Density Functional Theory
in the *abinit* code

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fnrs
FREEDOM TO RESEARCH

Hohenberg-Kohn theorem

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

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

Hohenberg and Kohn have demonstrated that the electronic density of the ground-state n(r) defined by:

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

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

- The external potential is thus a functional of the density.

Hohenberg-Kohn theorem

- It is also the case for all the quantities which can be formally obtained 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).

- The total electronic energy is also a functional of the density:

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

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:

$$E = \min_{\phi} \left\{ \langle \phi | \hat{H} | \phi \rangle \right\} = \min_{n} \left\{ \min_{\phi \to n} \left\{ \langle \phi | \hat{H} | \phi \rangle \right\} \right\}$$

$$= \min_{n} \left\{ \min_{\phi \to n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} + \sum_{i=1}^{N_e} V_{\text{ext}}(\mathbf{r}_i) | \phi \rangle \right\} \right\}$$

$$= \min_{n} \left\{ \min_{\phi \to n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} | \phi \rangle \right\} + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \right\}$$

$$= \min_{n} \left\{ F[n] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \right\}$$

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

density, but it is not known explicitly.

Kohn-Sham equations

- F[n] represents an important part of the total energy. It is thus critical to make a reasonable approximation for it

- Kohn and Sham tried to establish a connection with a system of non-interacting electrons in an effective potential V_{eff}, whose ground-state density equals the one of the interacting system:

$$E[n] = F[n] + \int n(\mathbf{r}) V_{eff}(\mathbf{r}) \, \mathrm{d}\mathbf{r} = F + E_{eff} \quad \text{with} \quad n(\mathbf{r}) = \sum_{}^{occ} \phi_i(\mathbf{r})^2$$

- For non-interacting particles, F reduces to the much simpler expression:

$$F[n] = \min_{\phi \to n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} | \phi \rangle \right\} \quad \longrightarrow \quad T_0[n] = -\frac{1}{2} \sum_i \langle \phi_i | \nabla^2 | \phi_i \rangle$$

- Ansatz for E_{eff}:

Unknown

$$E_{eff}[n] = E_{ext}[n] + E_H[n] + \boxed{E_{xc}[n]} \quad \text{with} \quad E_{\mathrm{H}}[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Kohn-Sham equation

- 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:

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

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

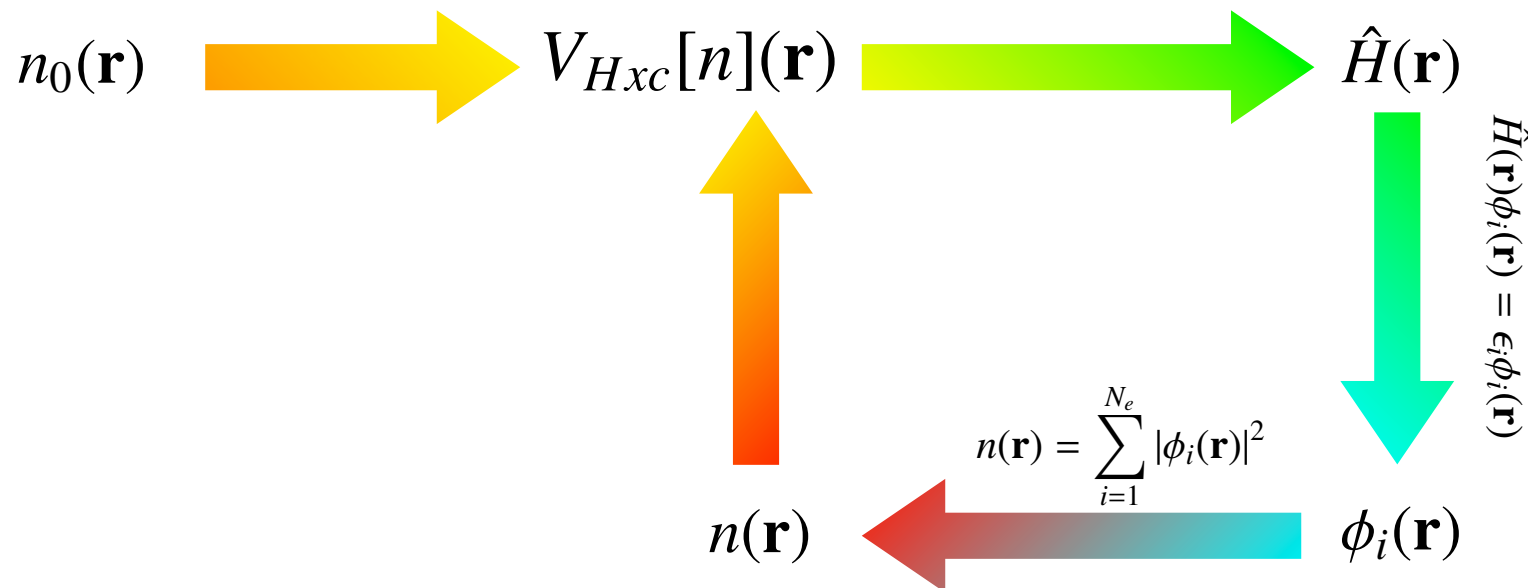- It is thus also equivalent to solve the 1-electron Schrödinger equation:

Lagrangian multipliers

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

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

The self-consistent cycle

- However, there is a new difficulty:

  – to obtain the potential $V_{Hxc}(r)$, the electronic density $n(r)$ and hence all the wavefunctions $\phi_i(r)$ are needed

  – to obtain the wavefunctions $\phi_i(r)$, the potential $V_{Hxc}(r)$ is required

- In practice, one starts from a trial electronic density and then iterates the equations until self-consistency is reached:

$$n_0(\mathbf{r}) \longrightarrow V_{Hxc}[n](\mathbf{r}) \longrightarrow \hat{H}(\mathbf{r})$$

$$\hat{H}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2$$

$$n(\mathbf{r}) \longleftarrow \phi_i(\mathbf{r})$$

Discretizing the KS equations

- Let $\{b_i\}$ be a set of vectors that span an appropriate Hilbert subspace

- The KS orbitals are expanded in this basis set using:

$$|\psi\rangle = \sum_i c_i |b_i\rangle \qquad \text{with} \qquad c_i \equiv \langle b_i|\psi\rangle$$

- The KS equation $H|\psi\rangle = \epsilon|\psi\rangle$ reduces to the solution of the generalized eigenvalue problem:

$$Hc = \epsilon Oc \qquad\qquad H_{ij} = \langle b_i|H|b_j\rangle$$

Vector of unknown coefficients

$$O_{ij} = \langle b_i|b_j\rangle$$

Overlap matrix

- The basis set should be

  - accurate

  - efficient (small size and/or $\langle b_i|H|b_j\rangle$ easy to compute)

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]

(a)　(b)
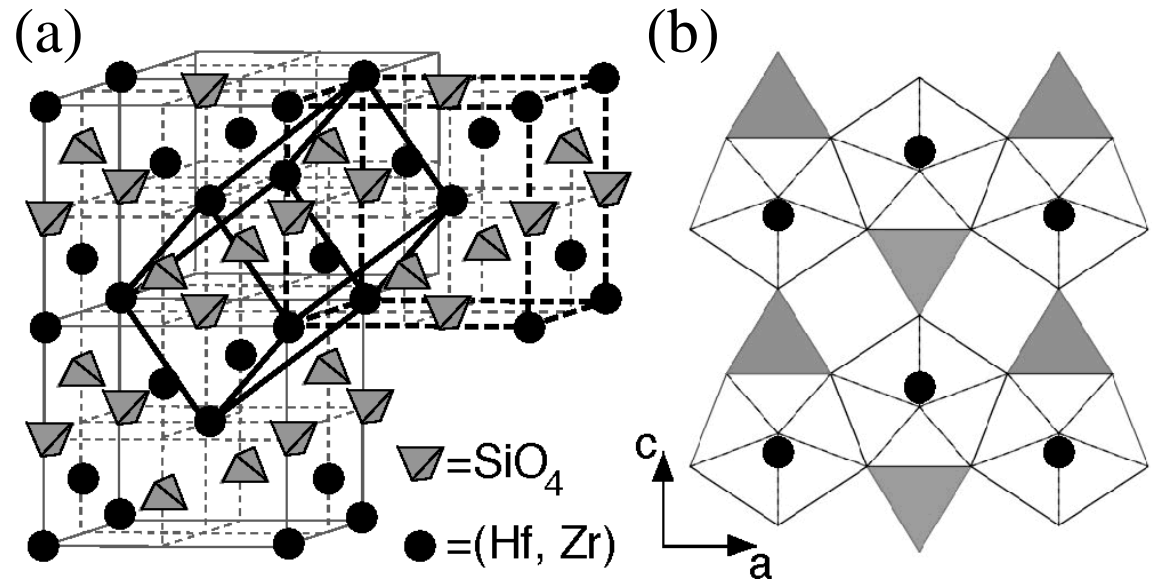
$\triangledown = SiO_4$　● = (Hf, Zr)

  - 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(Si-O)	1.62	1.61	1.61	1.62
d(M-O)	2.14	2.10	2.10	2.13
	2.27	2.24	2.24	2.27
$\angle$(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).

- hybrid functionals are obtained by mixing (using an empirically adjusted parameter) a part of exact exchange and an approximated correlated part (acronyms: B3LYP, HSE, ...).

- Another approximation consists in suppressing the self-interaction which is present in the Hartree term (acronym: SIC).

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 equations:

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

- No direct physical interpretation for the Kohn-Sham eigenvalue (they are simply Lagrange multipliers).

- However, the electronic bandstructures obtained within DFT (LDA or GGA) are in reasonably good agreement with the experimental data.

- The most notable exception is the band gap which is systematically underestimated by 30-50% (or even 100%).

DFT and the band gap problem

[adapted from van Schilfgaarde et al., PRL 96, 226402 (2006)]
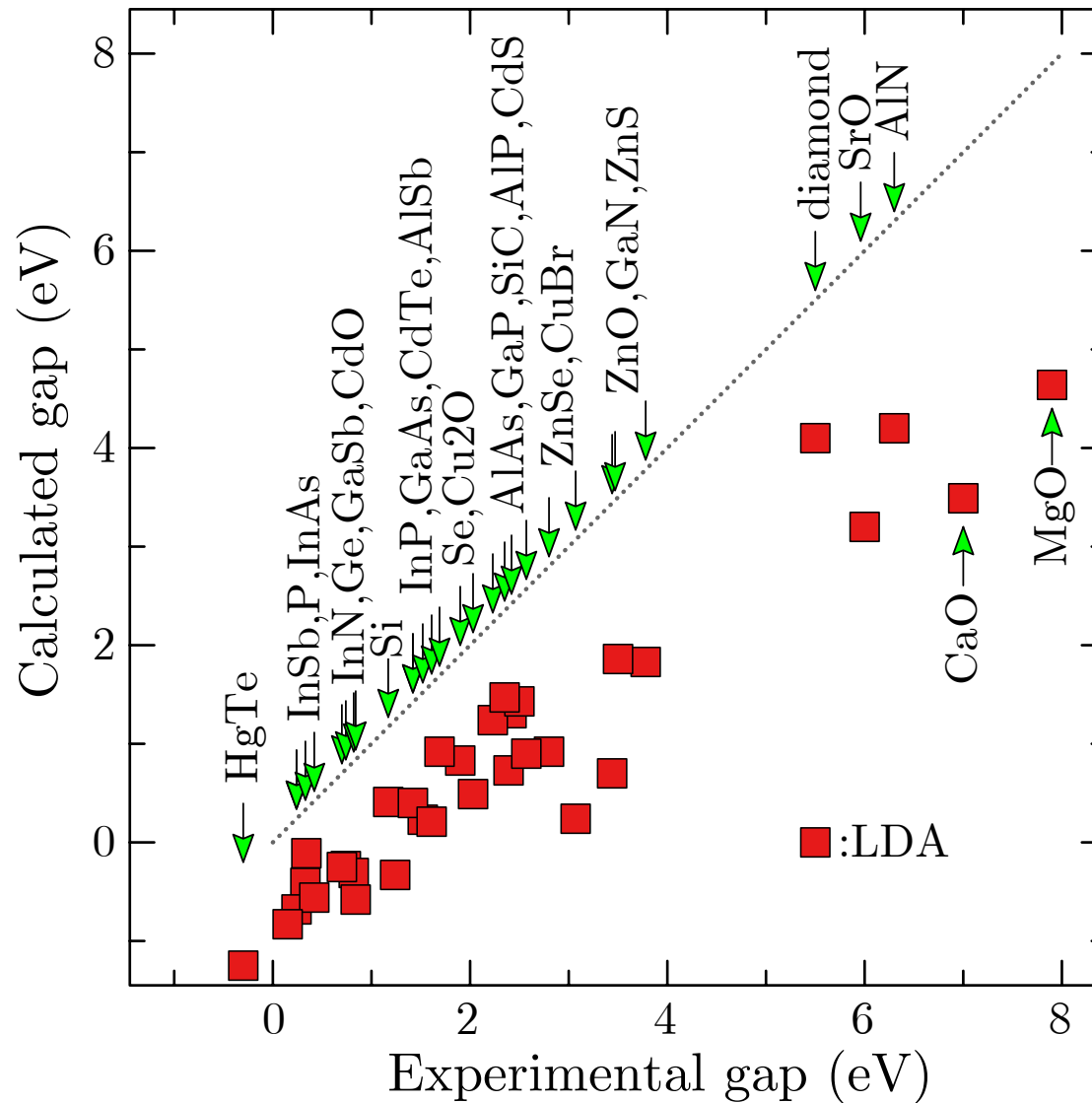
- This problem is related to the existence of a discontinuity in the derivative of the (exact) exchange-correlation potential.

Direct photoemission spectroscopy

- Energy measurement of electrons emitted from solids by the photoelectric effect (used to study occupied states)
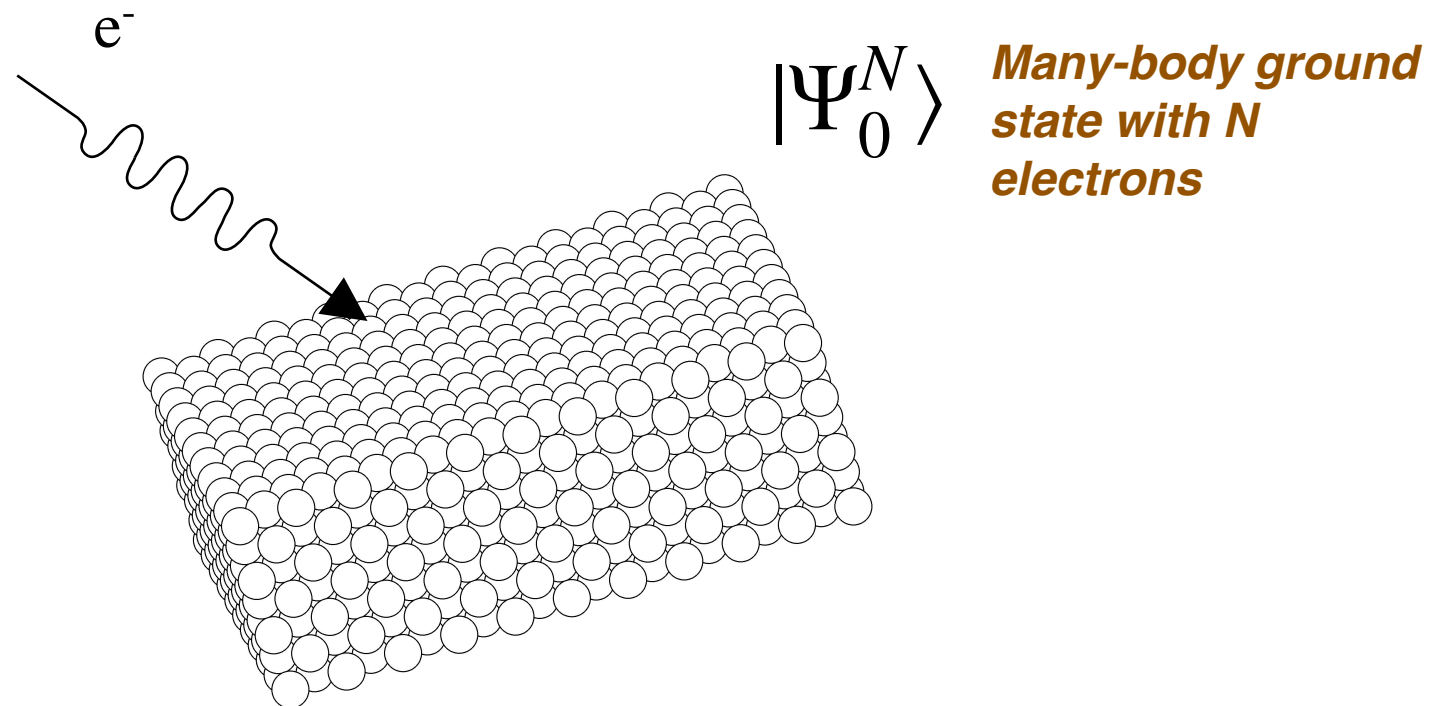
$h\nu$

$|\Psi_0^N\rangle$ *Many-body ground state with N electrons*

Direct photoemission spectroscopy

e$^-$
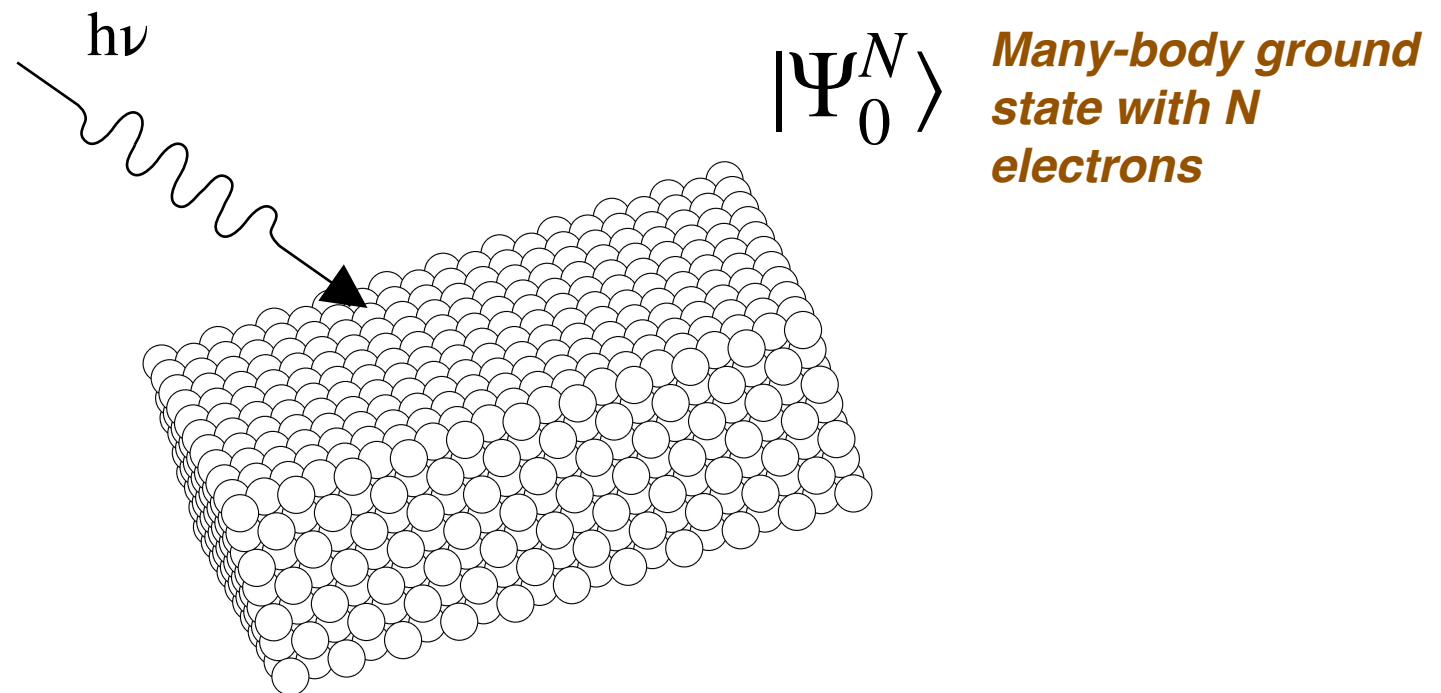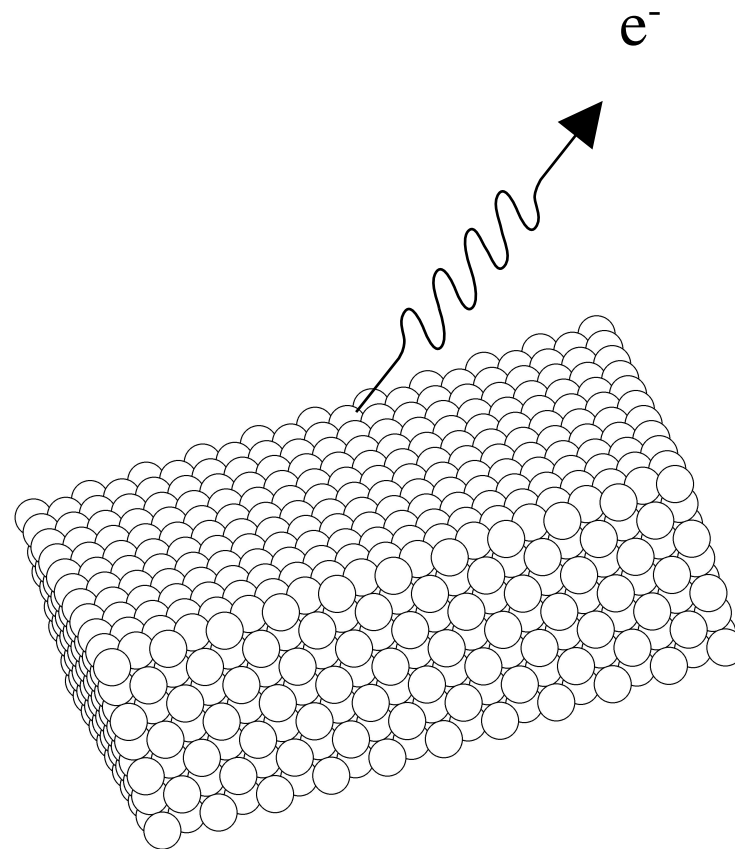
Excited Many-body
state with N-1
electrons

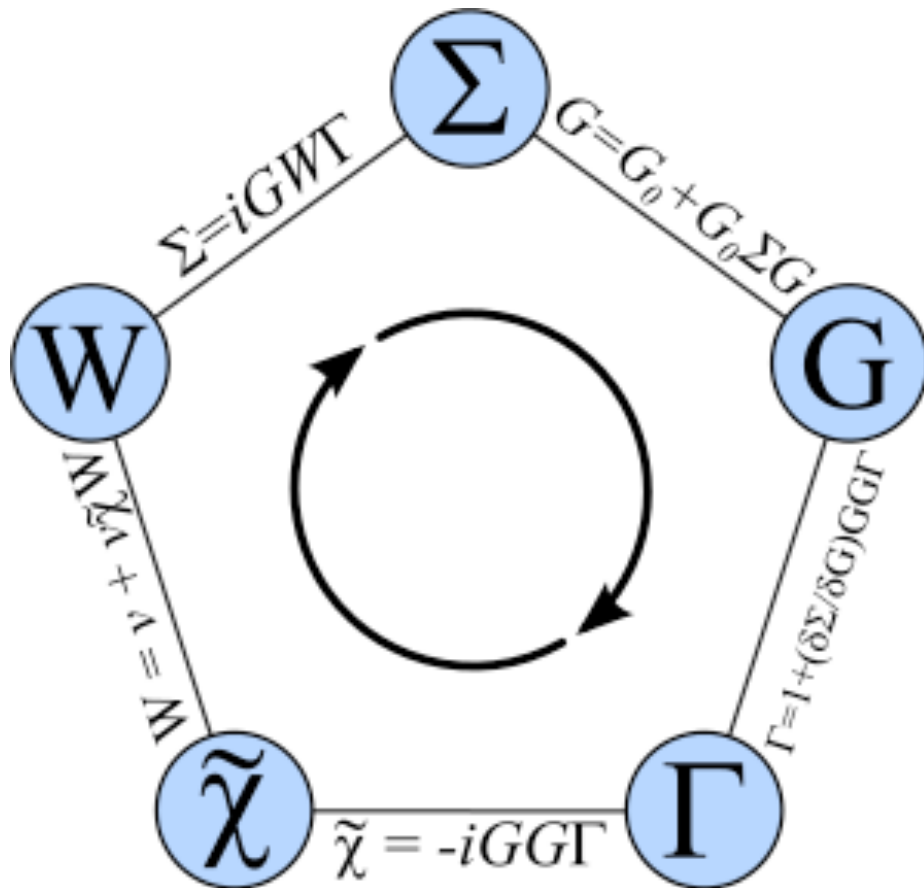$|\Psi_i^{N-1}\rangle$

Indirect photoemission spectroscopy

- Used to study empty states

e$^-$

$|\Psi_0^N\rangle$ *Many-body ground state with N electrons*

Indirect photoemission spectroscopy

hν

Excited Many-body state with N+1 electrons

$|\Psi_i^{N+1}\rangle$
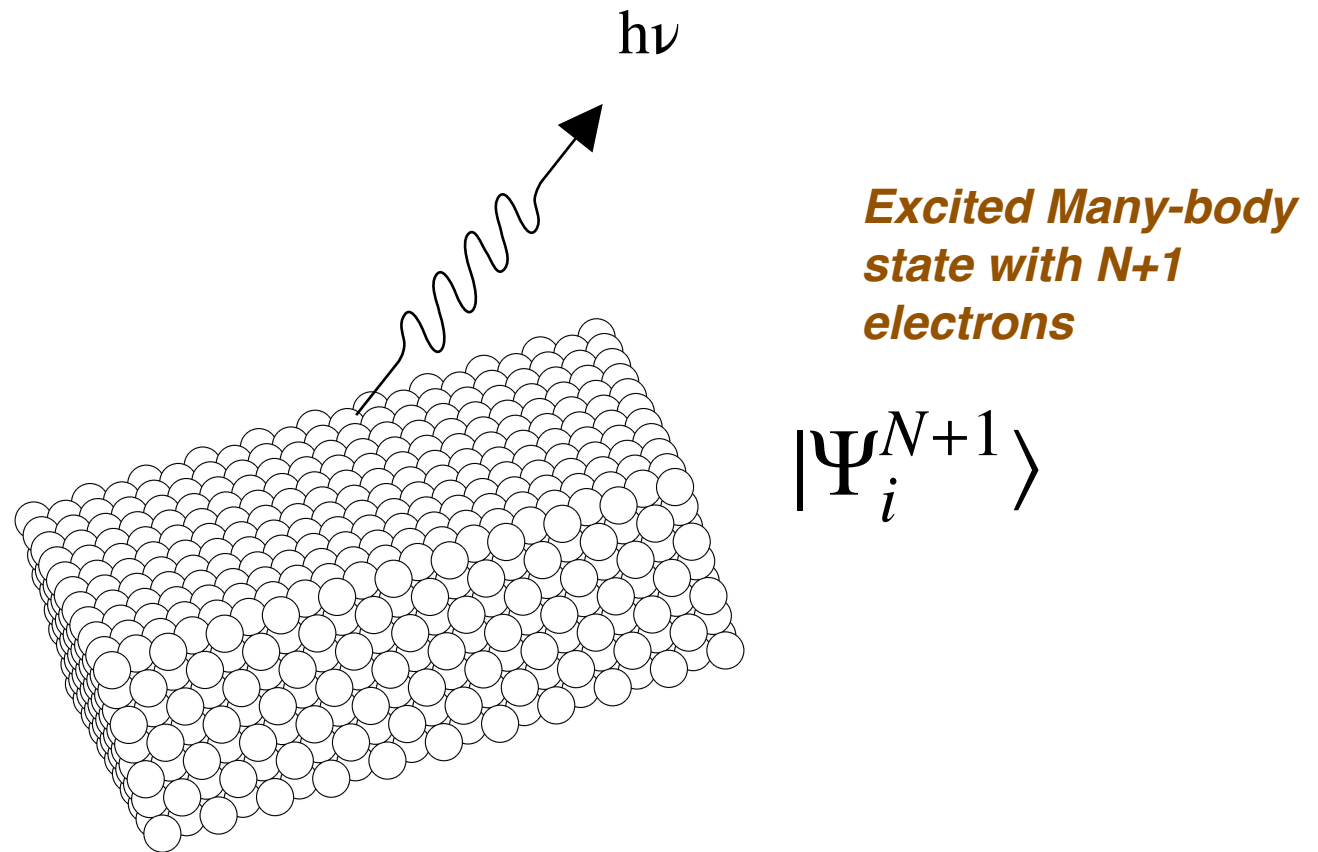
A different approach: Hedin's equations

Quasi-particle equation

$$\left[\hat{h}_0 + \Sigma(\epsilon^{\mathrm{QP}})\right]|\Psi^{\mathrm{QP}}\rangle = \epsilon^{\mathrm{QP}}|\Psi^{\mathrm{QP}}\rangle$$

Exact formalism but challenging problem that cannot be solved without resorting to approximations!

- The iteration starts by setting $\Sigma=0$, $G=G_0$

- Then the set of equations should be iterated until self-consistency in all terms is reached

- "True" quasi-particle band structures and optical properties

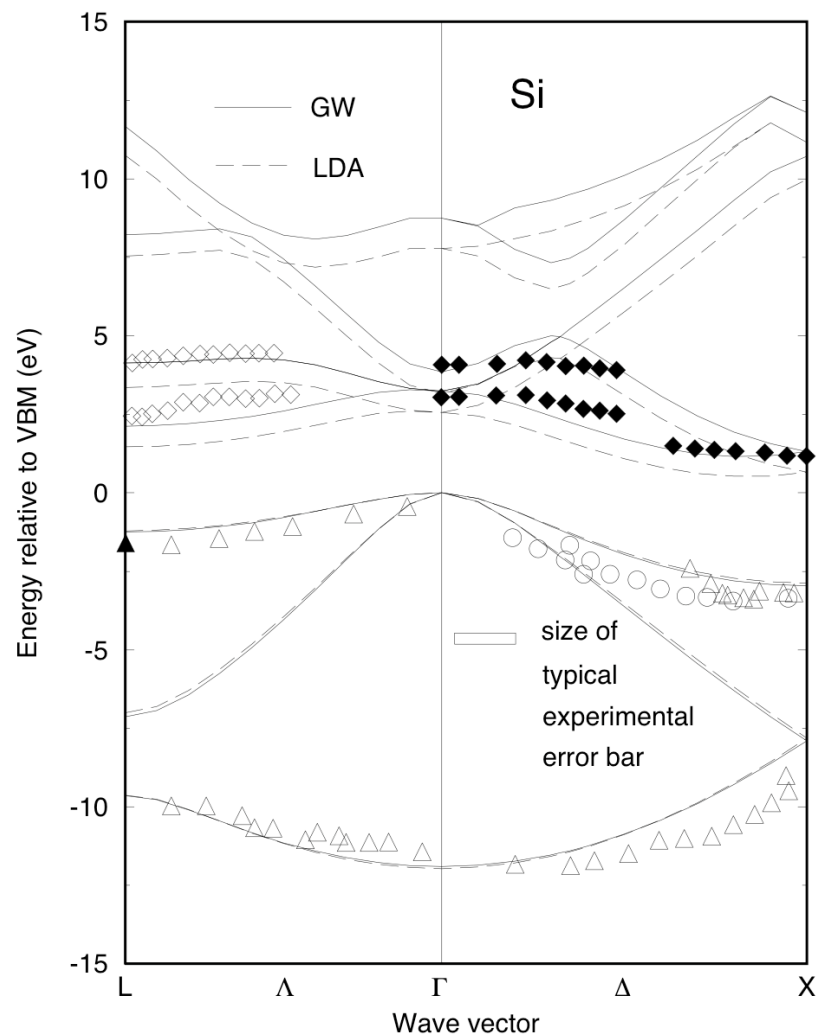# The band gap within G_0W_0

- The agreement with experiments is much better!
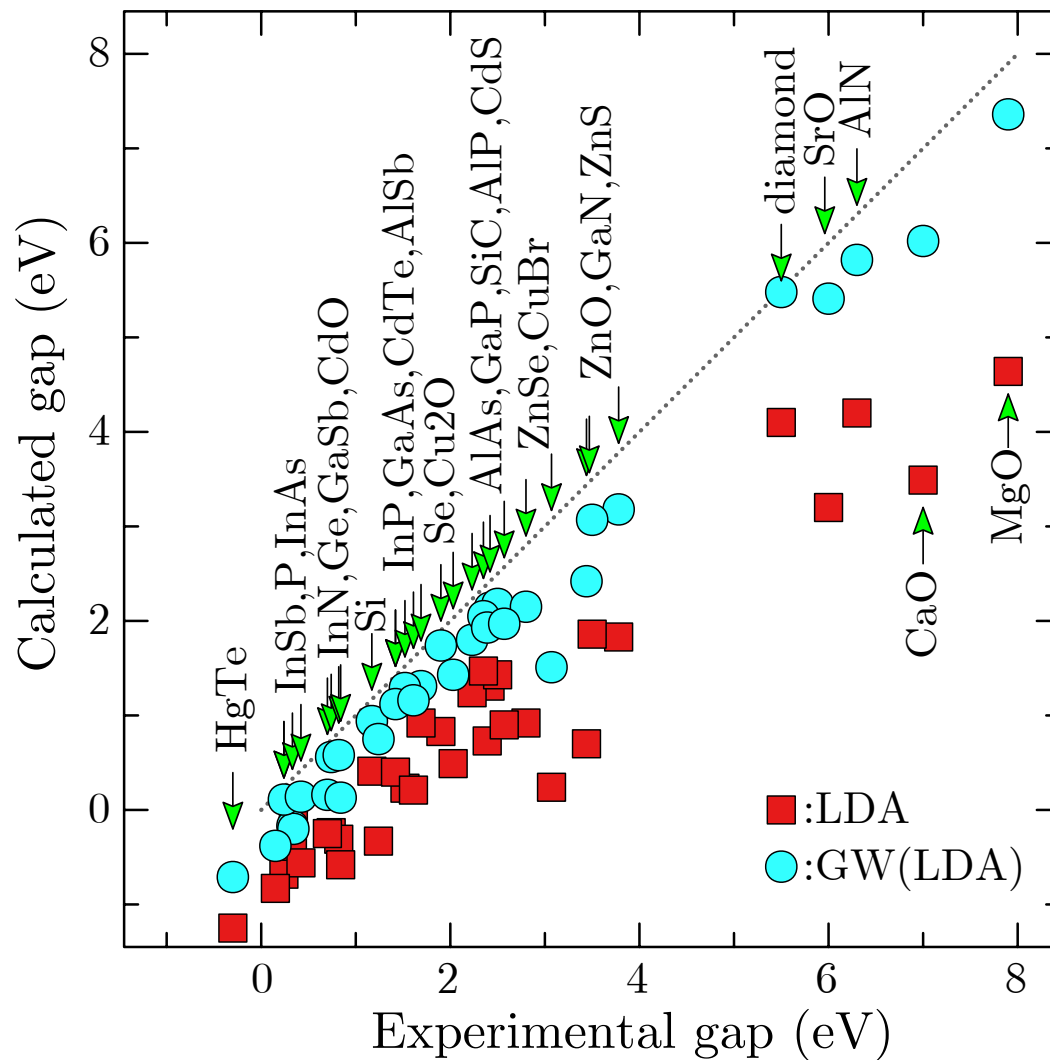
[adapted from van Schilfgaarde et al., PRL 96, 226402 (2006)]

The band gap within G_0W_0

- The calculated band structures are in excellent agreement with those measured experimentally.
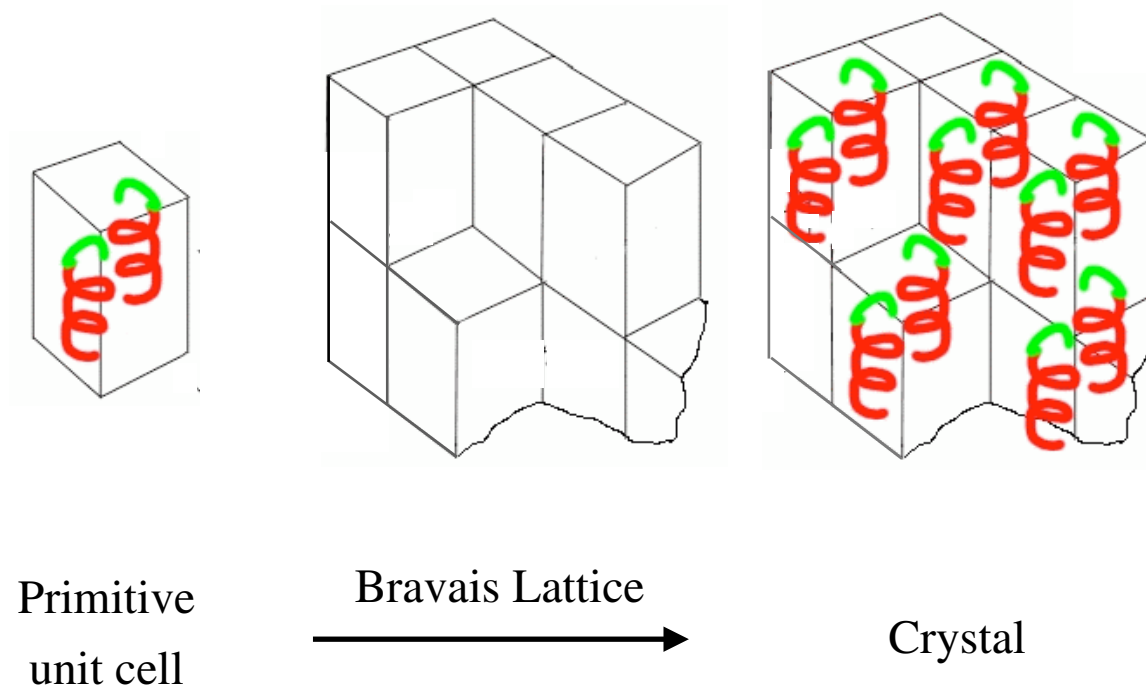

[from Aulbur et al., Solid State Physics 54, 1 (2000)]

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) expending in all three spatial dimensions.

Primitive unit cell → Bravais Lattice → Crystal

The Bravais lattice

- The lattice is defined by its primitive vectors a_1, a_2, and a_3 which are independent and such that each point of the lattice can be written as:

  $R = l\, a_1 + m\, a_2 + n\, a_3$ with $l, m, n \in \mathbb{Z}$
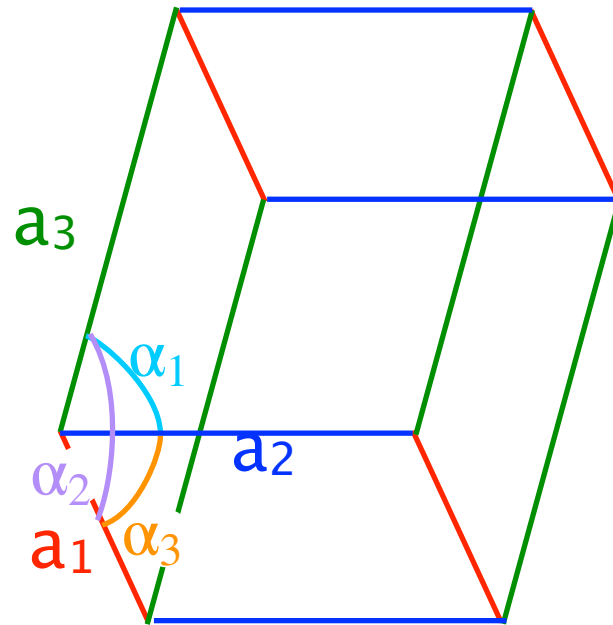
Primitive volume

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

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

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

- Reciprocal lattice: $G = l\, b_1 + m\, b_2 + n\, b_3$ with $l, m, n \in \mathbb{Z}$ and
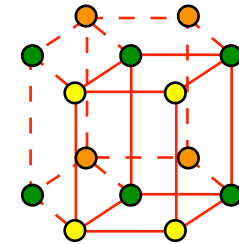
$$\mathbf{a_i} \cdot \mathbf{b_j} = 2\pi\delta_{ij}$$

The primitive vectors in ABINIT

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

hexagonal

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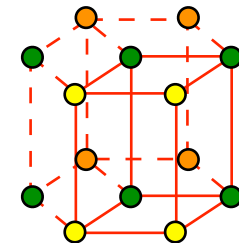
- $a_i \rightarrow$ acell(i) / $\alpha_i \rightarrow$ angdeg(i)

hexagonal

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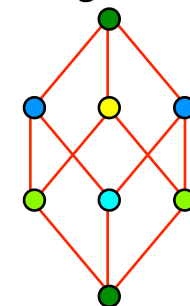
trigonal

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

The 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`

- Abinit assumes atomic units by default: lengths are in Bohr, energies are given in Hartree

Example 1: c-ZrO$_2$

- 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
```
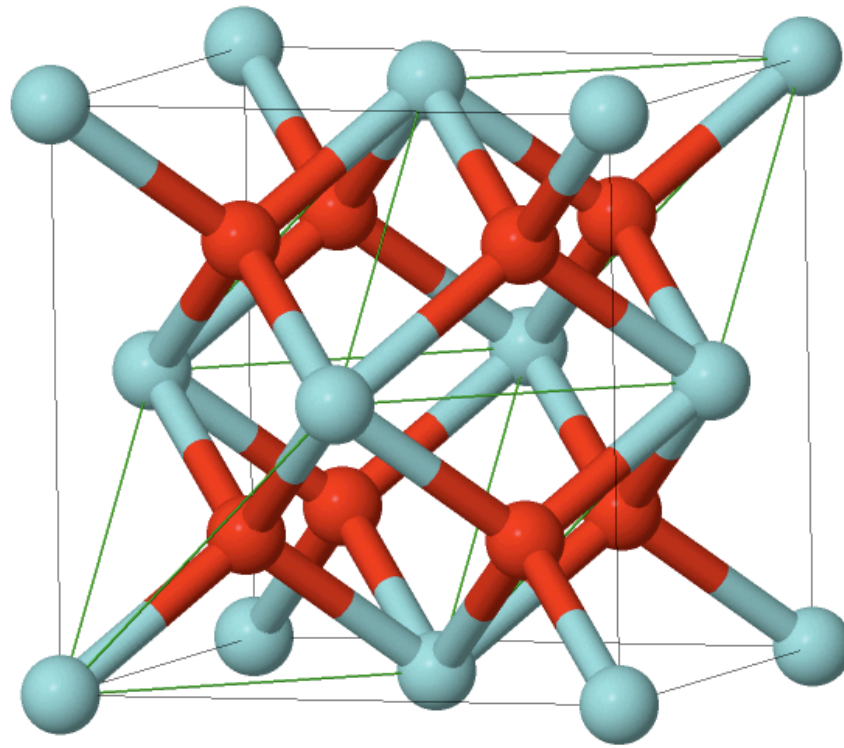
Example 1: c-ZrO$_2$

- 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 -1  0   0  0 -1
              0 -1  1   0 -1  0   1 -1  0       0  1 -1   0  1  0  -1  1  0


              ...                               ...


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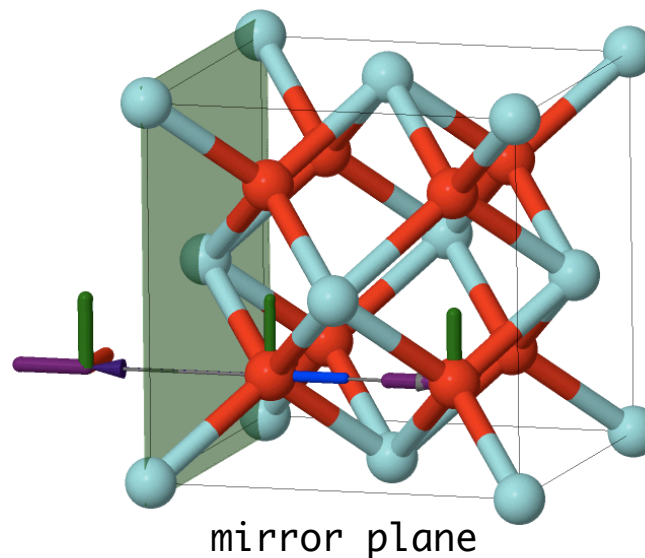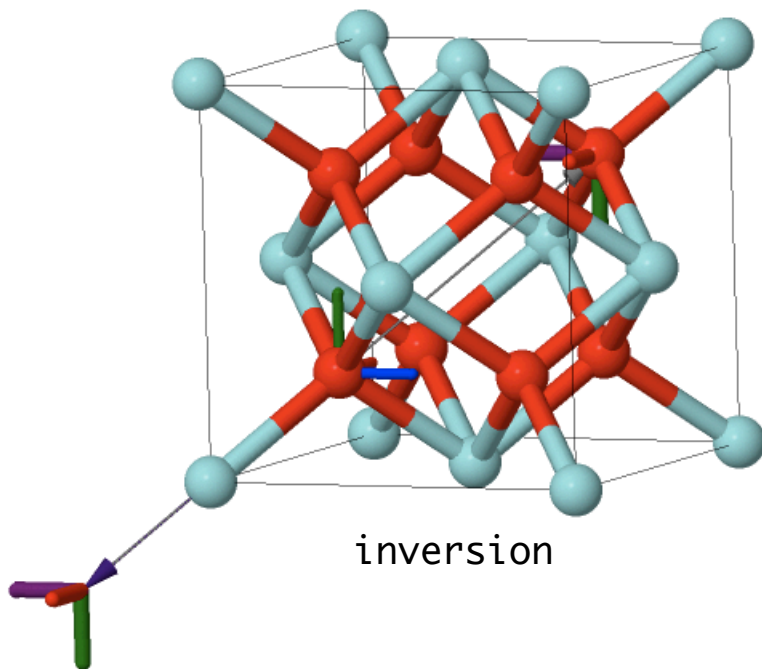

inversion   mirror plane

Example 1: c-ZrO$_2$

- 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
```
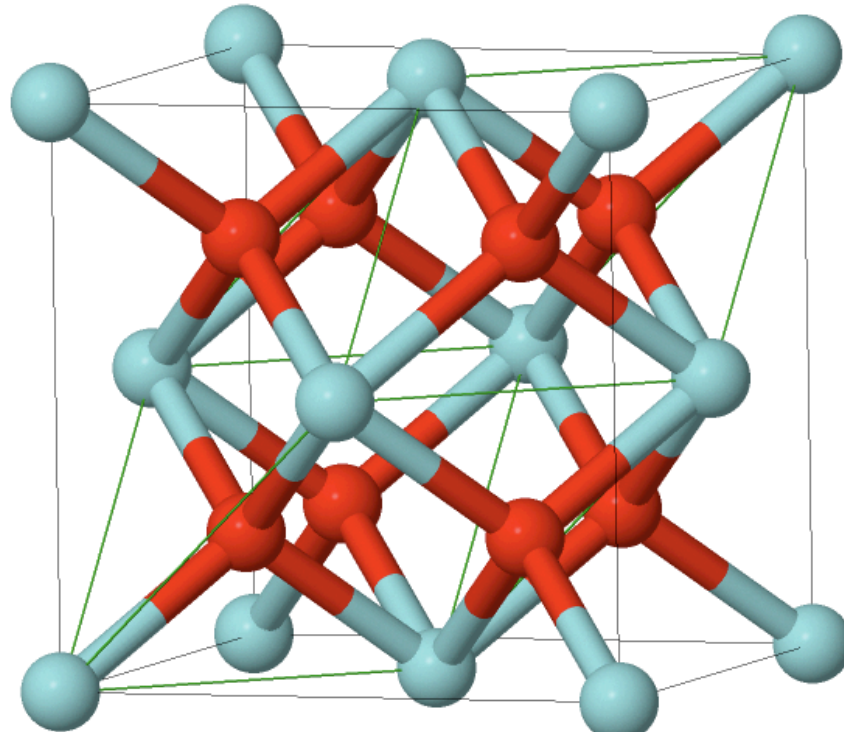
The plane-wave basis set

Treatment of periodic systems

- For periodic systems (with the lattice vectors 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 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:

$$u_{n\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega}\int_{\Omega} u_{n\mathbf{k}}(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r}$$

Kinetic energy cut-off

- The coefficients $u_{nk}(G)$ for the lowest-energy eigenfunctions decrease exponentially with the kinetic energy $(k+G)^2/2$.

- 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):

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

$$\uparrow$$

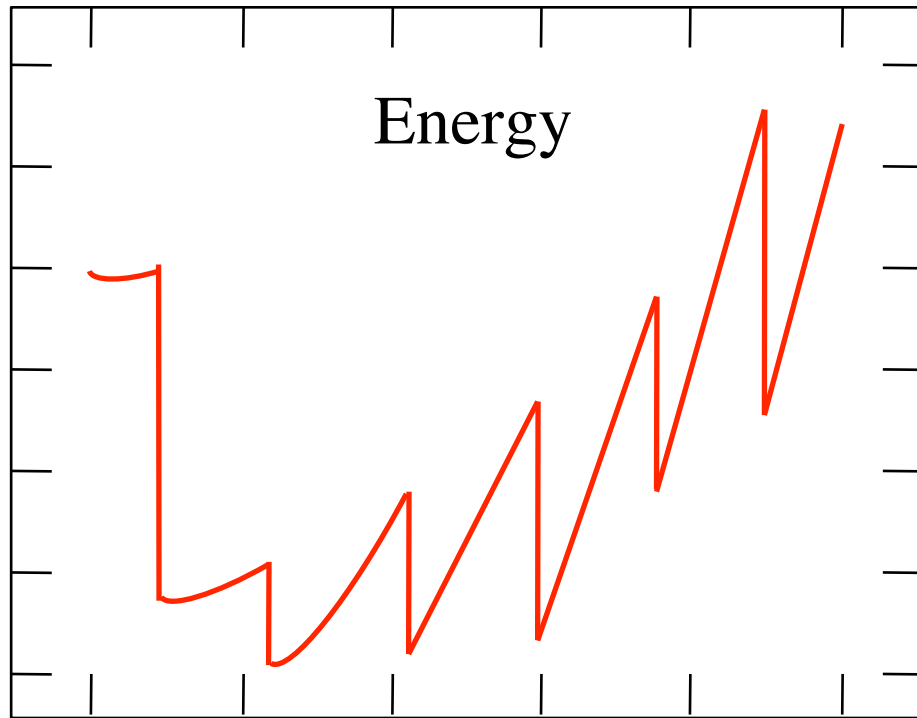$$-\frac{1}{2}\nabla^2 e^{i(\mathbf{k}+\mathbf{G})\cdot r}$$
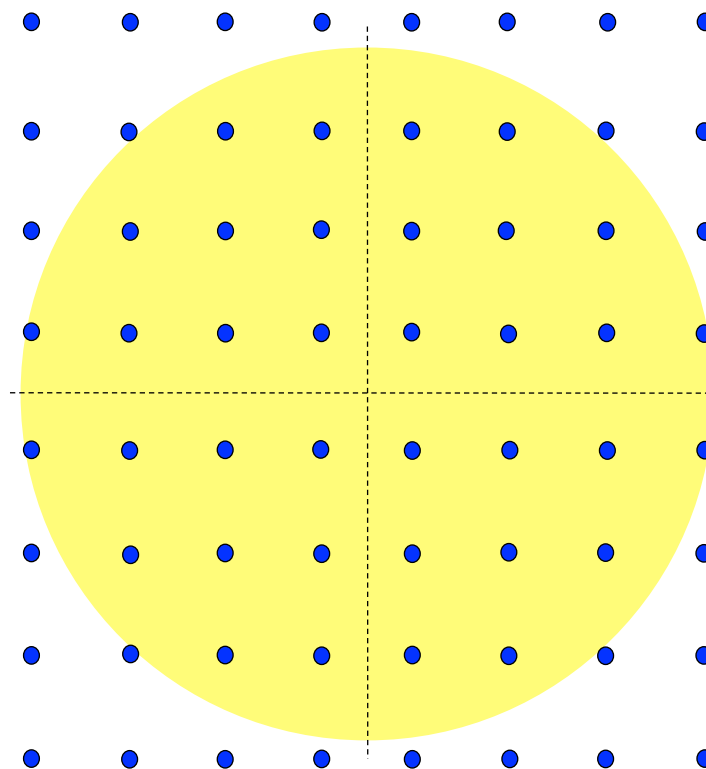
The number of plane-waves is not a continuous function of the cut-off energy...
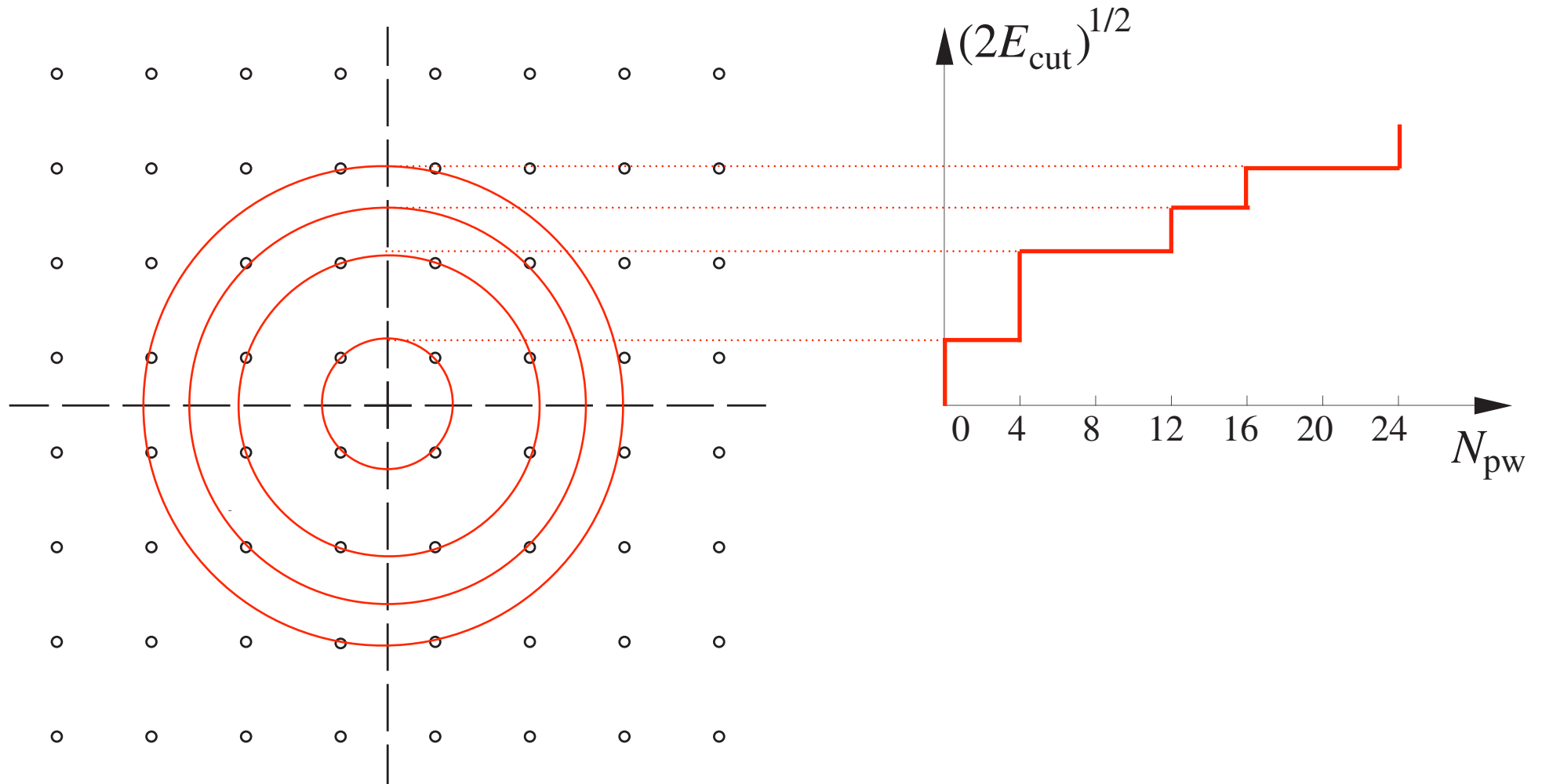
... nor it is as a function of the lattice parameter

There are discontinuities in the pressure and energy curves

Energy

Lattice parameter

Pressure
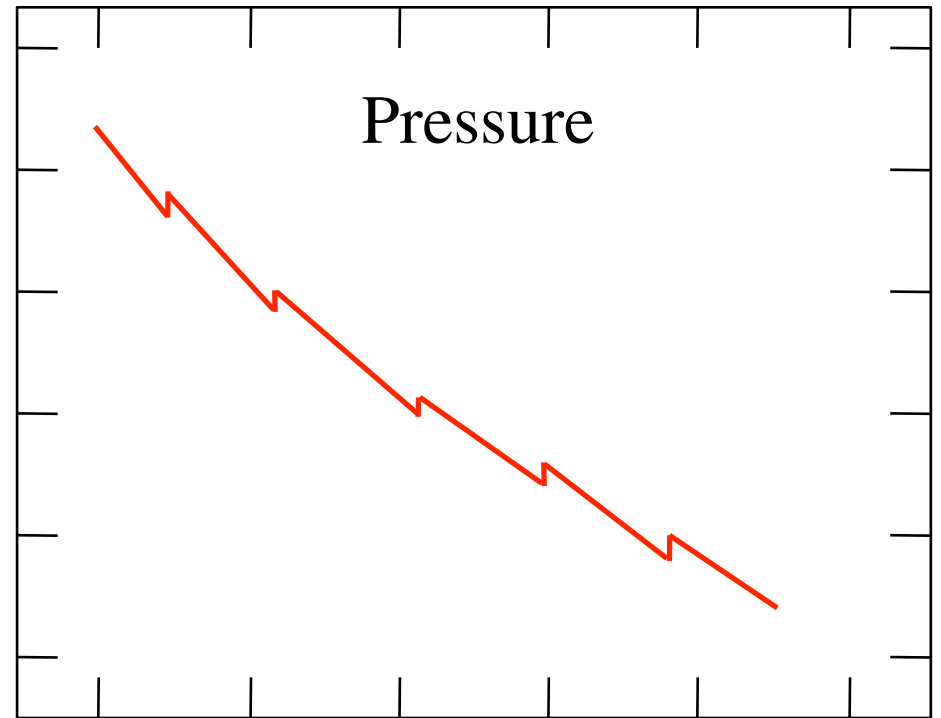
Lattice parameter

Use `ecutsm` to remove the discontinuities

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

- <u>Advantages</u>

  - orthonormal basis set

  - the quality of the basis set can be systematically increased by increasing the cut-off energy

  - Fast algorithms to go from G to r space and vice-versa (FFT)

  - Same accuracy in any region of the simulation box

  - Easy to implement (e.g. simple expression for the kinetic operator)

- <u>Problem:</u>

  - 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

The supercell technique for non-periodic systems
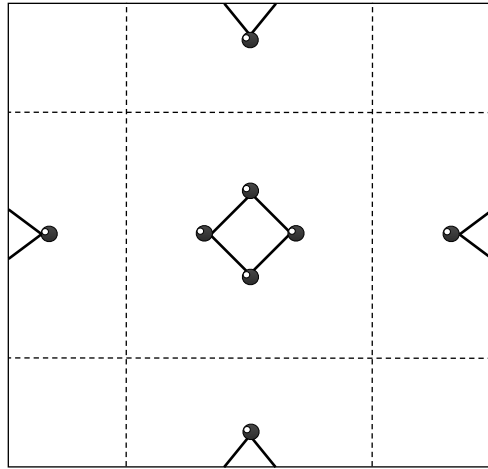
Molecule   Surface   Point defect in a bulk solid
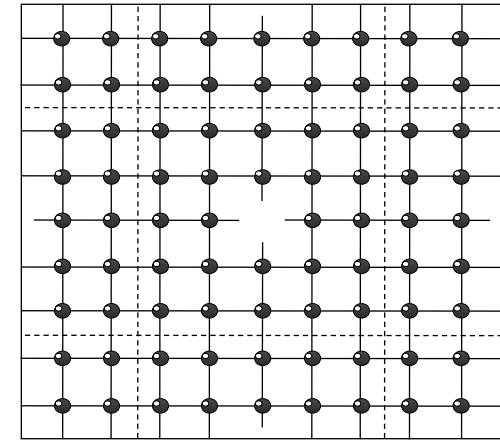
The supercell must be sufficiently large: convergence study

Representation of the density (I)

Density associated with one eigenfunction:

$$n_{b\mathbf{k}}(\mathbf{r}) = u^*_{b\mathbf{k}}(\mathbf{r})\, u_{b\mathbf{k}}(\mathbf{r})$$

In Fourier space:

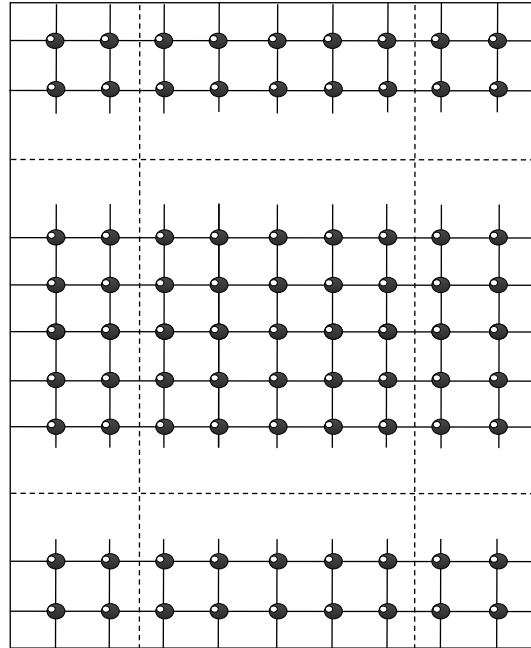$$n_{b\mathbf{k}}(\mathbf{r}) = \left(\sum_{\mathbf{G}} u^*_{b\mathbf{k}}(\mathbf{G}) e^{-i\mathbf{G}\mathbf{r}}\right)\left(\sum_{\mathbf{G}'} u_{b\mathbf{k}}(\mathbf{G}') e^{i\mathbf{G}'\mathbf{r}}\right) =$$

$$= \sum_{\mathbf{G}\mathbf{G}'} \left[u^*_{b\mathbf{k}}(\mathbf{G}) u_{b\mathbf{k}}(\mathbf{G}') \right] e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}}$$
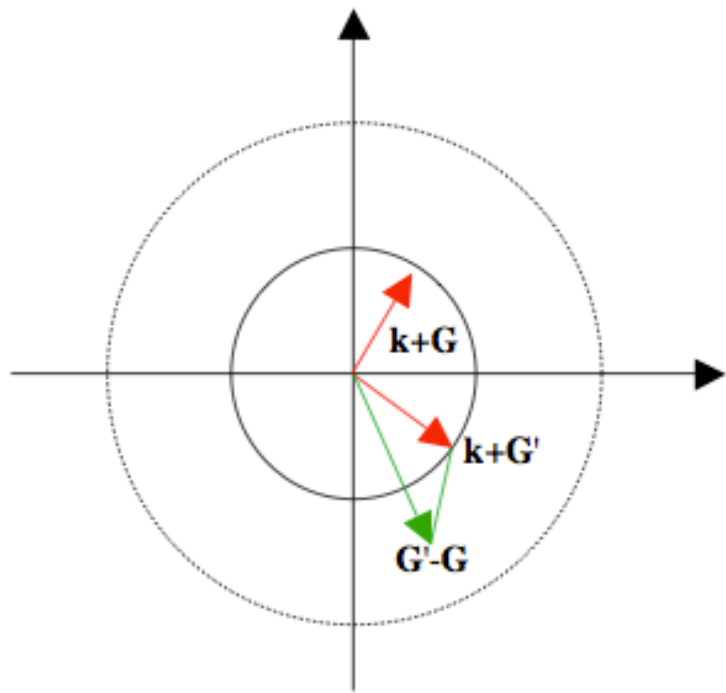
The sphere for $n(\mathbf{G})$ has a double radius

$n(\mathbf{G})$ is given by the convolution of $u(\mathbf{G})$

Representation of the density (II)

Fast transform $\{\mathbf{r}_i\} \leftrightarrow \{\mathbf{G}\}$ algorithm: Fast Fourier Transform

Reciprocal lattice
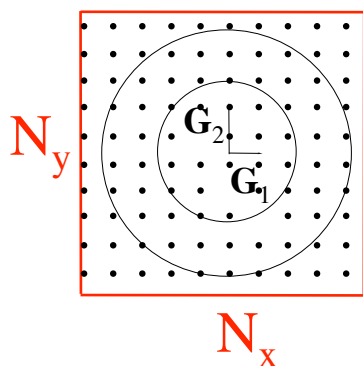
Real lattice: original cell
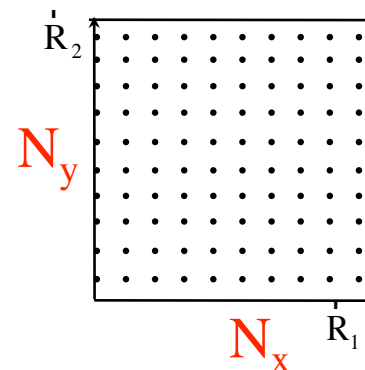
$\mathcal{O}(N \log N)$

$$u_{n\mathbf{k}}(\mathbf{G}) \xrightarrow{\text{FFT}} n(\mathbf{r}) = \sum_{n\mathbf{k}} f_{n\mathbf{k}}|u_{n\mathbf{k}}(\mathbf{r})|^2 \xrightarrow{\text{FFT}} n(\mathbf{G})$$

- Computational cost scales almost linearly with the number of points in the "dense" FFT mesh used for the density

Poisson's equation in G-space (I)

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \iff \nabla^2 V_H(\mathbf{r}) = -4\pi \, n(\mathbf{r})$$

Using: $\mathcal{F}(\nabla V_H) = i\mathbf{G} V_H(\mathbf{G})$ one obtains:

$$\mathbf{G}^2 V_H(\mathbf{G}) = 4\pi n(\mathbf{G}) \implies V_H(\mathbf{G}) = \frac{4\pi \, n(\mathbf{G})}{\mathbf{G}^2}$$

Poisson solver with $\mathcal{O}(N \log N)$ operations:

$$n(\mathbf{G}) \quad \Longrightarrow \quad V_H(\mathbf{G}) = \frac{4\pi \, n(\mathbf{G})}{\mathbf{G}^2} \quad \xrightarrow{\text{FFT}} \quad V_H(\mathbf{r})$$

Poisson's equation in G-space (II)

$$n(\mathbf{G} = 0) = \frac{1}{\Omega} \int_\Omega n(\mathbf{r}) \, d\mathbf{r}$$

Number of electrons per unit cell

$$V_H(\mathbf{G}) = \frac{4\pi \, n(\mathbf{G})}{\mathbf{G}^2}$$

$V_H(\mathbf{G} = 0)$ diverges at $G = 0$

- The divergence is compensated by a similar divergence due to the electron-ion interaction (charge neutrality)

Pros and Cons

Very efficient

Periodic conditions are automatically enforced even in isolated systems

Application of the Hamiltonian

- Kinetic part in G-space (exact and efficient):

$$\nabla^2 |\psi\rangle = \sum_{\mathbf{G}} \nabla^2 u(\mathbf{G}) e^{i\mathbf{Gr}} = -\sum_{\mathbf{G}} \mathbf{G}^2 u(\mathbf{G}) e^{i\mathbf{Gr}}$$

- $V_H |\psi\rangle$ is computed in real space

- $V_{\text{xc}}[n] |\psi\rangle$ is computed in real space. The derivatives of n needed for the GGA are computed exactly

- Iterative techniques (e.g. conjugate gradient method) to compute the lowest eigenstates. The basic steps of the algorithm are:

$$H|\psi\rangle \quad \text{and orthogonalization of} \quad \{|\psi_i\rangle\}$$

Brillouin zone integration

From discrete states to the Brillouin zone (BZ)

Discrete summations over states:

Kinetic energy: $\quad T = -\dfrac{1}{2} \sum\limits_{i}^{\text{occ}} \langle \psi_i | \nabla^2 | \psi_i \rangle$

Density: $\quad\quad n(\mathbf{r}) = \sum\limits_{i}^{\text{occ}} \psi_i(\mathbf{r})^* \psi_i(\mathbf{r})$

Periodic case: summation over bands and integration over the BZ

$$T = -\frac{1}{2} \sum_b \frac{1}{\Omega_{\mathbf{k}}} \int_{\Omega_{\mathbf{k}}} f(\epsilon_{b\mathbf{k}}) \langle \psi_{b\mathbf{k}} | \nabla^2 | \psi_{b\mathbf{k}} \rangle \, \mathrm{d}\mathbf{k}$$

$$n(\mathbf{r}) = \sum_b \frac{1}{\Omega_{\mathbf{k}}} \int_{\Omega_{\mathbf{k}}} f(\epsilon_{b\mathbf{k}}) \psi_{b\mathbf{k}}^*(\mathbf{r}) \psi_{b\mathbf{k}}(\mathbf{r}) \, \mathrm{d}\mathbf{k}$$

How to treat $\quad \dfrac{1}{\Omega_{\mathbf{k}}} \int_{\Omega_{\mathbf{k}}} X(\mathbf{k}) \, \mathrm{d}\mathbf{k}$?

Brillouin zone integration

$$\frac{1}{\Omega_{\mathbf{k}}} \int_{\Omega_{\mathbf{k}}} X(\mathbf{k})\, d\mathbf{k} \implies \sum_{\{\mathbf{k}\}} w_{\mathbf{k}} X(\mathbf{k}) \qquad\qquad \sum_{\mathbf{k}} w_{\mathbf{k}} = 1$$

Special points

Weights

If

- the integrand is periodic
- the integrand is continuous and differentiable at all orders
- homogeneous k-grids and weights all equal

Then exponential convergence with respect to Δk

- OK for semiconductors where the occupation number is independent of k within a band

- Convergence: one ought to test several grids with different Δk

Treatment of metals (I)

Behavior of $f(\varepsilon_F - \varepsilon_{nk})$?

Discontinuity of the integrand
at the Fermi level!

unoccupied $f = 0$

ε_F

occupied $f = 2$ (spin)
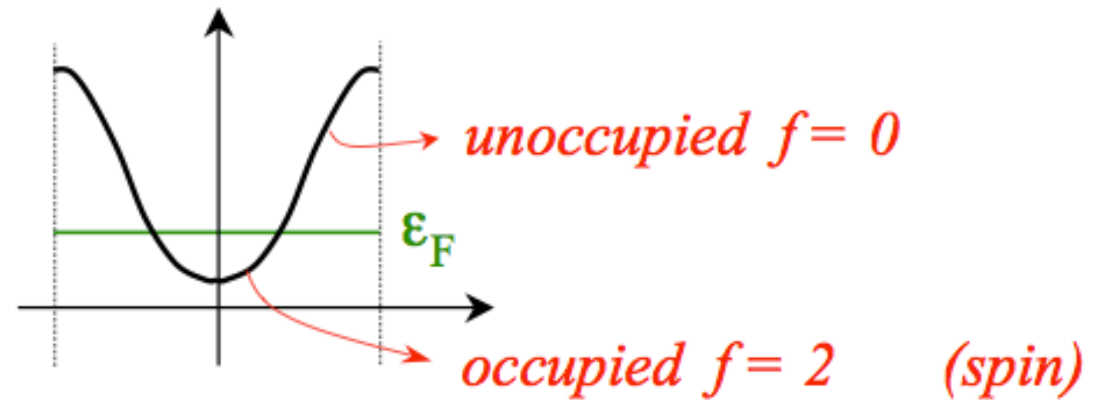
Smearing technique

First attempt: generalization of DFT to finite temperature

- $f(\varepsilon_{n\mathbf{k}}) = \dfrac{1}{1 + e^{(\varepsilon_{n\mathbf{k}} - \varepsilon_F)/kT}}$

  f goes from 0 to 2 in an energy range of width kT

- $E(T) \cong E(T=0) + \alpha T^2 + ...$

  $F(T) = E - TS$

Problem:

the T needed to recover the same convergence as for semiconductors is very high (>> 2000 K)

Treatment of metals (II)

Better technique: the goal is to obtain $E(\sigma = 0)$

from a total energy expression $E(\sigma)$ with modified occupation numbers, where σ is similar to a temperature

$$E(\sigma) \approx E(\sigma=0) + \alpha \, \sigma^2 + O(\sigma^3) \qquad \text{with} \ \alpha \ \text{small}$$

$$\text{or} \ E(\sigma) \approx E(\sigma=0) + \beta \, \sigma^n + O(\sigma^{n+1}) \quad \text{with} \ n > 2$$

$$f(\epsilon_{n\mathbf{k}}) = s \int_{\frac{\epsilon_{n\mathbf{k}} - \epsilon_F}{\sigma}}^{\infty} \tilde{\delta}(x) \, dx \qquad \qquad \int_{-\infty}^{\infty} \tilde{\delta}(x) \, dx = 1$$

Spin factor

Gaussian smearing: $\quad \tilde{\delta}(x) = \dfrac{1}{\sigma \sqrt{2\pi}} e^{-\left(\frac{x}{4\sigma}\right)^2}$

Other methods:
  Gauss - Hermite smearing,
  "Cold Smearing" (N. Marzari)

Crystal symmetries and k-points (I)

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

$$3\times3 \text{ real orthogonal matrix} \quad \{\mathbf{S}\,|\,\mathbf{v}(S)\}$$

$$\{S_{\alpha\beta}\,|\,v_\alpha(S)\} \quad \text{vector}$$

smaller than any primitive vector of the crystal

$$\underbrace{\phantom{3\times3 \text{ real orthogonal matrix}}}_{\text{rotation}} \quad \underbrace{\phantom{\text{vector}}}_{\text{translation}}$$

rotation — symrel
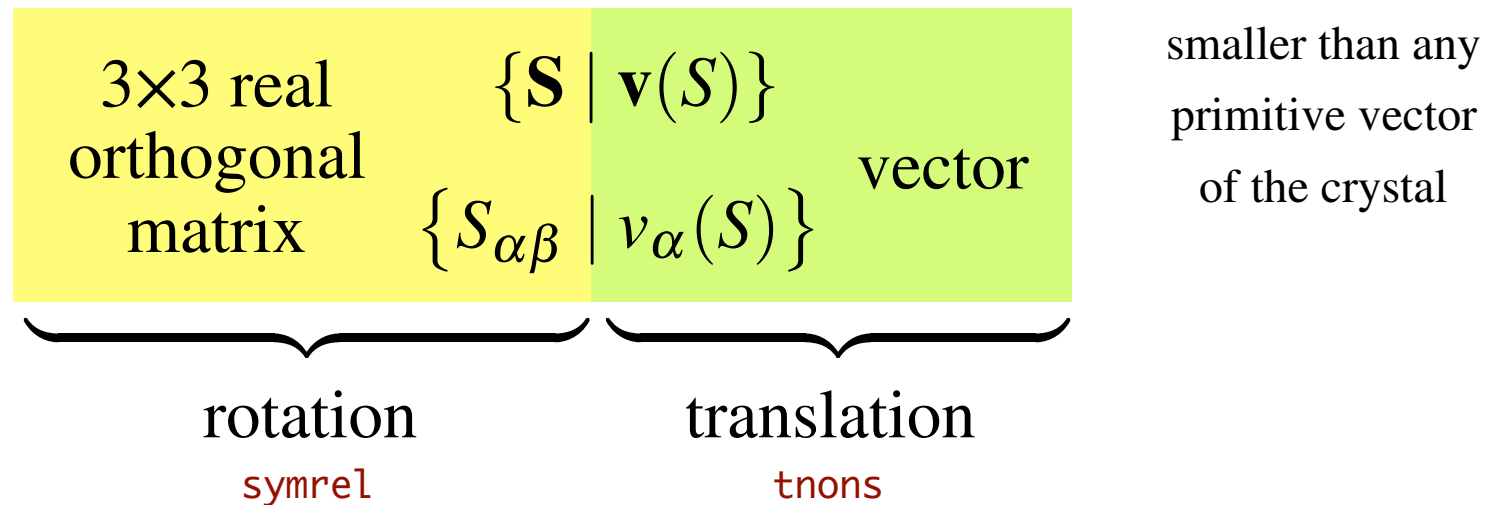
translation — tnons

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

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

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

Crystal symmetries and k-points (II)

The information in the full Brillouin zone can be reconstructed by symmetry from an appropriate irreducible wedge:

Irreducible wedge

$$
\begin{cases}
\epsilon_{\mathcal{S}\mathbf{k}} & = \quad \epsilon_{\mathbf{k}} \\
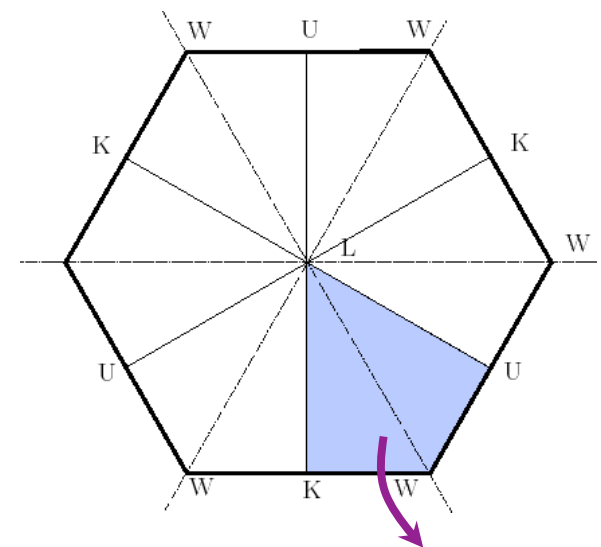u_{\mathcal{S}\mathbf{k}}(\mathbf{r}) & = \quad e^{-i\mathcal{S}\mathbf{k}\cdot\mathbf{t}}\, u_{\mathbf{k}}(\mathcal{S}^{-1}(\mathbf{r}-\mathbf{t})) \\
u_{\mathcal{S}\mathbf{k}}(\mathbf{G}) & = \quad e^{-i(\mathcal{S}\mathbf{k}+\mathbf{G})\cdot\mathbf{t}}\, u_{\mathbf{k}}(\mathcal{S}^{-1}\mathbf{G})
\end{cases}
$$

$$
\begin{cases}
\epsilon_{n\mathbf{k}} & = \quad \epsilon_{-\mathbf{k}} \\
u_{n\mathbf{k}}(\mathbf{r}) & = \quad u^{\dagger}_{n-\mathbf{k}}(\mathbf{r}) \\
u_{n\mathbf{k}}(\mathbf{G}) & = \quad u^{\dagger}_{n-\mathbf{k}}(-\mathbf{G})
\end{cases}
$$

- Monkhorst-Pack grids Phys. Rev. B 13, 5188 (1976)
- Tetrahedron method ...

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:

$$n(\mathbf{r}) = \sum_i^N \psi_i^*(\mathbf{r})\psi_i^*(\mathbf{r})$$

$$= \sum_{i \in \text{core}}^{N_{\text{core}}} \psi_i^*(\mathbf{r})\psi_i^*(\mathbf{r}) + \sum_{i \in \text{val}}^{N_{\text{val}}} \psi_i^*(\mathbf{r})\psi_i^*(\mathbf{r})$$

- « 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:

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

Frozen (imported from the atomic environment)

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

Computed until self-consistency is reached

$$+ \sum_{i\in val}^{N_{val}} \langle \psi_i | -\frac{1}{2}\nabla^2 | \psi_i \rangle + \int V_{ext}(\mathbf{r})n_{val}(\mathbf{r})\,d\mathbf{r} + \frac{1}{2}\int \frac{n_{val}(\mathbf{r}_1)n_{val}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,d\mathbf{r}_1 d\mathbf{r}_2$$

$$+ \int \frac{n_{val}(\mathbf{r}_1)n_{core}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}\left[n_{core} + n_{val}\right]$$

- The valence orbitals must still be orthogonal to core orbitals
- We need a "pseudopotentials" that mimics the quantum mechanical interaction between the frozen core orbitals and the valence electrons

Removing core electrons (I)

- Pseudopotentials try to remove completely the core orbitals from the simulation by removing the strong changes within a « cut-off radius r_{cut}

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

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

- $\epsilon_i^{ps} = \epsilon_i$
- $\psi_i^{ps}(\mathbf{r})$ smooth for $r < r_{cut}$ and $\psi_i^{ps}(\mathbf{r}) = \psi_i(\mathbf{r})$ for $r \geq r_{cut}$
- norm conservation: $\int_{r<r_{cut}} \left|\psi_i^{ps}(\mathbf{r})\right|^2 d\mathbf{r} = \int_{r<r_{cut}} \left|\psi_i(\mathbf{r})\right|^2 d\mathbf{r}$
- $\dfrac{d\psi_i^{ps}(\mathbf{r})}{d\mathbf{r}} = \dfrac{d\psi_i(\mathbf{r})}{d\mathbf{r}}$ for $r = r_{cut}$ D.R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979)
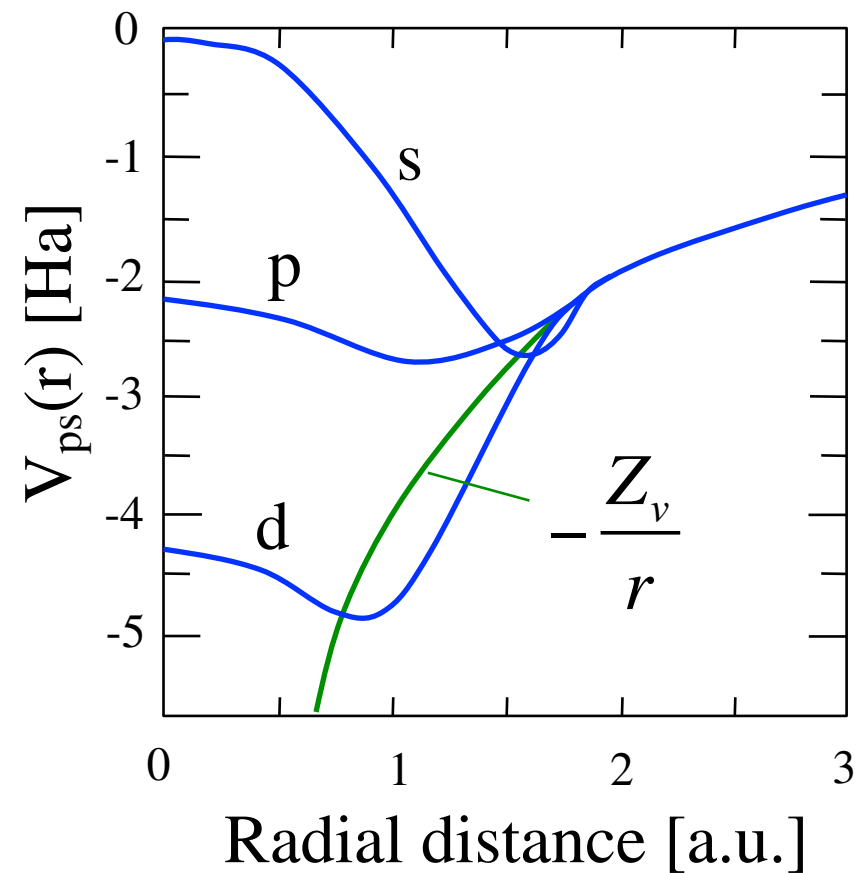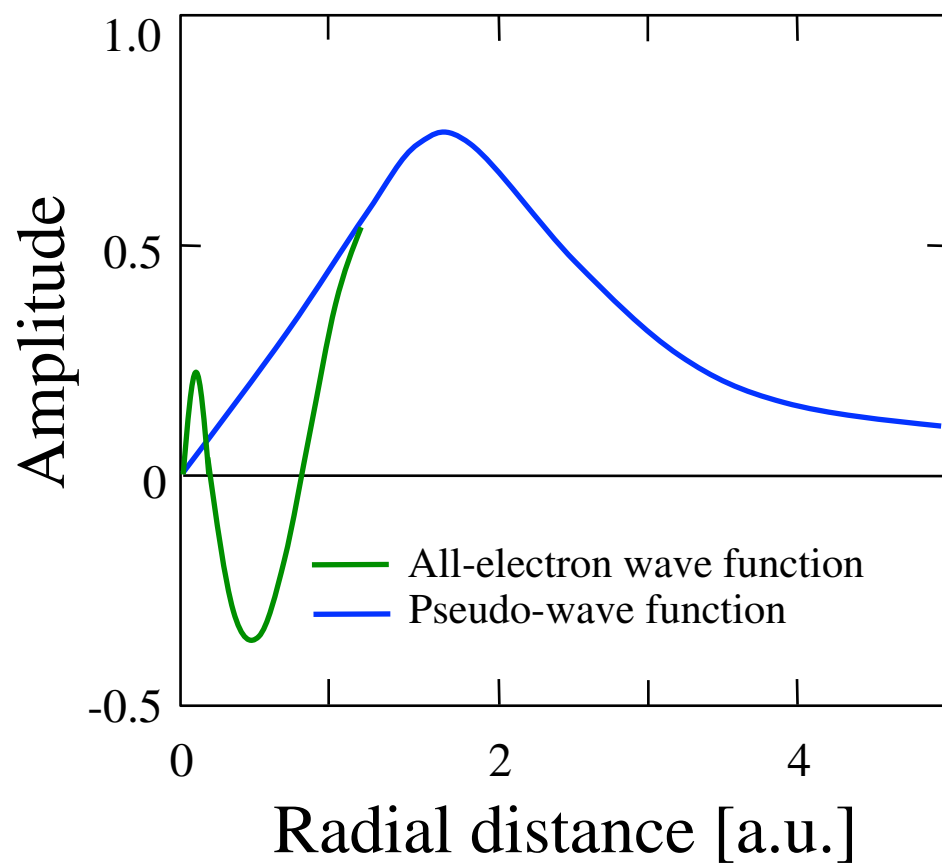
$$V_{ps} = \epsilon_i + \frac{1}{2}\frac{\nabla^2\psi_i^{ps}}{\psi_i^{ps}}$$

Different potentials for the different angular momenta

Example of pseudopotential

3s Radial wave function of Si

- $V_{ps}(\mathbf{r})$ smooth for $r < r_{cut}$ and $V_{ps}(\mathbf{r}) = V_{ion}(\mathbf{r})$ for $r \geq r_{cut}$
- Norm conservation implies transferability (atom --> crystal)

Removing core electrons (II)

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

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

kernel

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

Spherical Harmonics

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

- Pseudopotentials belong to two different classes:

  – the semi-local pseudopotentials for which:

  $$v_{\mathrm{NL},l}(r, r') = v_{\mathrm{SL},l}(r) \delta(r - r') \qquad \text{Phys Rev. B 26, 4199 (1982)}$$

  – the separable pseudopotentials for which:

  $$v_{\mathrm{NL},l}(r, r') = \xi_l^*(r) f_l \xi_l(r') \qquad \text{Phys. Rev. Lett. 48, 1425 (1982)]}$$

Forms of pseudopotentials

- Semi-local pseudopotentials are easily visualized, but separable ones are definitely more powerful for numerical techniques:

  - semi-local form:

  $$\langle \psi_{\mathbf{k}} | V_{nl} | \psi_{\mathbf{k}} \rangle = \sum_{\mathbf{GG'}} u^*(\mathbf{G}) V_{nl}^{\mathbf{k}}(\mathbf{G}, \mathbf{G'}) u(\mathbf{G'})$$

  - separable:

  $$\langle \psi_{\mathbf{k}} | V_{nl} | \psi_{\mathbf{k}} \rangle = \left[\sum_{\mathbf{G}} u(\mathbf{G}) F_{nl}^{\mathbf{k}}(\mathbf{G}) \right]^* \left[\sum_{\mathbf{G'}} F_{nl}^{\mathbf{k}}(\mathbf{G'}) u(\mathbf{G'}) \right]$$

- A technique was introduced to transform semi-local pseudopotentials into a separable form (caution: ghost states may appear).

Important papers

1979: Hamann, Schluter, and Chiang paper on the norm-conserving (NC) approach

1982: Pseudopotential table by Bachelet and al.

1982: Fully separable Kleinman-Bylander form

1989: Hamann's generalized pseudopotentials

1990: Troullier-Martins pseudization scheme

1991: Gonze's analysis of separable potentials

1990: Vanderbilt ultrasoft pseudopotentials (USPP)

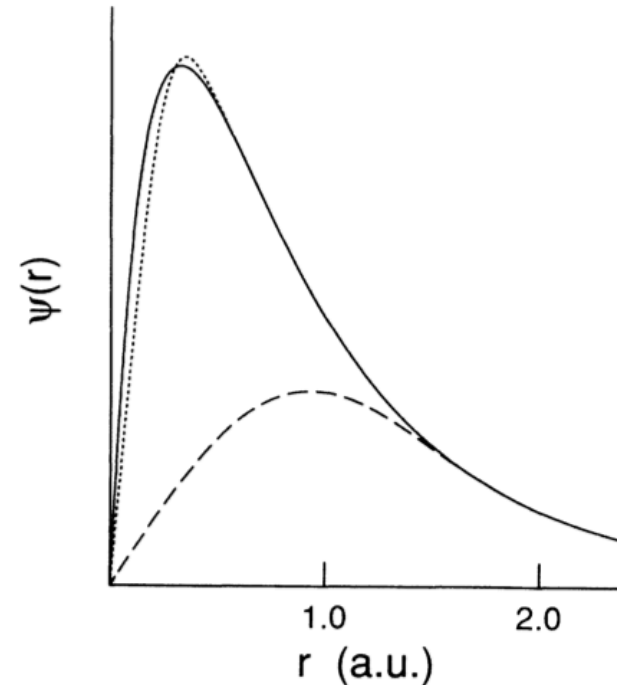**1991**: King-Smith real-space pseudopotentials

FIG. 1. Oxygen 2p radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

Unresolved problems

🔴 Hard compensation charges have to be used in the USPP formalism

🔴 Difficult to go beyond the frozen core (FC) approximation

🔴 Only pseudo quantities are accessible

Projector augmented-wave method

P. E. Blöchl

IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

An approach for electronic structure calculations is described that generalizes both the pseudopotential method and the linear augmented-plane-wave (LAPW) method in a natural way. The method allows high-quality first-principles molecular-dynamics calculations to be performed using the original fictitious Lagrangian approach of Car and Parrinello. Like the LAPW method it can be used to treat first-row and transition-metal elements with affordable effort and provides access to the full wave function. The augmentation procedure is generalized in that partial-wave expansions are not determined by the value and the derivative of the envelope function at some muffin-tin radius, but rather by the overlap with localized projector functions. The pseudopotential approach based on generalized separable pseudopotentials can be regained by a simple approximation.

- Correct nodal shape of the wavefunctions

- Flexible: all-electron, relaxed-core or different levels of frozen core

- Suitable for planewaves (PW), real space grids, wavelets, ...

- PW cutoff comparable to USPP

- Approximations involved in the theory can be easily tested

- NC and USPP are obtained under particular approximations

PAW TRANSFORMATION
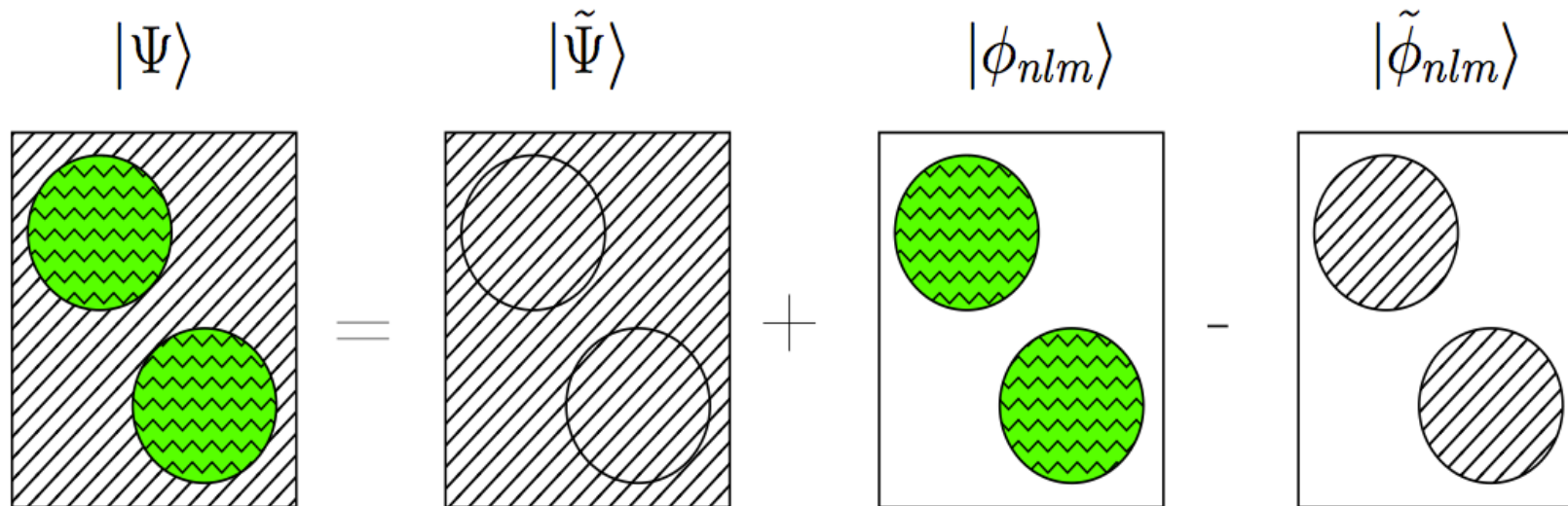
$$|\Psi\rangle = \hat{T}\,|\tilde{\Psi}\rangle$$

True wavefunction with strong oscillations difficult to describe

Smooth pseudo wave. Computationally efficient

▷ All-electron pseudopotential method

▷ KS equations are efficiently solved in the pseudized Hilbert space

▷ True matrix elements are obtained via $\langle\Psi|\hat{A}|\Psi\rangle = \langle\tilde{\Psi}|T^{\dagger}\hat{A}T|\tilde{\Psi}\rangle$

An efficient $\hat{T}$ is obtained by considering the behavior of electrons in solids:

- Atomic-like in the region around the ions

- Smooth behavior in the interstitial region

$$|\Psi\rangle \qquad |\tilde{\Psi}\rangle \qquad |\phi_{nlm}\rangle \qquad |\tilde{\phi}_{nlm}\rangle$$

All-electron wavefunction $\qquad$ Plane wave part $\qquad$ All-electron on-site part $\qquad$ Pseudized on-site part

$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^1\rangle - |\tilde{\Psi}^1\rangle \qquad\qquad |\tilde{\Psi}\rangle = |\tilde{\Psi}^1\rangle \quad \text{in } \Omega_a$$

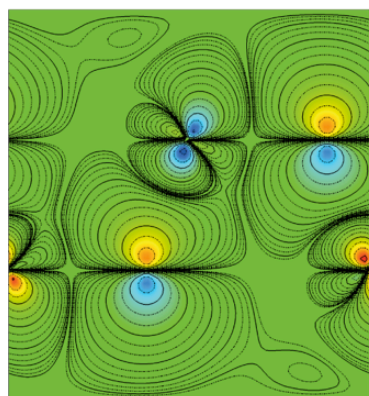**Smooth pseudo part** $\qquad$ **AE onsite term** $\qquad$ **PS onsite term** $\qquad\qquad$ **Provided that the basis set is complete**

$$\langle \tilde{p}_i^a | \tilde{\phi}_j^a \rangle = \delta_{ij} \qquad \xrightarrow{\textbf{Sufficient condition}} \qquad \sum_i |\tilde{\phi}_i^a\rangle\langle \tilde{p}_i^a| = \hat{1} \quad \text{in} \quad \Omega_a$$
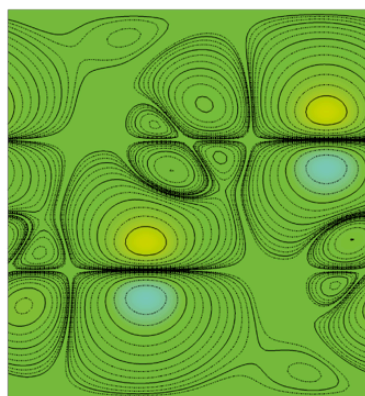
▷ Smooth $|\tilde{\phi}\rangle$ in reciprocal space lead to smooth $|\tilde{p}\rangle$

▷ Smooth $|\tilde{\phi}\rangle$ can be obtained with standard pseudization schemes

Components of the all-electron wavefunction in PAW

(Wurtzite ZnO in the 110 plane, highest occupied state at Gamma, log. contours)

$$\left| \Psi_\Gamma^{AE} \right\rangle = \left| \tilde{\Psi}_\Gamma^{PW} \right\rangle - \left| \tilde{\Psi}_\Gamma^{PS} \right\rangle_{SPH.} + \left| \Psi_\Gamma^{AE} \right\rangle_{SPH.}$$
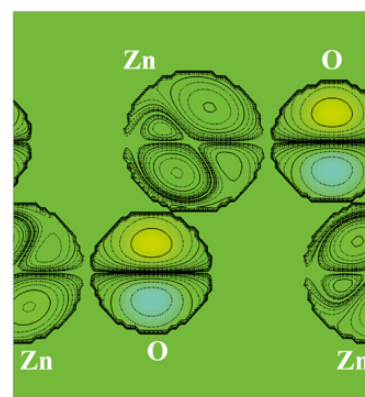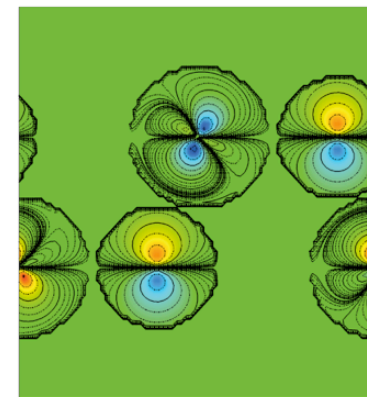
| All-electron wavefunction | Standard plane-wave part over unit cell | Pseudo-partial wave contribution in spheres | All-electron component in spheres |

(should exactly cancel PW part)

▷ Abinit supports NC pseudos generated by:

    (1) FHI code

    (2) APE

    (3) Opium

    (4) Quantum espresso (UPF format)

    (5) Hamann's code, Siesta format ...

▷ Abinit supports PAW files generated by:

(1) Atompaw
www.wfu.edu/~natalie/papers/pwpaw/man.html

(2) Vanderbilt's USPP code
www.physics.rutgers.edu/~dhv/uspp/

(3) PAWXML format
wiki3.fysik.dtu.dk/gpaw/setups/

■ Atomic data available
■ Atomic data non available

PAW atomic data

ABINIT table
Recommended atomic data

USppPAW table
From USPP code

AtomPAW table
From PWPAW code

User's contributions
PAW datasets produced by experienced ABINIT users

Old table
old atomic data (before may 07), for tests only

The ABINIT software project

What is ABINIT?

- It is a software that allows one to perform first-principles calculations in the framework of:

  - Density-Functional Theory (DFT)   → ground-state

    [P. Hohenberg & W. Kohn, Phys. Rev. 136, B864 (1964);

    W. Kohn & L.J. Sham, Phys. Rev. 140, A1133 (1965)]

  - Many-Body Perturbation Theory (MBPT)   → excited-states

    [L. Hedin, Phys. Rev. 139, A796 (1965);

    G. Onida, L. Reining, & A. Rubio, Rev. Mod. Phys. 74, 601 (2002)]

  - Density-Functional Perturbation Theory (DFPT)   → response

    [S. Baroni et al., Rev. Mod. Phys. 73, 515 (2001);

    X. Gonze, Phys. Rev. B 55, 10337 (1997);

    X. Gonze and C. Lee, Phys. Rev. B 55, 10355 (1997)]

ABINIT capabilities (I)

- Basis sets

    - planewaves

    - projector augmented waves (PAW)

    - wavelets (BIGDFT effort)

- Representation of atoms:

    - many norm-conserving pseudopotential types

    - different PAW generators

- Exchange-correlation functionals for DFT:

    - LDA
    } use LibXC
    - GGA

    - LDA+U (only with PAW)

    - + some advanced functionals (Meta-GGA, RPA)

ABINIT capabilities (II)

- Density-Functional Perturbation Theory :

  - Responses to atomic displacements, to static homogeneous electric field, and to strain perturbations

  - Second-order derivatives of the energy, giving direct access to: dynamical matrices at any q, phonon frequencies, force constants; phonon DOS, thermodynamic properties (quasi-harmonic approximation); dielectric tensor, Born effective charges; elastic constants, internal strain; piezoelectric tensor ...

  - Matrix elements, giving direct access to: electron-phonon coupling, deformation potentials, superconductivity

  - Non-linear responses thanks to the 2n+1 theorem - at present: non-linear dielectric susceptibility; Raman cross-section; electro-optic tensor

ABINIT capabilities (III)

- **Beyond DFT**

  - TDDFT: linear response (Casida) for finite systems excitation energies

  - GW for accurate electronic quasiparticles

    - ★ 4 plasmon pole models, analytic continuation, or contour integration

    - ★ non-self-consistent (G^0W^0), partly self-consistent (GW^0 or G^0W), quasiparticle self-consistent (QSGW), and vertex correction ($GW\Gamma$)

    - ★ susceptibility matrix by sum over states (Adler-Wiser)

    - ★ extrapolar and effective-energy technique to reduce the number of unoccupied states

  - Bethe-Salpeter for accurate optical properties calculations

ABINIT capabilities (IV)

- Insulators/metals - smearings: Fermi, Gaussian, Gauss-Hermite ...

- Collinear spin / non-collinear spin / spin-orbit coupling

- Forces, stresses, automatic optimization of atomic positions and unit cell parameters (Broyden and Molecular dynamics with damping)

- Molecular dynamics (Verlet or Numerov), Nosé thermostat, Langevin dynamics

- Electric field gradients

- Symmetry analyzer (database of the 230 spatial groups and the 1191 Shubnikov magnetic groups)

A bit of history...

- It all started in 1997...

  Idea: softwares for first-principles simulations become more and
           more sophisticated (not easy to develop and maintain).

  Solution: worldwide collaboration of specialized, complementary groups

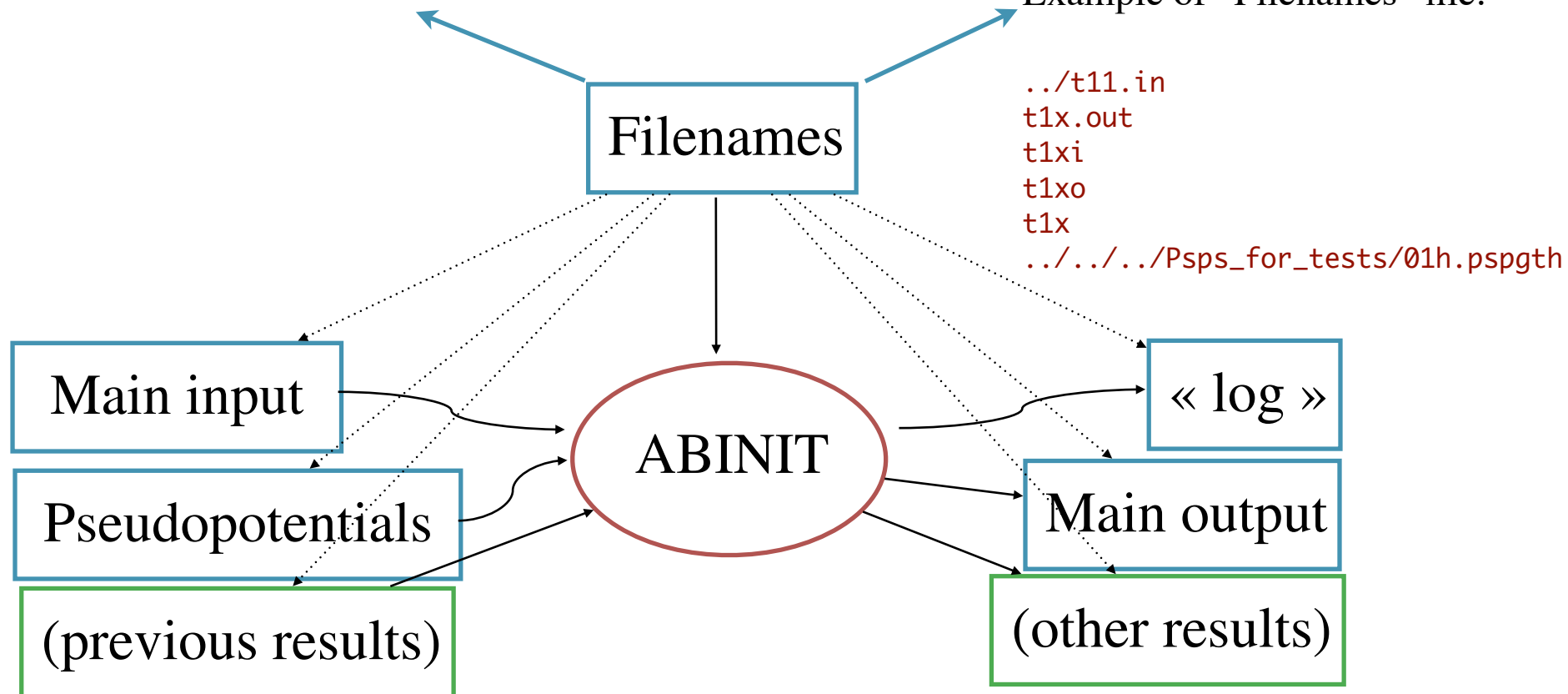 Model: Linux software development: 'free software' (GPL License)

- As of today (2014)

  - the software consists of more than 400 kLines of F90

  - more than 80 contributors

  - there are more than 1200 people on the users mailing list
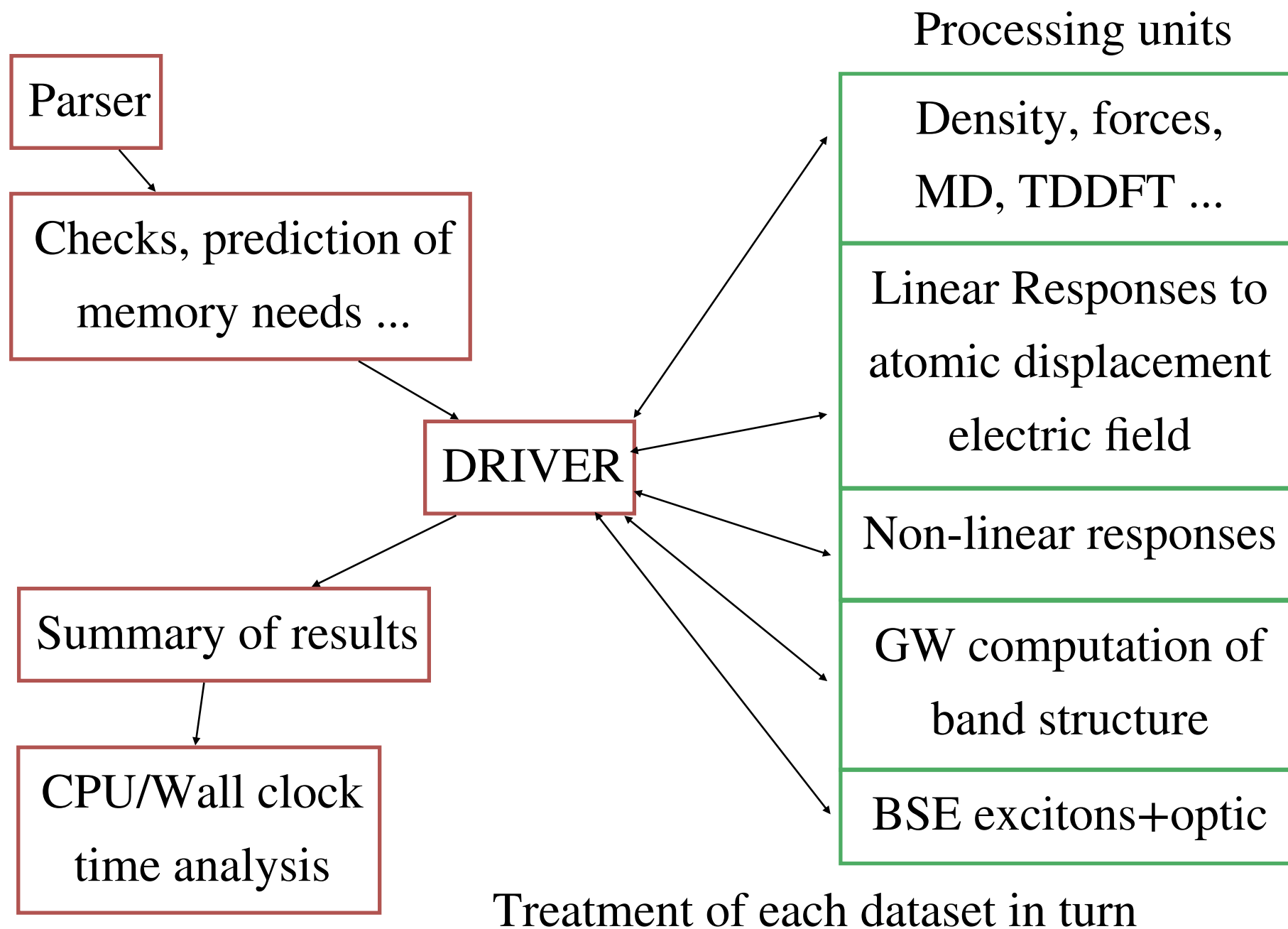
External files in a ABINIT run

prompt:> abinit < filenames > log 2> err &

Example of "Filenames" file:

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

Filenames

Main input

Pseudopotentials

(previous results)

ABINIT

« log »

Main output

(other results)

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

Functional structure of ABINIT

Parser

Checks, prediction of memory needs ...

DRIVER

Summary of results

CPU/Wall clock time analysis

Processing units

Density, forces, MD, TDDFT ...

Linear Responses to atomic displacement electric field

Non-linear responses

GW computation of band structure

BSE excitons+optic

Treatment of each dataset in turn

ABINIT tutorials

http://www.abinit.org/documentation/tutorials

ABINIT tutorials : layout and dependencies
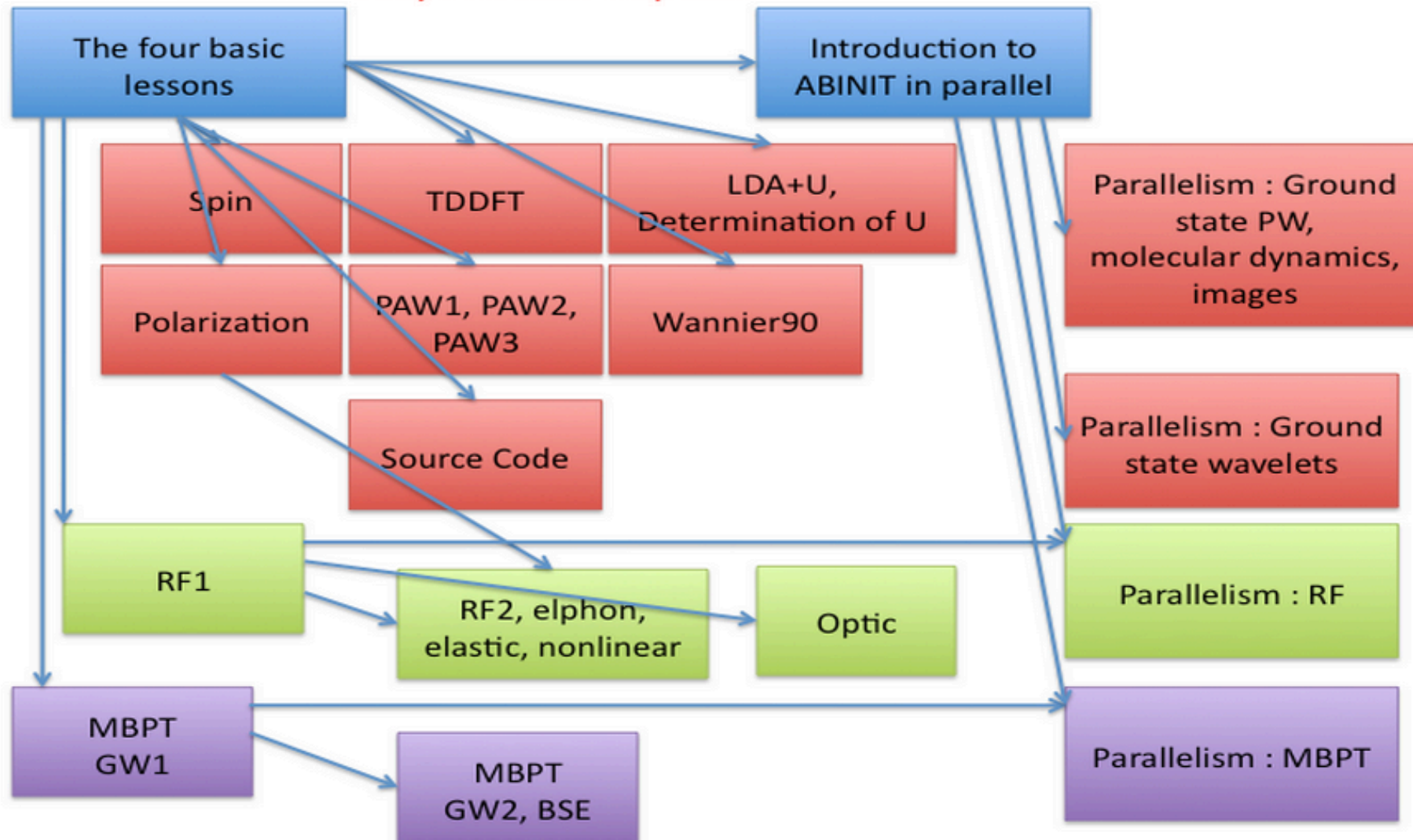
Parallelism in ABINIT

prompt:> mpirun -n 2 abinit < filenames > log 2> err &
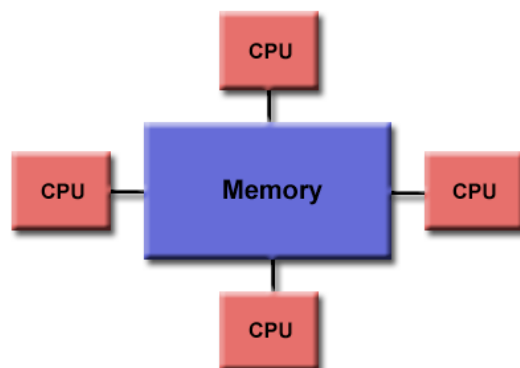
Two different parallel paradigms:

 For distributed-memory, shared-memory and hybrid architectures
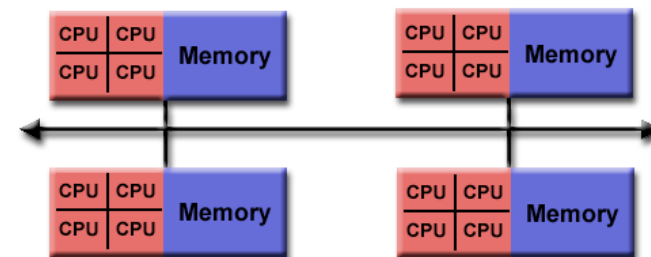
 For shared memory multiprocessing programming
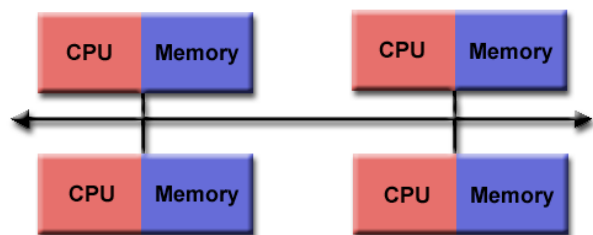
Distributed Memory

Shared Memory (UMA)

Hybrid Distributed-Shared Memory

Common configuration in supercomputing centers

Parallelism in ABINIT

MPI-parallelism of the DFT part of ABINIT:

- *Parallelism over k points and spins*: very efficient, memory is distributed but speedup is limited by nkpt * nsppol

- *Combined band/FFT/ k point/spin parallelism (paral_kgb=1)*: much better scalability. need excellent network and MPI-IO

- *Parallelism over bands* for linear-response calculations: efficient; can lead to large speed-ups; no memory gain; combined with k point and spin parallelization

- *Parallelism over perturbations* for linear-response calculations: very efficient, limited by the number of perturbation
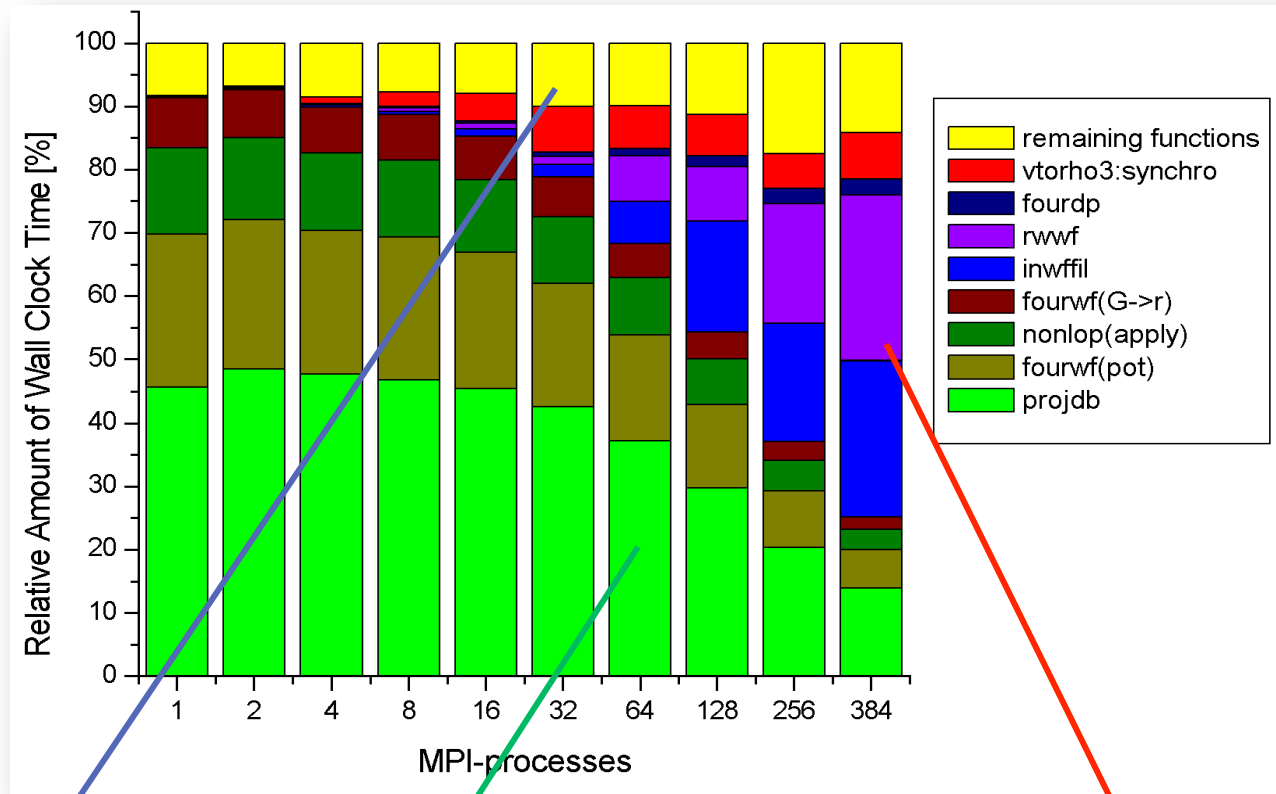
MPI-parallelism of the GW part of ABINIT:

- *k-point parallelism*: efficient but no memory gain

- *band parallelism*: very efficient; can lead to larger speed-ups; memory gain

ABINIT DFPT – PERFORMANCE ANALYSIS

Test done in october 2011 !

Repartition of time in response function calculations

A significant part of the overall wall-time is spent in FFTs and in linear algebra routines

IO becomes the main bottleneck when Ncpus > 64

Optimized libraries are needed for achieving optimal performance (Blas, Lapack, MPI-IO)

Libraries for High-Performance Computing

blas

Basic Linear Algebra Subprograms: a *de facto* standard to perform linear algebra operations such as vector and matrix multiplication

LAPACK

Linear Algebra PACKage: software library for numerical linear algebra (linear equations, eigenvalue problems, ...). It depends upon the BLAS in order to effectively exploit the caches

Implementations

- **Netlib BLAS:** The official reference implementation (written in Fortran77)
- **ACML:** for AMD architectures
- **ATLAS:** Automatically Tuned Linear Algebra Software, an open source implementation of BLAS
- **ESSL:** IBM's Engineering and Scientific Subroutine Library, supporting the PowerPC architecture
- **Goto BLAS:** Goto's implementation of BLAS
- **Intel MKL:** for Intel architectures
- and many others

FFTW

C library for computing the discrete Fourier transform of arbitrary input size, and of both real and complex data.

Wrappers with the same interface are provided by MKL and ESSL

How to link Abinit against MKL
(FFT+BLAS+LAPACK)

```
$> configure --with-config-file=myconf.ac && make -j4

$> cat myconf.ac

# FFT Library
with_fft_flavor="fftw3"

with_fft_libs="-L/opt/intel/mkl/lib/intel64 -lmkl_intel_lp64,
-lmkl_core -lmkl_intel_sequential -lpthread -lm"

with_fft_includes="-I/opt/intel/mkl/include"

# BLAS-LAPACK
with_linalg_flavor="mkl"
with_linalg_libs="-L/opt/intel/mkl/lib/intel64 -lmkl_lapack95_lp64 -
lmkl_blas95_lp64 -lmkl_intel_lp64 -lmkl_core -lmkl_intel_sequential -lpthread
-lm"

# consult the MKL link line advisor if you experience problems with MKL
# http://software.intel.com/en-us/articles/intel-mkl-link-line-advisor/
```

See also ~abinit/doc/build and ~abinit/doc/config/build-examples

The developers...

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Han-sur-Lesse (Belgium), April 2011