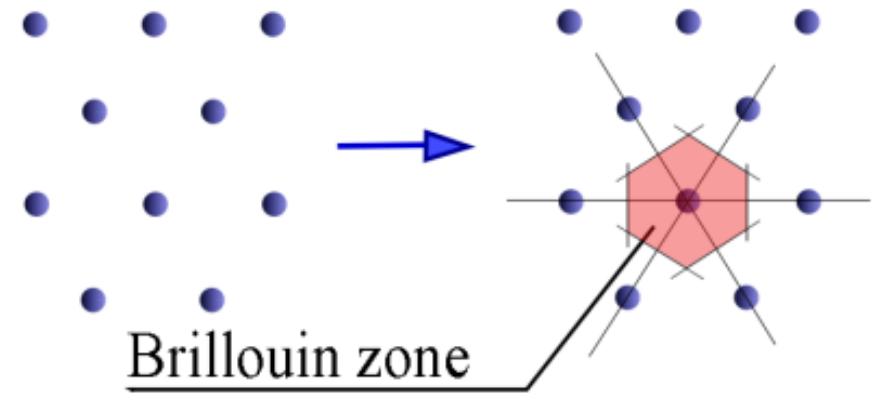
Bloch's Theorem states that:

$$\Phi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{i,\mathbf{k}}(\mathbf{r})$$

Wavefunction for
the entire crystal

Point in the 1st BZ

Wavefunction
with Bravais
lattice periodicity



Brillouin Zone Sampling

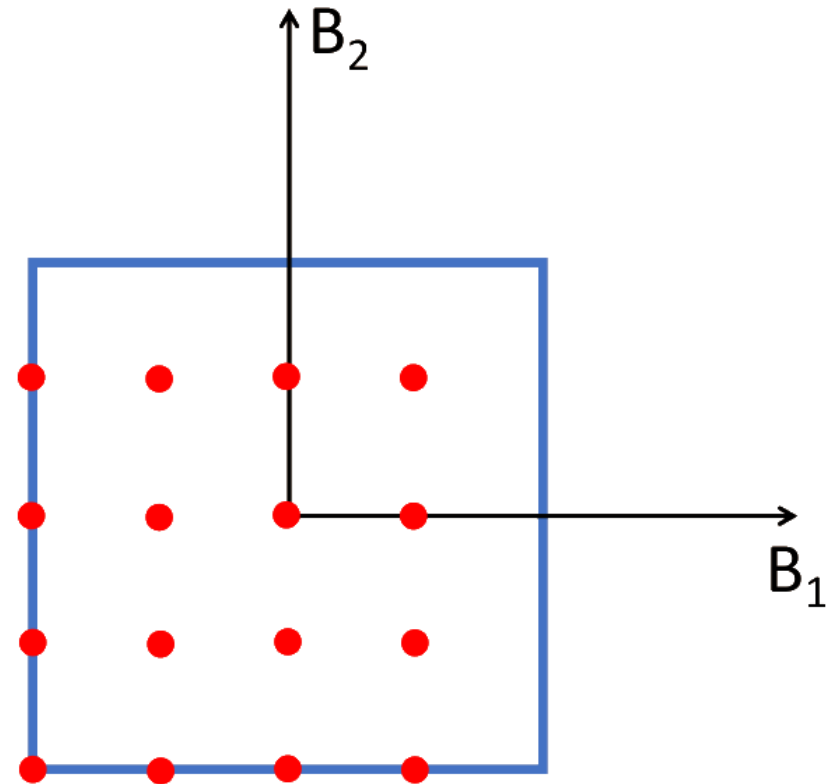
$$n(r) = \frac{V_{cell}}{(2\pi)^3} \int_{1BZ} \left(\sum_{i=1}^N | \phi_{i,k}(r) |^2 \right) dk = \frac{V_{cell}}{(2\pi)^3} \int_{1BZ} \left(\sum_{i=1}^N | u_{i,k}(r) |^2 \right) dk$$

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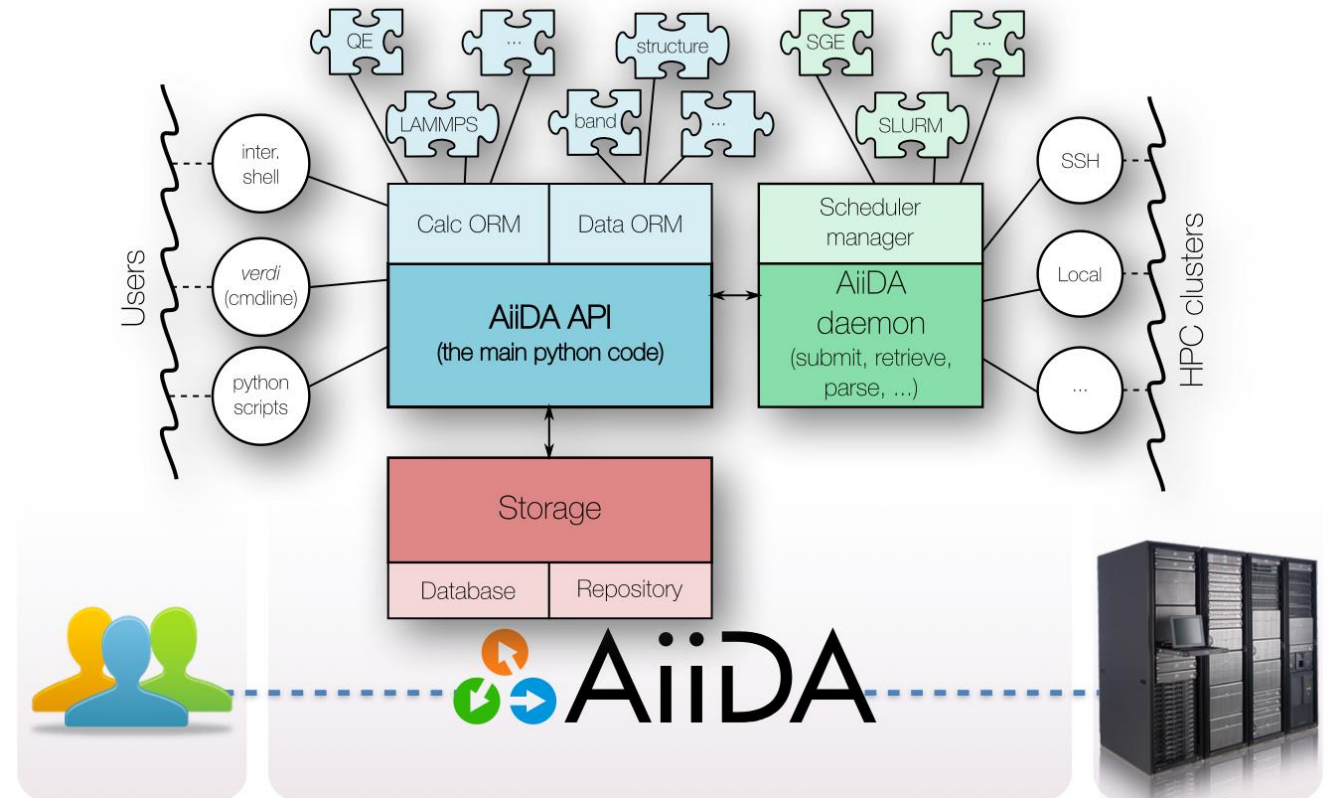
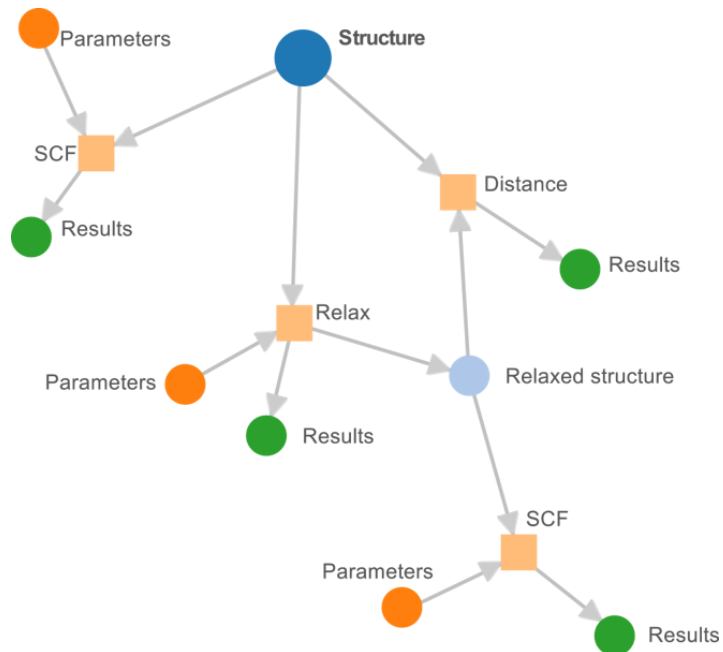
$$n(r) \approx \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k} \in 1st BZ} \left(\sum_{i=1}^N | u_{i,\mathbf{k}}(r) |^2 \right) d\mathbf{k}$$

The number of k-points can be further reduced by considering only the symmetry-inequivalent ones



Advanced Tools

Advanced informatic infrastructures



Advanced informatic infrastructures

