

*In honour of Walter Kohn, the “father” of the DFT*

# Introduction to Density Functional Theory and pseudo-potential concepts

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# Outlook

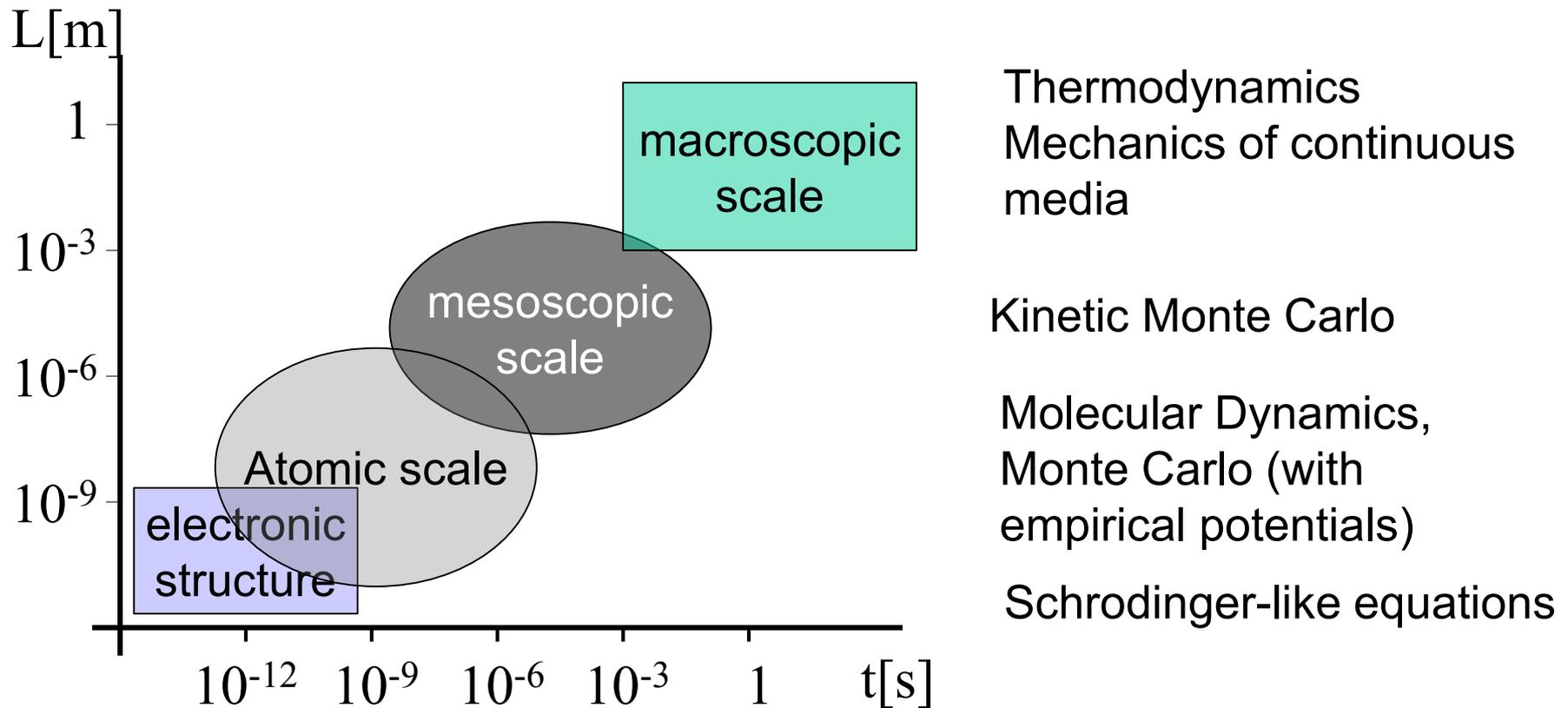
*Today, there are many available “ready-to-use” DFT-based codes :  
do we really know what is inside ?*

- 1) The electron density as the basic variable;** the energy as a density functional
- 2) Minimizing the energy functional;** the Kohn-Sham equations
- 3) The exchange-correlation energy:** basic definitions and the main approximations (LDA, GGA, hybrid functionals)
- 4) Plane-wave implementation**
- 5) Pseudo-potentials, an historical perspective:** core and valence electrons, norm-conserving and ultra-soft PSPs, PAW method

*The following lecture is for people having some previous experience with DFT :  
recalling main concepts, there are excellent books on DFT that provide more insight*

# Generalities

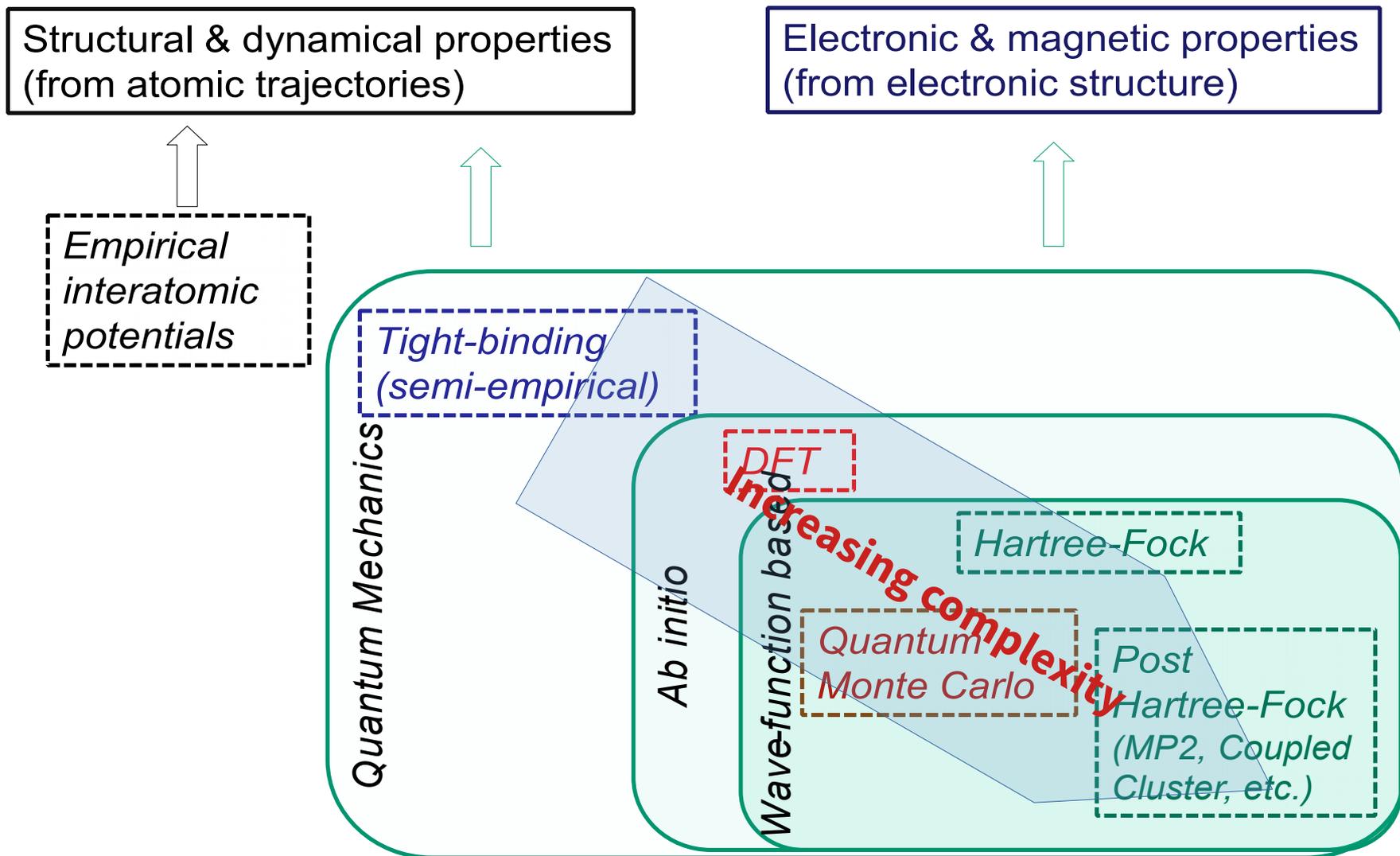
## *Time and length scales*



It is often necessary to combine different methods in order to tackle realistic problems

# Generalities

## Properties and methods



# Generalities

## *Ab initio methods*

Goal : Atom-atom interactions and material properties from first principles

- Energies : chemical accuracy = 1 kcal/mol = 43 meV / particle
- Atomic positions within 0.01 Å uncertainty
- Vibrational frequencies within 0.1 THz = 3.3 cm<sup>-1</sup>

What is actually affordable within ab initio methods

- Number of atoms < 1000
- Ab Initio Molecular Dynamics : shorter runs than 100 ps
- Accuracy crucially depends on the employed approximations

**AB INITIO == from the fundamental equations  
But the theory is necessarily approximated !**

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# I. The electron density as the basic variable

## *Fixed nuclei, search for the electronic wavefunction*

Time-independent Schrödinger equation for  $N$  electrons

The  $M$  nuclei are fixed in  $R_j$  (no spin, no relativistic effects)

$$\hat{H} = \sum_{i=1}^N \left[ -\frac{\hbar^2 \nabla_i^2}{2m} - \sum_{J=1}^M \frac{Z_J e^2}{|r_i - R_J|} \right] + \sum_{i < j} \frac{e^2}{|r_i - r_j|}$$

Ansatz:  $\Psi(r_1, r_2, \dots, r_N, R_1, \dots, R_M) = \psi(r_1, r_2, \dots, r_N; \{R_I\}) \chi(R_1, \dots, R_M)$



The electronic part of the wave function is too complex to be straightforwardly computed !!!

Ex:  $N=10$ ,  $P$  points to interpolate on each spatial coordinate  $\rightarrow P^{30}$  variables !!!

Is there any way to avoid the exponential growth of complexity with  $N$  ?

# I. The electron density as the basic variable

## *From density to Hamiltonian : an isolated atom*

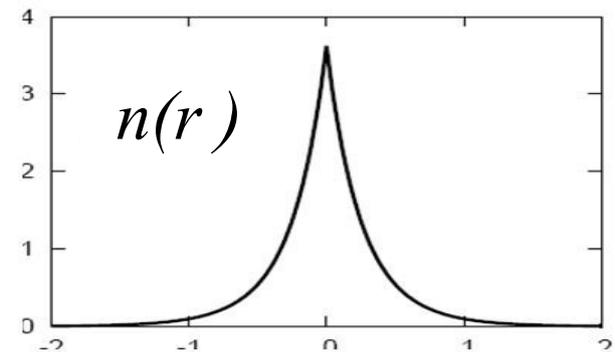
The (ground-state) electron density is a contraction over the spatial coordinates :

- Function of 3 coordinates, independently of  $N$
- It is in principle measurable

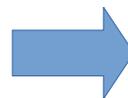
$$n(r) = \langle \psi_0 | \sum_{i=1}^N \delta(r - r_i) | \psi_0 \rangle$$

(almost) exact electron density for an isolated atom (ground state)

- Where is the nucleus ( $R$ ) ?
- How many electrons ( $N$ ) ?
- Atomic number  $Z$  ?



$$\hat{H} = \sum_{i=1}^N \left[ -\frac{\hbar^2 \nabla_i^2}{2m} - \frac{Z e^2}{|r_i - R|} \right] + \sum_{i < j} \frac{e^2}{|r_i - r_j|}$$



$R, N, Z$ , from  $n(r) \rightarrow$  the specific Hamiltonian is found !!!

# I. The electron density as the basic variable

## From density to Hamiltonian : Hohenberg-Kohn theorems

universal Hamiltonian  
for  $N$  electrons

System-specific one-  
electron operator

Careful: we work at constant  
number of electrons  $N$

$$\hat{H} = \sum_{i=1}^N \left[ -\frac{\hbar^2 \nabla_i^2}{2m} + \sum_{i < j} \frac{e^2}{|r_i - r_j|} \right] + \sum_{i=1}^N V_{ext}(r_i)$$

### HK theorem #1

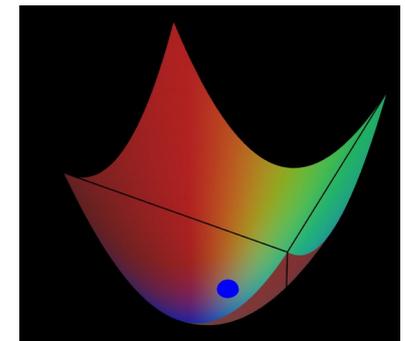
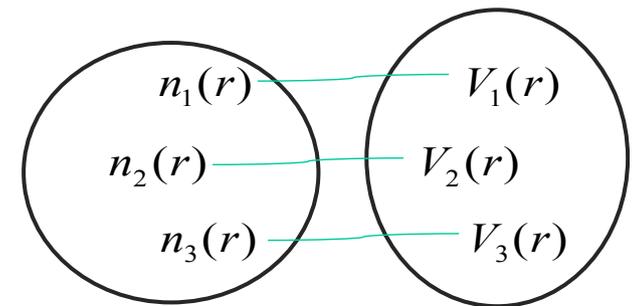
There is a one-to-one correspondence between  
**ground-state** electron densities and ext. potentials

$$E[n] = F[n] + \int dr n(r) V_{ext}(r)$$

### HK theorem #2

$E[n]$  has a minimum for the true **ground-state**  
electron density  $n_0(r)$  (among all possible ones)

→ find  $n_0(r)$  by minimizing  $E[n]$



# I. The electron density as the basic variable

## *Constrained search*

The “constrained-search” approach by Levy

M. Levy, PNAS 76 6062 (1979)

0. Search for the lowest energy among all  $N$ -electron wfs.

Be  $E$  the ground-state energy

$$E = \liminf_{\Psi} \langle \Psi | T + V_{ee} + V_{ext} | \Psi \rangle$$

1. Form classes of all  $N$ -electron wfs that give the same density  $n(r)$ , and minimize the energy

$$E_v[n] = \liminf_{\Psi \rightarrow n} \langle \Psi | T + V_{ee} | \Psi \rangle + \int dr n(r) v_{ext}(r)$$

2. Consider the wfs yielding  $E_v[n]$  and now minimize with respect to the density at fixed  $v(r)$

$$E = \liminf_n E_v[n]$$

“Conventional” step 0 is equivalent to steps 1+2

- 1) **The electron density as the basic variable**; the energy as a density functional
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- 4) **Plane-wave implementation**
- 5) **Pseudo-potentials, an historical perspective**: core and valence electrons, norm-conserving and ultra-soft PSPs, PAW method

## II. Minimizing $E[n]$

*variational approach*

$$\hat{H} = \sum_{i=1}^N \left[ -\frac{\hbar^2 \nabla_i^2}{2m} + \sum_{i < j} \frac{e^2}{|r_i - r_j|} \right] + \sum_{i=1}^N V_{\text{ext}}(r_i) \quad \longrightarrow$$

$$E[n] = T[n] + \frac{e^2}{2} \int dr_1 \int dr_2 \frac{n(r_1)n(r_2)}{|r_1 - r_2|} + U[n] + \int dr_1 n(r_1) V_{\text{ext}}(r_1)$$

Minimize  $E[n]$  at constant number  $N$  of electrons:

$$\frac{\delta}{\delta n(r)} \left[ E[n] + \mu \int dr n(r) \right] = \frac{\delta T[n]}{\delta n(r)} + e^2 \int dr_1 \frac{n(r_1)}{|r - r_1|} + \frac{\delta U[n]}{\delta n(r)} + V_{\text{ext}}(r) - \mu = 0$$

UNKNOWN FUNCTIONALS !!!

The Lagrange multiplier  $\mu$  on the number of electrons is the electron chemical potential :

$$\frac{\partial E[n]}{\partial N} = \mu$$

## II. Minimizing E[n]

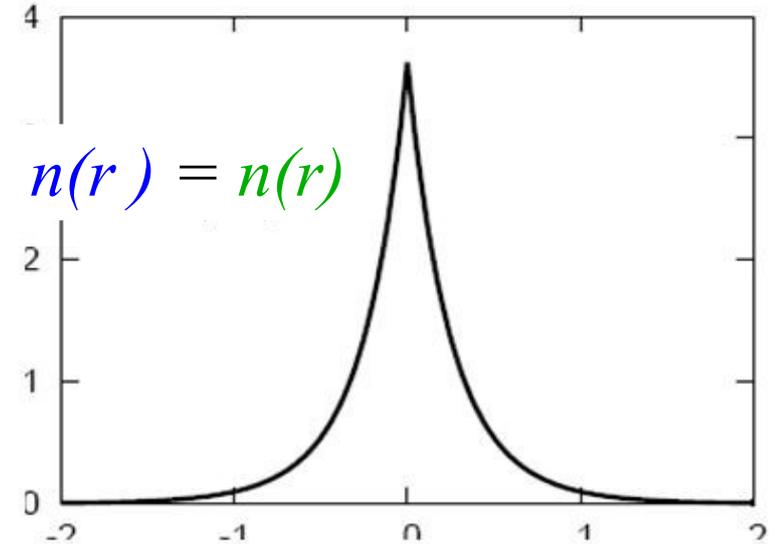
### *interacting vs. non-interacting electrons : density*

A year later (1965), Kohn and Sham had a brilliant idea: the density of the **physical system** (with e-e interaction) can be reproduced by a **fictitious system** (without e-e interaction) in a suitable one-electron external potential

Example: the He atom

$$-\frac{\hbar^2 \nabla_1^2}{2m} - \frac{\hbar^2 \nabla_2^2}{2m} - \frac{2e^2}{|r_1|} - \frac{2e^2}{|r_2|} + \frac{e^2}{|r_1 - r_2|}$$

$$-\frac{\hbar^2 \nabla_1^2}{2m} - \frac{\hbar^2 \nabla_2^2}{2m} - \frac{2e^2}{|r_1|} - \frac{2e^2}{|r_2|} + \delta V(r_1) + \delta V(r_2)$$



## II. Minimizing $E[n]$

### *interacting vs. non-interacting electrons : potential*

$$T[n] + U[n] = T_0[n] + E_{XC}[n] \quad \text{Interacting system (real)}$$

$$E[n] = T_0[n] + \frac{e^2}{2} \int dr_1 \int dr_2 \frac{n(r_1)n(r_2)}{|r_1 - r_2|} + E_{XC}[n] + \int dr n(r_1) V_{ext}(r_1)$$

$$\frac{\delta T_0[n]}{\delta n(r)} + e^2 \int dr_1 \frac{n(r_1)}{|r - r_1|} + \frac{\delta E_{XC}[n]}{\delta n(r)} + V_{ext}(r) = \mu$$

$$\frac{\delta T_0[n]}{\delta n(r)} + \delta V(r) + V_{ext}(r) = \mu$$

**Non-interacting system** (virtual)

The **non-interacting system** has the same electron density of the **real system** under the effective one-electron potential

$$V_{eff}(r) = e^2 \int dr_1 \frac{n(r_1)}{|r - r_1|} + \frac{\delta E_{XC}[n]}{\delta n(r)} + V_{ext}(r)$$

## II. Minimizing $E[n]$ the Kohn-Sham equations

Although  $T_0[n]$  is unknown, we can solve the **non-interacting**  $N$ -electron system !

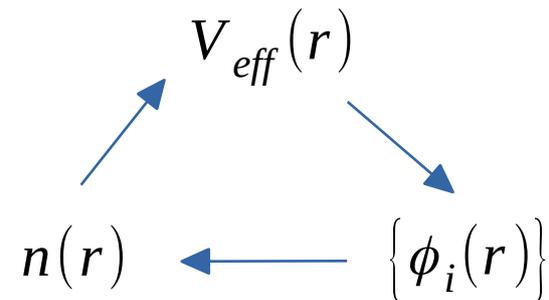
1. Expand the density in the virtual one-electron occupied orbitals

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

2. Each orbital obeys a Schrödinger equation in the effective one-electron potential

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{eff}}(r) \right] \phi_i(r) = \epsilon_i \phi_i(r) \quad \text{with} \quad V_{\text{eff}}(r) = e^2 \int dr_1 \frac{n(r_1)}{|r-r_1|} + \frac{\delta E_{XC}[n]}{\delta n(r)} + V_{\text{ext}}(r)$$

- Theoretical foundation of **one-electron equations** for  $N$  interacting electrons
- **Self-consistent equations**



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# III. Exchange-correlation density functional

## *basic definitions*

$$E[n] = T_0[n] + \frac{e^2}{2} \int dr_1 \int dr_2 \frac{n(r_1)n(r_2)}{|r_1 - r_2|} + E_{XC}[n] + \int dr n(r) V_{ext}(r)$$

$$E_{XC}[n] = \underbrace{T[n] - T_0[n]}_{\text{green}} + \underbrace{E_{e-e}[n] - \frac{e^2}{2} \int dr_1 \int dr_2 \frac{n(r_1)n(r_2)}{|r_1 - r_2|}}_{\text{blue}}$$

Difference between the kinetic energy of the interacting vs. the non-interacting electron gas at the same density

Difference between the e-e repulsion of the quantum and the classical electron gas :

- Exchange between paired electrons
- Correlation between electrons
- Self-interaction correction

**The exact  $E_{XC}[n]$  is unknown** apart from ideal systems (homogeneous electron gas) but there are many available approximations for the non-homogeneous electron gas

# III. Exchange-correlation density functional

## Example: the He atom, ground state

$$H = -\frac{\hbar^2 \nabla_1^2}{2m} - \frac{\hbar^2 \nabla_2^2}{2m} - \frac{2e^2}{|r_1|} - \frac{2e^2}{|r_2|} + \frac{e^2}{|r_1 - r_2|}$$

Singlet ground state (L=0, S=0)  
 $E_0 = -5.8075 \text{ Ryd}$

$$\psi(r_1, \sigma_1, r_2, \sigma_2) = \varphi(r_1, r_2) (\chi_{\uparrow}(1) \chi_{\downarrow}(2) - \chi_{\downarrow}(1) \chi_{\uparrow}(2)) / \sqrt{2}$$

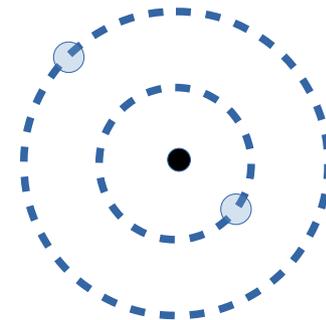
Trial #1:  $\varphi(r_1, r_2) = g_{\alpha}(r_1) g_{\alpha}(r_2)$  with  $g_{\alpha}(r) = \frac{\alpha^{3/2}}{\sqrt{\pi}} \exp(-\alpha r)$

$$E_0^{(1)} = \liminf_{\alpha} \langle \psi | H | \psi \rangle \rightarrow \alpha = 1.6875, E_0^{(1)} = -5.5695 \text{ Ryd}$$

Trial #2:  $\varphi(r_1, r_2) = g_{\alpha}(r_1) g_{\beta}(r_2) + g_{\beta}(r_1) g_{\alpha}(r_2)$

$$E_0^{(2)} = \liminf_{\alpha, \beta} \langle \psi | H | \psi \rangle \rightarrow \alpha = 2.18, \beta = 1.19, E_0^{(2)} = -5.5751 \text{ Ryd}$$

$\alpha \neq \beta \rightarrow$  the electrons are dynamically correlated  
and sit on different orbitals



# III. Exchange-correlation density functional

## *The spurious self-interaction*

### The H atom: a trivial case ?

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} - \frac{e^2}{r} \right] \phi(r) = \epsilon \phi(r)$$

The **exact** Schrödinger equation for the one-electron orbital

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} - \frac{e^2}{r} + e^2 \int dr_1 \frac{|\phi(r_1)|^2}{|r-r_1|} + \frac{\delta E_{XC}[n]}{\delta n(r)} \right] \phi(r) = \epsilon \phi(r)$$

The KS equation

The Kohn-Sham equation for the one-electron orbital is wrong, **unless the XC potential exactly compensates the self-interaction Coulomb term** (not automatic for any approximated functional)

The spurious self-interaction can be significant on localized orbitals (d and f states atomic-like states, trapped electrons, etc.).

It can be partially corrected via LDA+U (GGA+U) and hybrid functionals

# III. Exchange-correlation density functional

## *The Jacob's ladder*

Ooops ... we have to think the XC energy as a **functional of the electron density**

... ??? ...

**Meta-GGA**, including small dishomogeneity of the kinetic energy functional

$$n(r), \nabla n(r), \nabla^2 n(r), \sum_{i=1}^N |\nabla \phi_i(r)|^2$$

**Hybrid functionals** including a fraction of Fock exchange via the KS orbitals

$$n(r), \nabla n(r), \{\phi_i(r)\}$$

**DFT-vdW** including dispersion via the (approximate) response function of the electron gas

$$n(r), \nabla n(r), \frac{\delta n(r)}{\delta V(r')}$$

Generalized Gradient Approximations (**GGA**,  $\sigma$ -GGA)

$$n(r), \nabla n(r)$$

Local Density Approximations (**LDA**, LSDA)

$$n(r)$$

# III. Exchange-correlation density functional

## Formal properties

- Uniform coordinate scaling**  
 $r' = \lambda r$  and  $n'(r') = \lambda^{-3} n(r)$   
 $\Rightarrow E_X[n'] = \lambda^{-1} E_X[n]$  and  $T_0[n'] = \lambda^{-2} T_0[n]$
- Coupling-constant integration**  
( $e \rightarrow se$ )  
Varying the electron charge adiabatically, by keeping the electron density clamped at that of the interacting ( $s=1$ ) system  
$$E_{XC}[n] = \int_0^1 ds \langle \Psi_n^{(s)} | \hat{V}_{ee}^{(s)} | \Psi_n^{(s)} \rangle - U[n]$$
- Sum rules**  
$$E_{XC}[n] = \frac{e^2}{2} \int dr_1 \int dr_2 \frac{n(r_1) n_{XC}(r_1, r_2)}{|r_1 - r_2|}$$
  
 $\Rightarrow \int dr_2 n_{XC}(r_1, r_2) = -1 \quad \forall r_1$   
“XC” hole: conditional probability to have an electron at  $r_2$  when another is at  $r_1$
- Size consistency**  
$$E_{XC}[n_A + n_B] \rightarrow E_{XC}[n_A] + E_{XC}[n_B]$$
  
For spatially-separated A and B systems

# III. Exchange-correlation density functional

## Extension to spin (non-relativistic case)

1. Choose an (arbitrary) axis  $\mathbf{z}$  of quantization for the spin  $\rightarrow S_z$
2. Consider spin-up and spin-down KS orbitals  $\rightarrow$  spin-up and spin-down densities

$$n_{\uparrow}(r) = \sum_{i=1}^{N_{\uparrow}} |\phi_{i,\uparrow}(r)|^2 \qquad n_{\downarrow}(r) = \sum_{i=1}^{N_{\downarrow}} |\phi_{i,\downarrow}(r)|^2$$

3. The XC functional depends on both densities:  $E_{XC}[n_{\downarrow}, n_{\uparrow}]$

4. The KS spin-orbitals obey distinct Kohn-Sham equations

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + e^2 \int dr_1 \frac{n(r_1)}{|r-r_1|} + \frac{\delta E_{XC}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\downarrow}(r)} + V_{\text{ext}}(r) \right] \phi_{i,\downarrow}(r) = \epsilon_{i,\downarrow} \phi_{i,\downarrow}(r)$$
$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + e^2 \int dr_1 \frac{n(r_1)}{|r-r_1|} + \frac{\delta E_{XC}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\uparrow}(r)} + V_{\text{ext}}(r) \right] \phi_{i,\uparrow}(r) = \epsilon_{i,\uparrow} \phi_{i,\uparrow}(r)$$

# III. Exchange-correlation density functional

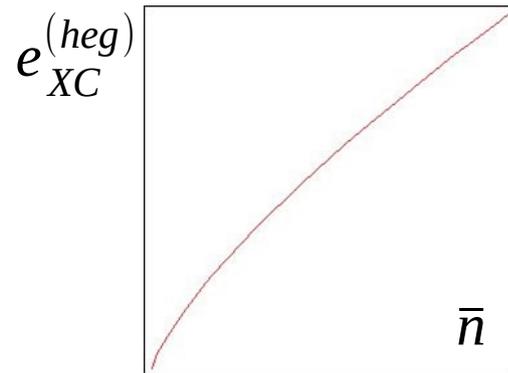
## *The homogeneous electron gas (heg)*

### A solvable model: the homogeneous electron gas

$$n(r) = \bar{n} = N/V \forall r \quad E_{XC}[n] \rightarrow E_{XC}^{(heg)} = N e_{XC}^{(heg)}(\bar{n})$$

The exchange-correlation energy per electron  $e_{XC}^{(heg)}(\bar{n})$  can be obtained from quantum MonteCarlo simulations of the heg for various mean densities  $\bar{n}$

(Ceperley & Alder, PRL 45, 566 (1980))



Note that the exchange energy of the heg can be easily computed

$$e_X^{(heg)}(\bar{n}) = -\frac{3}{4\pi} (3\pi^2 \bar{n})^{1/3}$$

# III. Exchange-correlation density functional

## The Local Density Approximation (LDA)

### The homogeneous electron gas

$$E_{XC}^{(heg)} = V \frac{N}{V} e_{XC}^{(heg)}(\bar{n})$$

LDA is not too bad in many systems with moderate XC effects (simple metals, elemental semiconductors, etc.)

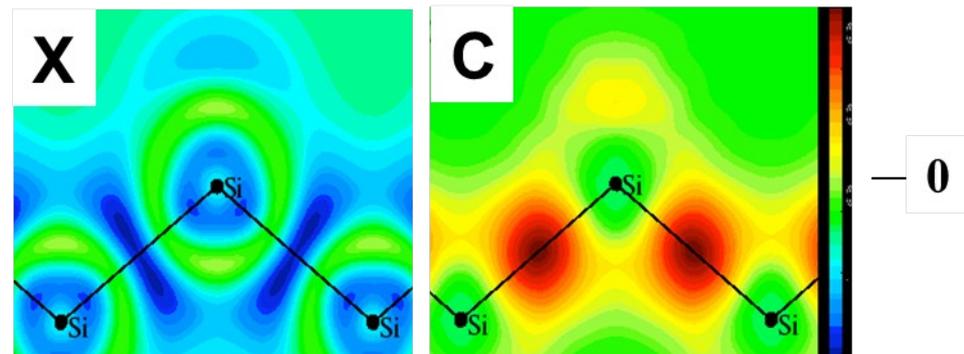
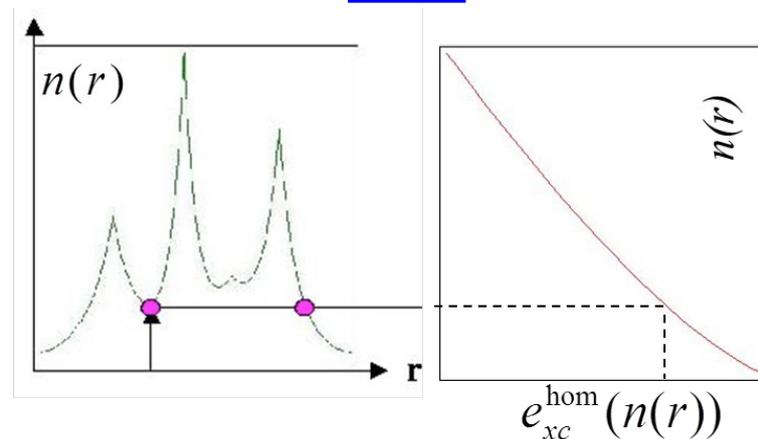
- Sum rule: the XC hole contains exactly an electron
- Good in the high-density limit
- Partial error compensation: underestimated  $|E_x^{(LDA)}|$  and overestimated  $|E_c^{(LDA)}|$

Difference between QMC and LDA exchange and correlation energies in Si (Hood et al. PRB 57, 8972)

### the inhomogeneous gas in the LDA

$$E_{XC}^{(LDA)} = \int dr n(r) e_{XC}^{(heg)}(n(r))$$

XC as a sum of local contributions



# III. Exchange-correlation density functional

## *The Generalized Gradient Approximation (GGA)*

Improving on the LDA via corrections depending on the density gradient

$$E_{XC}^{(GGA)} = E_{XC}^{(LDA)} + \int dr F_{XC}(n(r), s(r)) \quad \text{with} \quad s(r) = \frac{|\nabla n(r)|}{2k_F n(r)}$$

Distinct parametrizations of  $F_{XC}$  are available. Most of them behaves :

- $0 < s < 1$  : significant contributions to  $E_{XC}$
- $1 < s < 3$  : secondary contributions, still appreciable
- $s > 3$  : can be neglected, avoiding the unphysical divergence of the naïve gradient expansion for  $s \rightarrow \infty$

Main characteristics of GGAs (BP86, PW91, PBE, rPBE, PBEsol, etc.):

- Good description of weak bonds (H bonds)
- Atomic densities better described than in the GGA
- Often GGA outperforms LDA, sometimes GGA overcorrects LDA
- Long-range interactions (vdW) and strong correlated systems badly accounted for

# III. Exchange-correlation density functional

## Performances: GGA vs LDA

### Atoms:

Exchange-correlation energies in Ha

Atom	LSD	GGA	Exact
H	-0.29	-0.31	-0.31
He	-1.00	-1.06	-1.09
Li	-1.69	-1.81	-1.83
Be	-2.54	-2.72	-2.76
N	-6.32	-6.73	-6.78
Ne	-11.78	-12.42	-12.50

### Molecules:

Atomization energies in Ha

Molecule	LSD	GGA	Exact
H <sub>2</sub>	4.9	4.6	4.7
CH <sub>4</sub>	20.0	18.2	18.2
NH <sub>3</sub>	14.6	13.1	12.9
H <sub>2</sub> O	11.6	10.1	10.1
CO	13.0	11.7	11.2
O <sub>2</sub>	7.6	6.2	5.2

### Molecules and Solids:

mean relative errors	LSDA	GGA
• Bond lengths	-1%	+1%
• Strength of H bonds	+43%	+5%
• Frequencies	+3 %	-3%
• Electron affinity	+19%	+12%

A notable exception: the Au crystal

Au	$a_0$ (bohr)	$-E_{\text{coh}}$ (eV)
LDA	7.68	4.12
RLDA	7.68	4.09
GGA	7.87	2.91
RGGA	7.88	2.89
expt.	7.67	3.78

# III. Exchange-correlation density functional

## Performances: GGA vs LDA

Property	LSD	GGA
$E_x$	5% (not negative enough)	0.5%
$E_c$	100% (too negative)	5%
bond length	1% (too short)	1% (too long)
structure	overly favors close packing	more correct
energy barrier	100% (too low)	30% (too low)

Approximation	Mean absolute error (eV)
Unrestricted Hartree-Fock	3.1 (underbinding)
LSD	1.3 (overbinding)
GGA	0.3 (mostly overbinding)
Desired “chemical accuracy”	0.05

Perdew & Kurth, in “A primer in Density Functional Theory”, edited by C. Fiolhais, F. Nogueira and M.A.L. Marques, Springer (2003)

# III. Exchange-correlation density functional

## Orbital-dependent exchange

What about writing the exchange energy in terms of the Kohn-Sham orbitals instead of the density? *hum, not really a theory based on the density ...*

$$E_{XC} = E_C[n] + E_X[\phi_{1,\sigma}, \phi_{2,\sigma}, \dots, \phi_{N,\sigma}]$$

The Kohn-Sham equations become integral equations :

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + e^2 \int dr_1 \frac{n(r_1)}{|r-r_1|} + \frac{\delta E_C[n_\uparrow, n_\downarrow]}{\delta n_\sigma(r)} + V_{ext}(r) \right] \phi_{i,\sigma}(r) + e^2 \sum_{j>i} \int dr_1 \frac{\phi_{i,\sigma}(r_1) \bar{\phi}_{j,\sigma}(r_1) \phi_{j,\sigma}(r)}{|r-r_1|} = \epsilon_{i,\sigma} \phi_{i,\sigma}(r)$$

**This increases the numerical complexity** when:

- 1) Solving the KS equations at fixed potential
- 2) Iterating to self-consistency

# III. Exchange-correlation density functional

## Hybrid functionals : B3LYP

$E_{XC} = E_C^{(GGA)}[n] + E_X[\{\phi_{i,\sigma}\}] \Rightarrow$  worse results than in the GGA

*Fock theory has indeed many drawbacks ...*

Pragmatically (B3LYP) : try a linear combination of LSDA and “exact” exchange

$$E_{XC}^{(B3LYP)} = E_{XC}^{(LSDA)}[n] + a_0 \left( E_X[\{\phi_{i,\sigma}\}] - E_X^{(LSDA)}[n] \right) + a_X \Delta E_X^{(B88)}[n] + a_C \Delta E_C^{(LYP)}[n]$$

GGA correction to  $E_X^{(LDA)}$                       GGA correction to  $E_C^{(LDA)}$

Three free parameters     $a_0, a_X, a_C$

They were determined by a fit to a global set (“G2” set) of molecular properties

Pros and cons

- First XC approximation to provide reasonable energies for strongly correlated electron systems
- KS orbitals and eigenvalues closer to interacting-electron counterparts
- Numerical complexity, difficult to implement in plane-wave based codes
- Really ab initio ?

# III. Exchange-correlation density functional

## *Spatially-separated hybrid functionals : HSE06*

*Is bare (Fock) exchange suitable for solids? (e-e interaction is screened at long range)*

Heyd, Scuseria and Ernzerhof introduced in 2006 a hybrid functional, where the linear combination of GGA and Fock exchange is controlled by two parameters

$$E_{XC}^{(HSE06)} = \alpha E_X^{sr}[\{\phi_{i,\sigma}\}] + (1-\alpha) E_X^{(PBE-sr)}[n] + E_X^{(PBE-lr)}[n] + E_C^{(PBE)}[n]$$

Fock exchange, short-range    GGA exchange, short-range    GGA exchange, long-range

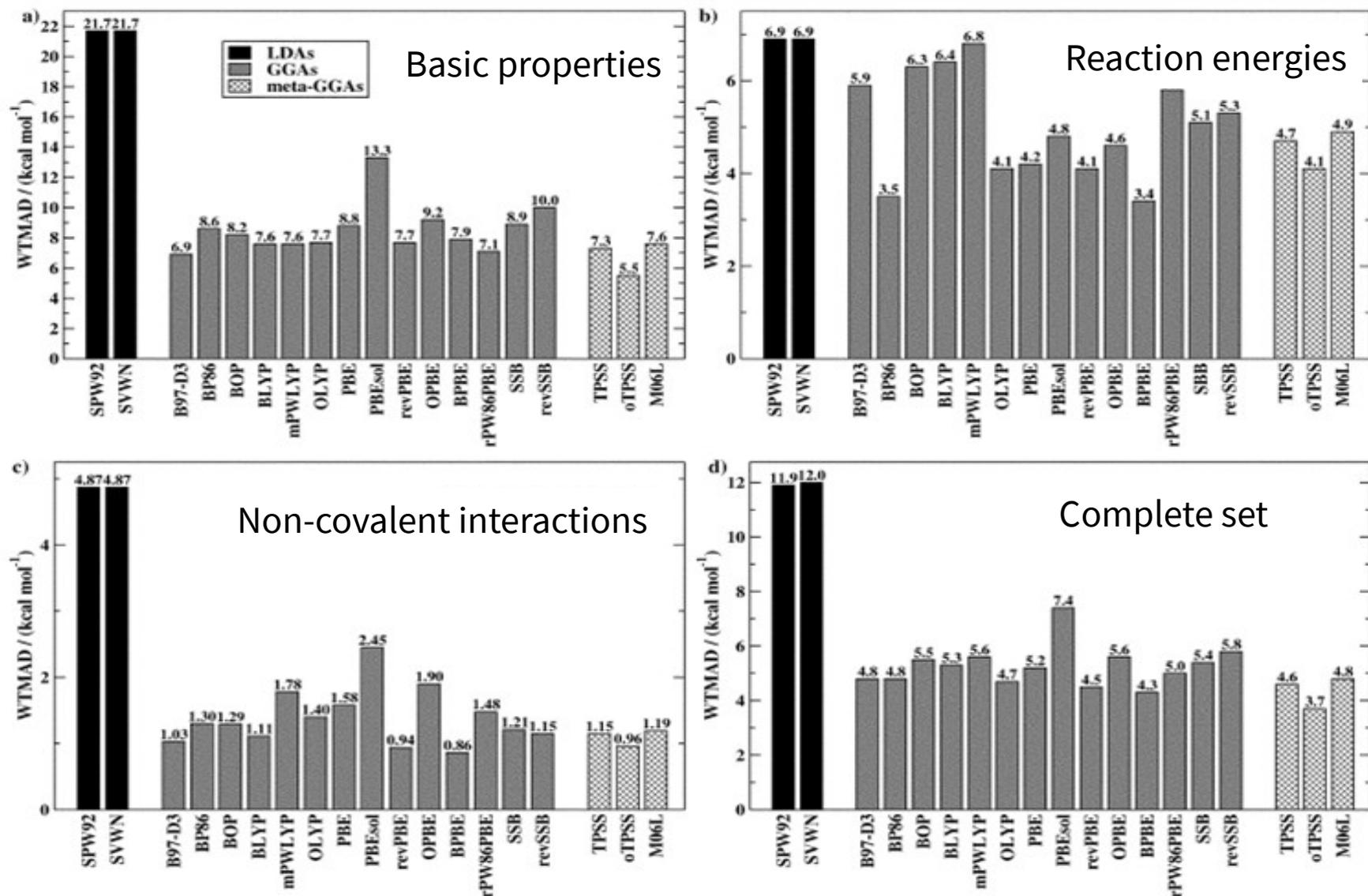
Typical values:     $\alpha \sim 0.25$  ;  $\omega \sim 0.20 \text{ \AA}^{-1}$      $\omega^{-1}$  defines the typical cutoff distance between short and long range

Pros and cons

- Often better than B3LYP in solids, not necessarily in finite systems (molecules)
- KS orbitals and eigenvalues rather close to interacting-electron counterparts
- Numerical complexity, difficult to implement in plane-wave based codes
- Physically sound, the range separation can be justified by many-body theories

# III. Exchange-correlation density functional

## Performances: LDA, GGA, meta-GGA



Grimme, PCCP 13, 6670 (2011)

- 1) **The electron density as the basic variable**; the energy as a density functional
- 2) **Minimizing the energy functional**; the Kohn-Sham equations
- 3) **The exchange-correlation energy**: basic definitions and properties and the main approximations (LDA, GGA, hybrid functionals)
- 4) **Plane-wave implementation**
- 5) **Pseudo-potentials, an historical perspective**: core and valence electrons, norm-conserving and ultra-soft PSPs, PAW method

# IV. Plane Waves

## *PW expansion : fundamentals*

Framework: solve the Kohn-Sham equations **at fixed effective potential**

*(for how to attain self-consistency, listen at the next lectures ...)*

1. Work in the crystal representation (i.e. **periodic boundary conditions**)

$$\phi_{i,k}(r) = e^{ik \cdot r} u_{i,k}(r) \quad \text{with} \quad u_{i,k}(r + \sum (l_1 a_1 + l_2 a_2 + l_3 a_3)) = u_{i,k}(r)$$

2. Expand the periodic part of the orbital in PWs with wave vector  $G = m_1 b_1 + m_2 b_2 + m_3 b_3$

$$\phi_{i,k}(r) = \sum_G c_i(k+G) e^{i(k+G) \cdot r} \theta(E_{cut}^{(1)} - \hbar^2 |k+G|^2 / 2m)$$

Fourier expansion coeffs: the dof in PW-based codes      The sum is truncated at the cutoff energy  $E_{cut}^{(1)}$

3. Expand the other periodic quantities (density, potential) in plane waves

$$n(r) = \sum_G \tilde{n}(G) \theta(E_{cut}^{(2)} - \hbar^2 G^2 / 2m) \quad \text{second cutoff energy} \quad E_{cut}^{(2)}$$

4. Adjust the two cutoff energies in order to attain converged quantities

**The higher the cutoff, the more accurate the results, the slower the calculations**

# IV. Plane Waves

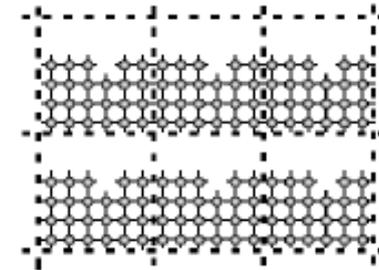
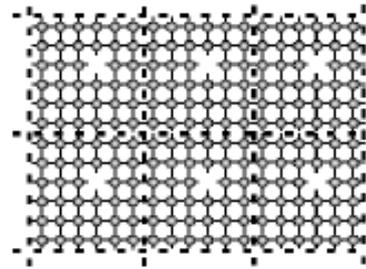
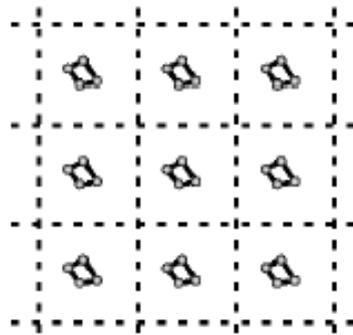
## *the super-cell*

PW's are a complete basis set for any *periodic* function ....

What about clusters,

defects,

surfaces ?



They are *artificially* made periodic !

☺ Some spurious interactions can be avoided by enlarging the unit cell

☹ Some others are long-range ( $\int d^3r |V(r)|$  diverges). Ex: charge-charge, charge-dipole, dipole-dipole → use of compensating background (uniform charge, dipole) or other numerical skills

# IV. Plane Waves

## *the calculation of the electron density*

Usually, about  $10^4$  PWs in a super-cell calculation: we must avoid any double sum over reciprocal (G) wave-vectors → **massive use of fast Fourier transforms (FFT)**

Example: the electron density

$$n(r) = \sum_{i,k} w_k |u_{i,k}(r)|^2$$

Product in **r-space** ↔ convolution in **G-space**

Instead:

$$c_i(k+G)$$



$$u_{i,k}(r)$$



$$n(r) = \sum_{i,k} w_k |u_{i,k}(r)|^2$$

$$\tilde{n}(G)$$

FFT



These operations are of the order of  $N M_{PW} \log M_{PW}$

Number of occupied orbitals

Number of Pws (grid 1)

# IV. Plane Waves

## *R-space (direct) and G-space (reciprocal)*

Some terms are easier to compute in the **direct ( $r$ -) space**, others in the **reciprocal ( $G$ -) space**

XC energy and potential (LDA)

$$E_{\text{xc}}[n(\mathbf{r})] = \int_{\Omega_0} (n(\mathbf{r}) + n_c(\mathbf{r})) \varepsilon_{\text{xc}}(n(\mathbf{r}) + n_c(\mathbf{r})) d\mathbf{r}$$
$$v_{\text{xc}}(n(\mathbf{r})) = \left. \frac{d((n + n_c) \varepsilon_{\text{xc}}(n + n_c))}{dn} \right|_{n=n(\mathbf{r}); n_c=n_c(\mathbf{r})}$$

Hartree potential

$$v_{\text{H}}^{(0)}(\mathbf{G}) = \begin{cases} 2\pi \Omega_0 \sum_{\mathbf{G}' \neq 0} \frac{n(\mathbf{G}')}{|\mathbf{G}'|^2} & \text{when } \mathbf{G} \neq 0, \\ 0 & \text{when } \mathbf{G} = 0. \end{cases}$$

Fast Fourier Transforms (FFT's) are used to avoid convolution products

$$\{\mathbf{r}\} \begin{array}{c} \xrightarrow{\text{FFT}} \\ \xleftarrow{\text{FFT}^{-1}} \end{array} \{\mathbf{G}\}$$

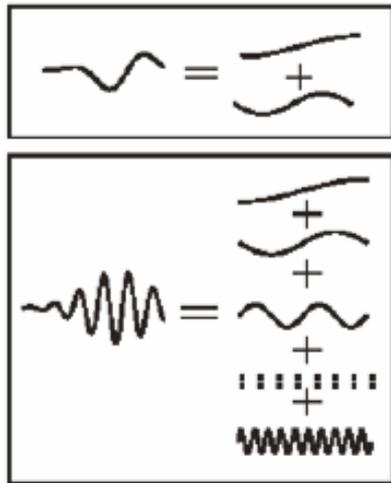
- 1) **The electron density as the basic variable**; the energy as a density functional
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# V. Pseudo-potentials

## Core and valence states

We aim at simulating material properties:

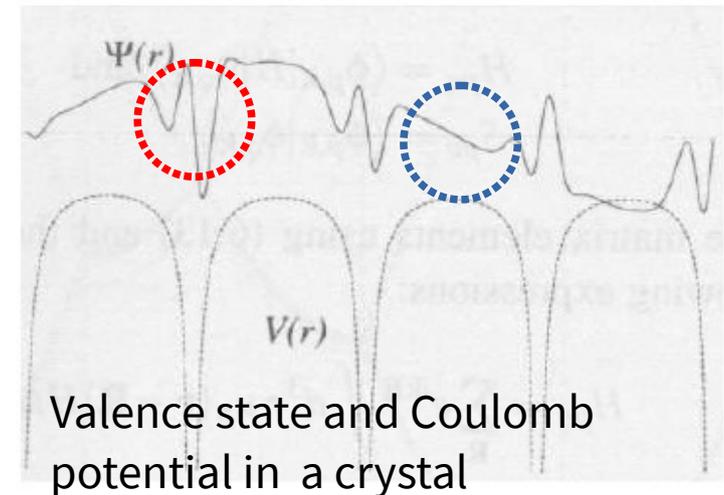
1. Do we really need to describe core states ?
2. For certain properties, is it possible to adopt a partial representation of valence states ?



Huge gradients  
Imply many plane  
waves for the orbital  
expansion ...

Core region:  
atomic-like, quick  
oscillations

Interstitial  
region(bonding)  
smooth variations



Valence state and Coulomb potential in a crystal

How to “get rid” of core states ?

How to properly “replace” the true valence states with smooth ones ?

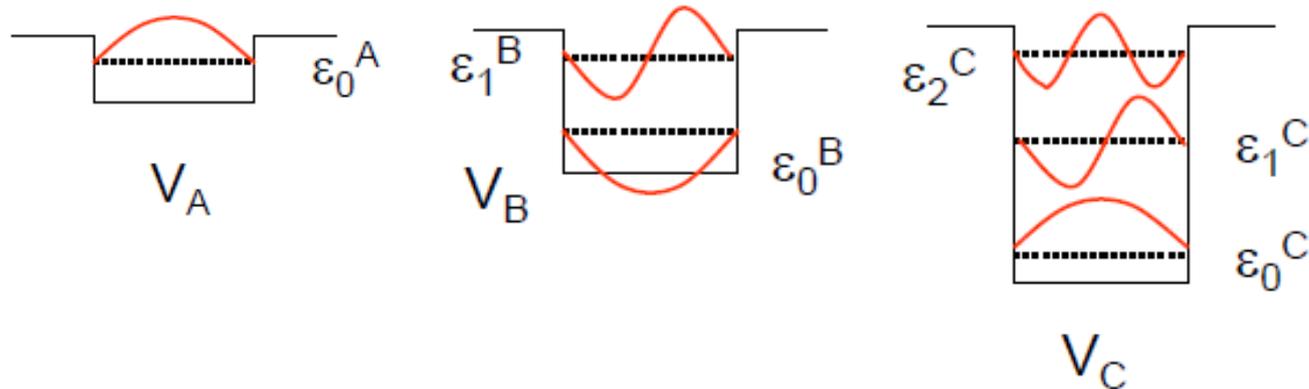
# V. Pseudo-potentials

## *The heuristic approach*

A simple model: the 1D potential well.

When varying the well depth, the number of bound states grows.

Among certain depths, the energy of the uppermost states coincides



The idea: replace  $V_C$  with  $V_A$ , by reproducing the relevant properties of the valence (uppermost) states.

An old idea: Fermi (1936), Philips & Kleinman (1959), and others ...

# V. Pseudo-potentials

## Phillips & Kleinman : projectors

$$|\psi_v\rangle \quad \text{“true” valence state} \quad \Longrightarrow \quad H|\psi_v\rangle = \epsilon_v|\psi_v\rangle \quad \text{and} \quad \langle\psi_c|\psi_v\rangle = 0$$

$$|\psi_v\rangle = |\phi_v\rangle - \sum_c |\psi_c\rangle \langle\psi_c|\phi_v\rangle \quad |\phi_v\rangle \quad \text{pseudo-valence state}$$

$$\text{Which equation for } |\phi_v\rangle ? \quad \left( H + \sum_c (\epsilon_v - \epsilon_c) |\psi_c\rangle \langle\psi_c| \right) |\phi_v\rangle = \epsilon_v |\phi_v\rangle$$

-  $|\phi_v\rangle$  has same eigenvalue as  $|\psi_v\rangle$  !

- The pseudo-Hamiltonian having  $|\phi_v\rangle$  as solution, contains now a projector on the core states, which is

(1) short-range, (2) non-local, and (3) repulsive

$$H_{ps} = H + \sum_c (\epsilon_v - \epsilon_c) |\psi_c\rangle \langle\psi_c|$$

Careful: non-unique solutions !!!

$$\text{ex. try with } |\phi'_v\rangle = |\phi_v\rangle - \sum_c \alpha_c |\psi_c\rangle$$

# Outlook

- 1) **The electron density as the basic variable**; the energy as a density functional
- 2) **Minimizing the energy functional**; the Kohn-Sham equations
- 3) **The exchange-correlation energy**: basic definitions and properties and the main approximations (LDA, GGA, hybrid functionals)
- 4) **Plane-wave implementation**
- 5) **Pseudo-potentials, an historical perspective**: core and valence electrons, norm-conserving and ultra-soft PSPs, PAW method

# V. Pseudo-potentials

## ”Ab initio” pseudopotentials: main ingredients

What are they made of ?

- A long-range Coulomb-like ionic potential by the nucleus and the core electrons

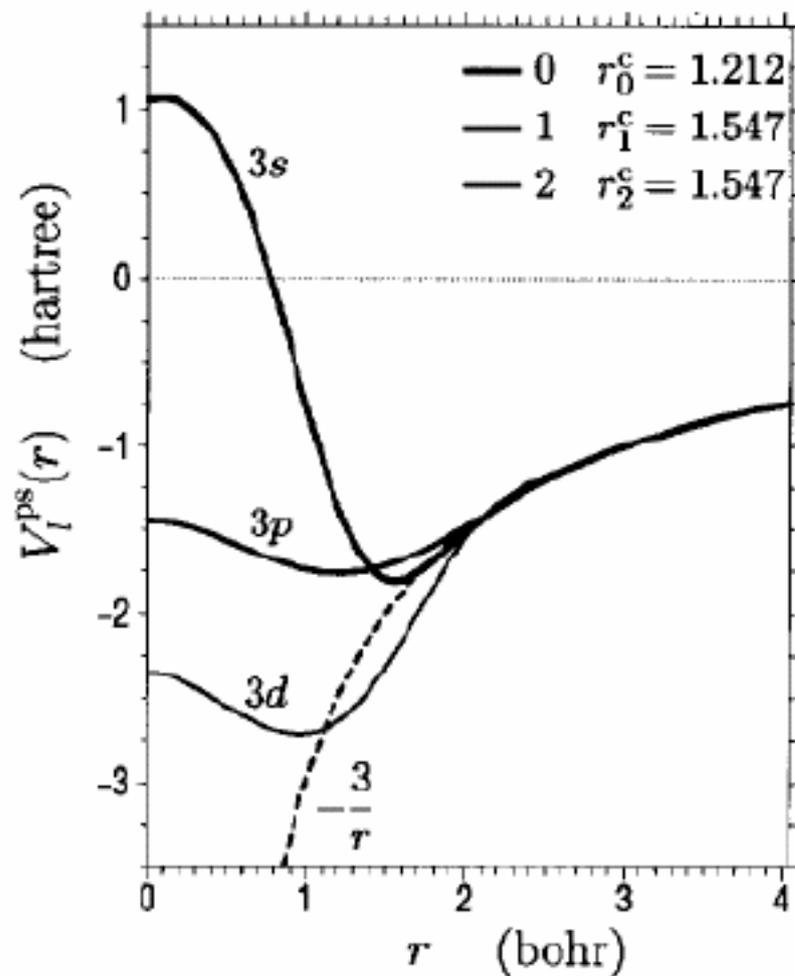
$$\hat{V}_{loc} = -\frac{(Z - N_c)}{r} \sim -\frac{Z_{ion}(r)}{r}$$

- A short-range, non-local projector, usually repulsive and different for each angular momentum

$$\hat{V}_{nl} = \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \Delta v_l^{(ps)}(r) \delta(r-r') |Y_{lm}\rangle \langle Y_{lm}|$$

Local in  $r$ , non-local on the angular coordinates

Norm-conserving pseudopotential, Al



Fuchs & Scheffler, Comp. Phys. Comm. 119 (1999) 67

# V. Pseudo-potentials

## Semi-local and separable pseudopotentials

A computational “trick”: The Fourier transform of fully non-local pseudopotentials (in  $r, \theta, \phi$ ) is simply the product of two matrix elements :

$$\langle G ( |f_{n,l} Y_{lm}\rangle \langle Y_{lm} f_{n,l}| ) G' \rangle = \langle G |f_{n,l} Y_{lm}\rangle \langle f_{n,l} Y_{lm} | G' \rangle$$

Fully non-local pseudopotentials are very desirable in plane-waves based codes

How to go from semi-local to fully non-local pseudopotentials ?

- 1) At given  $l$ , use the radial eigenstates as projectors
- 2) Define a dual space
- 3) And obtain, after some algebra

$$\sum_{n=0}^{\infty} |f_{nl}\rangle \langle f_{nl}| = \delta(r-r')$$

$$\langle \beta_{n'l'm'} | f_{nl} Y_{lm} \rangle = \delta_{n,n'} \delta_{l,l'} \delta_{m,m'}$$

$$\hat{V}^{(ps)} = \hat{V}_{local} \delta(r-r') + \sum_{i=nlm} \sum_{j=n'l'm'} B_{ij} |\phi_i\rangle \langle \phi_j|$$

with

$$B_{ij} = \langle \phi_i | \sqrt{\Delta v_i^{(ps)} \Delta v_j^{(ps)}} | \phi_j \rangle$$

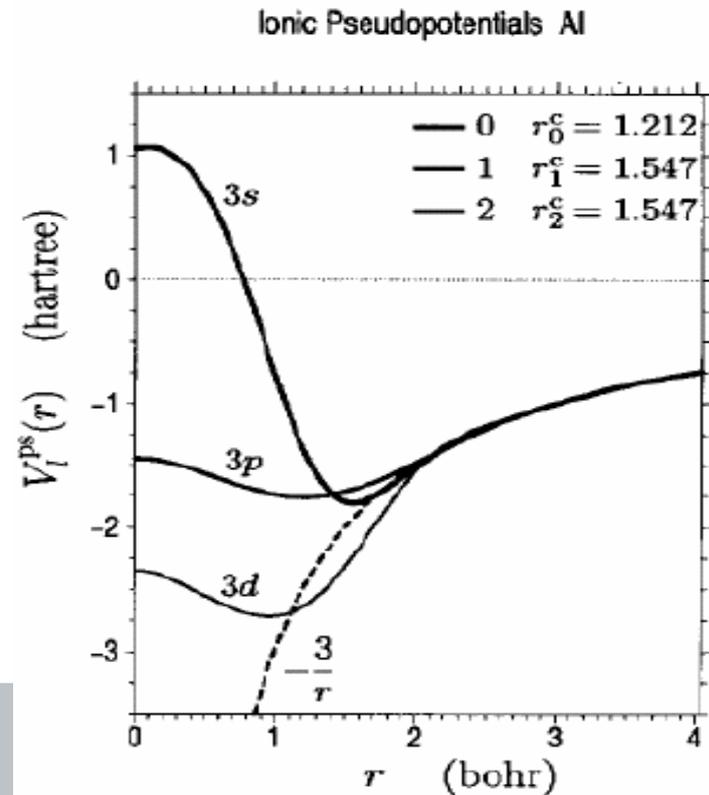
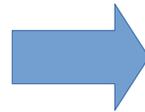
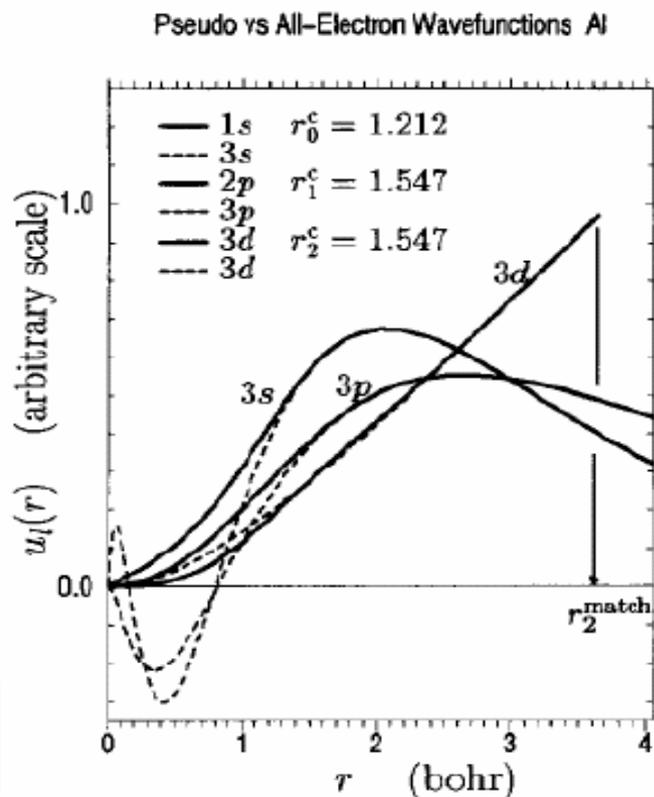
Actually, Kleinman & Bylander proposed in 1982 a similar transformation where only one term of the expansion in (1) was retained ... partial representation of the  $\delta$  function

**→ low-energy spurious solutions below the valence energies (“ghost states”)**

# V. Pseudo-potentials

## “Standard” recipe for norm-conserving pseudo-potential

- 1) Separation core/valence and choice of the reference atomic configuration  
→ true (“all-electron”) valence wave-function
- 2) Pseudization: from the true wf to the nodeless, smooth pseudo-wf
- 3) Modeling the core charge density (for non-linear core corrections)
- 4) Invert the atomic KS equation and find the effective potential
- 5) Subtract out from the effective potential the XC and Coulomb terms → ionic psp

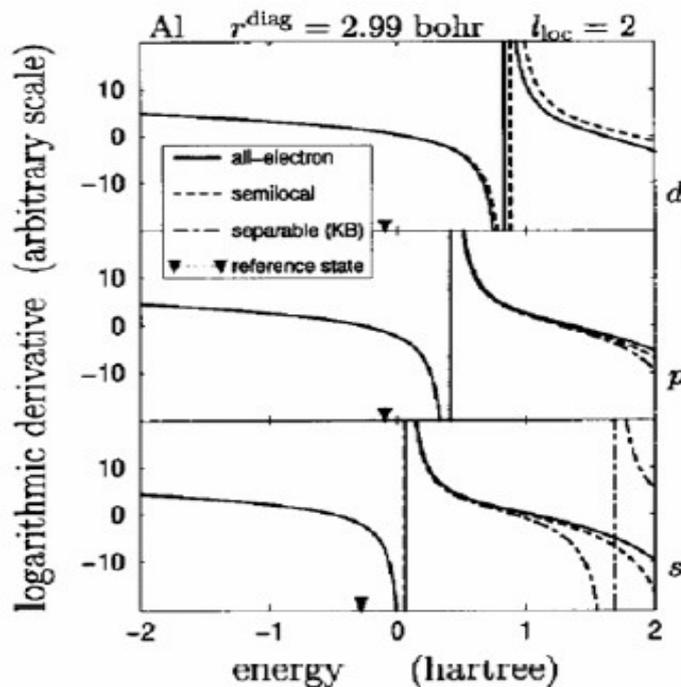


# V. Pseudo-potentials

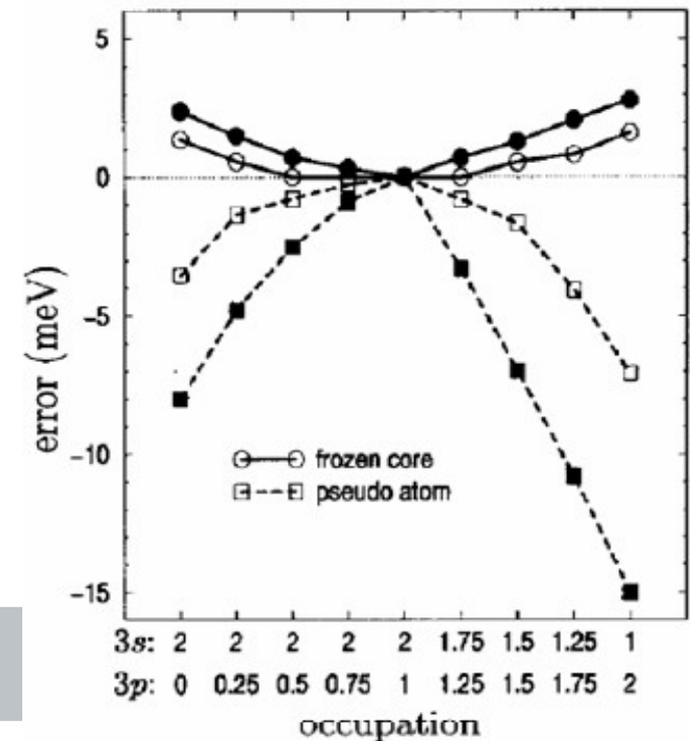
## Testing the pseudo-potential

- 1) Choice of the local component of the pseudo-potential in order to avoid ghost states - see Gonze et al, PRB 41 12264 (1991)
- 2) For the atom: compare all-electron valence states to valence states obtained by using the pseudo-potential
- 3) Compute the logarithmic derivatives (connected to the scattering properties of the pseudopotential on states at different energies)
- 4) For some reference systems : compare all-electron to psp observables

$$D(r; \varepsilon) = [d\phi_\varepsilon/dr]_r / \phi_\varepsilon(r)$$



**TRANSFERABILITY**  
=  
**How does the pseudo-potential work for different systems ?**



# V. Pseudo-potentials

## Ultra-soft pseudopotentials

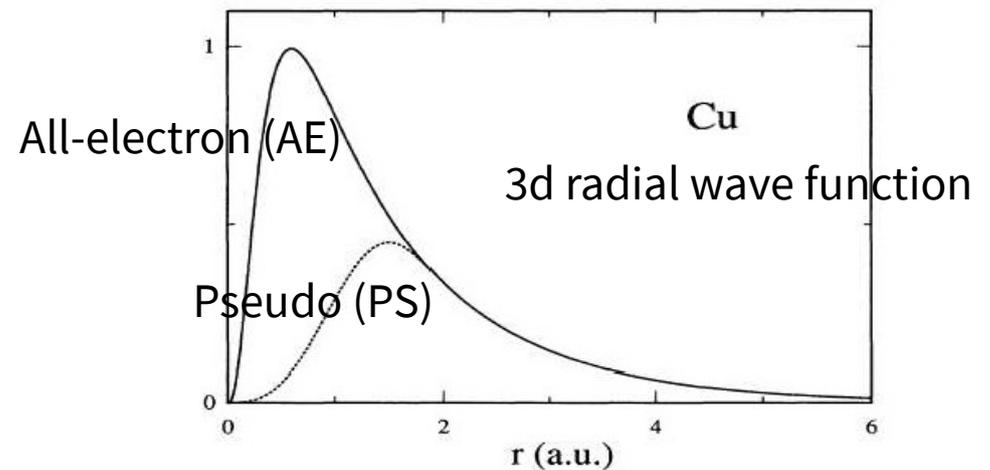
Up to now, we considered norm-conserving pseudo-potentials, that is

$$\langle f_{nl}^{(ps)} Y_{lm} | f_{nl}^{(ps)} Y_{lm} \rangle = \langle f_{nl}^{(AE)} Y_{lm} | f_{nl}^{(AE)} Y_{lm} \rangle = 1$$

Relaxing this condition allows the pseudo-wave-function to be smoother

→ low energy cutoff for PW expansion

But the norm conservation improves psp transferability ...



Vanderbilt PRB 41 7892 (1990)

1) Use several projectors at different energies for each angular channel

2) Augment the valence charge with pre-defined functions that are localized in the core region

$$\hat{V}^{(ps)} = \hat{V}_{local} \delta(r-r') + \sum_i \sum_j B_{ij} |\beta_i\rangle \langle \beta_j|$$

$$n(\mathbf{r}) = \sum_i \left[ |\phi_i(\mathbf{r})|^2 + \sum_{nm,I} Q_{nm}^I(\mathbf{r}) \langle \phi_i | \beta_n^I \rangle \langle \beta_m^I | \phi_i \rangle \right]$$

Ultra-soft  
Pseudo wf  
Small cutoff

Augmentation  
charge (fixed)  
Large cutoff

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# V. Projector-Augmented Waves (PAW)

Up to now, we have mainly tried to reproduce the valence wave-functions TAIL (i.e. the relevant part for bonding)....

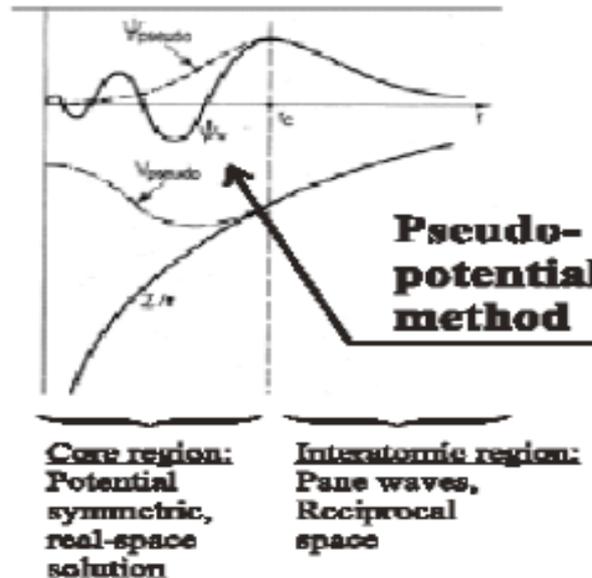
What about trying to shadow the TOTAL true wave-function  $\Psi$  ?

Within core:  $r < R_c$

Consider radial true (pseudo) orbitals  $\phi_i$  ( $\tilde{\phi}_i$ )

$$\Psi = \sum_i c_i \phi_i$$

$$\tilde{\Psi} = \sum_i c_i \tilde{\phi}_i$$



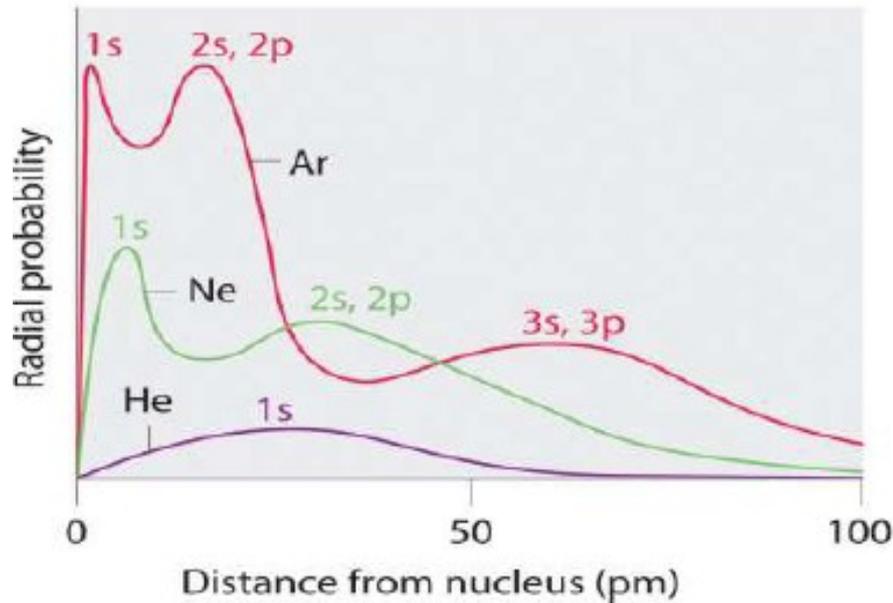
Outside core:  $r > R_c$

$$\tilde{\Psi} = \Psi$$

First (original) paper on PAW: Blochl, PRB 50, 17953 (1994)

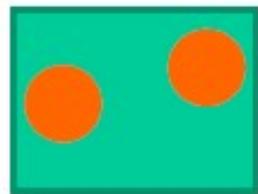
# V. Projector-Augmented Waves

## *The full electron density & the double grid*



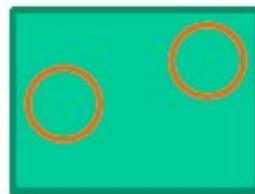
Core-electron density is a steep function  $\rightarrow$  expanded on a atom-centered **radial grid**

Valence-electron density is much softer  $\rightarrow$  expansion in **plane waves**



Full electron density

=



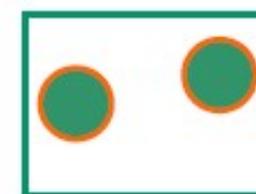
PW expansion

+



Expansion on the radial grid

-



Correction on the radial grid

# V. Projector-Augmented Waves

## *The representation of the full electron density*

$$n(r) = n_2^{\text{PS}}(r) + n_1(r) - \delta n_1(r)$$

$n_2^{\text{PS}}(r)$  : reproduces the smooth valence density outside the core region  $\rightarrow$  expanded on a PW (uniform) grid

$n_1(r) = \sum_{ij} \rho_{ij} \langle \psi_i | r \rangle \langle r | \psi_j \rangle$  : All-electron on-site density, short-ranged

$\delta n_1(r) = \sum_{ij} \rho_{ij} \langle \Phi_i | r \rangle \langle r | \Phi_j \rangle$  : correction, short-ranged

$n_1(r)$  ,  $\delta n_1(r)$  represented on a RADIAL mesh, centered on the nucleus

- As in linear methods (FLAPW) use of a double mesh (radial + uniform)
- At variance with linear methods, no need of taking into account the continuity of the function and its derivatives on the sphere border ( $\delta n_1(r)$  does the job !)

# V. Projector-Augmented Waves

## *Pros and cons*

- Necessarily, finite number of projectors  $\rightarrow n_1(r)$  (all-electron, on-site core density) does not have the right m-pole moments at any order  $\rightarrow$  introduction of another compensating charge distribution
- Four terms for the valence density, one more for the core density  $\rightarrow$  many terms appear in the expression of the total energy, which must be treated on different grids
- Derivatives of the total energy : even more involved expressions
  
- PAW can be considered as a bridge between all-electron linear methods and pseudopotential techniques: two worlds far apart coming together ...
- Exact correspondence between the US-PSP and PAW formalism, within the frozen-core approximation:
  - $\rightarrow$  US-PSP is shown to be exact at the 1<sup>st</sup> order changes in core density
  - $\rightarrow$  PAW enables systematic tests on US-PSP calculations
  - $\rightarrow$  US pseudopotentials can be built up with reference to PAW formalism

# V. Projector-Augmented Waves

## PAW versus Ultra Soft pseudo-potentials (USPsP)

US-PSP

$$n(\mathbf{r}) = \sum_i \left[ |\phi_i(\mathbf{r})|^2 + \sum_{nm,I} Q_{nm}^I(\mathbf{r}) \langle \phi_i | \beta_n^I \rangle \langle \beta_m^I | \phi_i \rangle \right]$$

Augmentation charge

$$Q_{nm}(r) = \psi_n^*(r)\psi_m(r) - \phi_n^*(r)\phi_m(r)$$

In PAW,  $Q_{nm}(\mathbf{r})$  is represented on a radial grid, while in current implementations of US-PSP, it is expanded on the finer PW grid

→ US-PSP can be as accurate as PAW at the expense of an enormous waste (very fine PW double grid)

Kresse's recipe to the simple generation of highly transferable US-PSP's:

- i. generate very accurate norm-conserving pseudopotentials and pseudowfs.  $\phi_i^{\text{NC}}(\mathbf{r})$  with very small cutoff radii
- ii. "Pseudize" the NC-PSP by defining the augmentation functions as:  
$$Q_{nm}(\mathbf{r}) = \phi_n^{\text{NC}}(\mathbf{r}) \phi_m^{\text{NC}*}(\mathbf{r}) - \phi_n(\mathbf{r}) \phi_m^*(\mathbf{r})$$
- iii. Restore the correct behavior of the all-electron wfs. on the radial grid

# V. Projector-Augmented Waves

## Results (1)

### Parameters of PAW dataset and USPsP

Kresse & Joubert, PRB 59, 1758 (1999)

	Valence	$r_c^l$ (a.u.)	$r_{\text{comp}}^l$ (a.u.)	$E_{\text{cut}}$ (eV)
H	1s	1.2	0.8	400
Li	1s2s2p	2.0	2.0	160
Be	2s2p	1.9	1.5	240
B	2s2p	1.5 <sub>s</sub> , 1.7 <sub>p</sub>	1.2	400
C	2s2p	1.3 <sub>s</sub> , 1.5 <sub>p</sub>	1.1	400
N	2s2p	1.3 <sub>s</sub> , 1.5 <sub>p</sub>	1.1	400
F	2s2p	1.3 <sub>s</sub> , 1.5 <sub>p</sub>	1.1	400
Na	2p3s	2.2	1.5	210
Si	3s3p	1.9	1.5	240
P	3s3p	1.9	1.5	240
Ca(1)	3p4s3d	3.0 <sub>s</sub> , 2.3 <sub>p,d</sub>	1.5	230
Ca(2)	3s3p4s3d	2.3		230
V	3p4s4p3d	2.3	2.1	260
Fe	4s4p3d	2.2	1.9 <sub>s,p</sub> , 1.5 <sub>d</sub>	300
Co	4s4p3d	2.2	1.9	300
Ni	4s4p3d	2.2	1.9	300

### Bond lengths in dimers and molecules

Kresse & Joubert, PRB 59, 1758 (1999)

	US-PP	PAW	AE
H <sub>2</sub>	1.447	1.447	1.446 <sup>a</sup>
Li <sub>2</sub>	5.127	5.120	5.120 <sup>a</sup>
Be <sub>2</sub>	4.524	4.520	4.521 <sup>a</sup>
Na <sub>2</sub>	5.667	5.663	5.67 <sup>a</sup>
CO	2.141 (2.127)	2.141 (2.128)	2.129 <sup>a</sup>
N <sub>2</sub>	2.077 (2.066)	2.076 (2.068)	2.068 <sup>a</sup>
F <sub>2</sub>	2.640 (2.626)	2.633 (2.621)	2.615 <sup>a</sup>
P <sub>2</sub>	3.570	3.570	3.572 <sup>a</sup>
H <sub>2</sub> O	1.840 (1.834)	1.839 (1.835)	1.833 <sup>a</sup>
$\alpha$ (H <sub>2</sub> O)	105.3°(104.8°)	105.3°(104.8°)	105.0°
BF <sub>3</sub>	2.476 (2.470)	2.476 (2.470)	2.464 <sup>b</sup>
SiF <sub>4</sub>	2.953 (2.948)	2.953 (2.948)	2.949 <sup>b</sup>

AE = All-electron

# V. Projector-Augmented Waves

## Results (2)

Cohesive properties of Si, bcc V, bcc Li  
Kresse & Joubert, PRB 59, 1758 (1999)

	$a$ ( $\text{\AA}^3$ )	$E_{\text{coh}}$ (eV)	$B$ (GPa)
silicon			
US-PP(current)	5.40	-5.96	95
PAW(current)	5.40	-5.96	95
PAW <sup>a</sup>	5.38	-6.03	98
LAPW <sup>a</sup>	5.41	-5.92	98
bcc V			
US-PP(current)	2.93	-9.41	206
PAW(current)	2.93	-9.39	210
PAW <sup>a</sup>	2.94	-9.39	200
LAPW <sup>a</sup>	2.94	-9.27	200
bcc Li			
PAW(1s val)	3.363	-2.034	15.0
PAW(1s frozen)	3.368	-2.037	15.0
PAW(s only)	3.368	-2.026	15.0
PAW(1s frozen, no pc)	3.349	-2.027	15.0
PAW(s only, no pc)	3.463	-1.711	12.6
AE <sup>b</sup>	3.36		15.0

Relative stability of some phases of Fe with respect to non-magnetic (NM) hcp Fe

	FLAPW <sup>a</sup>	PAW	US-AE	US-PP
bcc Fe NM		412 (373)	413 (372)	413 (369)
bcc Fe FM	133 (-73)	139 (-73)	139 (-73)	81 (-191)
fcc Fe NM	77 (78)	71 (61)	70 (62)	70 (62)
hcp Fe NM		0	0	0

LSDA results compared to sGGA in brackets

FLAPW="Fully Linear Augmented Plane Waves"  
(all-electron calculations for crystals)