

Density Functional Theory

Gian-Marco Rignanes

CECAM Tutorial

Theoretical Spectroscopy Lectures

Lausanne, 8-12 octobre 2018



Introduction

Born-Oppenheimer approximation

- Let us consider a crystalline solid with N electrons and N_N nuclei, the system will be completely quantum-mechanically described by its **wavefunction** Ψ :

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_N})$$

where \mathbf{r}_i ($i = 1, \dots, N_e$) and \mathbf{R}_α ($\alpha = 1, \dots, N_N$) are the coordinates of the electrons and of the nuclei, respectively.

- As the nuclei are much heavier (hence slower) than the electrons ($M_\alpha \gg 1$), their respective dynamics can be decoupled. Hence, the wavefunction of the system can be broken into its electronic and nuclear components:

$$\Psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \times \psi^N(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_N})$$

Electronic N -body problem

- In practice, it is thus assumed that the nuclei positions can be considered as fixed when studying the electrons dynamics.
- In the end, we have to consider a system of N interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$, such as the one generated by the nuclei.
- It is completely described by its **wavefunction**:

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

which is obtained by solving the **Schrödinger equation**:

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \psi = E\psi$$

$$\hat{T}_e = \sum_n -\frac{\nabla_n^2}{2} \qquad \hat{V}_{ee} = \sum_n \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|}$$

Variational Quantum Monte Carlo

- Basically, it is impossible to solve this Schrödinger equation for more than two electrons analytically.
- A first class of numerical methods relies on the variational principle for the ground-state energy of the electronic system:

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

- Namely, for any arbitrary function ϕ , called trial-wavefunction, its expectation value E_ϕ , which is defined as:

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

is such that $E_\phi \geq E$ and it reaches its minimum when:

$$\frac{\delta E_\phi}{\delta \phi} = 0$$

Variational Quantum Monte Carlo

- This variational principle can be exploited to approach the ground-state energy as much as possible.
- A trial-wavefunction $\phi(a)$ depending on one or more parameters is chosen. The different many-dimensional integrals are evaluated numerically (Monte Carlo methods) so as to obtain:

$$E(a) = \frac{\langle \phi(a) | \hat{H} | \phi(a) \rangle}{\langle \phi(a) | \phi(a) \rangle}$$

- The minimum is then located by varying the parameter(s):

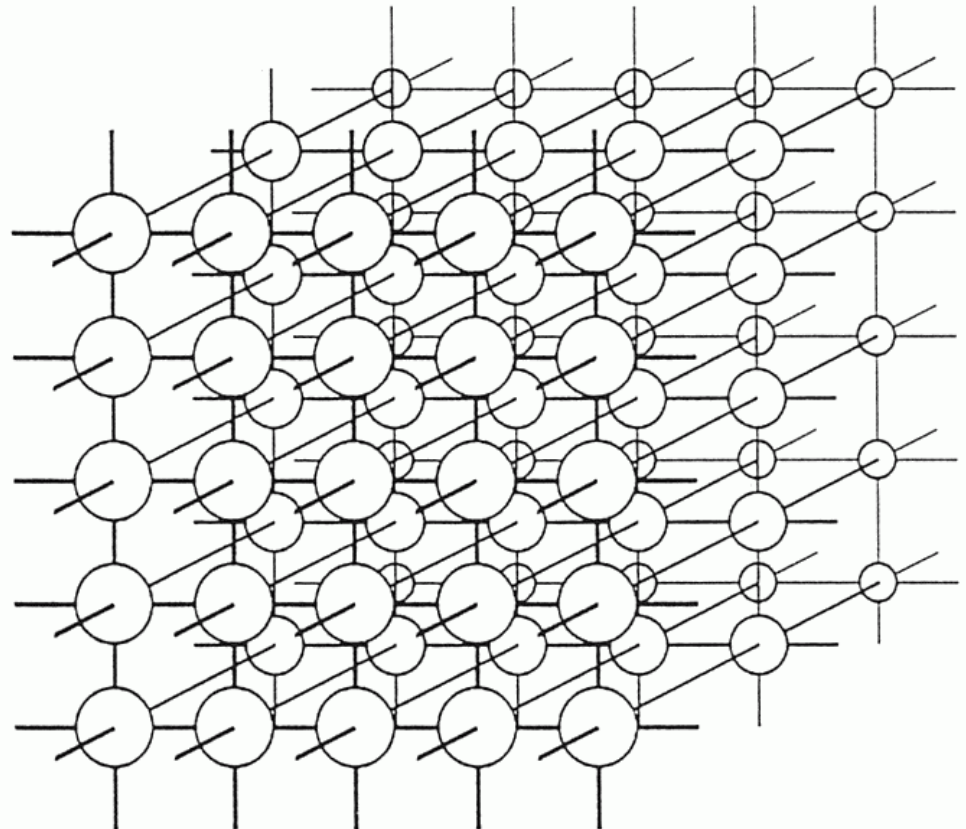
$$\frac{\partial E(a)}{\partial a} = 0$$

- The choice of the trial-wavefunction is obviously very critical.

Variational Quantum Monte Carlo

- Moreover, the N -electrons wavefunction soon becomes an object very difficult to handle in a computer.
- For instance, the wavefunction of the oxygen atom (with 8 electrons) defined on a $10 \times 10 \times 10$ real space-grid is an object which consists of 10^{24} real numbers.

Note: in classical mechanics, the very same system is fully described by 48 real numbers (the positions and the velocities of the 8 electrons).



One-particle approximations

Independent electron approximation

- In fact, electron-electron interactions are the real problem.

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \psi = E\psi$$

- Assuming that these are negligible with respect to the external potential (the electron-ion interactions), the problem simplifies to:

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) \right) \psi = E\psi$$

Separating the variables

- The form of the Hamiltonian calls for a separation of variables. The N -electrons wavefunction can be replaced by the product of N 1-electron wavefunctions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N)$$

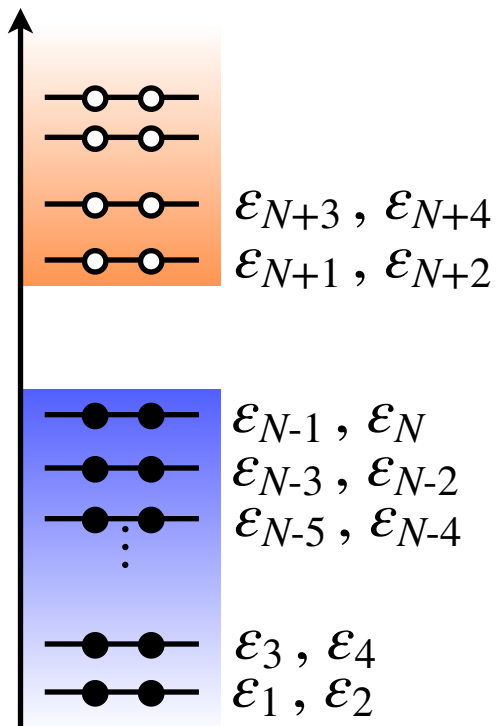
which are the solutions of a 1-electron Schrödinger equation:

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \varepsilon_n \phi_n(\mathbf{r})$$

- The total energy is simply given by:

$$E = \sum_n \varepsilon_n$$

$$E_{N,0} = \varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_{N-1} + \varepsilon_N$$

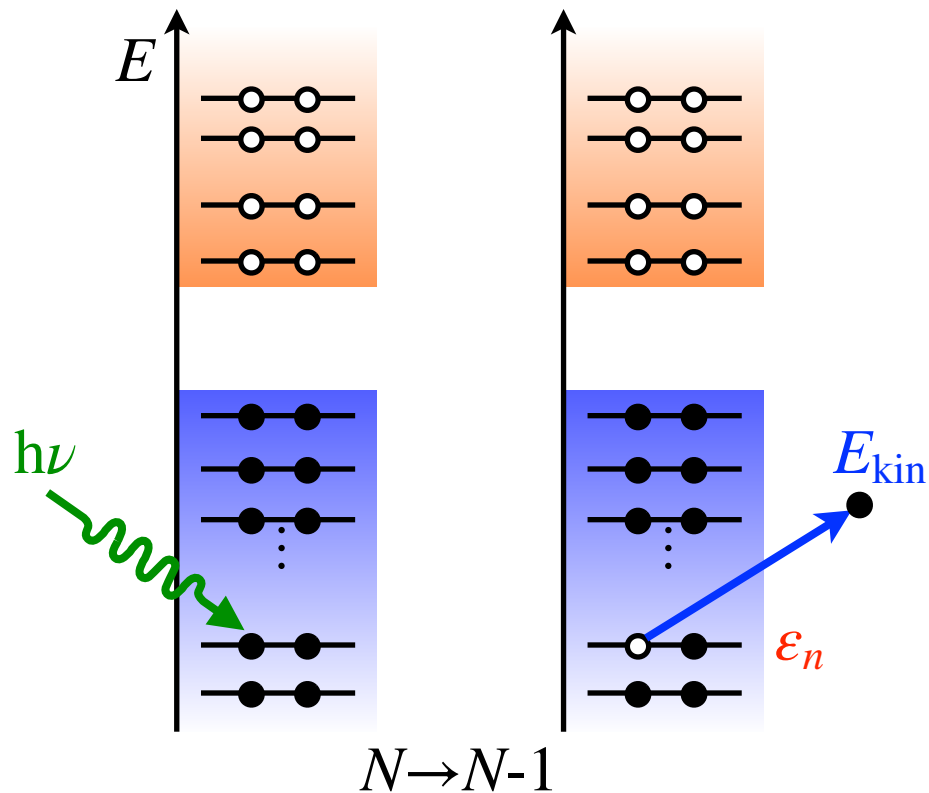


Connection to photoemission

- By solving the 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r})$$

we obtain the band structure ϵ_n which can be determined experimentally by photoemission or inverse photoemission (valence or conduction bands).



Energy conservation:

before $\rightarrow h\nu + E_{N,0}$

after $\rightarrow E_{\text{kin}} + E_{N-1,n}$

The binding energy is:

$$E_{\text{kin}} - h\nu = E_{N,0} - E_{N-1,n} = \epsilon_n$$

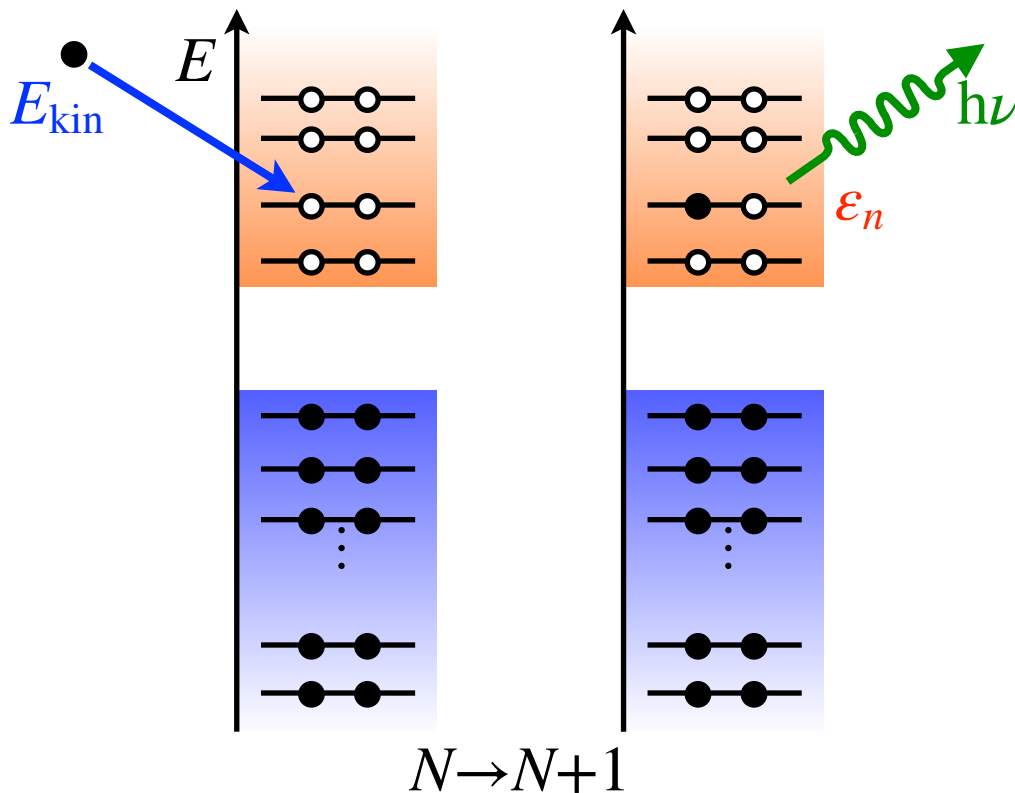
$$E_{N-1,n} = \epsilon_1 + \dots + \cancel{\epsilon_n} + \dots + \epsilon_N$$

Connection to inverse photoemission

- By solving the 1-electron Schrödinger equation:

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r})$$

we obtain the band structure ϵ_n which can be determined experimentally by photoemission or inverse photoemission (valence or conduction bands).



Energy conservation:

$$\text{before} \rightarrow E_{\text{kin}} + E_{N,0}$$

$$\text{after} \rightarrow h\nu + E_{N+1,n}$$

The binding energy is:

$$E_{\text{kin}} - h\nu = E_{N+1,n} - E_{N,0} = \epsilon_n$$

$$E_{N+1,n} = \epsilon_1 + \dots + \epsilon_N + \epsilon_n$$

Wavefunction methods

Hartree approximation

- The **Hartree approximation** assumes that the N -electrons wavefunction can be replaced by the product of N 1-electron wavefunctions even when the electron-electron interactions are not neglected.

- Hence, we need to find the 1-electron wavefunctions ϕ_i that minimize the total energy:

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

under the normalization constraint:

$$\langle \phi_n | \phi_n \rangle = 1$$

- Introducing Lagrange multipliers, we simply need to minimize a functional of the 1-electron wavefunctions:

$$\min_{\{\phi_n\}} F [\{\phi_n\}] = \langle \psi | \hat{H} | \psi \rangle - \sum_n \epsilon_n^H \langle \phi_n | \phi_n \rangle$$

Hartree approximation

- It can be shown that the 1-electron wavefunctions are the solutions of the following 1-electron Schrödinger equation:

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{m \neq n} \hat{J}_m \right] \phi_n(\mathbf{r}) = \epsilon_n^{\text{H}} \phi_n(\mathbf{r})$$

where \hat{J}_m is the **Coulomb operator** defined by:

$$\hat{J}_m \phi_n(\mathbf{r}) = \left\{ \int \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_m(\mathbf{r}') d\mathbf{r}' \right\} \phi_n(\mathbf{r})$$

Hartree approximation

- The electronic eigenenergies can be written as:

$$\epsilon_n^H = \langle \phi_n | -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) | \phi_n \rangle + \sum_{m \neq n} J_{nm}$$

where $J_{nm} = \int \phi_n^*(\mathbf{r}) \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_n(\mathbf{r}) \phi_m(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$

- So that the total electronic energy writes:

$$\begin{aligned} E = \langle \psi | \hat{H} | \psi \rangle &= \sum_n \langle \phi_n | -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) | \phi_n \rangle + \frac{1}{2} \sum_n \sum_{m \neq n} J_{nm} \\ &= \sum_n \epsilon_n^H - \frac{1}{2} \sum_n \sum_{m \neq n} J_{nm} \end{aligned}$$

Hartree approximation

- The 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{m \neq n} \hat{J}_m \right] \phi_n(\mathbf{r}) = \epsilon_n^{\text{H}} \phi_n(\mathbf{r})$$

$$\text{where } \hat{J}_m \phi_n(\mathbf{r}) = \left\{ \int \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_m(\mathbf{r}') d\mathbf{r}' \right\} \phi_n(\mathbf{r})$$

is almost identical (apart from the self-interaction) to:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \epsilon_n^{\text{H}} \phi_n(\mathbf{r})$$

with $V_{\text{H}}(\mathbf{r})$, the **Hartree potential**, defined by:

$$V_{\text{H}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

where $n(\mathbf{r}) = \sum_n |\phi_n(\mathbf{r})|^2$ is the electronic density.

Hartree approximation

- In this case, the total electronic energy is written as:

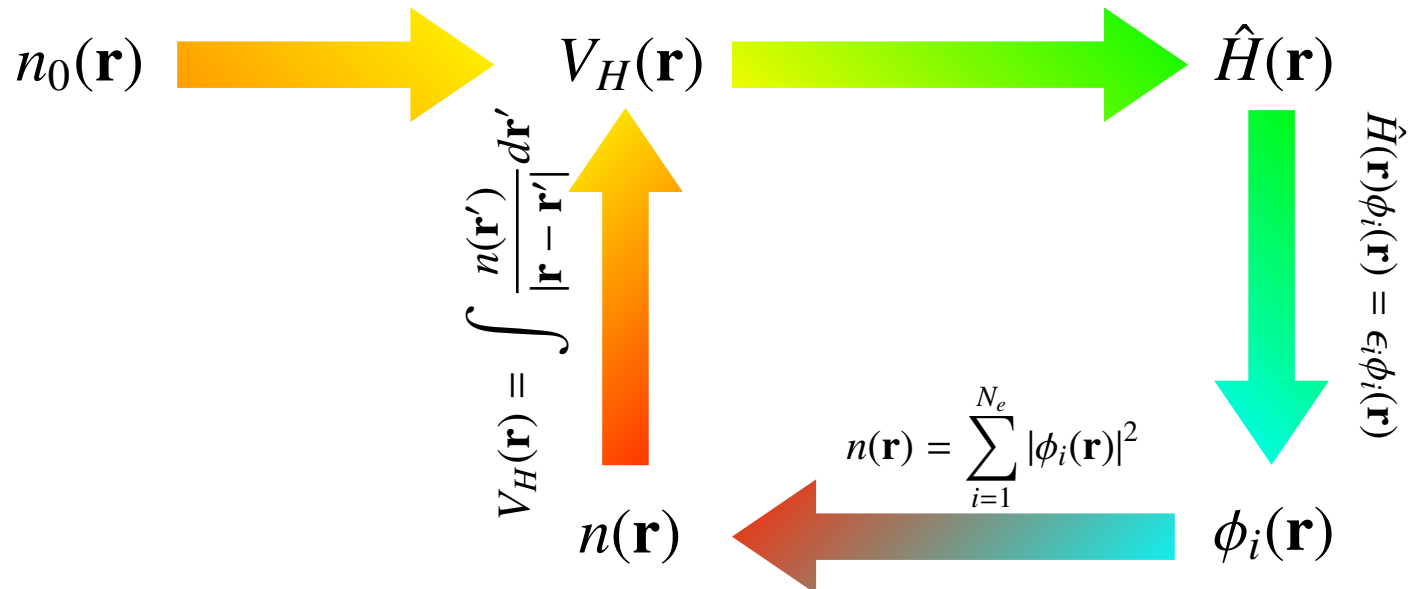
$$E = \sum_n \epsilon_n^{\text{H}} - E_{\text{H}}$$

where E_{H} is the **Hartree energy**, defined by:

$$E_{\text{H}} = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

Hartree approximation

- However, there is a new difficulty:
 - to obtain the Hartree potential $V_H(\mathbf{r})$, the electronic density $n(\mathbf{r})$ and hence all the wavefunctions $\phi_i(\mathbf{r})$ are needed
 - to obtain the wavefunctions $\phi_i(\mathbf{r})$, the Hartree potential $V_H(\mathbf{r})$ is required
- In practice, one starts from a trial electronic density and then iterates the equations until **self-consistency** is reached:



Hartree-Fock approximation

- In order to take Pauli exclusion principle into account, the product of N 1-electron wavefunctions should be replaced by a **Slater determinant**:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

That is the **Hartree-Fock** approximation.

- Again, we simply need to minimize a functional of the 1-electron wavefunctions with Lagrange multipliers:

$$\min_{\{\phi_n\}} F[\{\phi_n\}] = \langle \psi | \hat{H} | \psi \rangle - \sum_n \epsilon_n^{\text{HF}} \langle \phi_n | \phi_n \rangle$$

Hartree-Fock approximation

- It can be shown that the 1-electron wavefunctions are the solutions of the following 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{m \neq n} (\hat{J}_m - \hat{K}_m) \right] \phi_n(\mathbf{r}) = \epsilon_n^{\text{HF}} \phi_n(\mathbf{r})$$

where \hat{J}_m is the **Coulomb operator** defined by:

$$\hat{J}_m \phi_n(\mathbf{r}) = \left\{ \int \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_m(\mathbf{r}') d\mathbf{r}' \right\} \phi_n(\mathbf{r})$$

and \hat{K}_m is the **exchange operator** defined by:

$$\hat{K}_m \phi_n(\mathbf{r}) = \left\{ \int \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_n(\mathbf{r}') d\mathbf{r}' \right\} \phi_m(\mathbf{r})$$

Hartree-Fock approximation

- The electronic eigenenergies can be written as:

$$\varepsilon_n^{\text{HF}} = \langle \phi_n | -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) | \phi_n \rangle + \sum_{m \neq n} (J_{nm} - K_{nm})$$

where

$$J_{nm} = \int \phi_n^*(\mathbf{r}) \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_n(\mathbf{r}) \phi_m(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

and

$$K_{nm} = \int \phi_n^*(\mathbf{r}) \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_m(\mathbf{r}) \phi_n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

- So that the total electronic energy is:

$$E = \langle \psi | \hat{H} | \psi \rangle = \sum_n \varepsilon_n^{\text{HF}} - \frac{1}{2} \sum_n \sum_{m \neq n} (J_{nm} - K_{nm})$$

Hartree-Fock approximation

- The 1-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{m \neq n} (\hat{J}_m - \hat{K}_m) \right] \phi_n(\mathbf{r}) = \epsilon_n^{\text{HF}} \phi_n(\mathbf{r})$$

is identical (here, the self-interaction cancel in J and K) to:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + \hat{V}_{\text{x}} \right] \phi_n(\mathbf{r}) = \epsilon_n^{\text{HF}} \phi_n(\mathbf{r})$$

with \hat{V}_{x} , the **exchange potential** operator, defined by:

$$\hat{V}_{\text{x}} \phi_n(\mathbf{r}) = \sum_m \left\{ \int \phi_m^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_n(\mathbf{r}') d\mathbf{r}' \right\} \phi_m(\mathbf{r})$$

It is a non-local operator.

Hartree-Fock approximation

- A link with photoemission experiments can be established if we assume that the wavefunction of the $N-1$ electrons system can be written as:

$$\begin{aligned} |N-1, n\rangle &= \psi_{N-1, n}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}, \mathbf{r}_{n+1}, \dots, \mathbf{r}_{N-1}) \\ &= \frac{1}{\sqrt{!(N-1)}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_{n-1}(\mathbf{r}_1) & \phi_{n+1}(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \vdots & & \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_{n-1}) & \cdots & \phi_{n-1}(\mathbf{r}_{n-1}) & \phi_{n+1}(\mathbf{r}_{n-1}) & \cdots & \phi_N(\mathbf{r}_{n-1}) \\ \phi_1(\mathbf{r}_{n+1}) & \cdots & \phi_{n-1}(\mathbf{r}_{n+1}) & \phi_{n+1}(\mathbf{r}_{n+1}) & \cdots & \phi_N(\mathbf{r}_{n+1}) \\ \vdots & & \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \cdots & \phi_{n-1}(\mathbf{r}_N) & \phi_{n+1}(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix} \end{aligned}$$

(meaning that we neglect the relaxation of the 1-electron wavefunctions on electron removal).

- Indeed, we can write:

$$E_{N,0} - E_{N-1,n} = \langle N, 0 | \hat{H} | N, 0 \rangle - \langle N-1, n | \hat{H} | N-1, n \rangle = \epsilon_n^{\text{HF}}$$

Hartree-Fock approximation

- A link with inverse photoemission experiments can be established if we assume that the wavefunction of the $N+1$ electrons system can be written as:

$$\begin{aligned} |N+1, n\rangle &= \psi_{N+1, n}(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{r}_{N+1}) \\ &= \frac{1}{\sqrt{!(N+1)}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) & \phi_n(\mathbf{r}_1) \\ \vdots & & \vdots & \vdots \\ \phi_1(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) & \phi_n(\mathbf{r}_N) \\ \phi_1(\mathbf{r}_{N+1}) & \cdots & \phi_N(\mathbf{r}_{N+1}) & \phi_n(\mathbf{r}_{N+1}) \end{vmatrix} \end{aligned}$$

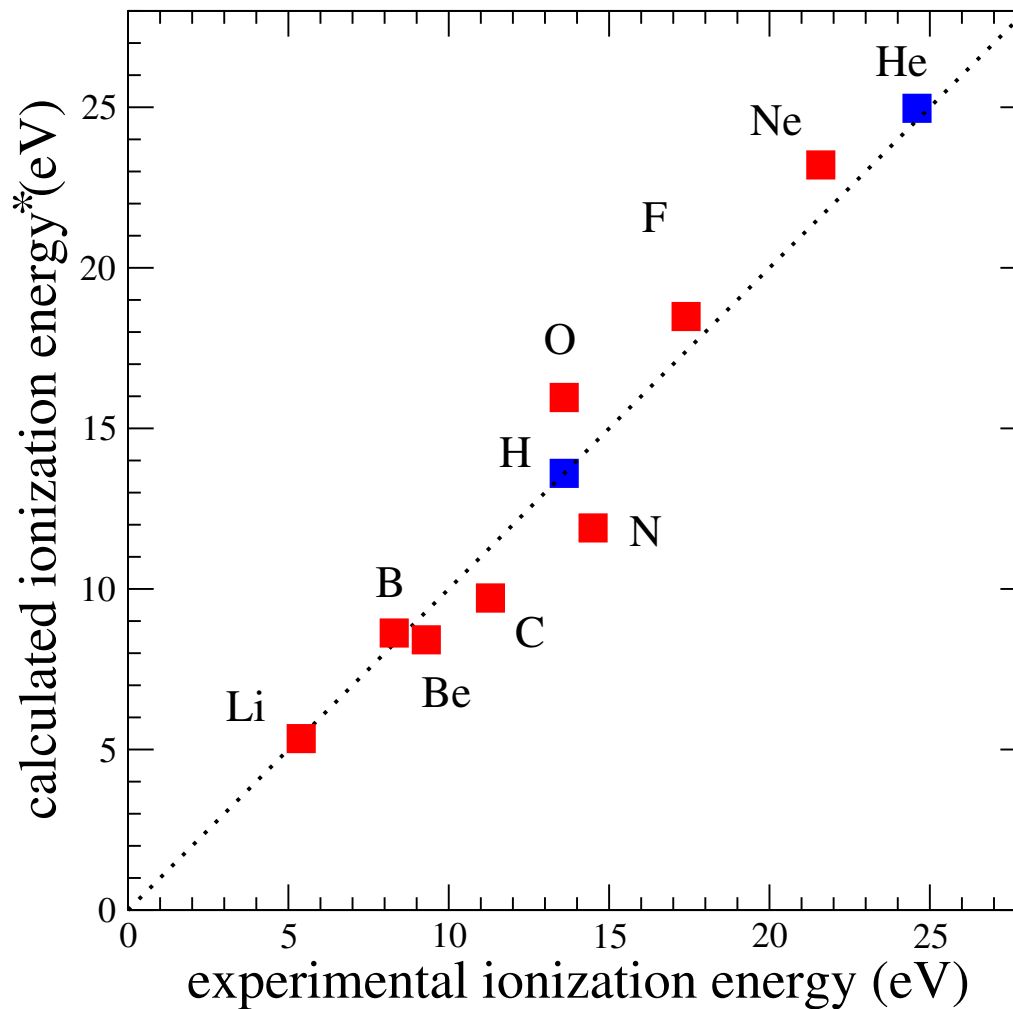
(meaning that we neglect the relaxation of the 1-electron wavefunctions on electron addition).

- Indeed, we can write:

$$E_{N+1, n} - E_{N, 0} = \langle N+1, n | \hat{H} | N+1, n \rangle - \langle N, 0 | \hat{H} | N, 0 \rangle = \epsilon_n^{\text{HF}}$$

Hartree-Fock approximation

- Results for the ionization energy

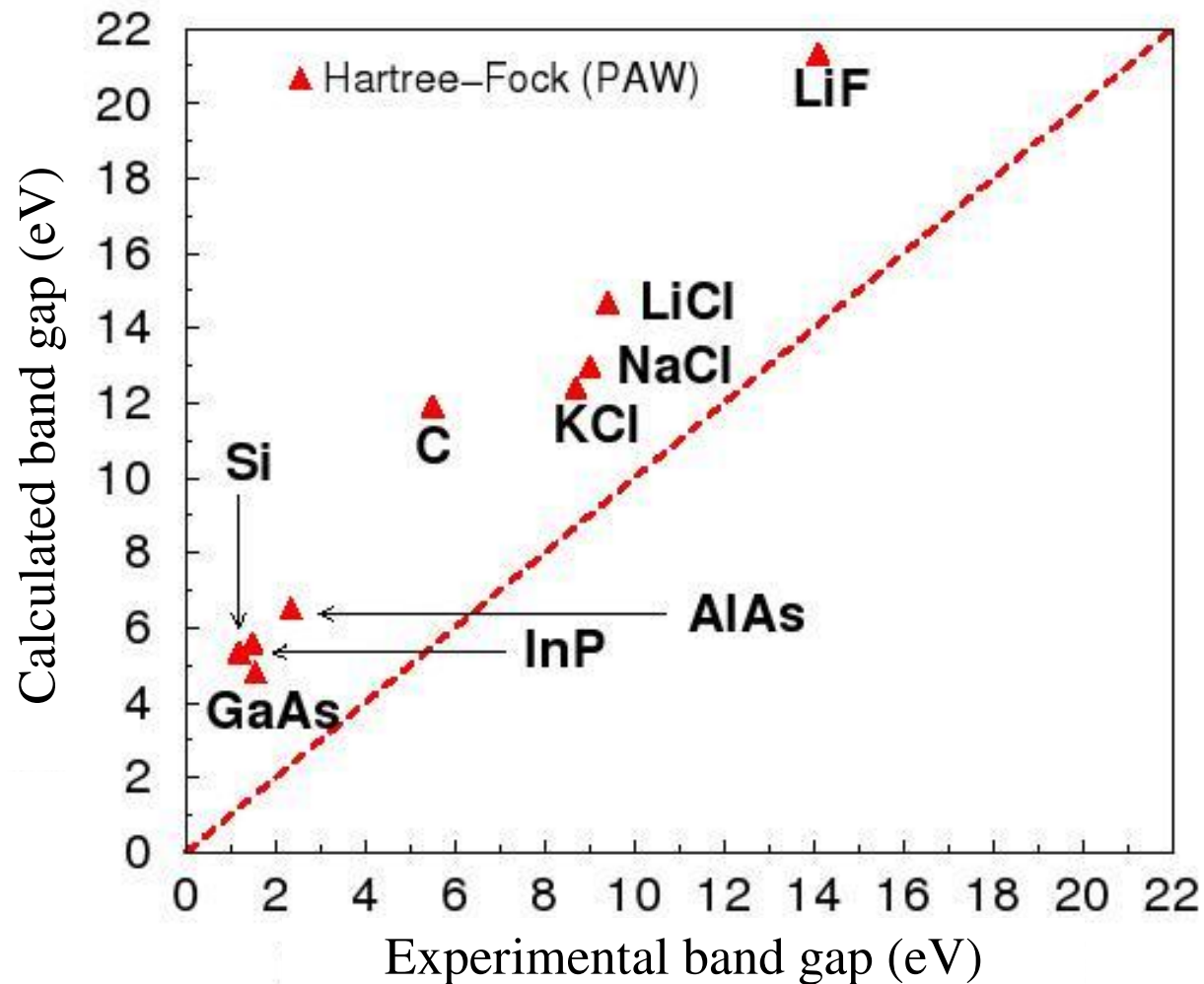


(*) HOMO energy computed with Gaussian03

[courtesy of Fabien Bruneval (CEA-DEN, Gif-sur-Yvette, France)]

Hartree-Fock approximation

- Band gap of semiconductors and insulators



[courtesy of Brice Arnaud (Université de Rennes, France)]

Post-Hartree-Fock methods

- **Configuration Interaction** (CI): the N -electrons wavefunction is approximated by a linear combination of Slater determinants (including 1-electron wavefunctions associated to excited states).
- **Coupled Cluster** (CC): the N -electrons wavefunction is obtained by applying an exponential of the excitation operator on the Slater determinant (hence producing a linear combination of excited Slater determinants).
- **Møller-Plasset** (MP): the N -electrons wavefunction is obtained by means of perturbation theory in terms of the correlation potential (i.e. the difference between the exact Hamiltonian and the one of Hartree-Fock approximation). The correlation potential does not contribute in first-order to the exact electronic energy. The higher-order terms are written on basis of doubly-excited Slater determinants (singly-excited do not contribute).

Density Functional Theory

Hohenberg-Kohn theorem

- Let us consider all possible Schrödinger equation for N_e electrons which only differ by the external potential $V_{\text{ext}}(\mathbf{r})$:

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \psi = E\psi$$

Hohenberg and **Kohn** have demonstrated that the electronic density of the ground-state $n(\mathbf{r})$ defined by:

$$n(\mathbf{r}) = N_e \int [\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})]^* \psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}) d\mathbf{r}_2 \dots d\mathbf{r}_{N_e}$$

determines uniquely the external potential $V_{\text{ext}}(\mathbf{r})$, modulo a global constant.

Hohenberg-Kohn theorem

- Lemma: Let us consider two local potentials $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$. Their ground-state wavefunctions may or may not be degenerate, but one wavefunction ψ cannot be common to both, except if the potentials differ only by a shift, or are identical everywhere (except at points of zero density - these points forming a set of measure zero).
- Indeed, the difference between the corresponding Schrödinger equations would imply that

$$\left(\sum_{i=1}^N [V_1(\mathbf{r}_i) - V_2(\mathbf{r}_i)] + \Delta E \right) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0$$

for each many-dimensional point (i.e. each configuration of electrons). Fixing the positions corresponding to the indices from 2 to N , one obtains that the difference between $V_1(\mathbf{r}_1)$ and $V_2(\mathbf{r}_1)$ must be a constant in space.

Hohenberg-Kohn theorem

- Let $\psi_1(\mathbf{r})$ the (or one of the) ground-state wavefunction(s) of \hat{H}_{V_1} , with associated charge density $n_1(\mathbf{r})$ and energy $E_1 = \langle \psi_1 | \hat{H}_{V_1} | \psi_1 \rangle$
 $\psi_2(\mathbf{r})$ the (or one of the) ground-state wavefunction(s) of \hat{H}_{V_2} , with associated charge density $n_2(\mathbf{r})$ and energy $E_2 = \langle \psi_2 | \hat{H}_{V_2} | \psi_2 \rangle$.
- Due to the variational principle, $E_1 = \langle \psi_1 | \hat{H}_{V_1} | \psi_1 \rangle < \langle \psi_2 | \hat{H}_{V_1} | \psi_2 \rangle$
- Here, a strict inequality holds, because ψ_2 cannot be one of the ground-state wavefunctions of \hat{H}_{V_1} (see previous slide) . The \hat{H}_{V_1} and \hat{H}_{V_2} Hamiltonians only differ by their one-electron local potential, so that

$$\langle \psi_2 | \hat{H}_{V_1} | \psi_2 \rangle = \underbrace{\langle \psi_2 | \hat{H}_{V_2} | \psi_2 \rangle}_{E_2} + \underbrace{\langle \psi_2 | \hat{H}_{V_1} - \hat{H}_{V_2} | \psi_2 \rangle}_{\int [V_1(\mathbf{r}) - V_2(\mathbf{r})] n_2(\mathbf{r}) d\mathbf{r}}$$

Hohenberg-Kohn theorem

- Finally, we have that:

$$E_1 < E_2 + \int [V_1(\mathbf{r}) - V_2(\mathbf{r})] n_2(\mathbf{r}) d\mathbf{r}$$

- With the same line of thought, interchanging 1 and 2, we get that:

$$E_2 < E_1 + \int [V_2(\mathbf{r}) - V_1(\mathbf{r})] n_1(\mathbf{r}) d\mathbf{r}$$

- Summing these two inequalities gives that:

$$0 < \int [V_2(\mathbf{r}) - V_1(\mathbf{r})] [n_1(\mathbf{r}) - n_2(\mathbf{r})] d\mathbf{r}$$

- Postulating $n_1(\mathbf{r})$ equal to $n_2(\mathbf{r})$ everywhere leads to $0 < 0$.

This is obviously wrong.

Hohenberg-Kohn theorem

- So, we have proven that the knowledge of the ground-state density defines the external potential up to a constant.
- The external potential is thus a functional of the ground-state density, as well as all the quantities that may be known formally once the potential is fixed modulo a global constant (for instance, the wavefunctions of the ground-state), hence the name of the theory (acronym: DFT).
- Moreover, if the arbitrary constant for the external potential is fixed through a simple condition (for instance, the potential goes to zero when the distance goes to infinity), the total electronic energy is also a functional of the density:

$$E = \langle \psi | \hat{H} | \psi \rangle = E[n]$$

Indeed, the Hamiltonian is uniquely defined by specifying the external potential, and its expectation value gives the total electronic energy.

Hohenberg-Kohn theorem

- Starting from the variational principle, it is possible to gain insight about this energy functional:

$$\begin{aligned} E &= \min_{\phi} \left\{ \langle \phi | \hat{H} | \phi \rangle \right\} = \min_n \left\{ \min_{\phi \rightarrow n} \left\{ \langle \phi | \hat{H} | \phi \rangle \right\} \right\} \\ &= \min_n \left\{ \min_{\phi \rightarrow n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} + \sum_{i=1}^{N_e} V_{\text{ext}}(\mathbf{r}_i) | \phi \rangle \right\} \right\} \\ &= \min_n \left\{ \min_{\phi \rightarrow n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} | \phi \rangle \right\} + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \right\} \\ &= \min_n \left\{ F[n] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \right\} \end{aligned}$$

where $F[n] = \min_{\phi \rightarrow n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} | \phi \rangle \right\}$ is a universal functional of the

density, but it is **not known explicitly**.

Kohn-Sham equation

- In fact, $F[n]$ represents an important part of the total electronic energy. It is thus critical to make a reasonable approximation for it in order to obtain a good value for $E[n]$
- **Kohn** and **Sham** tried to establish a connection with a system of non-interacting electrons with the same electronic density:

$$F[n] = \min_{\phi \rightarrow n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} | \phi \rangle \right\} \quad \longrightarrow \quad T_0[n] = \min_{\phi \rightarrow n} \left\{ \langle \phi | \hat{T}_e | \phi \rangle \right\}$$

The kinetic energy is a known functional $T_0[n]$ of the density.

Moreover, the functional for the associated Hartree energy is also known explicitly:

$$E_H[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

Kohn-Sham equation

- If these two pieces are subtracted from $F[n]$, the rest represents a much smaller part of the total electronic energy. This difference is called **exchange-correlation energy functional**:

$$E_{xc}[n] = F[n] - T_0[n] - E_H[n]$$

Indeed, it should contain an exchange term (see Hartree-Fock) and a correlation term. But, it also contains the difference between the kinetic energies of the systems of interacting and non-interacting electrons.

- Moreover, it is much easier to obtain a reasonable approximation for it (see below). Let us suppose that this functional is known.

Kohn-Sham equation

- The problem has now turned into minimizing the functional :

$$E[n] = T_0[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{\text{xc}}[n]$$

under constraint of a fixed number of electrons: $\int n(\mathbf{r})d\mathbf{r} = N_e$

- Introducing Lagrange multipliers, one has to solve:

$$\frac{\delta \left(E[n] - \lambda \left[\int n(\mathbf{r})d\mathbf{r} - N_e \right] \right)}{\delta n} = 0$$

$$\frac{\delta T_0[n]}{\delta n} + V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\text{xc}}[n]}{\delta n} = \lambda$$

Kohn-Sham equation

- This equation is strictly equivalent to that of a system of non-interacting electrons with the same electronic density in an external potential, called **Kohn-Sham potential**:

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \underbrace{\int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'}_{V_{\text{H}}(\mathbf{r})} + \underbrace{\frac{\delta E_{\text{xc}}[n]}{\delta n}}_{V_{\text{xc}}(\mathbf{r})}$$

where $V_{\text{xc}}(\mathbf{r})$ is the **exchange-correlation potential**.

- It is thus also equivalent to solve the 1-electron Schrödinger equation self-consistently:

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{KS}}(\mathbf{r}) \right] \phi_n^{\text{KS}}(\mathbf{r}) = \epsilon_n^{\text{KS}} \phi_n^{\text{KS}}(\mathbf{r})$$

with the electronic density $n(\mathbf{r}) = \sum_{i=1}^N |\phi_i^{\text{KS}}(\mathbf{r})|^2$

Kohn-Sham equation

- By construction, when self-consistency is reached, the electronic density and hence the total energy will be the exact ones (assuming the exchange-correlation functional to be exact).
- However, the Kohn-Sham wavefunctions and eigenenergies correspond to a fictitious set of independent electrons, so they do not correspond to any exact quantity.
- The solution of the Kohn-Sham self-consistent system of equations is equivalent to the minimization of

$$E[\{\phi_i\}] = \sum_i \left\langle \phi_i \left| -\frac{1}{2} \nabla^2 \right| \phi_i \right\rangle + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n]$$

under constraints of orthonormalization $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ for the occupied orbitals.

Local Density Approximation

- Let us come back to the problem of finding a reasonable approximation for the exchange-correlation energy functional.
- It is possible to show that this functional of the density can be written as the integral over the whole space of the density multiplied by the local exchange-correlation energy per electron:

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

- The Local Density Approximation (acronym: LDA), due to Kohn and Sham, consists in assuming that the local exchange-correlation energy per electron only depends on the local density and that it is equal to that of an homogeneous electron gas with the same density (in a neutralizing background – the “jellium”):

$$\varepsilon_{xc}^{LDA}(\mathbf{r}, n) = \varepsilon_{xc}^{\text{hom}}(n(\mathbf{r}))$$

Local Density Approximation

- The exchange part can be calculated analytically:

$$\varepsilon_x^{\text{hom}}(n(\mathbf{r})) = -\frac{3}{4\pi} \left[3\pi^2 n(\mathbf{r}) \right]^{1/3}$$

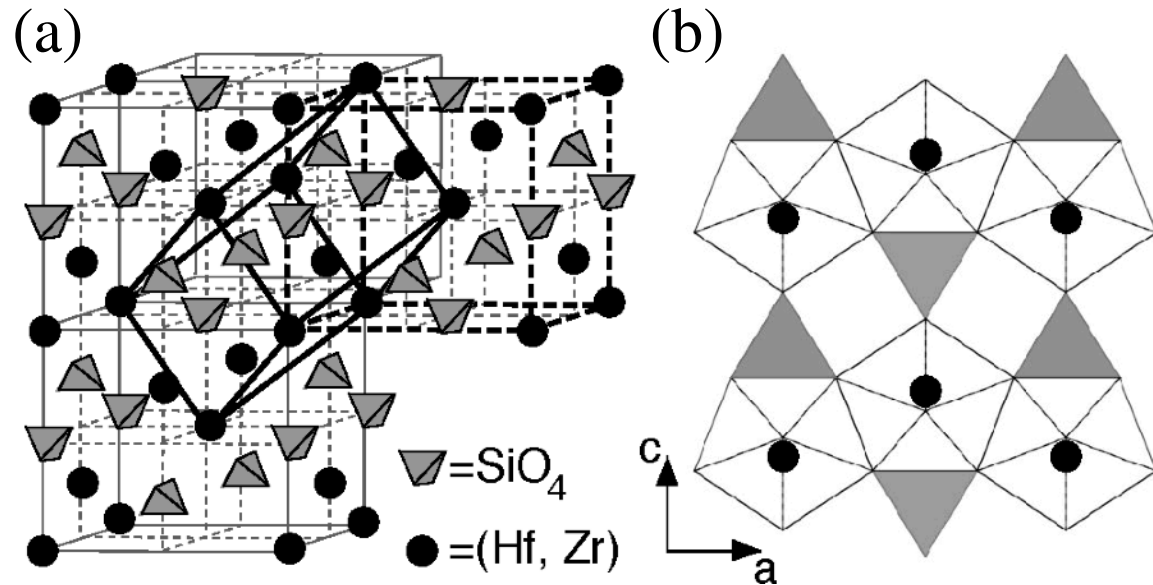
- The correlation part is obtained from accurate numerical simulations beyond DFT (e.g. Quantum Monte Carlo)

Local Density Approximation

- Globally, LDA works very well (hence, it is widely used).

Example: hafnon (HfSiO_4) / zircon (ZrSiO_4)

- body-centered tetragonal
- primitive cell with 2 formula units of MSiO_4
- alternating SiO_4 tetrahedra and MO_8 units, sharing edges to form chains parallel to $[0\ 0\ 1]$



- in the MO_8 units, four O atoms are closer to the Zr atoms than the four other ones
- O atoms are 3-fold coordinated

Local Density Approximation

- Globally, LDA works very well (hence, it is widely used).

Example: hafnon (HfSiO_4) / zircon (ZrSiO_4)

	HfSiO_4		ZrSiO_4	
	Th.	Expt.	Th.	Expt.
a	6.61	6.57	6.54	6.61
c	5.97	5.96	5.92	6.00
u	0.0672	0.0655	0.0645	0.0646
v	0.1964	0.1948	0.1945	0.1967
Volume	130.42	128.63	126.60	131.08
$d(\text{Si-O})$	1.62	1.61	1.61	1.62
$d(\text{M-O})$	2.14	2.10	2.10	2.13
	2.27	2.24	2.24	2.27
$\angle(\text{O-Si-O})$	97°	97°	97°	97°
	116°	117°	116°	116°

Lattice parameters are within 1 or 2% from the experimental values.

Beyond LDA

- However, in some particular cases (for instance, the hydrogen bond), it clearly shows its limits.
- Considerable efforts are dedicated to improving this approximation. One of the tracks that are pursued is to include a dependence on the gradients of the local density:

$$E_{xc}^{\text{approx}}[n] = \int n(\mathbf{r}) \varepsilon_{xc}^{\text{approx}} \left(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \nabla^2 n(\mathbf{r}) \right) d\mathbf{r}$$

This is the **generalized gradients approximation** (acronym: GGA).

- In this case, there is no model (such as the homogeneous electron gas) for which an analytic expression can be obtained.

Beyond LDA

- There exists a wide variety of GGA functionals which have been constructed trying to account for various sum rules (acronyms: PBE, PW86, PW91, LYP, ...).
- Another kind of approximation consists in obtaining a local form for the exchange potential by deriving the exchange term that appears in the Hartree-Fock approximation. This approach is referred to as **exact exchange** (acronym: EXX).
- Another approximation consists in suppressing the self-interaction which is present in the Hartree term (acronym: SIC).
- Finally, there are **hybrid functionals** which are obtained by mixing (using an empirically adjusted parameter) a part of exact exchange and an approximated part (acronyms: B3LYP, HSE, ...).

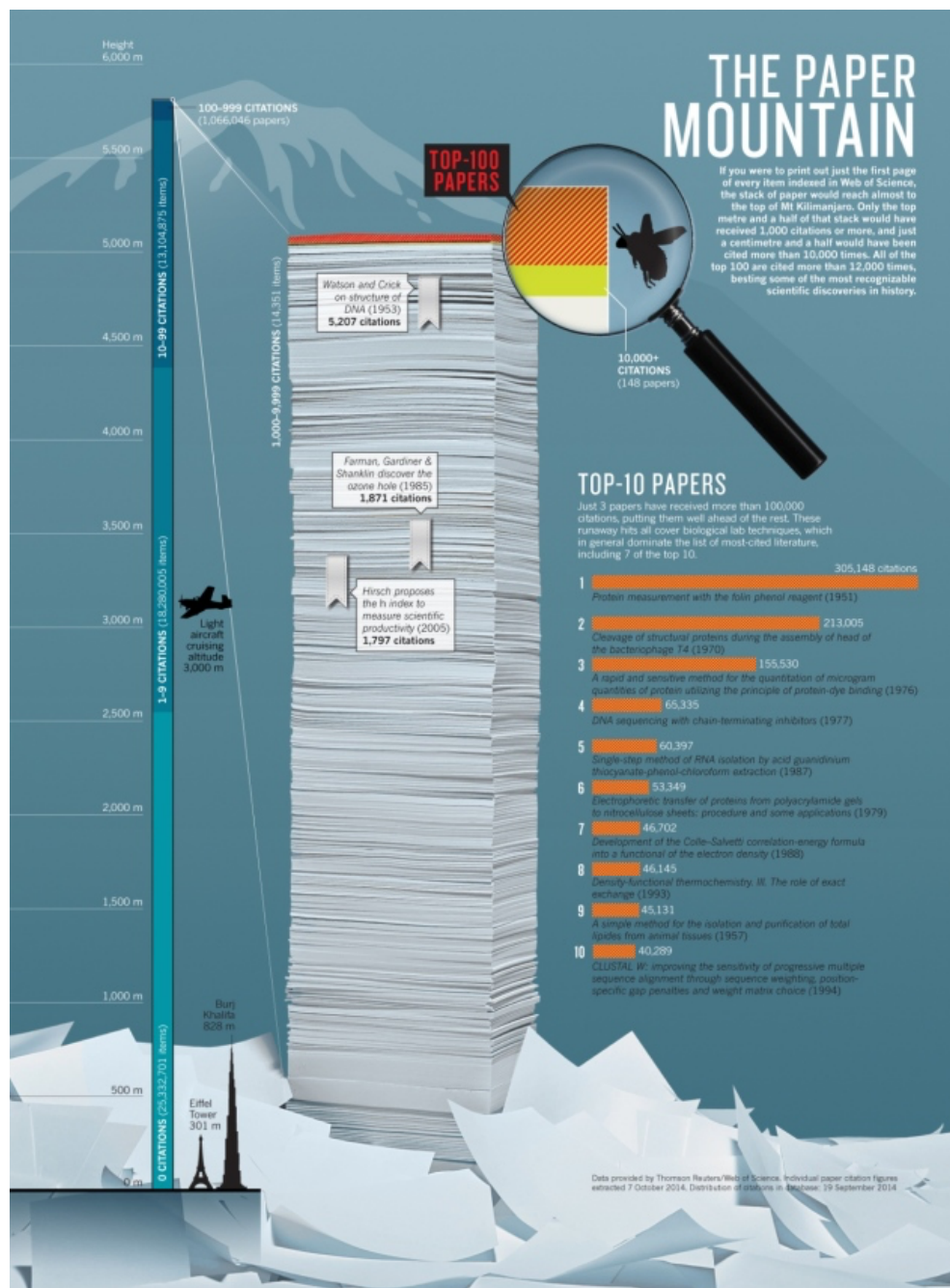
Importance of DFT

Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
<i>PR</i> 140, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
<i>PR</i> 136, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
<i>PRB</i> 23, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
<i>PRL</i> 45, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
<i>PR</i> 108, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
<i>PRL</i> 19, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
<i>PRB</i> 12, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
<i>PR</i> 124, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
<i>RMP</i> 57, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
<i>RMP</i> 54, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
<i>PRB</i> 13, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, *Physical Review*; *PRB*, *Physical Review B*; *PRL*, *Physical Review Letters*; *RMP*, *Reviews of Modern Physics*.

Importance of DFT



The top 100 papers

Nature explores the most-cited research of all time.

R. Van Noorden, B. Maher, & R. Nuzzo

(29 October 2014)

7. Lee, C., Yang, W. & Parr, R. G. Phys. Rev. B 37, 785–789 (1988). **46,702**
8. Becke, A. D. J. Chem. Phys. 98, 5648–5652 (1993). **46,145**
16. Perdew, J. P., Burke, K. & Ernzerhof, M. Phys. Rev. Lett. 77, 3865–3868 (1996). **35,405**
25. Becke, A. D. Phys. Rev. A 38, 3098–3100 (1988). **26,475**
34. Kohn, W. & Sham, L. J. Phys. Rev. 140, A1133 (1965). **23,059**
39. Hohenberg, P. & Kohn, W. Phys. Rev. B 136, B864 (1964). **21,931**
43. Kresse, G. & Furthmüller, J. Phys. Rev. B 54, 11169–11186 (1996). **18,856**
49. Monkhorst, H. J. & Pack, J. D. Phys. Rev. B 13, 5188–5192 (1976). **17,087**
77. Kresse, G. & Joubert, D. Phys. Rev. B 59, 1758–1775 (1999). **14,049**
85. Blöchl, P. E. Phys. Rev. B 50, 17953–17979 (1994). **13,330**
89. Kresse, G. & Furthmüller, J. Comput. Mater. Sci. 6, 15–50 (1996). **13,084**
93. Perdew, J. P. & Wang, Y. Phys. Rev. B 45, 13244–13249 (1992). **12,748**
96. Vosko, S. H., Wilk, L. & Nusair, M. Can. J. Phys. 58, 1200–1211 (1980). **12,583**

DFT and the band gap problem

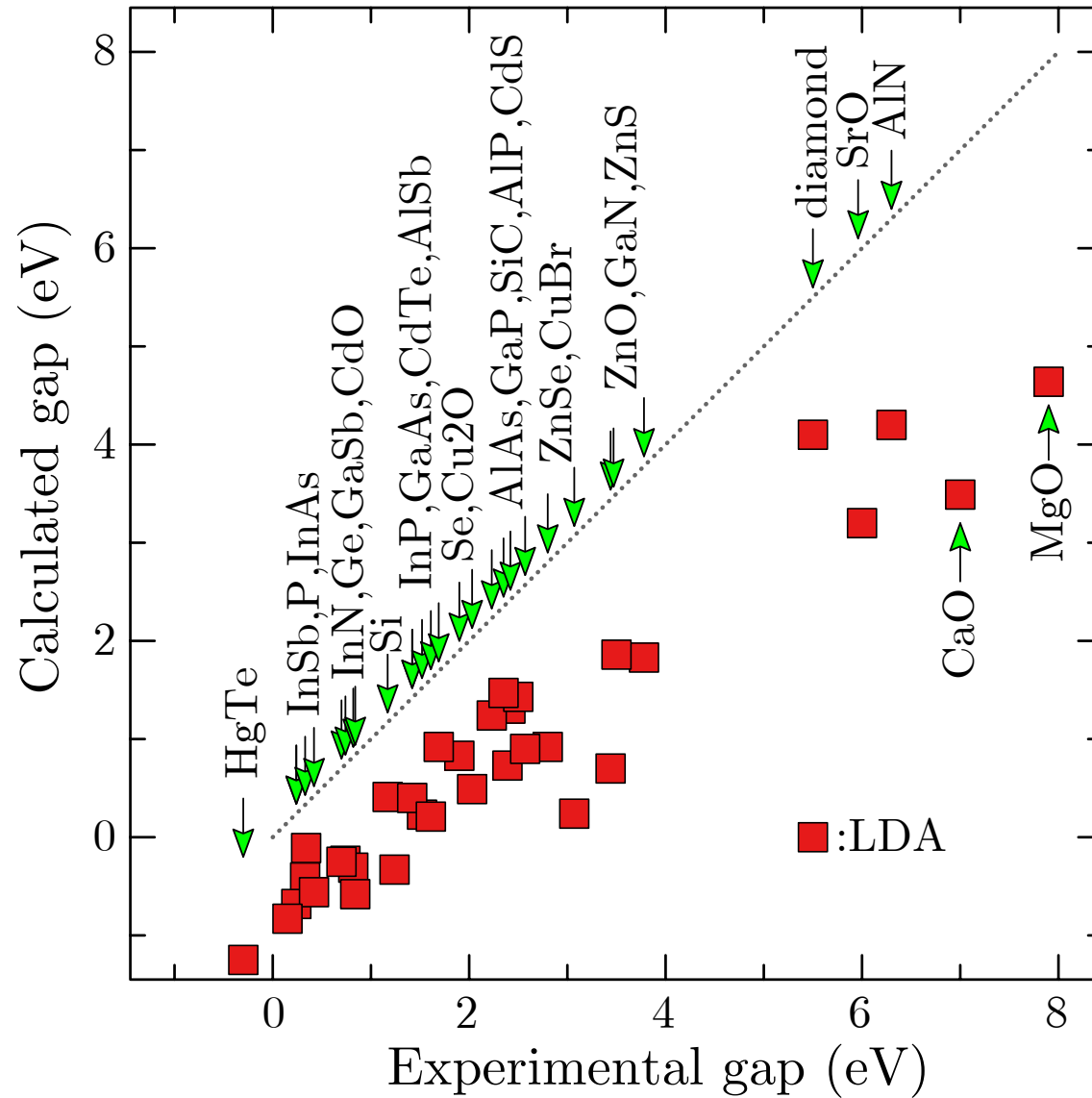
- The Density Functional Theory can (in principle) be used to compute exactly all the ground-state properties by solving the Kohn-Sham equation:

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \phi_{n\mathbf{k}}^{KS}(\mathbf{r}) = \epsilon_{n\mathbf{k}}^{KS} \phi_{n\mathbf{k}}^{KS}(\mathbf{r})$$

As already indicated, there is no direct physical interpretation for the Kohn-Sham eigenenergies (these are simply Lagrange multipliers).

- However, the electronic bandstructures obtained within DFT (LDA or GGA) are in quite good agreement with the experimental data. The most notable exception is the **band gap** which is **systematically underestimated** by 30-50% (or even 100%). This problem is related to the existence of a discontinuity in the derivative of the exchange-correlation potential functional.

DFT and the band gap problem



[adapted from van Schilfgaarde et al., PRL 96, 226402 (2006)]

DFT and the band gap problem

- In fact, the band gap can also be obtained from total energy differences
- The difference $E_{N+1,0} - E_{N,0}$ represents the minimum energy needed to add one electron to a system of N electrons.

It is the **electron affinity** (EA) :

$$\text{EA} = E_{N+1,0} - E_{N,0}$$

- The difference $E_{N,0} - E_{N-1,0}$ represents the minimum energy needed to remove one electron to a system of N electrons.

It is the **ionization energy** (IE) :

$$\text{IE} = E_{N,0} - E_{N-1,0}$$

DFT and the band gap problem

- It can be shown that $IE \leq EA$, so that if we define:

$$\begin{aligned}\varepsilon_g &= EA - IE \\ &= (E_{N+1,0} - E_{N,0}) - (E_{N,0} - E_{N-1,0})\end{aligned}$$

the quantity ε_g is positive.

- In an atomic or molecular system, we have:
IE (energy of HOMO) < EA (energy of LUMO).
- In a solid, we define the **chemical potential** μ such that:

$$IE \leq \mu \leq EA$$

In the thermodynamic limit ($N, V \rightarrow \infty$, with $N/V = \text{cst}$), we distinguish:

- metallic systems in which $\varepsilon_g = 0$ ($IE \simeq \mu \simeq EA$)
- insulating systems in which $\varepsilon_g > 0$ ($IE < \mu < EA$)

DFT and the band gap problem

- DFT can be extended to non-integer numbers of electrons by considering a zero temperature grand-canonical ensemble.
- For fractional numbers of electrons $N + \delta$ ($0 \leq \delta \leq 1$), the exact density and exact energy are given by ensemble averages of the integers from either side (N and $N + 1$):

$$n_{N+\delta}(\mathbf{r}) = (1 - \delta)n_N(\mathbf{r}) + \delta n_{N+1}(\mathbf{r})$$

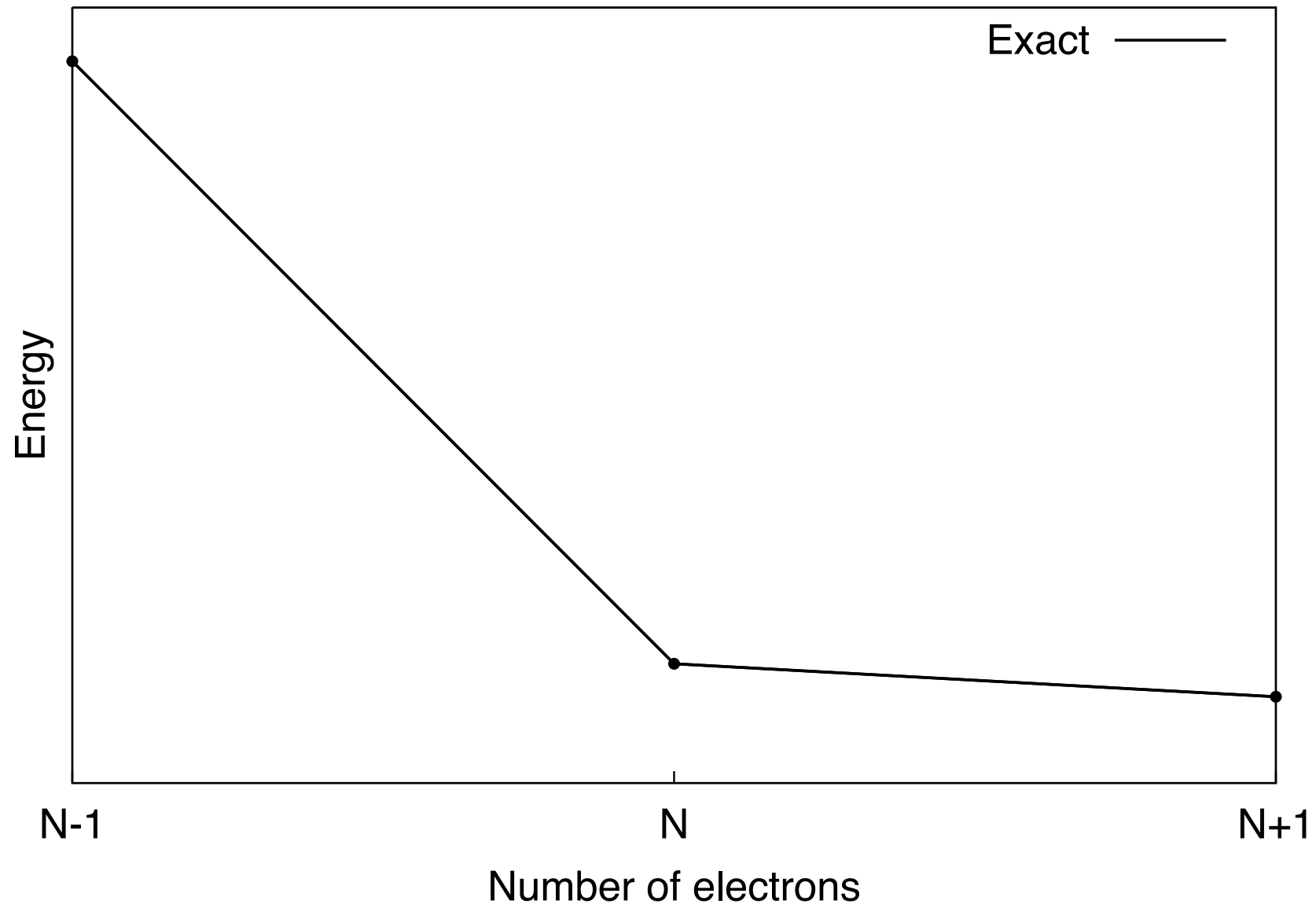
$$E_{N+\delta} = (1 - \delta)E_N + \delta E_{N+1}$$

$$\left. \frac{\partial E}{\partial N} \right|_{N-\delta} = \text{IE} \qquad \left. \frac{\partial E}{\partial N} \right|_{N+\delta} = \text{EA}$$

- The gap is thus related to the existence of a discontinuity in the derivative of the energy (and more precisely the exchange-correlation potential functional).

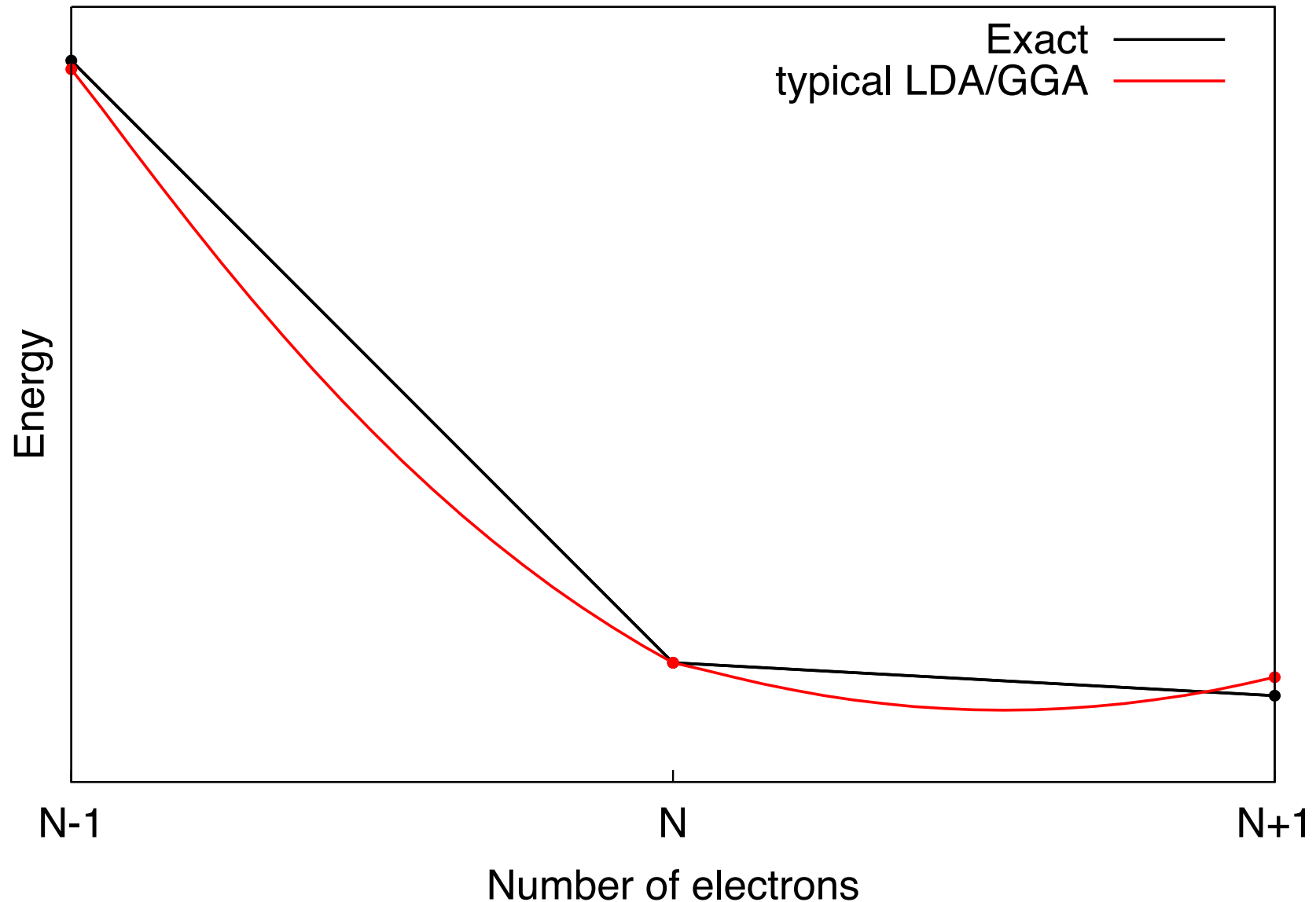
DFT and the band gap problem

- The exact DFT energy is discontinuous w.r.t. to the number of electrons



DFT and the band gap problem

- LDA or GGA often give good energies at integer number of electrons (esp. for finite systems) but have an incorrect convex behavior for $N + \delta$



Density Functional Theory

with ABINIT

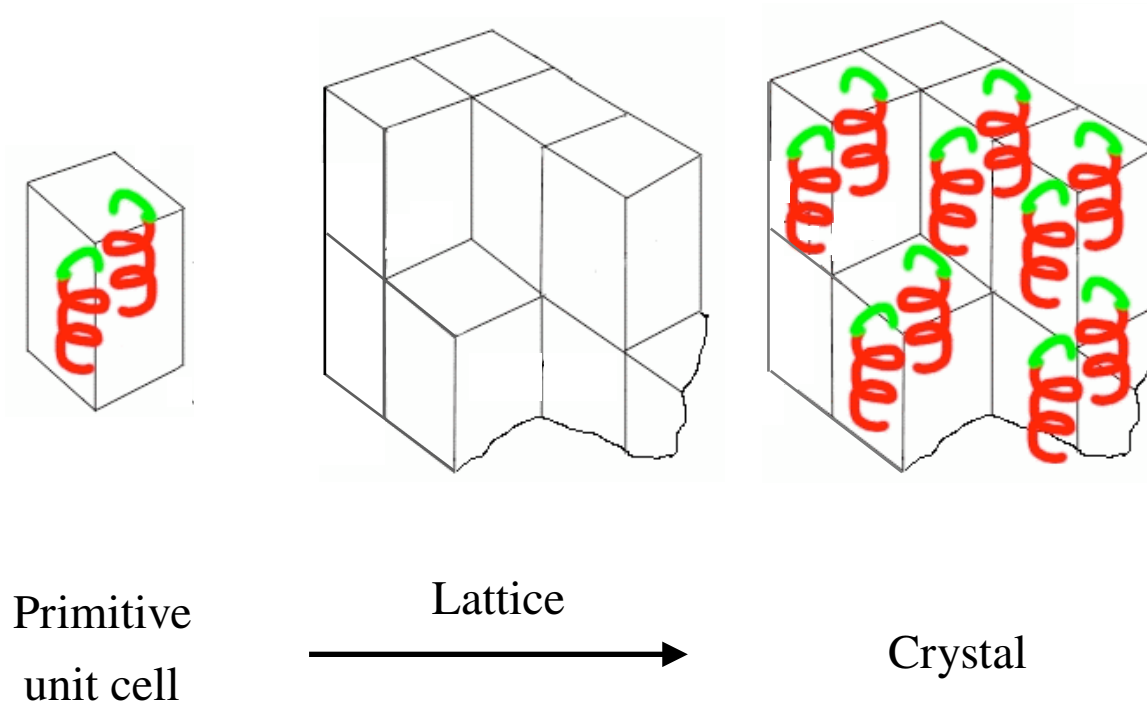
What is ABINIT?

- ABINIT is a package whose main program allows one to find the total energy, charge density and electronic structure of systems made of electrons and nuclei (molecules and periodic solids) within Density Functional Theory (DFT), using pseudopotentials and a plane-wave basis-set [...].
- ABINIT also includes options to optimize the geometry according to the DFT forces and stresses [...].
- Excited states can be computed within the Many-Body Perturbation Theory (the *GW* approximation and the Bethe-Salpeter equation) [...].
- ABINIT is a project that favors development and collaboration.

**Describing the structure
of the system to be investigated**

The primitive cell

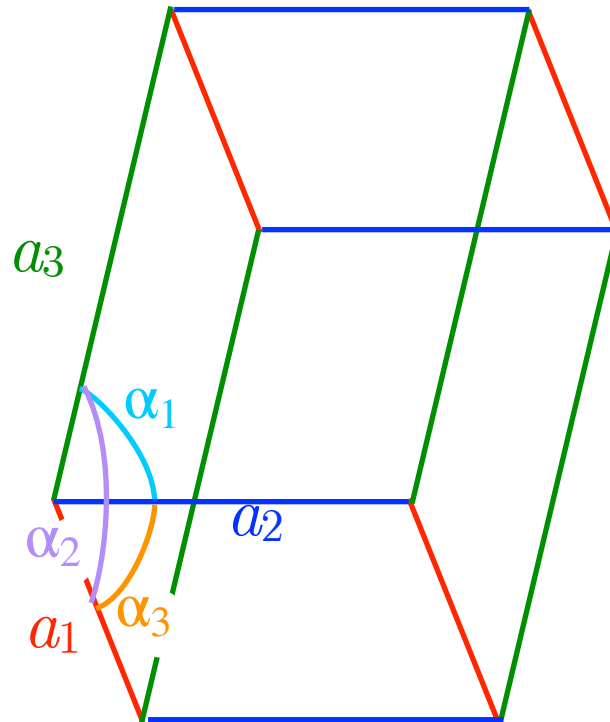
- A crystal is a solid in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating pattern (called the primitive cell) extending in all three spatial dimensions.



The lattice

- The lattice is defined by its primitive vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 which are independent and such that each point of the lattice can be written as:

$$\mathbf{R} = l \mathbf{a}_1 + m \mathbf{a}_2 + n \mathbf{a}_3 \text{ avec } l, m, n \in \mathbb{Z}$$



Primitive volume

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$

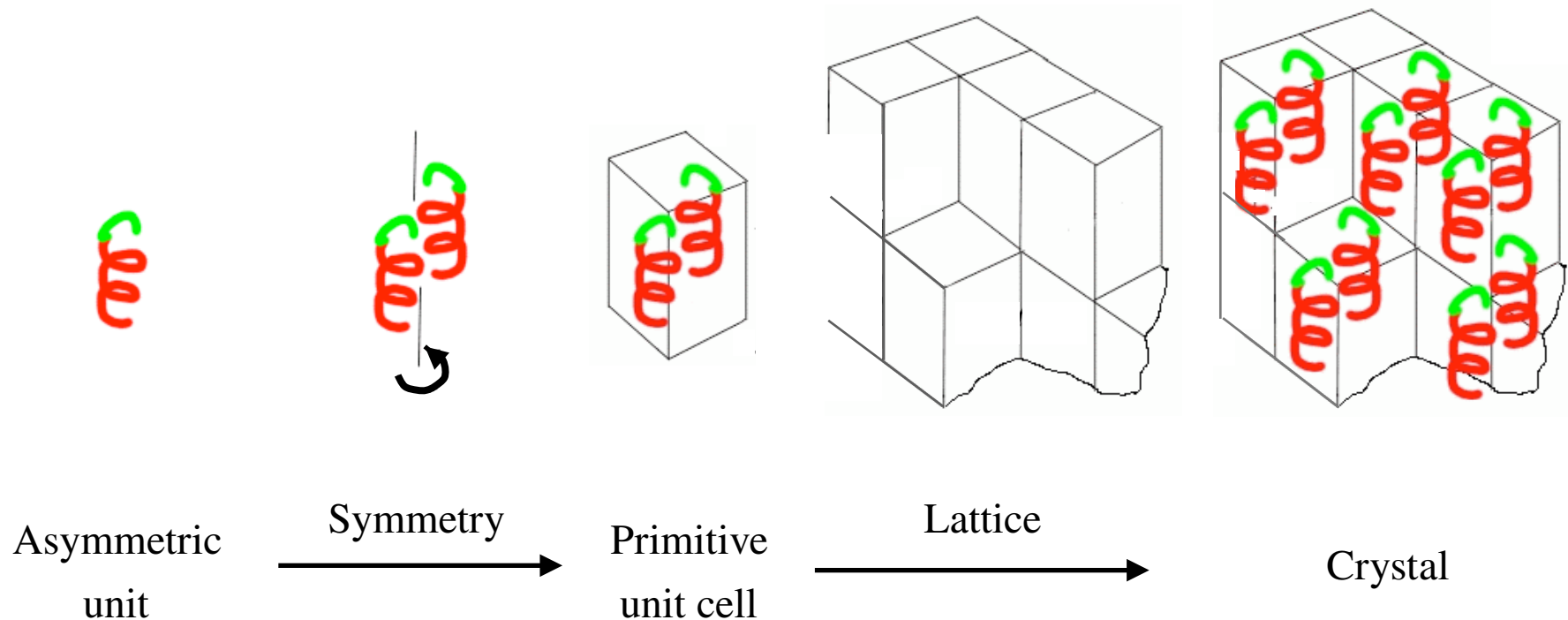
$$= \mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)$$

$$= \mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)$$

- Examples: triclinic ($a_1 \neq a_2 \neq a_3$ and $\alpha_1 \neq \alpha_2 \neq \alpha_3$)
cubic ($a_1 = a_2 = a_3$ and $\alpha_1 = \alpha_2 = \alpha_3 = 90^\circ$)

The asymmetric unit

- The asymmetric unit is the smallest part of the cell from which it is possible to built completely the primitive cell applying the symmetry operations of the system (space group).

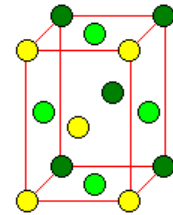


The primitive vectors in ABINIT

- $a_i(j) \rightarrow rprimd(j,i) = scalecart(j) \times rprim(j,i) \times acell(i)$

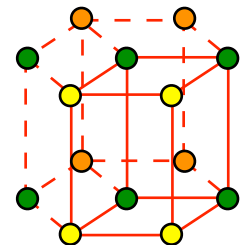
scalecart	9.5000000000E+00	9.8000000000E+00	1.0000000000E+01
rprim	0.0000000000E+00	5.0000000000E-01	5.0000000000E-01
	5.0000000000E-01	0.0000000000E+00	5.0000000000E-01
	5.0000000000E-01	5.0000000000E-01	0.0000000000E+00

face-centered
orthorhombic



acell	9.5000000000E+00	9.5000000000E+00	1.0000000000E+01
rprim	0.8660254038E+00	5.0000000000E-01	0.0000000000E+00
	-0.8660254038E+00	5.0000000000E-01	0.0000000000E+00
	0.0000000000E+00	0.0000000000E+00	1.0000000000E+00

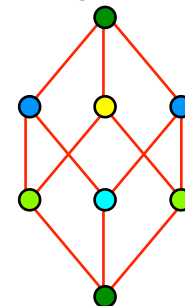
hexagonal



- $a_i \rightarrow acell(i) / \alpha_i \rightarrow angdeg(i)$

acell	9.5000000000E+00	9.5000000000E+00	1.0000000000E+01
angdeg	120 90 90		

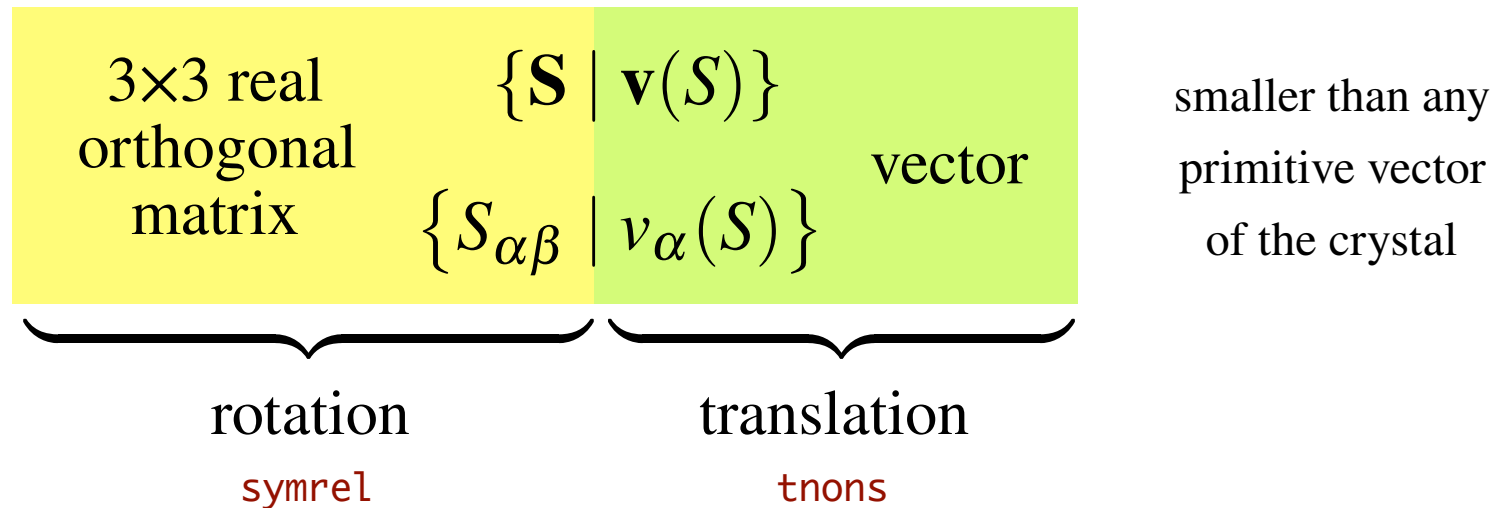
trigonal



acell	9.0000000000E+00	9.0000000000E+00	9.0000000000E+00
angdeg	48 48 48		

The symmetries in ABINIT

- We adopt the **Seitz notation** for the symmetry operations of the crystal:



- Applied to the equilibrium position vector of atom κ relative to the origin of the cell τ_{κ} , this symmetry transforms it as:

$$\{\mathbf{S} \mid \mathbf{v}(S)\} \tau_{\kappa} = \mathbf{S} \tau_{\kappa} + \mathbf{v}(S) = \tau_{\kappa'} + \mathbf{R}^a$$

$$\{S_{\alpha\beta} \mid v_{\alpha}(S)\} \tau_{\kappa\alpha} = S_{\alpha\beta} \tau_{\kappa\alpha} + v_{\alpha}(S) = \tau_{\kappa'\alpha} + R_{\alpha}^a$$

where \mathbf{R}^a is a translation vector of the crystal.

The atomic positions in ABINIT

- number of atoms → `natom`
- reduced coordinates → `xred`
- cartesian coordinates → `xcart` (in Bohr) / `xangst` (in Å)
- type of atoms → `typat`
- space group → `spgroup` + `natrd`
- number of symmetries → `nsym`
- symmetry operations → `symrel` + `tnons`

Example 1: c-ZrO₂

- with WPASSIGN on the Bilbao Crystallographic Server:

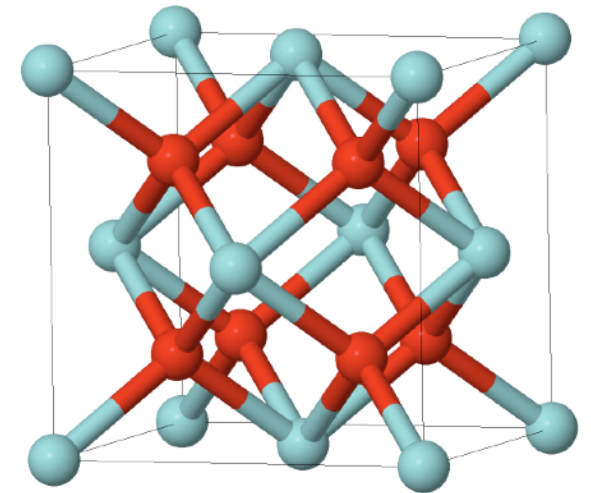
Bilbao Crystallographic Server → Assignment of Wyckoff Positions

Assignment of Wyckoff Positions

Atoms Data:

AT.	WP	SS	Representative	Atomic orbit
Zr1	4a (0,0,0)	m-3m	(0.000000,0.000000,0.000000)	(0.000000,0.000000,0.000000) (0.000000,0.500000,0.500000) (0.500000,0.000000,0.500000) (0.500000,0.500000,0.000000)
O2	8c (1/4,1/4,1/4)	-43m	(0.250000,0.250000,0.250000)	(0.250000,0.250000,0.250000) (0.750000,0.750000,0.250000) (0.750000,0.250000,0.750000) (0.250000,0.750000,0.750000) (0.250000,0.250000,0.750000) (0.750000,0.750000,0.750000) (0.250000,0.750000,0.250000) (0.750000,0.250000,0.250000)

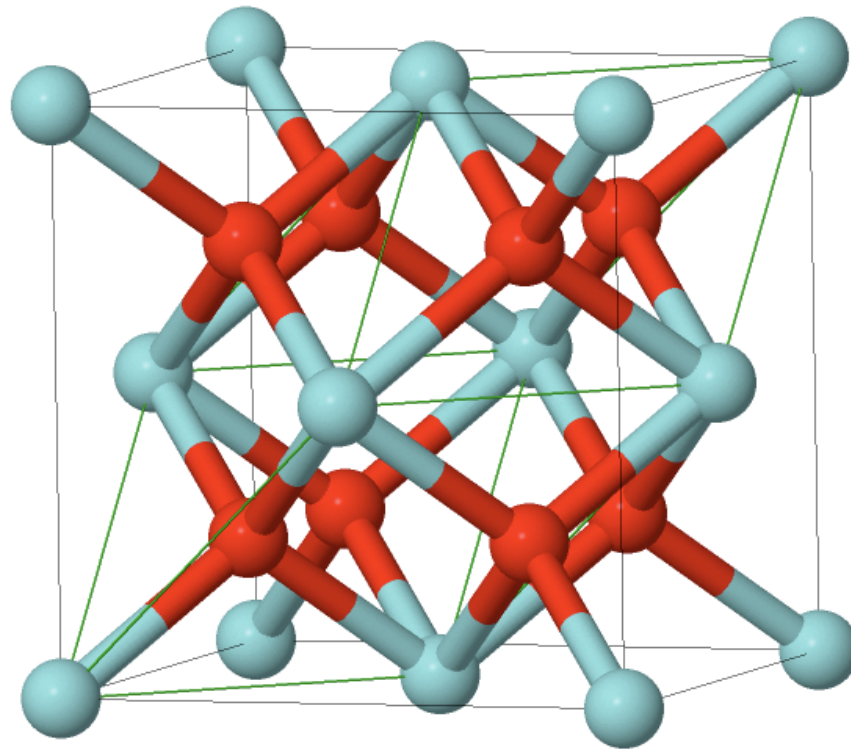
Fm-3m
a=5.010Å
b=5.010Å
c=5.010Å
α=90.0°
β=90.0°
γ=90.0°



Example 1: c-ZrO₂

- with ABINIT (input file):

```
natom      3
acell      5.0100000000E+00  5.0100000000E+00  5.0100000000E+00  ANGST
rprim      0.0000000000E+00  5.0000000000E-01  5.0000000000E-01
           5.0000000000E-01  0.0000000000E+00  5.0000000000E-01
           5.0000000000E-01  5.0000000000E-01  0.0000000000E+00
typat      1  2  2
xred       0.0000000000E+00  0.0000000000E+00  0.0000000000E+00
           2.5000000000E-01  2.5000000000E-01  2.5000000000E-01
           -2.5000000000E-01 -2.5000000000E-01 -2.5000000000E-01
```



Example 1: c-ZrO₂

- with ABINIT (output file):

Symmetries : space group Fm -3 m (#225); Bravais cF (face-center cubic)

spgroup 225

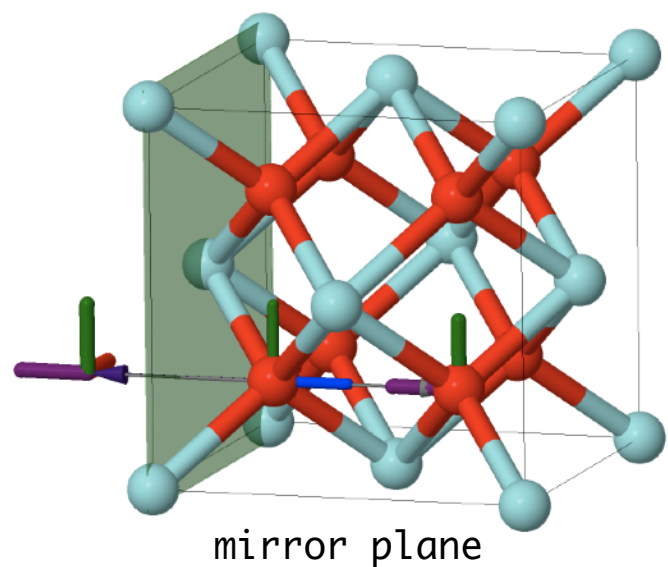
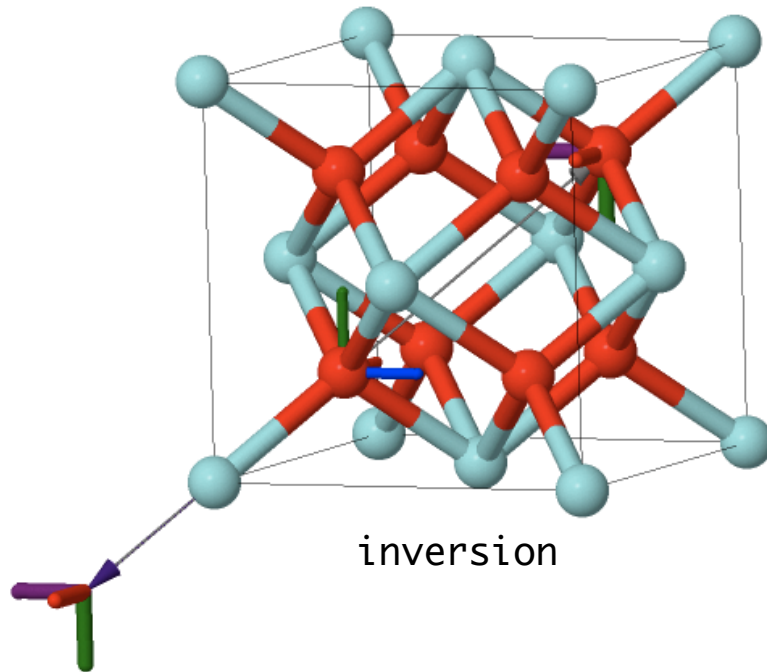
```
symrel 1 0 0 0 1 0 0 0 1 -1 0 0 0 0 -1
        0 -1 1 0 -1 0 1 -1 0 0 1 -1 0 -1 0
```

...

```
0 0 -1 1 0 -1 0 1 -1
-1 1 0 -1 0 1 -1 0 0
```

...

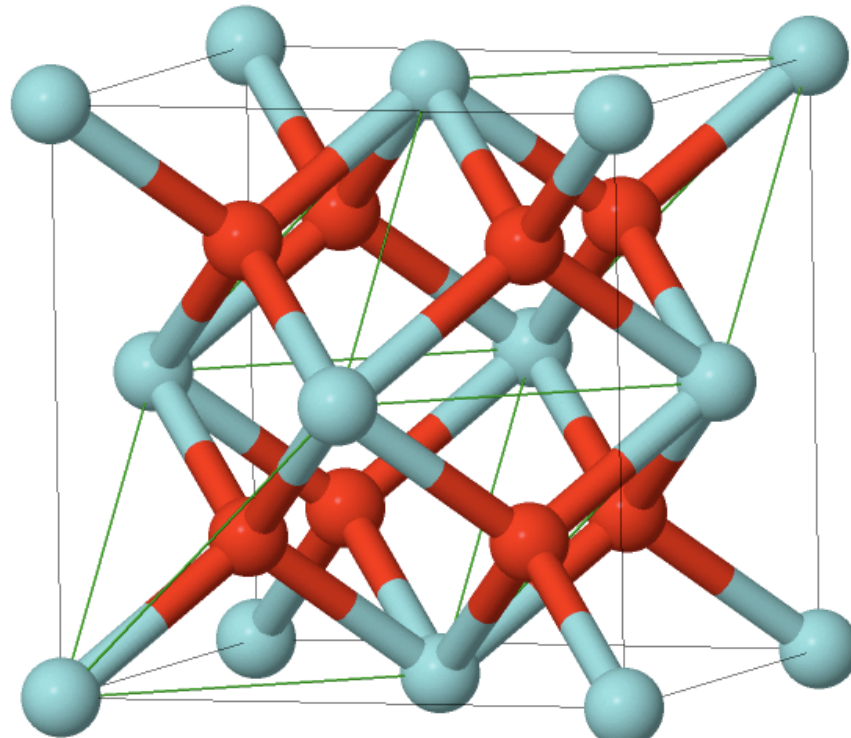
```
0 0 1 -1 0 1 0 -1 1
1 -1 0 1 0 -1 1 0 0
```



Example 1: c-ZrO₂

- with ABINIT (input file):

```
natom          3
acell    5.0100000000E+00  5.0100000000E+00  5.0100000000E+00  ANGST
rprim    0.0000000000E+00  5.0000000000E-01  5.0000000000E-01
         5.0000000000E-01  0.0000000000E+00  5.0000000000E-01
         5.0000000000E-01  5.0000000000E-01  0.0000000000E+00
typat      1  2  2
spgroup    225
natrd      2
xred       0.0000000000E+00  0.0000000000E+00  0.0000000000E+00
         2.5000000000E-01  2.5000000000E-01  2.5000000000E-01
```



Example 2: Si

- with WPASSIGN on the Bilbao Crystallographic Server:

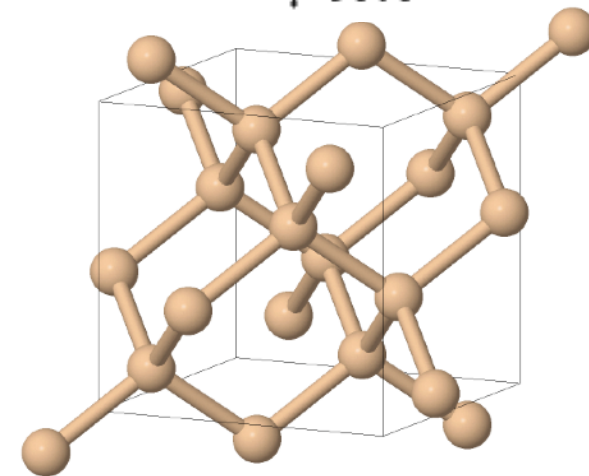
Bilbao Crystallographic Server → Assignment of Wyckoff Positions

Assignment of Wyckoff Positions

Atoms Data:

AT.	WP	SS	Representative	Atomic orbit
Si1	8a (1/8,1/8,1/8)	-43m	(0.125000,0.125000,0.125000)	(0.125000,0.125000,0.125000) (0.625000,0.125000,0.625000) (0.125000,0.625000,0.625000) (0.625000,0.625000,0.125000) (0.875000,0.375000,0.375000) (0.875000,0.875000,0.875000) (0.375000,0.375000,0.875000) (0.375000,0.875000,0.375000)

F d 3 m
 a=5.431Å
 b=5.431Å
 c=5.431Å
 $\alpha=90.0^\circ$
 $\beta=90.0^\circ$
 $\gamma=90.0^\circ$



```

natom      2
acell      5.4310000000E+00  5.4310000000E+00  5.4310000000E+00  ANGST
rprim      0.0000000000E+00  5.0000000000E-01  5.0000000000E-01
           5.0000000000E-01  0.0000000000E+00  5.0000000000E-01
           5.0000000000E-01  5.0000000000E-01  0.0000000000E+00
typat      1  1
xred       1.2500000000E-01  1.2500000000E-01  1.2500000000E-01
           8.7500000000E-01  8.7500000000E-01  8.7500000000E-01
    
```

Example 2: Si

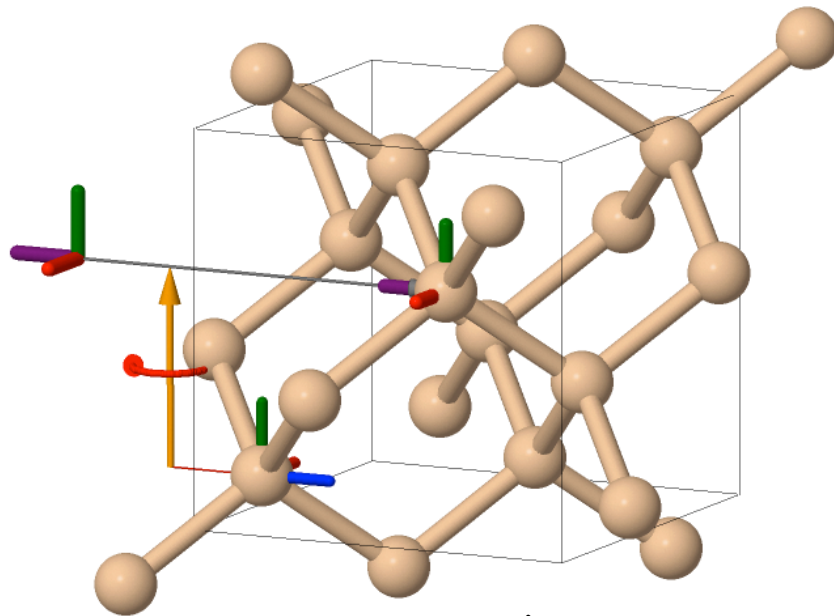
- with ABINIT (output file):

Symmetries : space group Fd -3 m (#227); Bravais cF (face-center cubic)

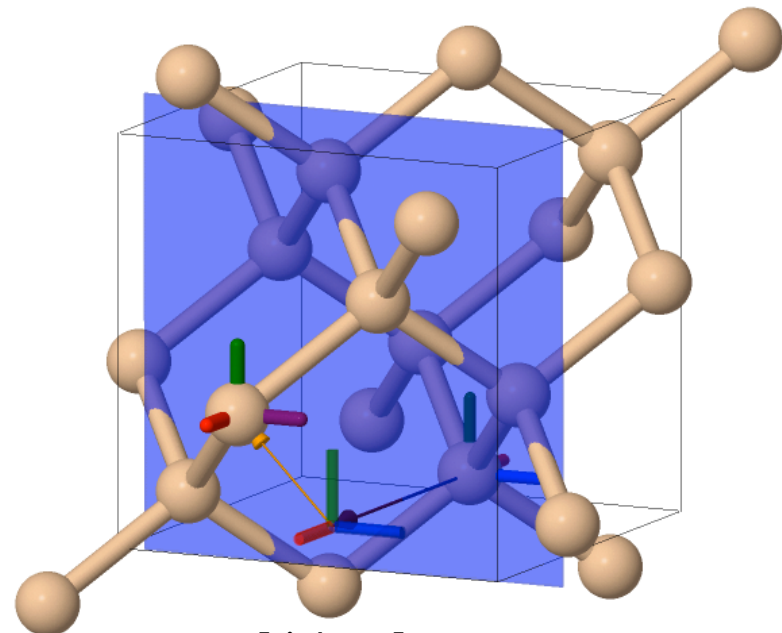
spgroup 227

symrel	1	0	0	0	1	0	0	0	1	-1	0	0	0	-1	0	0	0	-1
	0	-1	1	0	-1	0	1	-1	0	0	1	-1	0	1	0	-1	1	0
...										...								

tnons	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.5000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.5000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
...										...								



screw axis



glide plane

The plane-wave basis set

Treatment of periodic systems

- For periodic systems (with the lattice vectors \mathbf{R}), Bloch theorem's states:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r})$$

- If we define the reciprocal lattice (with the lattice vectors \mathbf{G}), such that:

$$e^{i\mathbf{G}\cdot\mathbf{R}} = 1$$

the periodic part of the Bloch's function can be written:

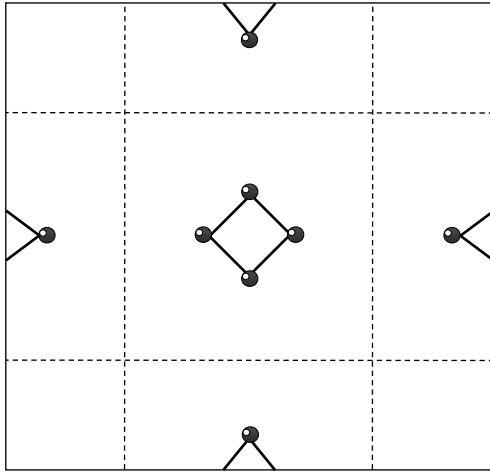
$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

where the coefficients $u_{n\mathbf{k}}(\mathbf{G})$ are obtained by a Fourier transform:

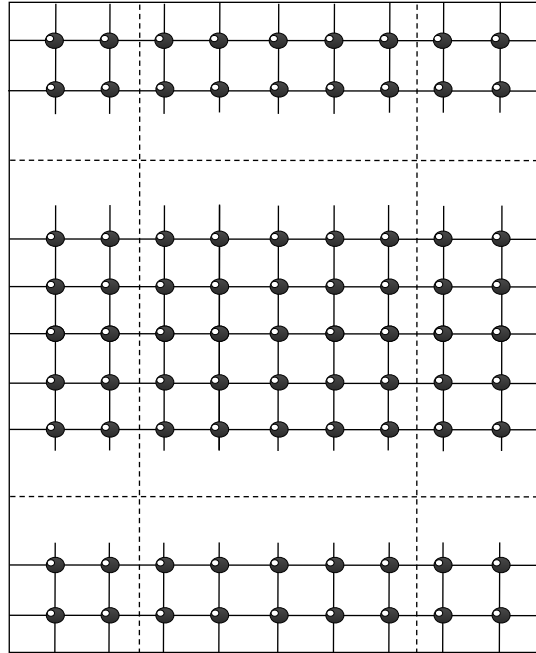
$$u_{n\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} u_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} d\mathbf{r} \quad \text{and} \quad \psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

The supercell technique for non-periodic systems

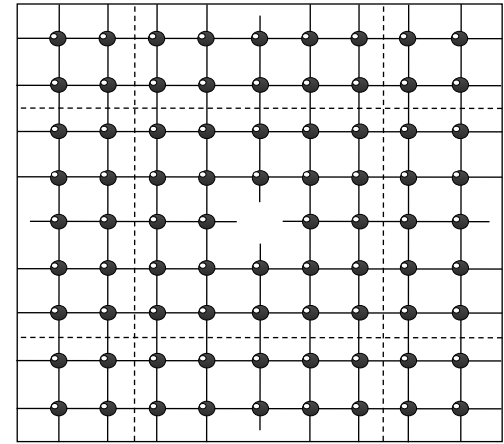
Molecule



Surface



Point defect in a bulk solid



The supercell must be sufficiently big : convergence study

Kinetic energy cut-off

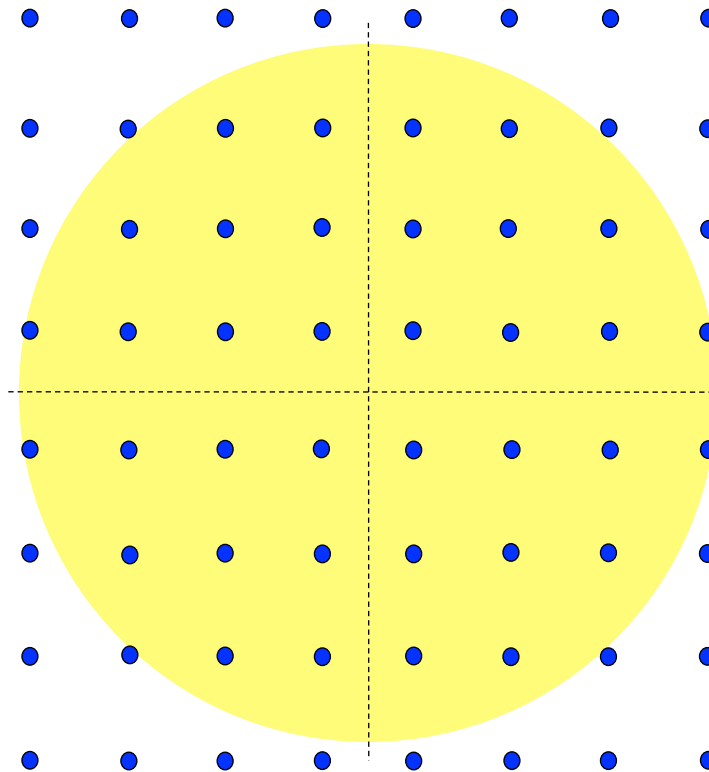
- The coefficients $u_{n\mathbf{k}}(\mathbf{G})$ for the lowest-energy eigenfunctions decrease exponentially with the kinetic energy $(\mathbf{k}+\mathbf{G})^2/2$.
- The plane-waves to be considered in the sum are selected using a kinetic energy cut-off E_{cut} (which defines the plane-wave sphere):

$$\frac{(\mathbf{k} + \mathbf{G})^2}{2} < E_{cut}$$

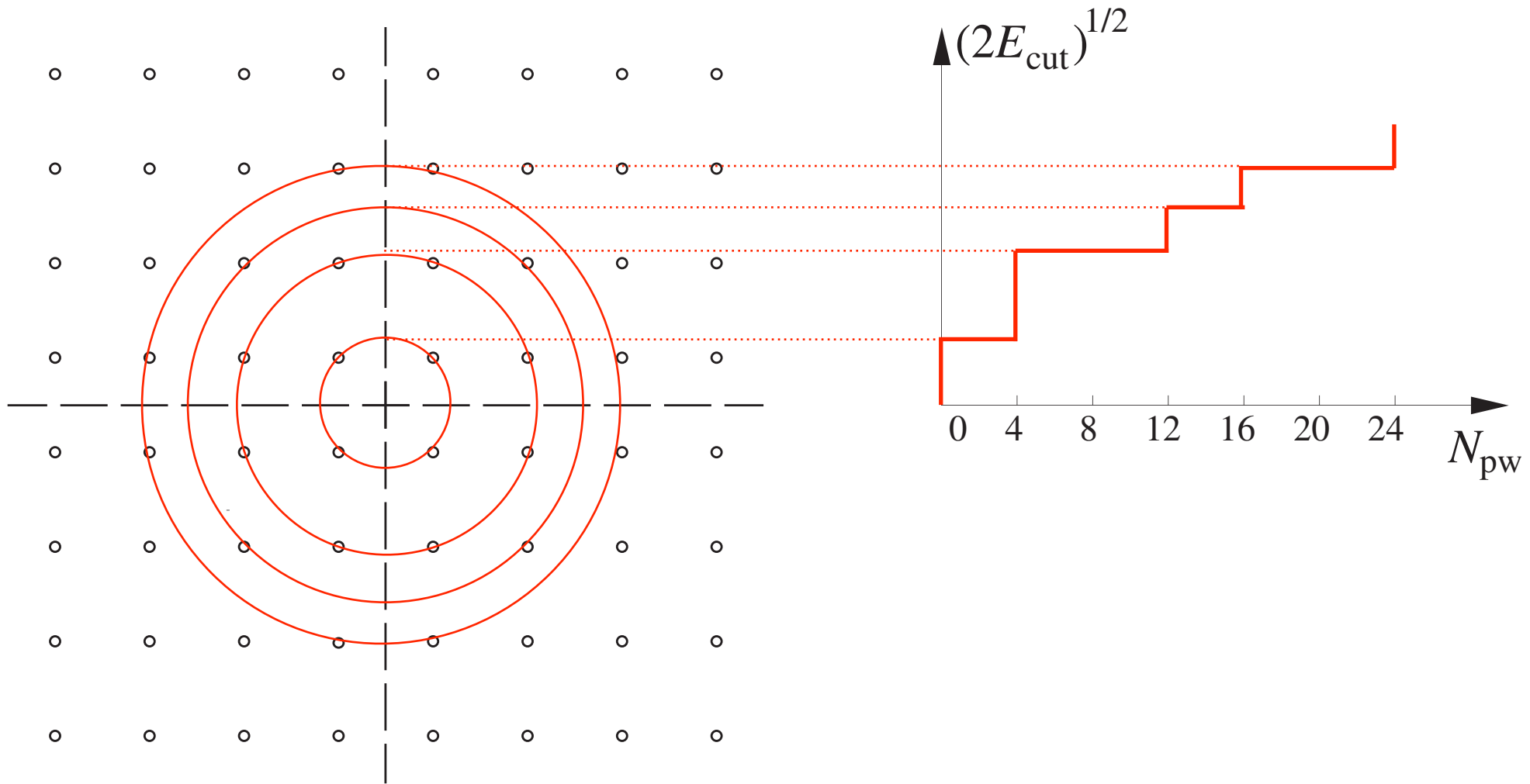
↑

$$-\frac{1}{2}\nabla^2 e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

ecut

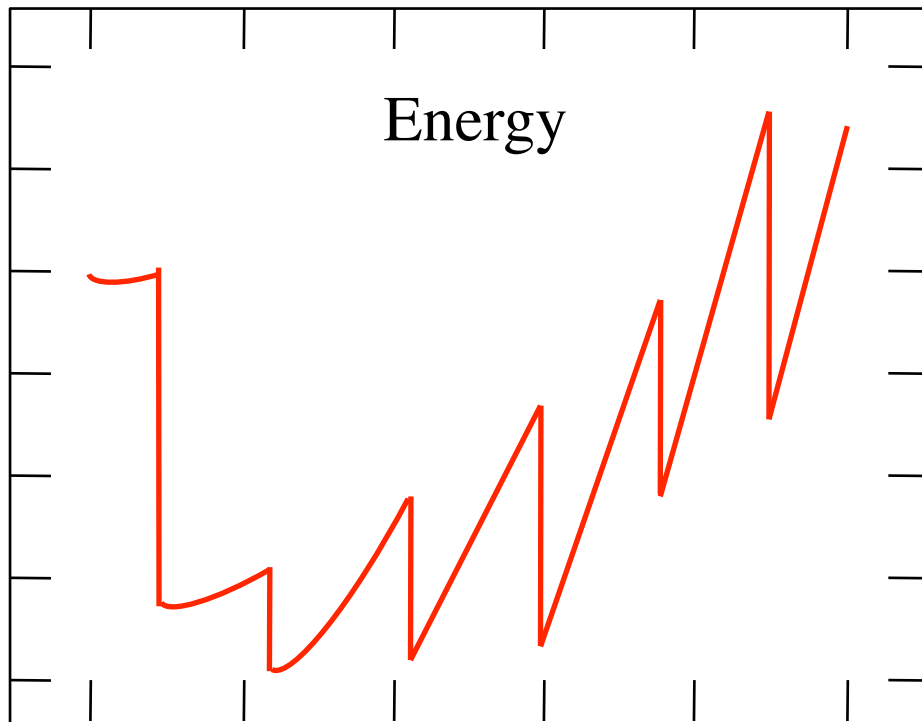


The number of plane-waves is not a continuous function of the cut-off energy...

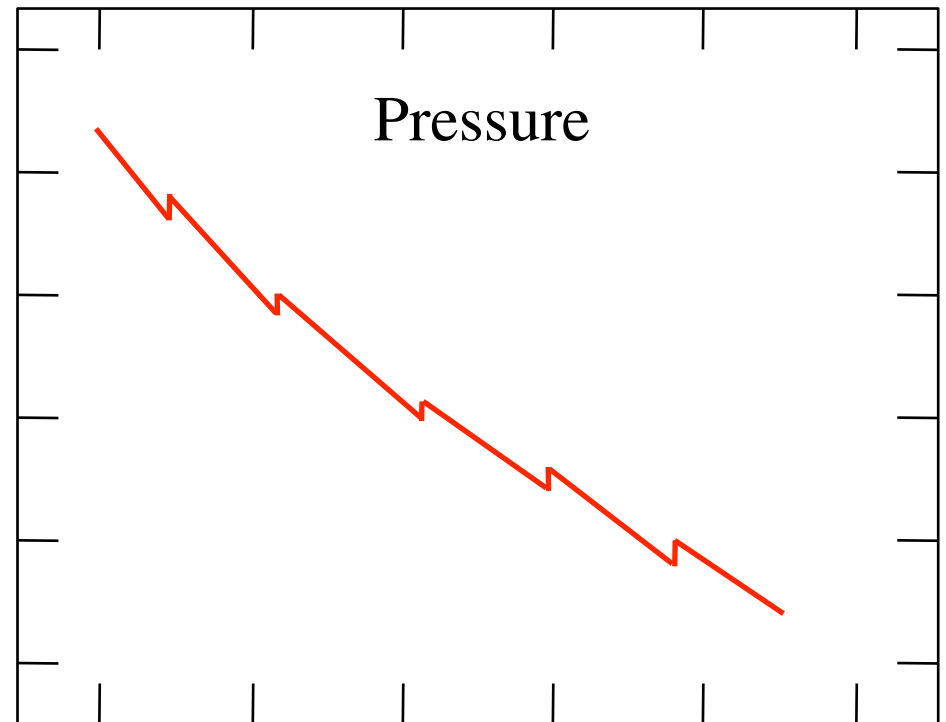


... nor it is as a function of the lattice parameter

There are discontinuities in the pressure and energy curves



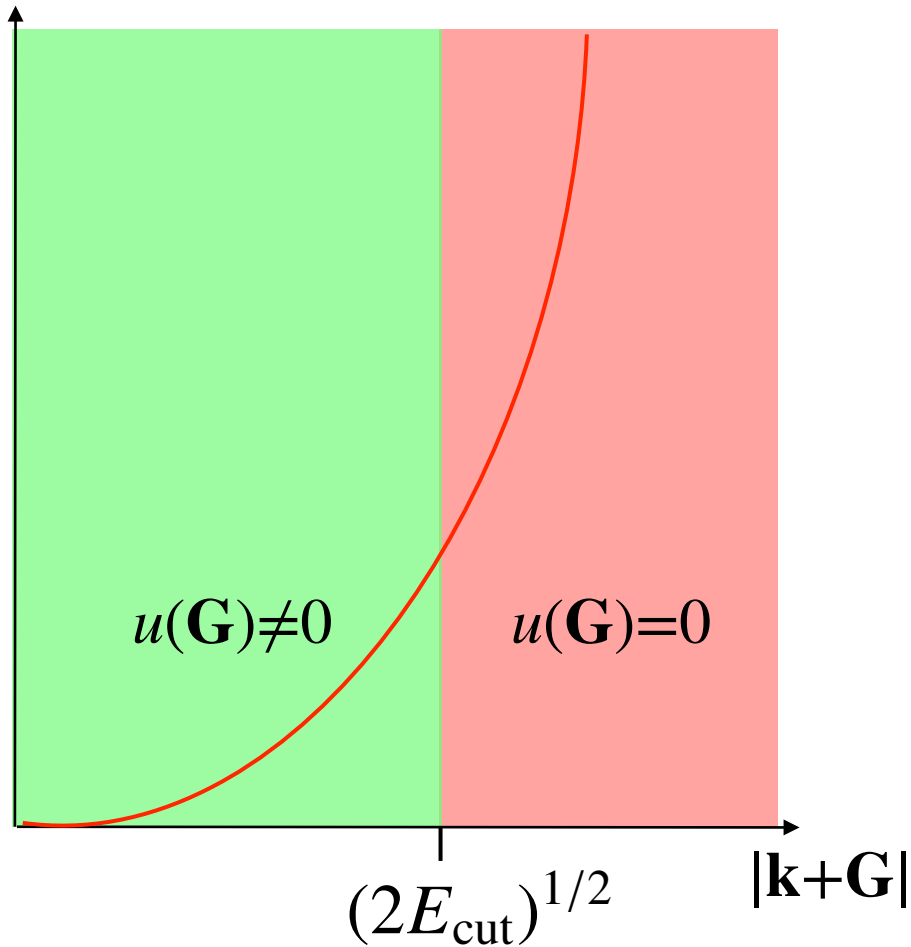
Lattice parameter



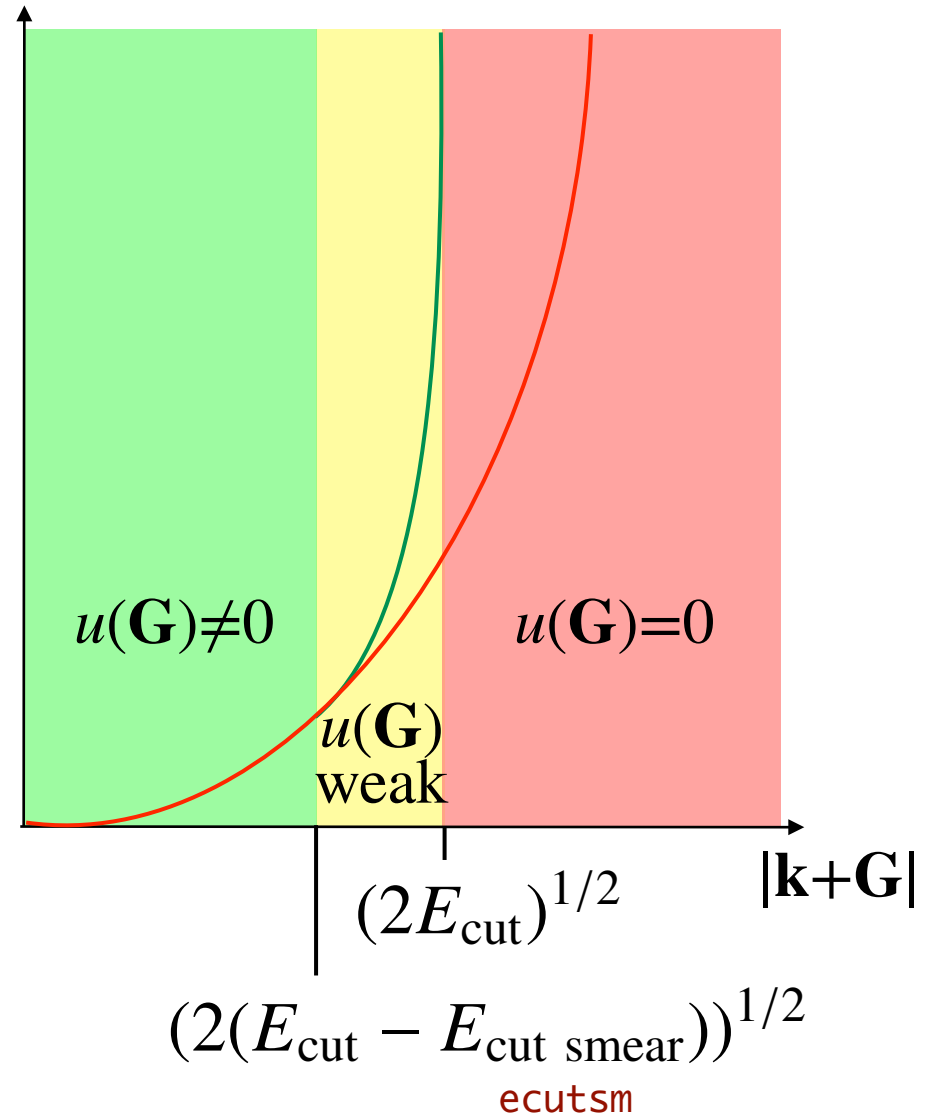
Lattice parameter

Removal of the discontinuities

Kinetic energy



Kinetic energy



Plane-waves are a natural and simple basis...

- The Fourier transform theory teaches us that:
 - details in real space are described if their characteristic length is larger than the inverse of the largest wave-vector norm (roughly speaking)
 - the quality of a plane wave basis set can be systematically increased by increasing the cut-off energy
- Problem: huge number of PWs is required to describe localized features (core orbitals, oscillations of other orbitals close to the nucleus)
- Pseudopotentials (or, in general, « pseudization ») are needed to eliminate the undesirable small wavelength features

Pseudopotentials

Core and valence electrons (I)

- Idea: Exploit the fact that core electrons occupy orbitals that are the « same » in the atomic environment or in the bonding environment
- Separation between core and valence orbitals for the density:

$$\begin{aligned}n(\mathbf{r}) &= \sum_i^N \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \\ &= \sum_{i \in \text{core}}^{N_{\text{core}}} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) + \sum_{i \in \text{val}}^{N_{\text{val}}} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})\end{aligned}$$

- « Frozen core » approximation: for $i \in \text{core}$: $\psi_i(\mathbf{r}) = \psi_i^{\text{atom}}(\mathbf{r})$
This approximation obviously influences the accuracy of the calculation !

Small / large core

- It depends on the target accuracy of the calculation !
- For some elements, the core/valence partitioning is obvious:

F atom: $1s^2$ $2s^2 2p^5$
IP 1keV 10-100 eV

- For some others, it is not:

Ti atom: $1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2 3d^2$ small core
 $1s^2 2s^2 2p^6 3s^2 3p^6$ $4s^2 3d^2$ large core
IP 99.2 eV 43.3eV

- Gd atom: small core with $n=1,2,3$ shells, might include $4s$, $4p$, and $4d$ in the core, $4f$ partially filled

Core and valence electrons (II)

- Separation between core and valence orbitals for the energy:

$$E_{\text{KS}} [\{\psi_i\}] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}} [n]$$

$$\begin{aligned} E_{\text{KS}} [\{\psi_i\}] &= \sum_{i \in \text{core}}^{N_{\text{core}}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n_{\text{core}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n_{\text{core}}(\mathbf{r}_1) n_{\text{core}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &+ \sum_{i \in \text{val}}^{N_{\text{val}}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n_{\text{val}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n_{\text{val}}(\mathbf{r}_1) n_{\text{val}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &+ \int \frac{n_{\text{val}}(\mathbf{r}_1) n_{\text{core}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}} [n_{\text{core}} + n_{\text{val}}] \end{aligned}$$

- One needs an expression for the energy of the valence electrons ...

Valence electrons in a screened potential

- The potential of the nuclei κ is screened by the core electrons:

$$V_{\text{ion},\kappa}(\mathbf{r}) = -\frac{Z_{\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \int \frac{n_{\text{core},\kappa}(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1$$

$$V_{\text{ion},\kappa}(\mathbf{r}) = -\frac{Z_{\text{val},\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \left(-\frac{Z_{\text{core},\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \int \frac{n_{\text{core},\kappa}(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 \right)$$

- The total energy becomes

$$E = \left(E_{\text{val}} + \sum_{\kappa} E_{\text{core},\kappa} \right) + \frac{1}{2} \sum_{\substack{(\kappa, \kappa') \\ \kappa \neq \kappa'}} \frac{Z_{\text{val},\kappa} Z_{\text{val},\kappa'}}{|\mathbf{R}_{\kappa} - \mathbf{R}_{\kappa'}|}$$

$$\text{with } E_{\text{val,KS}}[\{\psi_i\}] = \sum_{i \in \text{val}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int \left(\sum_{\kappa} V_{\text{ion},\kappa}(\mathbf{r}) \right) n_{\text{val}}(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \int \frac{n_{\text{val}}(\mathbf{r}_1) n_{\text{val}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n_{\text{core}} + n_{\text{val}}]$$

Non-linear XC
core correction

Removing core electrons (I)

- The valence orbitals must still be orthogonal to core orbitals
⇒ oscillations, slope at the nucleus, ...
- Pseudopotentials try to remove completely the core orbitals from the simulation by removing the strong changes within a « cut-off radius »

($r < r_{\text{cut}}$):

$$\left(-\frac{1}{2}\nabla^2 + V\right) |\psi_i\rangle = \epsilon_i |\psi_i\rangle$$

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{ps}}\right) |\psi_i^{\text{ps}}\rangle = \epsilon_i^{\text{ps}} |\psi_i^{\text{ps}}\rangle$$

with $V_{\text{ps}}(\mathbf{r})$ smooth for $r < r_{\text{cut}}$ and $V_{\text{ps}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r})$ for $r \geq r_{\text{cut}}$

$\psi_i^{\text{ps}}(\mathbf{r})$ smooth for $r < r_{\text{cut}}$ and $\psi_i^{\text{ps}}(\mathbf{r}) = \psi_i(\mathbf{r})$ for $r \geq r_{\text{cut}}$

$$\frac{d\psi_i^{\text{ps}}(\mathbf{r})}{d\mathbf{r}} = \frac{d\psi_i(\mathbf{r})}{d\mathbf{r}} \text{ for } r = r_{\text{cut}} \text{ and } \epsilon_i^{\text{ps}} = \epsilon_i$$

Removing core electrons (II)

- Various conditions can be imposed: e.g. norm conservation

[D.R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979)]

$$\int_{r < r_{\text{cut}}} |\psi_i^{\text{ps}}(\mathbf{r})|^2 d\mathbf{r} = \int_{r < r_{\text{cut}}} |\psi_i(\mathbf{r})|^2 d\mathbf{r}$$

- The general form of pseudopotential acts on the wavefunctions as follows:

$$\langle \mathbf{r} | V_{\text{ps}} | \psi \rangle = \int v_{\text{ps}}(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}'$$

kernel

with

$$v_{\text{ps}}(\mathbf{r}, \mathbf{r}') = v_{\text{loc}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') + v_{\text{NL}}(\mathbf{r}, \mathbf{r}')$$

and

$$v_{\text{NL}}(\mathbf{r}, \mathbf{r}') = \sum_{l,m} Y_{l,m}^*(\theta, \phi) v_{\text{NL},l}(r, r') Y_{l,m}(\theta', \phi')$$

Forms of pseudopotentials

- The most widely used pseudopotentials belong to two different classes:
 - the semi-local pseudopotentials for which:

$$v_{\text{NL},l}(r, r') = v_{\text{SL},l}(r)\delta(r - r')$$

[G.B. Bachelet, D.R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982)]

- the separable pseudopotentials for which:

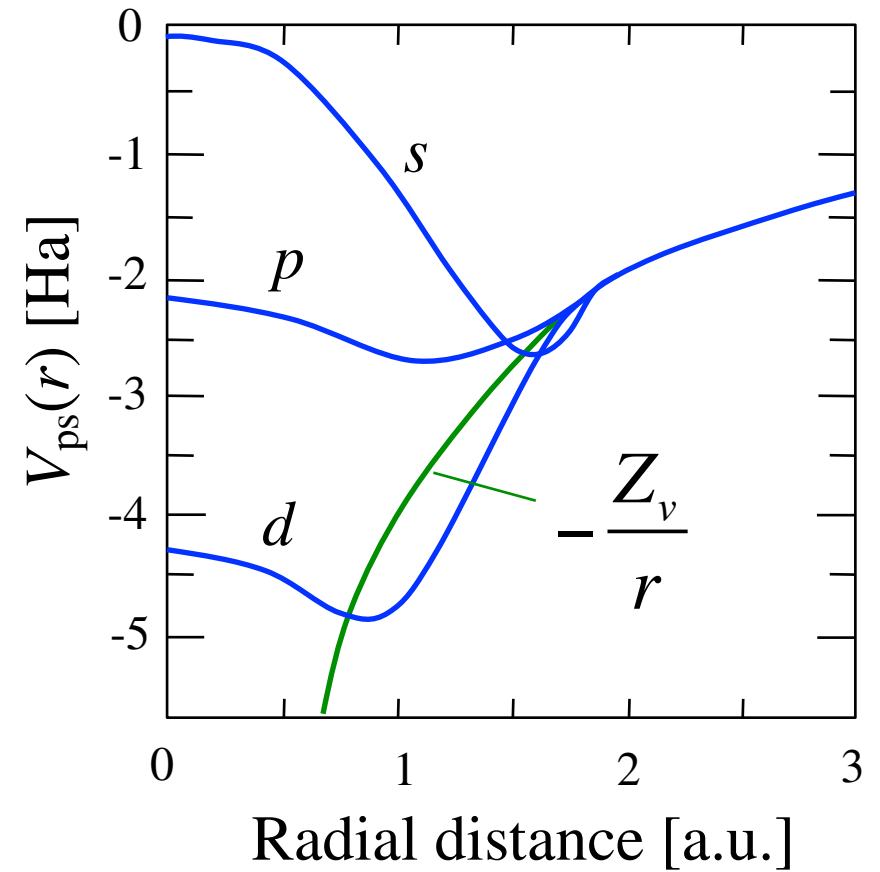
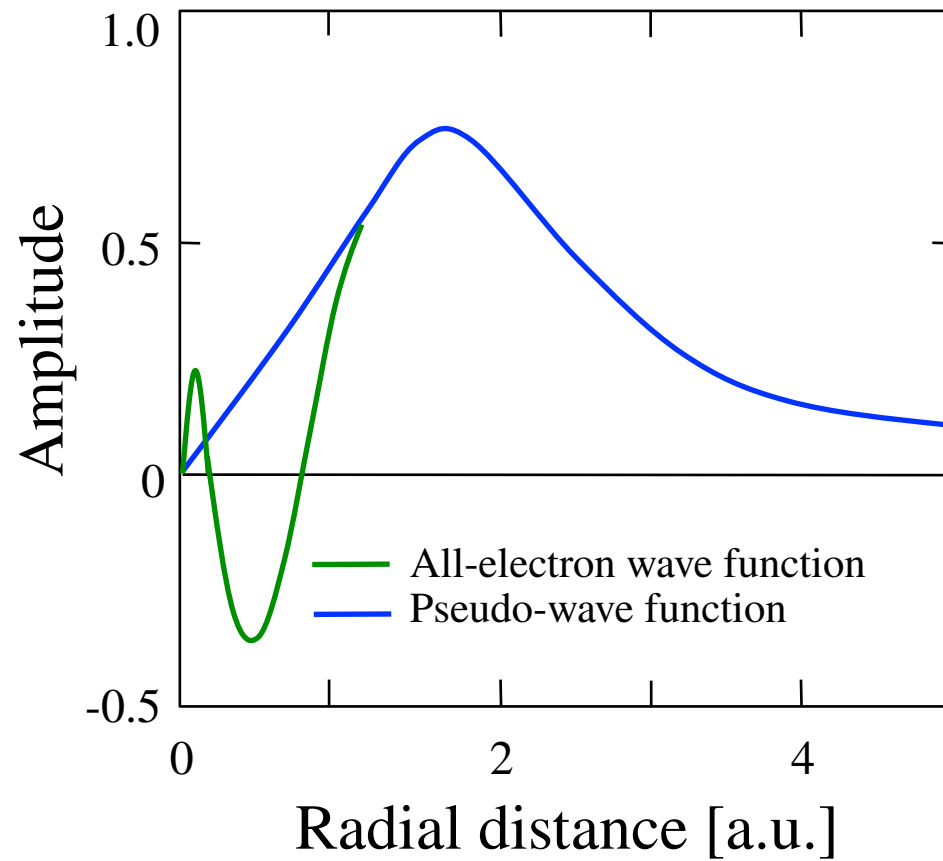
$$v_{\text{NL},l}(r, r') = \xi_l^*(r)f_l\xi_l(r')$$

[L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982)]

- Semi-local pseudopotentials are easily visualized, but separable ones are definitely more powerful for numerical techniques.
- A technique was introduced to transform semi-local pseudopotentials into a separable form (caution: ghost states may appear).

Example of pseudopotential

3s Radial wave function of Si



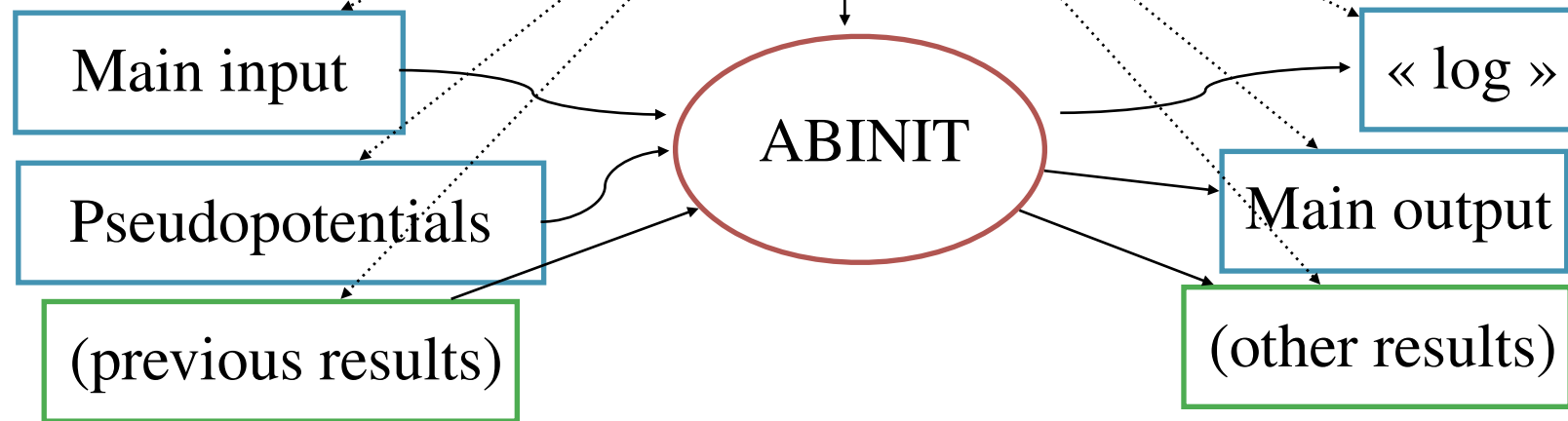
External files in a ABINIT run

prompt:> abinit < t1x.files >& log

Example of "Filenames" file:

Filenames

```
../t11.in  
t1x.out  
t1xi  
t1xo  
t1x  
../../../../Pspg_for_tests/01h.pspgth
```



Results : density (`_DEN`), potential (`_POT`),
wavefunctions (`_WFK`), ...