# Introduction to Numerical Simulations and High Performance Computing: From Materials Science to Biochemistry





Mauro Boero





Institut de Physique et Chimie des Matériaux de Strasbourg University of Strasbourg - CNRS, F-67034 Strasbourg, France







(a) Dept. of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Tokyo 113-8656, Japan

# Part 2: First Principles Molecular Dynamics

## **First Principles MD:**

instead of looking for a potential  $V(\mathbf{R}_I)$ , we try to include quantum electrons and classical nuclei and to compute forces from fundamental quantum mechanics



These electronic orbitals are what we want to describe. So what can we do with our Hamiltonian ?

$$\hat{H} = \frac{1}{2}\nabla^2 + V_{ee}(\mathbf{x}) + V_{eI}(\mathbf{x} - \mathbf{R}_I) \qquad (\mathbf{R}_I = nuclear \ position)$$

In principle, we have *simply* to solve the Schrödinger equation

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

But in case of many electrons the many body interaction  $V_{ee}$  is <u>very complicated</u> and the calculation of the many-body  $\psi_i$  <u>not</u> <u>possible</u> even with the most powerful computer... so we need some tricks...(and some mathematics)

## The Born-Oppenheimer method - I

The Born-Oppenheimer approximation (M. Born and J. R.
Oppenheimer, *Ann. der Physik, 4 Folge,* 1927) assumes that
Nuclei are much heavier than electrons, so that their kinetic energy can be neglected in computing the electronic structure,

$$M_{Nucl} >> m_e \implies \mathbf{p}^2 / (2M_{Nucl}) << \mathbf{p}^2 / (2m_e)$$

• The true many-body wavefunction  $\Psi(\mathbf{x}, \mathbf{R}_I)$  can be written as a product of separate wavefunctions

$$\Psi(\mathbf{x},\mathbf{R}_{I}) = \psi(\mathbf{x}) \cdot \phi(\mathbf{R}_{I})$$

• The same electronic state (ground state) is unaffected by small changes in the nuclear positions  $\mathbf{R}_I$  (adiabatic theorem)

• So the time-independent Schrödinger equation holds.

## The Born-Oppenheimer method - II

Practical applications of the BO method have been historically successful in the so-called Hartree-Fock approach.

- 1) The *electron* many-body wavefunction  $\Psi(\mathbf{q})$  is too complicated.  $\mathbf{q} = (\mathbf{x}_{1s}, \mathbf{x}_{2s}, \dots, \mathbf{x}_{Ns})$  is a multi-dimensional vector defining position and spin state *s* of each electron in the system.
- 2) Then, one has to solve the associated Schrödinger equation

$$\hat{H}(\mathbf{q}, \mathbf{R}_I)\Psi(\mathbf{q}) = E\Psi(\mathbf{q})$$

3) ...and it is assumed that  $\Psi(\mathbf{q})$  is an antisymmetric combination of single-particle orbitals  $\psi_{i\sigma}(\mathbf{x})$  (Slater determinant)

$$\Psi(\mathbf{q}) = \frac{1}{\sqrt{N!}} \det[\psi_{i\sigma}(\mathbf{x}_{j})] = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{1\uparrow}(\mathbf{x}_{1}) & \psi_{1\downarrow}(\mathbf{x}_{1}) & \dots & \psi_{1\downarrow}(\mathbf{x}_{N}) \\ \psi_{2\uparrow}(\mathbf{x}_{1}) & \psi_{2\downarrow}(\mathbf{x}_{1}) & \dots & \psi_{2\downarrow}(\mathbf{x}_{N}) \\ \dots & \dots & \dots \\ \psi_{N\uparrow}(\mathbf{x}_{1}) & \psi_{N\downarrow}(\mathbf{x}_{1}) & \dots & \psi_{N\downarrow}(\mathbf{x}_{N}) \end{vmatrix}$$

## The Born-Oppenheimer method - III

The many-body Schrödinger equation, written in terms of singleparticle orbitals

$$\left\{-\frac{1}{2}\nabla^2 + V_H(\mathbf{x}) + V_{eI}(\mathbf{x}) + \right\} \psi_{i\sigma}(\mathbf{x}) - \sum_{j\sigma'} \int d^3 x' \frac{\psi_{j\sigma'}^*(\mathbf{x}')\psi_{i\sigma}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \cdot \psi_{j\sigma'}(\mathbf{x}) = \varepsilon_i \psi_{i\sigma}(\mathbf{x})$$

Where the first part in { } includes:

- the electron kinetic term
- the Hartree (Coulomb) potential
- the electron-ion interaction

The integral part, instead has *no classical analog* and represents the quantum exchange interaction.

## The Born-Oppenheimer method - IV

Orbitals  $\psi_{i\sigma}(\mathbf{x})$  are generally expressed as linear combinations of known analytic functions

$$\psi_{i\sigma}(\mathbf{x}) = \sum_{k=1}^{M} c_{i\sigma}^{k} f_{k}(\mathbf{x}; \{\mathbf{R}_{I}\})$$

and in practical applications, a very popular, but somehow minimal, basis set is represented by Slater-type orbitals (STO)

$$\phi_k(\mathbf{x}, \{\mathbf{R}_I\}) \equiv \phi_k^{\text{STO}}(\mathbf{x} - \mathbf{R}_I) = \phi_k^{\text{STO}}(\mathbf{r}) = N_k \cdot r_x^{k_x} r_y^{k_y} r_z^{k_z} \exp\left(-\zeta_k |\mathbf{r}|\right)$$

or Gaussian-type orbitals (GTO)

$$\phi_k(\mathbf{x}, \{\mathbf{R}_I\}) \equiv \phi_k^{\text{GTO}}(\mathbf{x} - \mathbf{R}_I) = \phi_k^{\text{GTO}}(\mathbf{r}) = N_k \cdot r_x^{k_x} r_y^{k_y} r_z^{k_z} \exp\left(-\alpha_k \cdot r^2\right)$$

## The Born-Oppenheimer method - V

 $\rightarrow$ 1) Compute the electronic structure as usual:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle \implies \det(\langle\psi_i|\hat{H}|\psi_j\rangle - E_i\delta_{ij}) = 0$$

this implies a computationally (very) expensive diagonalization 2) Move the ions according to their equations of motion

$$\mathbf{R}_{I}(t+\delta t) = \mathbf{R}_{I} + \mathbf{v}_{I}(t)\delta t + \frac{\delta t^{2}}{2M_{I}}\mathbf{f}_{I}$$
$$\mathbf{v}_{I}(t) = \left[\mathbf{R}_{I}(t+\delta t) - \mathbf{R}_{I}(t-\delta t)\right]/2\delta t$$

in the velocity Verlet scheme.

→ 3) Re-orthogonalize the wavefunctions after moving the atoms  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$  ...and go back to 1)

### The Born-Oppenheimer method - VI

Computing the electronic structure

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle \implies \det(\langle\psi_i|\hat{H}|\psi_j\rangle - E_i\delta_{ij}) = 0$$

implies a computationally procedure of the steepest descent (SD), preconditioned conjugate gradient (PCG), diagonalization in iterative subspace (DIIS), etc.. All these methods can be regarded as solving the wavefunctions updating algorithm

$$\mu_{BO} |\dot{\Psi}_i\rangle = -\frac{\delta E[\Psi_i, \mathbf{R}_I]}{\delta \langle \Psi_i |} + constr. \Rightarrow |\Psi_i(t + \Delta t)\rangle \cong |\Psi_i(t)\rangle - \frac{\Delta t}{\mu_{BO}} \frac{\delta E[\Psi_i, \mathbf{R}_I]}{\delta \langle \Psi_i(t) |}$$

i.e. 1st order differential equations

## Hellmann-Feynman forces: How to compute $\mathbf{f}_I$

Hellmann, H. (1937) "Einfürung in die Quantenchemie", Deuticke, Vienna R. P. Feynman, *Phys. Rev.* **56**, 340 (1939)

To Compute the forces on the atoms one should compute

$$\nabla_{\mathbf{R}_{I}} \langle \psi_{i} | \hat{H} | \psi_{i} \rangle = \left( \nabla_{\mathbf{R}_{I}} \langle \psi_{i} | \hat{H} | \psi_{i} \rangle + \langle \psi_{i} | \nabla_{\mathbf{R}_{I}} \hat{H} | \psi_{i} \rangle + \langle \psi_{i} | \hat{H} ( \nabla_{\mathbf{R}_{I}} | \psi_{i} \rangle \right)$$

However, an important simplification can be used if:

1) 
$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

2) 
$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

## Hellmann-Feynman forces: How to compute $\mathbf{f}_I$

Hellmann, H. (1937) "Einfürung in die Quantenchemie", Deuticke, Vienna R. P. Feynman, *Phys. Rev.* **56**, 340 (1939)

Hence... 
$$\left( \nabla_{\mathbf{R}_{I}} \langle \psi_{i} | \hat{H} | \psi_{i} \rangle + \langle \psi_{i} | \nabla_{\mathbf{R}_{I}} \hat{H} | \psi_{i} \rangle + \langle \psi_{i} | \hat{H} (\nabla_{\mathbf{R}_{I}} | \psi_{i} \rangle) \right) = \left( \nabla_{\mathbf{R}_{I}} \langle \psi_{i} | \hat{E}_{i} | \psi_{i} \rangle + \langle \psi_{i} | \nabla_{\mathbf{R}_{I}} \hat{H} | \psi_{i} \rangle + \langle \psi_{i} | E_{i} (\nabla_{\mathbf{R}_{I}} | \psi_{i} \rangle) \right) = E_{i} \cdot \left[ \left( \nabla_{\mathbf{R}_{I}} \langle \psi_{i} | \hat{\Psi}_{i} \rangle + \langle \psi_{i} | (\nabla_{\mathbf{R}_{I}} | \psi_{i} \rangle) \right] + \langle \psi_{i} | \nabla_{\mathbf{R}_{I}} \hat{H} | \psi_{i} \rangle = E_{i} \cdot \nabla_{\mathbf{R}_{I}} \langle \psi_{i} | \psi_{i} \rangle + \langle \psi_{i} | \nabla_{\mathbf{R}_{I}} \hat{H} | \psi_{i} \rangle = E_{i} \cdot \nabla_{\mathbf{R}_{I}} 1 + \langle \psi_{i} | \nabla_{\mathbf{R}_{I}} \hat{H} | \psi_{i} \rangle = \langle \psi_{i} | \nabla_{\mathbf{R}_{I}} \hat{H} | \psi_{i} \rangle$$

namely, the derivative of the operator is identical to the derivative of the corresponding eigenvalue

# Interlude: (before going on) Function vs. Functional

Function : A number (*y*) that depends on a number (*x*)

$$y = f(x)$$

Example:  $y = x^n$ (a line n=1, parabola n=2etc...). y changes if x changes Functional:

A number (*F*) that depends on a function (f(x))

$$F = \int_{a}^{b} f(x) dx$$

Example: an integral over a fixed interval (*a*,*b*).*F* changes if *f*(*x*) changes

## Variational (functional) derivative: an euristic (practical) point of view

Consider a simple example known to everybody in physics: the scalar product of two vectors

$$|a\rangle = \begin{pmatrix} a_1 \\ \dots \\ a_N \end{pmatrix} \qquad |b\rangle = \begin{pmatrix} b_1 \\ \dots \\ b_N \end{pmatrix}$$

$$F = \left\langle a \left| b \right\rangle = \sum_{i=1}^{N} a_i b_i$$

The scalar product F is simply a number that depends on the two (set of) numbers  $a_i$  and  $b_i$ .

# Variational (functional) derivative: an euristic (practical) point of view

We want now to compute the derivative of the scalar product F with respect to  $b_j$ , the *j*-th component of |b>

$$\frac{dF}{db_j} = \frac{d}{db_j} \langle a | b \rangle = \sum_{i=1}^N a_i \frac{db_i}{db_j} = \sum_{i=1}^N a_i \delta_{ij} = a_j$$

The derivative simply selects the *j*-th component of |a> and *kills* the sum operation.

We do now something that physicists always do *without telling* to mathematicians.

# We consider formally similar a discrete and a *continuous* index



## A simple example of functional: the integral

In a way similar to the scalar product of two vectors, a functional is a number that *depends on one or more functions* (not numbers): e.g. the product a(x) b(x)

$$F[a,b] = \int a(x)b(x)dx$$

And the derivative with respect to b(y) reads:

$$\frac{\delta F[a,b]}{\delta b(y)} = \int a(x) \frac{\delta b(x)}{\delta b(y)} dx = \int a(x) \delta(x-y) dx = a(y)$$

...and now we are equipped for the next steps: Density Functional Theory and Car-Parrinello method.

# Density Functional Theory: brief review

• Define the electronic density  $\rho(\mathbf{x})$  as a superposition of single particle Kohn-Sham (KS) orbitals

$$\boldsymbol{\rho}(\mathbf{x}) = \sum_{i}^{occ} \boldsymbol{f}_{i} |\boldsymbol{\psi}_{i}(\mathbf{x})|^{2}$$

• Write the total energy functional as

 $E[\psi_i, \mathbf{R}_I] = E_k + E_H + E_{xc} + E_{ps} + E_M$ i.e. sum of the interactions electron-electron + electron-ion + ion-ion

after W. Kohn\* and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965) \*Nobel Prize for Chemistry in 1998



# Density Functional Theory: brief review

• Electron-electron interaction:

$$\begin{split} E_{k} &= -\frac{1}{2} \sum_{i} f_{i} \int d^{3}x \, \psi_{i}^{*}(\mathbf{x}) \nabla^{2} \psi_{i}(\mathbf{x}) \\ E_{H} &= \frac{1}{2} \int d^{3}x \, d^{3}x' \, \frac{\rho(\mathbf{x})\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \\ E_{xc} &= \int d^{3}x \, \epsilon_{xc}(\rho, \nabla \rho) \rho(\mathbf{x}) \end{split}$$

•  $E_k$  = kinetic energy,  $E_H$  = Coulomb interaction,  $E_{xc}$  = exchange-correlation interaction (= what we do not know: The many-body interaction)

# Density Functional Theory: brief review

• Electron-ion interaction:

$$\boldsymbol{E}_{\mathbf{ps}} = \sum_{I} \int d^{3}x \, V^{ps} \left( \mathbf{x} - \mathbf{R}_{I} \right) \boldsymbol{\rho} \left( \mathbf{x} \right)$$

the core-valence interaction is described by pseudopotentials

• Ion-ion interaction:

$$\boldsymbol{E}_{\mathbf{M}} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I \cdot Z_J}{\left| \mathbf{R}_I - \mathbf{R}_J \right|}$$

## The Exchange-Correlation problem: a few points

- The exchange interaction and the electron correlations are due to many-body effects and represented by the term  $E_{xc}[\rho]$
- The exact analytical expression is unfortunately unknown
- It is often assumed that exchange and correlation contributions can be computed separately and then linearly added as

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

• Approximate analytical expressions are generally derived from the homogeneous electron gas limit, for the exchange interaction (Becke, 1988)

$$E_{x}[\rho] = \frac{1}{2} \sum_{\sigma} \int \varepsilon_{x}^{\sigma}(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) d^{3}r \qquad \lim_{r \to \infty} \varepsilon_{x}^{\sigma}(\mathbf{r}) = -\frac{1}{r}$$

• So, the exchange part of the functional, can be written in the so-called *local density approximation* (LDA) as

$$E_{x}[\rho] = -\frac{3}{2} \left(\frac{3}{4\pi}\right)^{1/3} \sum_{\sigma} \int d^{3}r \left[\rho_{\sigma}(\mathbf{r})\right]^{4/3} \qquad \sigma = \uparrow, \downarrow$$

This is the *simplest possible form* and the name comes from the fact that  $\rho$  is given by the local density  $\rho(\mathbf{x})$  at a specific point  $\mathbf{x}$ .

• Similarly, the LDA version of the correlation energy, originally proposed by Kohn and Sham (1965) and refined by Perdew and Zunger (1981), reads

$$E_c[\rho] = \int d^3x \,\rho(\mathbf{x}) \cdot \varepsilon_c(\rho(\mathbf{x}))$$

where the explicit analytic form of the function  $\varepsilon_c(\rho(\mathbf{x}))$  comes from a parameterization from random phase approximation.

Due to the insufficiency of a simple LDA approximation in the treatment of many real systems, approximations including the gradient of the density, *ρ*(x) are often adopted and the exchange-correlation functional becomes

$$E_{xc}[\rho,\nabla\rho] = \int d^3x \,\varepsilon_{xc}(\rho(\mathbf{x}),\nabla\rho(\mathbf{x}))$$

# Why gradient correction/approximation?

• It is the first derivative of the density w.r.t. **x** 

$$\rho(\mathbf{x} + \delta \mathbf{x}) = \rho(\mathbf{x}) + \nabla \rho(\mathbf{x}) \cdot \delta \mathbf{x} + O(\delta \mathbf{x}^2)$$

- However it is not a Taylor expansion, not a perturbation expansion, not an analytical continuation, not etc....
- It is just an empirical way to include *something* beyond **x**-locality based on a (more or less) physical meaning

- In practical applications, however, *the gradient enters* only with its modulus  $|\nabla \rho(\mathbf{x})|$  thus adding only a modest computational cost
- These generalized gradient corrections (GGA) are a bit arbitrary, i.e. they are not a perturbation expansion
- Accuracy is assessed *a posteriori* by test calculations and comparisons with both exact results and experiments.
- Exchange: Becke (1988) still regarded as a standard. Subsequently refined and improved by the same author (Becke 1992, Becke 1993)
- Correlation: From several research groups, sometimes including also the exchange (Perdew 1986, Perdew and Wang 1992, Perdew et al. 1992, Perdew et al. 1996, Vosko et al. 1980, Lee et al 1988, Hamprecht et al. 1998, Handy and Cohen 2002, Xu and Goddard III 2004).

#### **Example of GGA on the exchange (after Becke):**

• The lowest order GGA on the exchange is determined only by dimensional analysis (i.e it is not an analytical expansion)

$$E_x^{GGA} = E_x^{LDA} - \beta \sum_{\sigma} \int \frac{\left[\nabla \rho_{\sigma}(\mathbf{x})\right]^2}{\left[\rho_{\sigma}(\mathbf{x})\right]^{4/3}} d^3x$$

- **Problem**: asymptotical divergence in atoms and molecules
- Workaround: A. D. Becke, *Phys. Rev. B* 38, 3098 (1988)  $E_x^{GGA} = E_x^{LDA} - \beta \sum_{\sigma} \int [\rho_{\sigma}(\mathbf{x})]^{4/3} \frac{\xi_{\sigma}^2}{(1+6\beta \cdot \xi_{\sigma} \cdot \sinh^{-1}\xi_{\sigma})} d^3x$ where  $\xi_{\sigma} = \frac{|\nabla \rho_{\sigma}(\mathbf{x})|}{[\rho_{\sigma}(\mathbf{x})]^{4/3}}$

and  $\beta$  (=0.0042) is fixed by a least-square fit procedure on a set of training atoms / molecules.

#### Example of GGA on the correlation (after Perdew *et al.*):

• As in the case of the exchange correlation is written as a linear combination of density and gradient dependent addends

$$E_c^{GGA} = \int \rho(\mathbf{x}) \cdot \left[ \varepsilon_c^{LDA}(r_s, \zeta) + \varepsilon_c^{GC}(r_s, \zeta, t) \right]$$
  
where  $r_s$  is the Wigner-Seitz radius  $\rho^{-1} = \frac{V}{N_c} = \frac{4}{3}\pi \cdot r_s^3$ 

 $\zeta = \frac{\rho_{\uparrow}(\mathbf{x}) - \rho_{\downarrow}(\mathbf{x})}{\rho(\mathbf{x})} \implies \text{Dimensionless spin polarization (LSD)}$  $t = \frac{|\nabla \rho(\mathbf{x})|}{2\varphi \cdot k_s \cdot \rho(\mathbf{x})} \implies \text{Dimensionless gradient}$  $\varphi = \frac{(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}}{2} \qquad k_s = \sqrt{4k_F / \pi a_0} \quad a_0 = \hbar^2 / me^2$ 

#### **Example of GGA on the correlation (after Perdew** et al.):

- $\varepsilon_c^{GC}$  has to satisfy three conditions:
- 1) Slow varying limit  $(t \rightarrow 0)$ . For  $r_s \rightarrow 0 \implies$  (high density)

$$\varepsilon_c^{GC} \rightarrow \frac{e^2}{a_0} \beta \varphi^3 t^2 \quad \beta = 0.066725$$

2) Rapid varying limit ( $t \rightarrow \infty$ )  $\implies$  (low density = *no corr*.)

$$\varepsilon_c^{GC} \rightarrow -\varepsilon_c^{LDA}$$

3) Uniform scaling to high density

(i) 
$$\forall r_s \to 0; \lambda \to \infty$$
  $\rho(\mathbf{x}) \to \lambda^3 \rho(\lambda \mathbf{x})$   
(ii)  $r_s \to 0$  as  $O(\lambda^{-1})$   
(iii)  $t \to \infty$  as  $O(\lambda^{-1/2})$   
then  $E_c^{GGA} = \text{constant}$ 

#### **Example of GGA on the correlation (after Perdew** *et al.*):

ε<sub>c</sub><sup>GC</sup> becomes then the PBE expression after *Phys. Rev. Lett.* 77, 3865 (1996)

$$\varepsilon_c^{GC} = \frac{e^2}{a_0} \gamma \cdot \varphi^3 \ln \left[ 1 + \frac{\beta}{\gamma} t^2 \left( \frac{1 + A \cdot t^2}{1 + A \cdot t^2 + A^2 t^4} \right) \right]$$

where  

$$A = \frac{\beta}{\gamma} \left\{ \exp\left[-\varepsilon_{c}^{LDA} / \left(\gamma \cdot \varphi^{3} e^{2} / a_{0}\right)\right] - 1 \right\}^{-1}$$

$$\gamma = \frac{1 - \ln 2}{\pi}$$

In general: A series of plausible hypotheses and a lot of algebra ...and good luck !

#### **Small warning about GGAs:**

So far it seems that GGA exchange correlation functionals are just linear combinations of density and gradient dependent functionals, i.e.

$$E_{xc}[\rho,\nabla\rho] = E_x^{LDA}[\rho] + E_x^{GGA}[\nabla\rho] + E_c^{LDA}[\rho] + E_c^{GGA}[\nabla\rho]]$$

Well it is almost true but not always ! Counter-example: HCTH\*

$$E_{xc}[\rho,\nabla\rho] = \sum_{j} c_{j} \int \varepsilon_{j}^{xc} (\rho_{\uparrow}, \rho_{\downarrow}, |\nabla\rho_{\uparrow}|, |\nabla\rho_{\downarrow}|) d^{3}x$$

densities and gradients are mixed together and the coefficients  $c_j$  are computed by self-consistent least-squares procedure on a "training set" of atoms and molecules...

\*J. Chem. Phys. 109, 6264 (1998)

# A simple example of GGA effect: Magnetite

Spinel fcc structure carrying octahedral and tetrahedral Fe



© M. Friak, A. Schindlmayr, M. Scheffler, New J. Phys. 9, 5 (2007)

# GGA effects on bond lengths

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt. <sup>a</sup>
H <sub>2</sub>				1004 - 10 - 1480 1			1999 C			
r(HH)	0.781	0.765	0.774	0.755	0.740	0.748	0.730	0.738	0.746	0.741
LiH										
r(LiH)	1.683	1.640	1.646	1.663	1.624	1.628	1.636	1.640	1.653	1.595
BeH										
r(BeH)	1.392	1.370	1.377	1.371	1.349	1.355	1.348	1.348	1.357	1.343
CH										
r(CH)	1.175	1.152	1.159	1.162	1.140	1.146	1.108	1.120	1.131	1.120
$CH_{2}(^{3}B_{1})$										
r(CH)	1.110	1.093	1.097	1.101	1.085	1.089	1.071	1.077	1.082	1.078
a(HCH)	132.9	134.8	135.3	131.7	133.1	133.5	130.7	131.6	132.2	136.0
$CH_2(^1A_1)$										
r(CH)	1.158	1.135	1.141	1.148	1.127	1.132	1.097	1.109	1.117	1.111
a(HCH)	98.3	99.1	98.7	98.7	99.5	99.1	103.0	102.1	101.5	102.4
CH3										
r(CH)	1.109	1.093	1.097	1.102	1.086	1.090	1.073	1.078	1.083	1.079
CH <sub>4</sub>										
r(CH)	1.118	1.101	1.105	1.114	1.097	1.100	1.084	1.090	1.094	1.086
NH				or sorting to			1755-1111-1548			
r(NH)	1.083	1.063	1.068	1.074	1.055	1.060	1.024	1.039	1.048	1.045
NH <sub>2</sub>										
r(NH)	1.064	1.045	1.050	1.060	1.042	1.046	1.013	1.028	1.034	1.024
a(HNH)	100.9	101.7	101.4	100.6	101.4	101.1	104.4	103.4	102.9	103.4
NH <sub>3</sub>										
r(NH)	1.044	1.027	1.031	1.043	1.026	1.030	1.002	1.017	1.020	1.012
a(HNH)	104.9	106.0	105.8	104.0	105.0	104.8	107.2	106.4	106.0	106.0
OH										
<i>r</i> (OH)	1.008	0.993	0.997	1.006	0.991	0.995	0.959	0.979	0.984	0.971
S-null = S	Slater exe	change, E	<b>B-</b> null = E	Becke ex	change					32

## GGA effects on vibrational frequencies

$\begin{array}{c c c c c c c c c c c c c c c c c c c $		S-null	II S-VWN		P B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt.	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Molecule			S-LYP							Obs. <sup>a</sup>	Harm. <sup>b</sup>
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$H_2(D_{\infty h})$			057		61555 41	6090 - S			0.0000	- 2222 - 223	2
Liff $(C_{\infty v})$ $\Sigma$ 1270 1353 1338 1304 1385 1373 1416 1392 1331 1360 1406 BeH $(C_{\infty v})$ $\Sigma$ 1919 1984 1958 1981 2049 2023 2151 2135 2059 1986 2059 CH $(C_{\infty v})$ $\Sigma$ 2534 2682 2647 2569 2718 2684 3058 2944 2818 2733 2862 CH <sub>2</sub> $(^{3}B_{1})$ $(C_{2v})$ $A_{1}$ 2961 3078 3048 2989 3102 3073 3325 3250 3186 1015 1010 985 1089 1093 1069 1239 1192 1149 963° $B_{2}$ 3173 3311 3284 3192 3327 3301 3525 3471 3398 3190 CH <sub>2</sub> $(^{1}A_{1})$ $(C_{2v})$ $A_{1}$ 2614 2757 2726 2639 2784 2754 3129 3001 2903 2806° 1363 1392 1374 1425 1457 1437 1564 1499 1470 1353 $B_{2}$ 2694 2844 2814 2695 2847 2819 3192 3085 2980 2865 CH <sub>3</sub> $(D_{3h})$ $A_{1}$ 2950 3069 3044 2971 3092 3068 3285 3220 3159 3005° $A_{2}''$ 396 488 492 346 449 456 308 406 434 606 E' 3123 3252 3227 3129 3260 3237 3461 3409 3336 3161 1320 1356 1337 1378 1416 1395 1540 1481 1454 1396 CH <sub>4</sub> $(T_{a})$ $A_{1}$ 2879 2988 2969 2887 2999 2980 3197 3112 3066 2917 3137 E 1487 1526 1508 1535 1576 1557 1703 1626 1603 1534 1567 $T_{2}$ 3000 3121 3104 2974 3098 3083 3302 3250 3188 3019 3158 1260 1293 1272 1327 1362 1339 1488 1414 1400 1306 1357	$\Sigma_{g}$	4035	4207	4119	4286	4461	4373	4646	4534	4367	4160	4401
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	LiH (C.	)										
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Σ	1270	1353	1338	1304	1385	1373	1416	1392	1331	1360	1406
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	BeH (Car	)								15		Sec.
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Σ	1919	1984	1958	1981	2049	2023	2151	2135	2059	1986	2059
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	CH (C. v)					53	2					9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Σ	2534	2682	2647	2569	2718	2684	3058	2944	2818	2733	2862
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$CH_2 ({}^3B_1)$	$(C_{2v})$				), ),	19					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$A_1$	2961	3078	3048	2989	3102	3073	3325	3250	3186		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1015	1010	985	1089	1093	1069	1239	1192	1149	963°	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	B <sub>2</sub>	3173	3311	3284	3192	3327	3301	3525	3471	3398	3190	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$CH_2({}^{1}A_1)$	$(C_{2v})$										
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A	2614	2757	2726	2639	2784	2754	3129	3001	2903	2806 <sup>c</sup>	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1363	1392	1374	1425	1457	1437	1564	1499	1470	1353	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	B <sub>2</sub>	2694	2844	2814	2695	2847	2819	3192	3085	2980	2865	S 95
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CH3 (D3h)	)										
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	A'	2950	3069	3044	2971	3092	3068	3285	3220	3159	3005 <sup>c</sup>	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	A''	396	488	492	346	449	456	308	406	434	606	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	E'	3123	3252	3227	3129	3260	3237	3461	3409	3336	3161	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1320	1356	1337	1378	1416	1395	1540	1481	1454	1396	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$CH_4(T_d)$								205			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	A	2879	2988	2969	2887	2999	2980	3197	3112	3066	2917	3137
T2         3000         3121         3104         2974         3098         3083         3302         3250         3188         3019         3158           1260         1293         1272         1327         1362         1339         1488         1414         1400         1306         1357	E	1487	1526	1508	1535	1576	1557	1703	1626	1603	1534	1567
1260 1293 1272 1327 1362 1339 1488 1414 1400 1306 1357	$T_2$	3000	3121	3104	2974	3098	3083	3302	3250	3188	3019	3158
		1260	1293	1272	1327	1362	1339	1488	1414	1400	1306	1357

## GGA effects on dipole moment

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt. <sup>a</sup>
LiH	5.357	5.514	5.346	5.521	5.662	5.501	5.981	5.776	5.563	5.88
BeH	0.222	0.216	0.194	0.298	0.293	0.273	0.337	0.218	0.167	
CH	1.285	1.368	1.349	1.234	1.314	1.296	1.582	1.507	1.371	1.46 <sup>b</sup>
$CH_2(^1A_1)$	1.814	1.903	1.895	1.702	1.789	1.783	2.016	1.965	1.802	
$CH_2({}^{3}B_1)$	0.610	0.689	0.694	0.547	0.631	0.638	0.582	0.636	0.635	
NH	1.522	1.599	1.580	1.458	1.529	1.511	1.750	1.709	1.658	1.389 <sup>c</sup>
NH <sub>2</sub>	1.999	2.067	2.057	1.875	1.945	1.937	2.135	2.120	2.080	
NH <sub>3</sub>	1.979	1.969	1.980	1.885	1.893	1.902	1.920	1.965	1.959	1.47
OH	1.745	1.793	1.784	1.652	1.701	1.693	1.884	1.862	1.833	1.66
OH <sub>2</sub>	2.109	2.146	2.141	2.000	2.042	2.037	2.199	2.200	2.179	1.85
FH	1.860	1.894	1.886	1.776	1.812	1.805	1.972	1.948	1.934	1.82
LiF	5.216	5.386	5.239	5.330	5.510	5.359	6.173	5.850	5.864	6.33
CN	1.168	1.048	1.025	1.149	1.031	1.009	2.182	2.113	1.378	1.15 <sup>b</sup>
HCN	2.827	2.873	2.860	2.762	2.808	2.796	3.209	2.949	2.976	2.98
COd	0.214	0.189	0.209	0.148	0.122	0.145	-0.264	0.192	-0.011	0.112
HCO	1.349	1.436	1.401	1.355	1.438	1.401	2.083	1.584	1.665	
H <sub>2</sub> CO	1.932	2.039	1.994	1.964	2.069	2.022	2.666	2.275	2.333	2.33
H <sub>3</sub> COH	1.592	1.643	1.619	1.601	1.651	1.622	1.867	1.834	1.830	1.70
H <sub>2</sub> NNH <sub>2</sub>	2.196	2.148	2.129	2.214	2.206	2.200	2.243	2.312	2.302	1.75
NO <sup>d</sup>	0.195	0.201	0.217	0.121	0.130	0.147	-0.210	0.078	0.057	0.153
HOOH	1.826	1.858	1.878	1.608	1.650	1.680	1.951	1.796	1.825	2.2
Mean deviation	-0.076	-0.035	0.062	-0.113	-0.069	-0.094	0.239	0.133	0.052	
Mean absolute deviation	0.280	0.252	0.278	0.255	0.227	0.251	0.289	0.277	0.233 -	

## GGA effects on dissociation energies

Molecule	S-null	S-VWN	S-LYP	B-null	B-VWN	B-LYP	HF	MP2	QCISD	Expt. <sup>a</sup>
H <sub>2</sub>	76.8	107.5	100.2	79.5	110.8	103.2	75.9	86.6	91.2	103.3
LiH	31.4	57.5	52.5	33.6	60.3	54.9	30.4	39.8	44.1	56.0
BeH	46.4	57.7	54.4	46.1	57.6	53.9	48.8	45.3	38.3	46.9
CH	61.0	86.7	85.4	56.6	82.4	79.9	50.0	63.6	66.6	79.9
$CH_{2}({}^{3}B_{1})$	163.8	201,0	198.1	144.7	181.8	177.7	142.9	161.7	160.7	179.6
$CH_2(^1A_1)$	135.6	185.1	181.7	121.0	170.8	166.1	112.3	141.2	145.0	170.6
CH <sub>3</sub>	255.2	320.5	316.7	227.2	292.5	287.3	223.3	259.4	259.4	289.2
CH4	347.5	436.8	432.1	306.6	396.0	389.9	300.4	354.2	353.9	392.5
NH	58.8	87.7	86.2	54.4	83.3	81.8	43.0	60.6	62.5	79.0
NH <sub>2</sub>	133.2	189.1	186.6	117.6	173.4	170.8	98.8	137.8	139.0	170.0
NH <sub>3</sub>	224.9	306.0	302.6	192.7	273.5	270.1	170.2	232.4	230.7	276.7
OH	85.5	112.9	112.8	72.4	99.7	98.6	57.7	84.7	83.9	101.3
OH,	188.1	240.8	239.9	156.6	209.1	207.3	131.7	188.8	183.7	219.3
FH	119.3	146.2	145.6	99.5	125.3	124.4	82.1	118.2	114.0	135.2
Li <sub>2</sub>	5.6	22.5	21.8	3.4	20.5	19.8	2.2	14.1	20.9	24.0
LiF	125.9	151.3	152.6	110.5	134.9	135.6	85.2	129.5	123.5	137.6
HCCH	363.9	438.6	444.0	305.5	380.1	383.4	271.9	365.6	351.2	388.9
H <sub>2</sub> CCH <sub>2</sub>	489.8	600.9	603.0	417.5	528.5	528.1	394.2	489.4	481.7	531.9
H <sub>3</sub> CCH <sub>3</sub>	604.7	752.1	751.2	517.7	664.9	660.9	506.0	608.5	603.1	666.3
CN	172.9	213.5	221.5	138.8	179.1	186.0	84.4	150.6	155.4	176.6
HCN	281.6	346.5	352.6	236.5	301.2	306.2	184.9	287.3	269.7	301.8
CO	258.2	293.4	301.9	215.9	250.9	257.4	168.3	254.3	237.4	256.2

# A few warnings:

- The explicit form adopted to describe the exchange and correlation interactions represents a delicate step in the setup of the simulation and must be carefully tested and benchmarked (see e.g. *Acc. Chem. Res.* **39**, 151 (2006) for an instructive example... OH<sup>-</sup> in water).
- Keep in mind that **no one** of the present versions of  $E_{xc}$  includes van der Waals interactions. In the cases in which they are dominant, special corrections *ad hoc* must be included (Langreth *et al.* 2005, Grimme 2006, Schwabe and Grimme 2007, Silvestrelli 2008)
- They are not entirely (or not at all) self-consistent with the DFT formulation.
#### Example of Hybrid Functional (1): B3LYP

The hybrid exchange-correlation functional B3LYP is a linear combination of the Hartree-Fock exact exchange functional  $E_x^{\rm HF}$  with the GGA exchange-correlation gradient-corrected (GGA=PBE, BLYP, HCTH, etc...) energy  $E_{xc}$  as provided by DFT.

$$E_{xc}^{\text{B3LYP}} = E_{xc}^{\text{LDA}} + a_0 \left( E_x^{\text{HF}} - E_x^{\text{LDA}} \right) + a_1 \left( E_x^{\text{GGA}} - E_x^{\text{LDA}} \right) + a_2 \left( E_c^{\text{GGA}} - E_c^{\text{LDA}} \right)$$

where  $a_0 = 0.20$ ,  $a_1 = 0.72$  and  $a_2 = 0.81$  are empirical parameters determined by fitting the computed values of atomization energies, ionization potentials, proton affinities, and total atomic energies to experiments and higher level quantum chemical calculations (CI, Coupled Cluster, multi-determinant methods,...) for a set of training molecules.

#### Example of Hybrid Functional (2): HSE & PBE0

Also the hybrid functionals HSE and PBE0 rely on calculation of the exact Hartree-Fock exchange functional at least at short range  $E_x^{\text{HF,SR}}$ . More precisely, the Coulomb potential is split into a short (SR) and a long range (LR) part as

$$\frac{1}{r} = \frac{1 - \operatorname{erf}(\omega r)}{\underset{\mathbf{SR}}{r}} + \frac{\operatorname{erf}(\omega r)}{\underset{\mathbf{LR}}{r}}$$

The mostly used HSE0 functional assumes (empirically)  $\omega$ =0.2 and a mixing coefficient *a* = 0.25

$$E_{xc}^{HSE} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE}$$

And the PBE0 is the limit  $\omega = 0$ 

$$E_{xc}^{PBE0} = aE_{x}^{HF}(0) + (1-a)E_{x}^{PBE}(0) + E_{c}^{PBE}$$

Namely only the exchange term is affected, not the correlation

#### Wannier functions technique: a useful tool

Define, after G. H. Wannier, Phys. Rev. 52, 191 (1937)

$$w_i(\mathbf{x} - \mathbf{R}) = \frac{V}{(2\pi)^3} \int d^3k \, \psi_{i,\mathbf{k}}(\mathbf{x}) e^{-i\mathbf{k}\cdot\mathbf{R}}$$

being **R** the atomic site position. With  $\mathbf{k} = \mathbf{0}$  ( $\Gamma$  point):

$$w_i(\mathbf{x}) = \prod_{p=0}^{\infty} \exp(-A^{(p)}) \cdot \psi_i^{KS}(\mathbf{x})$$

using the initial condition  $w_i^{(0)}(\mathbf{x}) = \psi_i^{\text{KS}}(\mathbf{x})$  for the iterative solution at step p = 0

References: R. Resta, *Phys. Rev. Lett.* **80**, 1800 (1998) N. Marzari and D. Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997)

#### WFC iterative scheme:

Minimize the spread of  $\Omega = \sum_{n} [\langle w_n | \mathbf{r}^2 | w_n \rangle - \langle w_n | \mathbf{r} | w_n \rangle^2]$ 

Step p = 0: using the initial condition  $w_i^{(0)}(\mathbf{x}) = \psi_i^{\text{KS}}(\mathbf{x})$  write  $X_{mn}^{(0)} = \left\langle w_m^{(0)} \left| \exp(-i2\pi x/L) \right| w_n^{(0)} \right\rangle$ 

Step p = 1: construct the matrix  $X^{(1)}$  (analogously  $Y^{(1)}$  and  $Z^{(1)}$ ) as  $X^{(1)} = \exp(-A^{(1)}) \cdot X^{(0)} \cdot \exp(A^{(1)})$ 

where  $A^{(1)}$  is an antihermitian matrix corresponding to a finite step in the direction of the gradient of  $\Omega$ 

$$A^{(1)} = \Delta t \cdot \frac{d\Omega}{dA^{(0)}}$$

and  $\frac{d\Omega}{dA_{mn}} = X_{mn} \left( X_{nn}^* - X_{mm}^* \right) - X_{mn}^* \left( X_{mm} - X_{nn} \right)$ 

40

The Wannier functions, in practice, minimize the spread

$$\Omega = \sum_{n} \left( \left\langle w_{n} \left| \mathbf{r}^{2} \right| w_{n} \right\rangle - \left\langle w_{n} \left| \mathbf{r} \right| w_{n} \right\rangle^{2} \right)$$

and are given by a unitary transformation of the KS orbitals

$$\left| w_{n} \right\rangle = \sum_{i} U_{in} \left| \psi_{i}^{KS} \right\rangle$$

the center of mass of a Wannier orbital is a useful quantity to characterize a system

**Wannier Function Center**  $\langle r_{\alpha,n} \rangle = -\frac{1}{G_{\alpha}} \operatorname{Im} \log \langle w_n | e^{-iG_{\alpha} \cdot x} | w_n \rangle$ 



$$\alpha = x, y, z \quad G_{\alpha} = 2\pi/L$$

#### WFCs technique in a nutshell:

• Unitary transform the KS orbitals as

 $W_n(\mathbf{x}) = \prod_p \exp(-\mathbf{A}^{(p)}) \psi^{KS} (\mathbf{x})$ 

• The coordinate  $x_n$  of the n<sup>th</sup> WFC reads

 $\begin{aligned} \mathbf{x}_{n} &= -(L/2\pi)Im \log \langle \mathbf{w}_{n} | \exp(-i2\pi \mathbf{x}/L) | \mathbf{w}_{n} \rangle \\ \text{and similar definition for } y_{n} \text{ and } z_{n}. \text{ Hence} \\ \mathbf{r}_{n} &= (x_{n}, y_{n}, z_{n}) \end{aligned}$ 

• The dipole moment P of the system reads

$$\mathbf{P} = \mathbf{P}_{\text{ion}} + \mathbf{P}_{e} = \sum_{I} Z_{I} \mathbf{R}_{I} - \sum_{n} f_{n} \mathbf{r}_{n}$$

## Wannier functions and WFC for a water molecule



## General expressions for vdW interaction: Adding to DFT what is missing

In (e.g.) a Grimme's scheme (D2) the vdW interaction is written as

$$E_{vdW}^{D2} = -s_6 \cdot \sum_{i,j>i}^{Nal} \frac{C_6}{r_{ij}^6} \cdot f_{damp}(r_{ij})$$
$$f_{damp}(r_{ij}) = \left[1 + e^{-\alpha_6 (r_{ij} / R_{vdW} - 1)}\right]^{-1}$$

- $s_6$  depends on the functional (training set fit)
- Very good approximation in many cases...
- ...but it looks like an *analytical restrain* on the atomic coordinates (**only**) preventing the system to actually reach its own ground electronic state (*whether correct or incorrect*)

## vdW interaction from first principles: One possible way

• Use the maximally localized Wannier functions scheme

$$S = \sum_{n} S_{n} = \sum_{n} (\langle w_{n} | r^{2} | w_{n} \rangle - \langle w_{n} | \mathbf{r} | w_{n} \rangle^{2})$$
$$\Rightarrow x_{n} = -\frac{L}{2\pi} \operatorname{Im} \ln \langle w_{n} | e^{-i(2\pi/L)x} | w_{n} \rangle$$

• From the WFCs positions  $\mathbf{r}_n$  and spread  $S_n$  define:

$$w_n(|\mathbf{r} - \mathbf{r}_n|) = \frac{3^{3/4}}{\sqrt{\pi}S_n^{3/2}} e^{-(\sqrt{3}/S_n)|\mathbf{r} - \mathbf{r}_n|}$$

## vdW interaction from first principles

From the auxiliary analytical Wannier functions  $w_{n}(|\mathbf{r} - \mathbf{r}_{n}|) = \frac{3^{3/4}}{\sqrt{\pi}S_{n}^{3/2}}e^{-(\sqrt{3}/S_{n})|\mathbf{r} - \mathbf{r}_{n}|}$   $C_{6nl} = \frac{3}{32 \cdot \pi^{3/2}} \int_{|\mathbf{r}| \le r_{c}} d^{3}r \int_{|\mathbf{r}'| \le r_{c}'} \frac{\sqrt{\rho_{n}(\mathbf{r}) \cdot \rho_{l}(\mathbf{r}')}}{\sqrt{\rho_{n}(\mathbf{r}) + \sqrt{\rho_{l}(\mathbf{r}')}}}$  $= \frac{3}{32 \cdot \pi^{3/2}} \int d^3 r \int d^3 r' \frac{w_n(\mathbf{r}) \cdot w_l(\mathbf{r}')}{w_n(\mathbf{r}) + w_l(\mathbf{r}')}$   $E_{\text{VdW}} = -\sum_{n,l} f_{nl}(r_{nl}) \frac{C_{6nl}}{r_{nl}^6} \quad f_{nl}(r) = \frac{1}{1 + \exp[-a(r/R_s - 1)]}$ 

46

# (Not the only) possible vdW alternative first-principles scheme

• vdW interaction written as usual

$$E_{vdW}^{WC} = -\sum_{l,n
$$f_{nl}(r_{nl}) = \left[1 + e^{-\alpha(r_{nl}/R_s - 1)}\right]^{-1}$$$$

- Results are almost independent on  $\alpha$  (~20)
- $R_s = R_{vdW} + R'_{vdW}$ , sum of the VdW radii of the MLWFs, which determined as the radii of the 0.01 electron density  $R_{vdW} = (1.475 - 0.866 \cdot \ln S_n) \cdot S_n$   $S_n =$  Wannier spread ...from  $w_n(|\mathbf{r} - \mathbf{r}_n|) = \frac{3^{3/4}}{\sqrt{\pi}S_n^{3/2}}e^{-(\sqrt{3}/S_n)|\mathbf{r} - \mathbf{r}_n|}$

## How to use this vdWC scheme

• Method 1: Self-consistent time consuming but "exact"

$$\min\{E^{DFT,m}\} \Rightarrow \psi_i \Rightarrow w_n = U_n^i \psi_i \Rightarrow E^{DFT,m+1} = E^{DFT,m} + E_{vdW}^{WC}$$
  
re-loop at each t

- Method 2: compute vdWC non self-consistently at each t  $\min \left\{ E^{DFT} \right\}_{\forall t} \Rightarrow \psi_i \Rightarrow w_n = U_n^i \psi_i \Rightarrow E^{DFT} = E^{DFT} + E_{vdW}^{WC}$
- Method 3: if  $|\mathbf{R}_{I}(t^{2} t) \mathbf{R}_{I}(t)| > tolerance$ , compute vdWC as above. Otherwise use the old  $C_{nl}^{6}$  and extrapolate WCs according to the movement of  $\mathbf{R}_{I}(t^{2} t)$

Futher numerical details in T. Ikeda & M.B. J. Chem. Phys. 143, 194510 (2015)

Do we really need all the electrons of every atom to describe a chemical bond ?



## This crucial observation led to pseudopotentials: core electrons are eliminated

a potential describing the core-valence interaction is built by fitting to the all-electron solutions of the Schrödinger or Dirac equation

D. R. Hamann, M. Schluter, C. Chang, C. Phys. Rev. Lett. 43, 1494 (1979)

$$E_{eI}[\rho] = \int d^3 x V_{ps}(\mathbf{x} - \mathbf{R}_I) \cdot \rho(\mathbf{x})$$

The elimination of the core electron from the calculation allows one to get rid of the *short length scale* problem

#### Pseudopotential (PP): general scheme to get one

PP generation is a three-step process:

- 1) In the first step one solves a Schrödinger-like / Dirac-like spherical equation for the all-electron (AE) system, computing eigenvalues  $\varepsilon_{nlm}$  and eigenfunctions  $\psi_{nlm}(\mathbf{r})$
- 2) In the second step one fits potentials /valence wavefunctions of the same atom without core electrons to this one. Generally, these potentials / wavefunctions angularmomentum dependent must match the AE ones beyond a given radius  $r_c$ .
- 3) In the third step ("*closer to cooking than to science*" © P. Giannozzi, 1998) one must test what she/he has generated from the former steps to see if it makes sense.

## Pseudopotential generation checklist:

- 1) Select the DFT level (GGA / LDA) you need / wish
- 2) Select valence and core states
- 3) Select a reference electron configuration (occupation)
- 4) Generate the AE wavefunctions
- 5) Select the matching radii  $r_c$  (and core corrections if needed)
- 6) Generate the PP
- 7) Check if it works in your molecule / liquid / solid, i.e. on atomic configurations differing from the starting one (this is what people call "transferability")
- 8) Check the required basis-set convergence (cut-off in PW)
- 9) Check its separable form

Warning: Do not even think to do any of the above if you do not have experience

#### **Separable form ? What ?**

The computational cost can be further reduced, provided that a separable form is chosen for the pseudopotential (PP) L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982)

$$V_{ps}(\mathbf{r}) = V_{loc}(\mathbf{r}) + \sum_{l,m} \phi_{lm}(\mathbf{r}) V_{NL}^{lm} \phi_{lm}^{*}(\mathbf{r})$$

- $\mathbf{r} = \mathbf{x} \mathbf{R}_I$
- $V_{loc}(\mathbf{r})$  depends only on the position  $\mathbf{r}$
- A non-local (NL) part depends on angular momenta *l,m*.
- The functions  $\phi_{lm}(\mathbf{r}) = f_l(r)Y_{lm}(\Omega)$  are eigenfunctions of the atomic Hamiltonian in which the core-valence interaction has been replaced by the PP

#### Norm-conserving pseudopotentials:

1) The PP (radial) wavefunction  $\phi^{PP}(r)$  is nodeless 2) The PP (radial) wavefunction matches the all-electron one  $\phi^{AE}(r)$  only beyond a certain distance  $r_0$  from the nucleus (cut-off radius)

$$\begin{cases} \phi^{AE}(r) = \phi^{PP}(r) & \forall r > r_0 \\ \phi^{AE}(r) \neq \phi^{PP}(r) & \forall r < r_0 \end{cases}$$

3) the square norm of the wavefunction is preserved in the pseudopotential construction

$$\int_{0}^{\infty} \left| \phi^{AE}(r) \right|^{2} r^{2} dr = \int_{0}^{\infty} \left| \phi^{PP}(r) \right|^{2} r^{2} dr$$



## Choosing valence and core states:

## This seems to be trivial, and often it is: Valence states contribute to bonding, core states do not. But....

- in transition metals, whose typical outer electronic configuration is  $nd^i(n + 1)s^j(n+1)p^k$ , it is not always evident that the *ns* and *np* states can be safely put into the core. The problem is that *nd* states are localized in the same spatial region as *ns* and *np* states, deeper than (n + 1)s and (n + 1)p states. This may lead to intolerable loss of transferability.
- Heavy alkali metals (Rb, Cs, maybe also K) have a large polarizable core. PP's with just one electron may not work properly (even with the core correction, see below)
- 3d states in GaAs may safely be left in the core (maybe with a core correction for Ga), not so in GaN.
- In ZnSe and other II-VI the d state of the cation has a nonnegligible contribution to the bonding.

In all these cases, promoting the highest core states ns and np, or nd (the "semicore" states) into valence may be a computationally expensive but obliged

<sup>©</sup> P. Giannozzi, 1998

#### Atomic calculations:

1) Non-relativistic case: The Kohn-Sham (Schrödinger-like) equation in spherical coordinates has to be solved

$$\begin{pmatrix} -\frac{\hbar^2}{2m} \nabla^2 + V(r) - \epsilon \end{pmatrix} \psi(\mathbf{r}) = 0$$
Your LDA/GGA choice here !
$$- \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial Y_{lm}(\hat{\mathbf{r}})}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y_{lm}(\hat{\mathbf{r}})}{\partial\phi^2} \right) = l(l+1)Y_{lm}(\hat{\mathbf{r}})$$

$$- \frac{\hbar^2}{2m} \frac{d^2 R_{nl}(r)}{dr^2} + \left(\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + V(r) - \epsilon\right) R_{nl}(r) = 0$$
providing the AE solution  $\psi(\mathbf{r}) = \left(\frac{R_{nl}(r)}{r}\right) Y_{lm}(\hat{\mathbf{r}})$ 

57

#### Atomic calculations:

2) Fully relativistic case: The Kohn-Sham (Dirac-like) equation in spherical coordinates has to be solved for large components  $R_{nlj}(r)$  and small ones  $S_{nlj}(r)$ 

$$c\left(\frac{d}{dr} + \frac{\kappa}{r}\right) R_{nlj}(r) = \left(2mc^2 - V(r) + \epsilon\right) S_{nlj}(r)$$
$$c\left(\frac{d}{dr} - \frac{\kappa}{r}\right) S_{nlj}(r) = \left(V(r) + \epsilon\right) R_{nlj}(r)$$

where  $j = \frac{1}{2} (l = 0)$  or  $j = \frac{l+1}{2}$ ; l-1/2 (otherwise) and  $\kappa$  is the Dirac quantum number  $\kappa = -1$  if l = 0, and  $\kappa = -l-1$ , l otherwise.

#### Atomic calculations:

3) Scalar relativistic case: The Kohn-Sham (Dirac-like) equation in spherical coordinates is solved only for the large components  $R_{nli}(r)$  and averages over the spin-orbit component, thus reading

$$-\frac{d^2 R_{nl}(r)}{dr^2} + \left(\frac{l(l+1)}{r^2} + M(r)\left(V(r) - \epsilon\right)\right) R_{nl}(r)$$
$$-\frac{\alpha^2}{4M(r)} \frac{dV(r)}{dr} \left(\frac{dR_{nl}(r)}{dr} + \langle\kappa\rangle\frac{R_{nl}(r)}{r}\right) = 0$$

where  $\alpha = 1/137.036$  is the fine structure constant and  $\langle \kappa \rangle = -1$  is the degeneracy-weighted Dirac quantum number, whereas

$$M(r) = 1 - \frac{\alpha^2}{4} \left( V(r) - \epsilon \right)$$

A practical (milestone) example: Analytic form of a Bachelet-Hamann-Schlüter (BHS) PP

$$V^{PP}(\mathbf{r}) = V_{loc}(\mathbf{r}) + \sum_{l} \Delta V_{l}^{NL}(\mathbf{r})$$
  
Not depending on angular momentum

$$V_{loc}(\mathbf{r}) = -\frac{Z_{v}}{r} \left[ \sum_{i=1}^{2} c_{i}^{loc} \operatorname{erf}\left(\sqrt{\alpha_{i}^{loc}} \cdot r\right) \right]$$
$$\Delta V_{l}^{NL}(\mathbf{r}) = \sum_{j=1}^{3} \left( c_{j,l}^{NL} + c_{j+3,l}^{NL} \cdot r^{2} \right) \cdot \exp\left(-\alpha_{j,l}^{NL} \cdot r^{2} \right)$$

Parameters to fit:  $\{\alpha_{i}^{loc}, c_{i}^{loc}, \alpha_{j,l}^{NL}, c_{j,l}^{NL}\}_{j=1,2,3}^{i=1,2}$  l = s, p, d, ...

#### A simple comparison of AE vs. PP calculation: CH<sub>2</sub>

CH<sub>2</sub> in the singlet and triplet states (interatomic distances are in Å, angles in degrees). Note that our AE calculations use a 6-311G<sup>\*\*</sup> and the others a 6-31G<sup>\*</sup> basis set.  $\Delta E = E({}^{1}A_{1}) - E({}^{3}B_{1})$  is the singlet-triplet energy difference in kcal/mol

Method	Singlet				Triplet					
	С-Н		ĤCH		С-Н		ĤCH		ΔΕ	
	AE	РР	AE	РР	AE	РР	AE	PP	AE	PP
LSD	1.130	1.125	100	101	1.091	1.091	137	137	15	14
BP	0.	1.122	-	101	-	1.086	1222	135		13
BLYP	1,123	1.117	101	102	1.086	1.087	135	135	11	12
BLYP <sup>a</sup>	1.132		99.1		1.089		133.5		11.6	
SCF	1.100	-	103	-	1.075	-	135	-	29	-
SCF <sup>a</sup>	1.109		102.1		1.077		131.6		30.6	
<b>OCISD</b> <sup>a</sup>	1.117		101.5		1.082		132.2		15.7	
MP2+G2b	1.109		102.1		1.077		131.6		6.6	
Exp.	1.111°		102.4 <sup>c</sup>		1.078 <sup>c</sup>		136.0°		9.0 <sup>d</sup>	

a,b = done by somebody else

(PW cut-off = 40 Ry, 60 Ry, 80 Ry)

© M.B. and W. Andreoni, Chem. Phys. Lett. 265, 24 (1997)

#### Most popular norm-conserving pseudopotentials:

- G. B. Bachelet, D. R. Hamann, M. Schluter, Phys. Rev. B 26, 4199 (1982)
- X. Gonze, R. Stumpf, M. Scheffler, M. Phys. Rev. B 44, 8503 (1991)
- N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991)
- S. Goedecker, M. Teter, J. Hutter, Phys. Rev. B 54, 1703 (1996)

#### Alternatives:

 The norm-conservation can be released leading to ultra-soft pseudopotentials. <u>But</u>, an augmented charge has to be added in order to restore the total charge density as obtained upon integration of the square modulus wavefunction.
 Vanderbilt *Phys. Rev. B* 41, 7892(1990))
 The inner electron wavefunctions are considered as frozen orbitals and

described with appropriate angular momentum projectors (PAW)

(P. E. Blöchl Phys. Rev. B 50, 17953 (1994)).

Chemical bonds: the atomic orbitals  $\psi_i(\mathbf{x})$  are modified as a consequence of the interactions of the valence electrons of the atoms involved



63





- If no up-down levels splitting occurs, then  $E^{tot}[LDA] = E^{tot}[LSD]$
- If the ground state of the system includes an energy-levels splitting between an up-spin level and the corresponding down-spin one, then  $E^{\text{tot}}[\text{LDA}] > E^{\text{tot}}[\text{LSD}]$
- ...then LDA is unable to converge to the proper ground state because of the spin restriction

#### Quantum Electrons in Molecular Dynamics

In 1985, Roberto Car (*Princeton University*) and Michele Parrinello (*Swiss Federal Institute of Technology*) proposed to use the fundamental quantum mechanics to write  $V(\mathbf{R}_I)$  in an *ab initio* way

$$V(\mathbf{R}_{I}) = E[\boldsymbol{\psi}_{i}, \mathbf{R}_{I}] = \sum_{i=1}^{K} \langle \boldsymbol{\psi}_{i} | \hat{H}(\mathbf{x}, \mathbf{R}_{I}) | \boldsymbol{\psi}_{i} \rangle$$

So no model potentials (analytic *ad hoc* functions) are needed and electronic structure modifications can be directly described by QM ...

...but how to compute at the same time the electronic structure and the dynamic displacement of the atoms ?

R. Car, M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985)

- Instead of using the "brute" force way, we can generalize the classical MD lagrangean by adding the electronic degrees of freedom  $\psi_i$
- a constraint for keeping the orthogonality of the wavefunctions
- and any external additional variables  $\alpha_q$  (e.g. thermostats, stress, etc.)

$$\mathcal{L}^{CP} = \sum_{i} \mu \int d^{3}x \, |\dot{\psi}_{i}|^{2} + \frac{1}{2} \sum_{I} M_{I} \dot{\mathbf{R}}_{I}^{2}$$
$$+ \frac{1}{2} \sum_{q} \mu_{q} \dot{\alpha}_{q}^{2} - E^{DFT} [\psi_{i}, \mathbf{R}_{I}, \alpha_{q}]$$
$$+ \sum_{ij} \Lambda_{ij} \left( \int d^{3}x \, \psi_{i}^{*} \psi_{j} - \delta_{ij} \right)$$

• Solve the related Euler-Lagrange EOM

$$\frac{d}{dt}\frac{\delta \mathcal{L}^{CP}}{\delta \dot{\psi}_{i}^{*}} - \frac{\delta \mathcal{L}^{CP}}{\delta \psi_{i}^{*}} = 0 \quad \Longrightarrow \quad \text{Electrons}$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}^{CP}}{\partial \dot{\mathbf{R}}_{I}} - \frac{\partial \mathcal{L}^{CP}}{\partial \mathbf{R}_{I}} = 0 \quad \Longrightarrow \quad \text{Ions}$$

$$\frac{d}{dt} \frac{\partial \mathcal{L}^{CP}}{\partial \dot{\alpha}_q} - \frac{\partial \mathcal{L}^{CP}}{\partial \alpha_q} = 0 \quad \Longrightarrow \quad \text{external additional variables}$$



• Instead of using the "brute" force way, we can generalize the classical MD Lagrangean by adding the electronic degrees of freedom  $\psi_i$ 



That the entire field of *ab initio* molecular dynamics has grown mature is also evidenced by a separate PACS classification number (71.15.Pd "Electronic Structure: Molecular dynamics calculations (Car–Parrinello) and other numerical simulations") that was introduced in 1996 into the *Physics and Astronomy Classification Scheme* 

• Let us observe that it is straightforward to give a Hamiltonian, instead of a Lagrangean, with a simple Legendre transform after defining the momenta

$$\pi_i(\mathbf{x}) = \frac{\delta \mathcal{L}^{CP}}{\delta \dot{\psi}_i^*(\mathbf{x})} = \mu \dot{\psi}_i(\mathbf{x}) \qquad \pi_i^*(\mathbf{x}) = \frac{\delta \mathcal{L}^{CP}}{\delta \dot{\psi}_i(\mathbf{x})} = \mu \dot{\psi}_i^*(\mathbf{x})$$

$$\mathbf{p}_{i} = \nabla_{\dot{\mathbf{R}}_{I}} \mathcal{L}^{\mathrm{CP}} = M_{I} \dot{\mathbf{R}}_{I}$$

$$\dot{\zeta}_q = \frac{\partial \mathcal{L}^{CP}}{\partial \dot{\alpha}_q} = \mu_q \dot{\alpha}_q$$

• so that the Hamiltonian reads

$$H^{CP} = \sum_{I} \frac{\dot{\mathbf{p}}_{I}^{2}}{2M_{I}} + \sum_{i} \int d^{3}x \frac{\pi_{i}^{*}(\mathbf{x}) \pi_{i}(\mathbf{x})}{\mu} + \sum_{q} \frac{\dot{\zeta}_{q}^{2}}{2\eta_{q}} - E^{tot} \left[ \rho, \{\mathbf{R}_{I}\}, \alpha_{q} \right]$$
$$- \sum_{ij} \lambda_{ij} \left( \int d^{3}x \psi_{i}^{*}(\mathbf{x}) \psi_{j}(\mathbf{x}) - \delta_{ij} \right)$$

and the CPMD equations of motion will be given by the corresponding Hamilton equations for each set of variables and momenta.


$$|\mathbf{R}_{I}^{CP}(t) - \mathbf{R}_{I}^{BO}(t)| < C \ \mu^{1/2} \qquad (C > 0)$$
  
if  $\omega_{0} = \sqrt{2 \cdot \left(\varepsilon^{LUMO} - \varepsilon^{HOMO}\right)/\mu} > 0 \qquad \Delta t_{\max} \propto \sqrt{\frac{\mu}{\Delta E_{gap}}}$ 

F.A. Bornemann and C. Schütte, Numerische Mathematik 78, N. 3, p. 359-376 (1998)

### Practical implementation

To implement the CP-EOM numerically, the KS orbitals are ulletgenerally expanded in plane waves

$$\boldsymbol{\psi}_{i}(\mathbf{x}) = \sum_{\mathbf{G}} c_{i}(\mathbf{G}) e^{i\mathbf{G}\mathbf{x}}$$

**G** are the reciprocal space vectors. The Hilbert space spanned • by **PWs** is truncated to a suitable cut-off  $E^{cut}$  such that

 $G^{2}/2 < E^{cut}$ 

- PWs have so far been the most successful basis set, in particular for extended systems requiring periodic boundary conditions
- The basis set accuracy can be systematically improved in a fully • variational way
- PWs are independent from atomic positions (no Pulay forces) •
- However they are *not* localized and can be inefficient, e.g., for • small molecules or clusters in a large simulation cell

Plane wave expansion:  $\psi_i(\mathbf{x}) = \sum_{\mathbf{G}} c_i(\mathbf{G}) e^{i\mathbf{G}\mathbf{x}}$ 

For each electron i=1,...,N, G=1,...,M are the reciprocal space vectors. The Hilbert space spanned by PWs is truncated to a cut-off  $G_{cut}^2/2 < E^{cut}$ 



#### Practical implementation

• Verlet's algorithm on EOM gives  $(\boldsymbol{\mu}/\Delta t^2) = [|\psi_i(t+\Delta t)\rangle + |\psi_i(t-\Delta t)\rangle - 2 |\psi_i(t)\rangle] = -(\mathcal{H}^{CP}+\Lambda) |\psi_i(t)\rangle$ or, in G-space,

$$\frac{\mu}{\Delta t^2} \Big[ c_i(\mathbf{G}, t + \Delta t) + c_i(\mathbf{G}, t - \Delta t) - 2c_i(\mathbf{G}, t) \Big] = -\sum_{\mathbf{G}'} \Big\langle \mathbf{G} \Big| H^{CP} \Big| \mathbf{G}' \Big\rangle c_i(\mathbf{G}') + \sum_j \Lambda_{ij} c_j(\mathbf{G})$$

- The ionic degrees of freedom  $\mathbf{R}_{t}(t)$  are updated at a rate (speed)  $\Delta t$  while the electronic degrees of freedom  $|\psi(t)\rangle$  are updated at a rate  $\Delta t/\mu^{1/2}$  ( $\Delta t \sim 5$  a.u.,  $\mu \sim 500$  a.u.), hence they are much slower (adiabatic) with respect to the ions.
- The parameter that controls the adiabaticity (BO) is  $\mu$
- However this  $\Delta t$  is driven by QM and is much shorter than  $\delta t$  in • classical MD

### Practical implementation

• To achieve computational efficiency, pseudopotentials are written in the Kleinmann-Bylander separable form

$$V^{\rm ps}(\mathbf{x},\mathbf{x'}) = V^{\rm loc}(\mathbf{x}) \,\delta(\mathbf{x}-\mathbf{x'})$$

+ 
$$\Sigma_{\rm lm} \phi_{\rm lm}(\mathbf{x}) \Delta V_{\rm lm} \phi^*_{\rm lm}(\mathbf{x'})$$

being  $V^{loc}$  the local part and  $\Delta V_{lm}$  the non-local  $V^{NL}$  angular momentum dependent part.

- Core electrons, as we have seen before, are not taken into account explicitly...
- ...unless partial core corrections or semicore states are needed (e.g. core polarization effects)



#### Practical implementation: orthogonalization (i)

To keep the wavefunction orthogonal to each other during the dynamics, the Lagrange multipliers  $\Lambda = [\lambda_{ij}]$  are computed in an iterative self-consistent way.

1) first propagate the wavefunction in an unconstrained way

$$\widetilde{\psi}_{i}(t+\Delta t) = -\psi_{i}(t-\Delta t) + 2\psi_{i}(t) + \frac{\Delta t^{2}}{\mu} \left[-H\psi_{i}(t)\right]$$

2) correct the updated wavefunction with the constraint

$$\psi_i(t + \Delta t) = \widetilde{\psi}_i(t + \Delta t) + \sum_j x_{ij} \psi_i(t)$$

where  $x_{ij} = (\Delta t^2 / \mu) \lambda_{ij}$ 

#### Practical implementation: orthogonalization (*ii*)

3) This gives us an equation for the Lagrange multipliers

$$\mathbf{X}\mathbf{X}^{+} + \mathbf{X}\mathbf{B} + \mathbf{B}^{+}\mathbf{X}^{+} = 1 - \mathbf{A}$$
  
where  $A_{ij} = \left\langle \widetilde{\psi}_{i}(t + \Delta t) \middle| \widetilde{\psi}_{j}(t + \Delta t) \right\rangle, B_{ij} = \left\langle \psi_{i}(t) \middle| \widetilde{\psi}_{j}(t + \Delta t) \right\rangle$ 

4) Note that  $\mathbf{A} = \mathbf{1} + O(\Delta t^2)$  and  $\mathbf{B} = \mathbf{1} + O(\Delta t)$ . We can then solve iteratively

$$\mathbf{X}^{(n)} = \frac{1}{2} \Big[ \mathbf{1} - \mathbf{A} + \mathbf{X}^{(n-1)} \big( \mathbf{1} - \mathbf{B} \big) + \big( \mathbf{1} - \mathbf{B}^{+} \big) \mathbf{X}^{(n-1)} - \mathbf{X}^{(n-1)2} \Big]$$

with the initial condition  $\mathbf{X}^{(0)} = \frac{1}{2} (\mathbf{1} - \mathbf{A})$ 

Generally 2-6 iterations are necessary between two subsequent simulation steps if  $\Delta t \sim 5-6$  a.u. or less <sup>80</sup>

### Practical implementation

- **G=1,...,***M* (*loop on reciprocal vectors*) distributed in a parallel processing in bunches of *M*/(*nproc*) or via MPI or hybrid MPI+OMP
- *i* =1,...,*N* (*loop on electrons*) distributed (MPI / OMP)
- $k = 1,...,N_{kpt}$  (loop on k-points) distributed (MPI / OMP)
- $I = 1, ..., N_{Atoms}$  (loop on atoms) distributed (MPI / OMP), particularly useful in QM/MM simulations where MM ~ O(N)
- The scaling of the algorithm is O(NM) for the kinetic term,  $O(NM \log M)$  for the local potential and  $O(N^2M)$  for the non-local term and orthogonalization procedure (*all other quantum chemical methods scale as*  $O(MN^3)$  *M*=basis set)

(see e.g. http://www.cpmd.org)

General scheme of a computer code for First Principles MD:



#### Car-Parrinello & Born-Oppenheimer MD their respective (dis)advantages - I

	CPMD	BO
Conservation of constants of motion	Good	Convergence dependent
Electronic optimization	Not needed	Needed
Hamiltonian diagonalization	Not needed	Needed
Integration step	Small	Large
Minimum of the BO surface	Approximate	Exact

- CP-like  $\psi_i$  propagation  $\longrightarrow$  Stability
- Large  $\Delta t$  with no SCF cycle  $\longrightarrow$  Efficiency
- BO deviation under control  $\longrightarrow$  Min. Error
- Stability
   Efficiency
   Accuracy
   Min. Error

Car-Parrinello & Born-Oppenheimer MD their respective (dis)advantages - II

BO:

- Diagonalization / minimization of  $E^{DFT}$  are required in BO
- Hellman-Feynman forces are just one component, Pulay forces exist if local basis set are used
- Residual forces components appear *unless strong convergence criteria are imposed*.  $\Delta \rho = \rho \rho^{BO}$

$$\mathbf{F}^{extra} - \int d^3x \left( \frac{\partial V_{xc}[\rho^{BO}]}{\partial \rho^{BO}} \cdot \Delta \rho + V_H[\Delta \rho] \right) \cdot \nabla_{\mathbf{R}_I} \rho^{BO}$$

CP:

- Only Hellman-Feynman forces (at least in PWs)
- No residual SCF forces because of the fully Lagrangean (variational) equations of motion



- What are the effects of the presence of ions ?
- Do they have a detectable influence ?
- What can we learn ?

#### Why should we care ?

Hydration properties of monovalent and divalent metal cations are a key issue in the understanding of several chemical and biochemical processes, such as, for instance,



# **Computational Details:**

- Car Parrinello MD with BLYP and Troullier Martins pseudopotentials
- Basis set: PWs; 70 Ry for pure water; 80 Ry for NaCl + H<sub>2</sub>O (semicore states included for Na)
- $\mu = 340.0$  a.u.  $\Delta t = 4.0$  au T = 300 K using Nosé-Hoover Thermostat
- NaCl: 126 water molecules + 1 Na<sup>+</sup> and 1 Cl<sup>-</sup> cubic cell with PBC



(same concentration used in experiments and present in extracellular environments)

- IR spectrum obtained via Fourier transform of the dipole-dipole autocorrelation function
- Molecular dipoles via MLWF

# NaCl in water



# Wannier Centers (WFCs) of $H_2O$ Lone pairO-H $\sigma$ bond



The dipole moment P of the system reads

$$\mathbf{P} = \mathbf{P}_{\text{ion}} + \mathbf{P}_{e} = \sum_{I} Z_{I} \mathbf{R}_{I} - \sum_{n} f_{n} \mathbf{r}_{n}$$

**IR** absorption spectrum after WFCs

• Compute the dipole-dipole autocorrelation function

 $< \mathbf{P}(t) \mathbf{P}(0) > = < d\mathbf{P}(t)/dt \cdot d\mathbf{P}(0)/dt > /\omega^{2}$ 

• The IR absorption coefficient reads  $\alpha(\omega) = [4\pi\omega \tanh(\beta\hbar\omega)] \int e^{-i\omega t} \langle \mathbf{P}(t)\mathbf{P}(0) \rangle dt$ 

•  $1/3\hbar n(\omega)cV$ 

 $\beta = 1/k_{\rm B}T$ , being *T* the simulation temperature, V= volume of the system,  $n(\omega) =$  refractive index

## Pure and salty water



# Observation ...



- Theoretical Overcorrection systematic shift of theory vs. experiment
- Both experiments and theory suggest a shift.
- From pure water to NaCl, low wavenumbers are reduced and high wavenumbers are enhanced

# **Dipole Moment distribution**



Shift towards higher wavenumbers shift towards lower dipole moment

Indication that the distribution for NaCl @ H<sub>2</sub>O moves towards lower values of dipole moments

#### Example 2 : random walk of a proton in water

Continuous breaking and formation of chemical bonds... ...we shall see it later in more detail



#### Example 3: an electron solvated in water

- The excess electron in solution  $(e_{aq})$  was studied since the early 60s due to its fundamental interest in a large class of aqueous reactions
- It is of practical importance in various areas of : Physics (e.g. M. J. Tauber and R. A. Mathies, J. Am. Chem. Soc. 125, 1394 (2003) - Raman spectroscopy of e<sup>-</sup><sub>aq</sub>), Chemistry (e.g. I. B. Martini et al., Science 293, 462 (2001) - optical control of electrons during electron transfer in solution) Biology (e.g. C. J. Fischer et al., J. Am. Chem. Soc. 124, 10359 (2002) - Phosphorescence in proteins due to solvated electrons)
- It is the basic example of electron (anionic) dynamics of solutes in water
- It is a probe for water properties, H-bond network topology and ability of  $H_2O$  in solvating

#### Detection of hydrated electrons in liquid water



Transient absorption measurements made with fs laser pulses (A. E. Bragg *et al. Science* **306**, 669 (2004)) across the 3 states of  $e_{aq}$ : localized s-like ground state, near-degenerate LUMO p-like states and delocalized conduction band (CB) state (P. J. Rossky *et al. Phys. Rev. Lett.* **60**, 456 (1988)).

The s  $\leftarrow$  p relaxation is generally the detected quantity.

#### Electronic structure of water at different densities



Adding one electron in water:



• When an electron is added to the first unoccupied electronic state, it becomes partly localized and forms a solvation shell

# One extra electron in normal liquid water ...after ~1.6 ps



# Density of states (DOS) for water at different densities



#### HOMO (s-like) / LUMO (p-like) transitions



# What can we compute to compare with experiments ?

The optical spectrum given by

$$\sigma(\omega) = C \frac{1}{\omega} \sum_{i,j} (f_i - f_j) \left| \left\langle \psi_i \left| \mathbf{p} \right| \psi_j \right\rangle \right|^2 \delta\left(\varepsilon_i - \varepsilon_j - \hbar\omega\right)$$

where *C* is a constant,  $f_i$  the occupation number,  $\psi_i$  the KS eigenfunction and  $\varepsilon_i$  the corresponding eigenvalue. All these variables and parameters are available from the simulation.

#### Optical absorption spectra



103

#### What can we get out of a CPMD simulation?

- Electronic structure evolution during the dynamics<sup>#</sup>
- Radial distribution function / pair correlation functions  $g_{ij}(r)$
- Diffusion coefficients
- Vibrational, Infrared<sup>#</sup> (from dipole autocorrelation function) and Raman<sup>#</sup> spectra
- NMR chemical shifts<sup>#</sup> and hyperfine<sup>#</sup> ESR parameters
- Dynamical averages (statistical averages) of several physical quantities as in classical MD: total and free energy, molecular velocity distributions, etc.
- Breaking and formation of chemical bonds<sup>#</sup> if the barrier is zero or very little (~  $k_BT$ ).



#### Suggestions for further readings:

- An Introduction to Computational Physics, T. Pang, Cambridge University Press, Cambridge, 1997
- R. Car and M. Parrinello, "Unified approach for molecular dynamics and density-functional theory". *Phys. Rev. Lett.* **55**, 2471-2474 (1985)
- Modern Methods and Algorithms of Quantum Chemistry http://www.fz-juelich.de/nic-series/Volume3/Volume3.html (freely downloadable)
- D. A. Schmidt, R. Scipioni and M. B. J. Phys. Chem. A 113, 7725 (2009)
- M. B., T. Ikeshoji and K. Terakura, ChemPhysChem. 6, 1775 (2005)
- M. B., M. Parrinello, K. Terakura, T. Ikeshoji and C. C. Liew, *Phys. Rev. Lett.* **90**, 226403 (2003)

#### Thermodynamic control methods: constant temperature on electrons and ions

As in the case of the Nosé-Hoover thermostat, a thermostat can be used for electrons to preserve the adiabaticity and keeping separate temperatures for ions and electrons.

This extension of the thermostat was originally proposed by Blöchl and Parrinello (*Phys. Rev. B* **45**, 9413 (1992)) and was applied in case of zero-gap systems, e.g. metals (molten Al).

As in the ionic case, a single variable  $\xi$  is introduced, along with s

$$\dot{\mathbf{R}}_{I} \to s \cdot \dot{\mathbf{R}}_{I}$$
$$\dot{\psi}_{i}(\mathbf{x}) \to \xi \cdot \dot{\psi}_{i}(\mathbf{x})$$

to rescale electronic and ionic velocities.

#### Thermodynamic control methods: constant temperature on electrons and ions

Both  $\xi$  and *s* become dynamic variables and the extended Lagrangean reads

#### Thermodynamic control methods: constant temperature on electrons and ions

This does not add too much computational workload. We just have one new equation of motion for the electronic thermostat

$$\mu \cdot \ddot{\psi}_{i}(\mathbf{x}) = -\frac{\delta E^{DFT}}{\delta \psi_{i}^{*}} + \sum_{j} \Lambda_{ij} \psi_{j}(\mathbf{x}) - \frac{\dot{\xi}}{\xi} \mu \cdot \dot{\psi}_{i}(\mathbf{x}) \quad \text{electrons}$$

$$M_{I} \ddot{\mathbf{R}}_{I} = \frac{1}{s^{2}} \nabla_{\mathbf{R}_{I}} E^{DFT} - 2\frac{\dot{s}}{s} M_{I} \dot{\mathbf{R}}_{I} \quad \text{ions}$$

$$Q_{e} \ddot{\xi} = \frac{2}{\zeta} \left( \zeta^{2} \sum_{i} \mu \int |\dot{\psi}_{i}(\mathbf{x})|^{2} d^{3}x - E_{e}^{kin} \right) \quad \text{electronic thermostat}$$

$$Q \ddot{s} = \frac{1}{s} \cdot \left[ s^{2} \sum_{I} M_{I} \dot{\mathbf{R}}_{I}^{2} - (3N+1)k_{B}T \right] \quad \text{ionic thermostat}$$
# Thermodynamic control methods: constant temperature on electrons and ions

Analogously to the Nosé-Hoover thermostat, the choice of  $Q_e$  and of the target kinetic energy  $E_e^{kin}$  is equivalent to the choice of a characteristic  $\omega_e$  frequency at which the thermostat oscillates :

$$\omega_e = \sqrt{\frac{2E_e^{\kappa in}}{Q_e}}$$



Electrons at finite (electronic) temperature: Free Energy Molecular Dynamics approach

A system of *N* electrons is generally described in quantum mechanics by its hamiltonian *H*, whose Schrödinger/Kohn-Sham equation reads

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$
  $i = 1,...,N$ 

- Each state  $\psi_i$  can be either occupied (occupation number  $f_i=1$ ) or unoccupied ( $f_i=0$ ).
- Ok for ground state and/or for materials with a wide band gap.
- However if a (quantum) system is **not** at  $T_e = 0$  K, but at a *finite temperature*  $T_e > 0$ , then each state  $E_i$  has, (in the simplest case of a Boltzmann distribution) a finite probability

$$e^{-E_i/k_BT_e}$$

of being occupied.

With such a finite occupation probability

$$e^{-E_i/k_B T_e}$$

a sum over all the states  $1, \ldots, N$ , gives

$$e^{-\beta F} = \frac{1}{N} \sum_{i=0}^{N} e^{-\beta E_i} = \left\langle e^{-\beta \hat{H}} \right\rangle = Z \quad \Longrightarrow \quad F = -\frac{1}{\beta} \log Z$$

where  $\beta = 1/(k_B T_e)$  and Z is the partition function.

For a *fermionic* system, the partition function is given by

$$Z(\beta,\mu,\upsilon) = \det\left\{1 + \exp\left[-\beta(\hat{H}-\mu)\right]\right\}$$

Then, the free energy is just the logarithmic functional

$$\Omega = -\frac{1}{\beta} \log Z$$

Why is this the free energy ? Simply because of its *definition*:

$$e^{-\beta F} = \frac{1}{\upsilon} \sum_{i=0}^{N} e^{-\beta E_i} = \left\langle 1 + e^{-\beta \hat{H}} \right\rangle = \det\left(1 + e^{-\beta \hat{H}}\right)$$

including the constraint  $+\mu N$  to fix the number of electrons (microcanonical ensemble)

The ionic contribution  $(E_{II})$  must still be added to complete the *free energy* functional of the whole system

$$F[\rho, \{\mathbf{R}_I\}] = \Omega[\rho] + \mu N_e + E_{II}$$

Now we have all the ingredients to compute: 1) The *forces* on the electrons in the DFT-like fashion

$$\frac{\delta F}{\delta \langle \boldsymbol{\psi}_i |} = \frac{\delta F}{\delta \rho(\mathbf{x})} | \boldsymbol{\psi}_i \rangle$$

2) The forces on the ions in a molecular dynamics fashion

$$\mathbf{f}_I = -\nabla_{\mathbf{R}_I} F$$

• FEMD-PBE based molecular dynamics with  $\beta = 1/(k_B T_e)$ 

$$F = \Omega[\rho(\mathbf{x})] + \mu N_e + E_{II}$$
$$\Omega[\rho(\mathbf{x})] = -\frac{2}{\beta} \ln \det\{1 + \exp[-\beta(H - \mu)]\}$$
$$-\int d^3x \,\rho(\mathbf{x}) \left[\frac{V_H(\mathbf{x})}{2} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{x})}\right] + E_{xc}$$

• Hamiltonian given by

$$H = -\frac{1}{2}\nabla^2 + V_H(\mathbf{x}) + \sum_I V_{ps}(\mathbf{x} - \mathbf{R}_I) + \delta E_{xc}/\delta\rho(\mathbf{x})$$

where  $V_H$  = Hartree potential and a pseudopotential approach accounts for the valence-core interaction ( $V_{ps}$ ): core electrons are supposed not to be involved in the excitations

• The electronic density given by KS orbitals and Fermi statistics reads

$$\rho(\mathbf{x}) = \sum_{i} f_{i} |\psi_{i}(\mathbf{x})|^{2}$$
$$f_{i} = \frac{1}{\left[1 + \exp\left(\frac{E_{i} - \mu}{k_{B}T_{e}}\right)\right]}$$

And the fs relaxation time of e<sup>-</sup> is << t<sup>relx</sup><sub>Ions</sub> so that the adiabatic theorem holds also in this case
(see Phys. Rev. B 42, 2842 (1990))

#### **Example of application of FEMD: Pure Si generated in SiO<sub>2</sub>**

Synthetic silicon produced in a cheaper and more tunable way.



New techniques for producing silicon might make this technologically crucial element cheaper.

It could also give engineers new ways to design silicon chips, stripes, dots & co.

• Nohira, T., Yasuda, K. & Ito, Y. *Nature Materials*, **2**, 397 (2003).

#### Experimental background (and motivation):

- Making silicon for electronic devices requires extreme (expensive) conditions:  $SiO_2$  is melted T > 1883 K and reacted with C to produce *impure* Si that has to be purified and re-crystallized.
- Immersing pristine SiO<sub>2</sub> in a molten salt at *T*~1000 K and touching it with a metal wire injecting *e<sup>-</sup>* (*Nature Materials* 2, 397 (2003))
- Or irradiating SiO<sub>2</sub> with femtosecond laser pulse (*App. Phys. Lett* 87, 3495 (2003); Hirao's & Murakami's exp.), Si islands can be created in SiO<sub>2</sub> below the melting point
- The laser pulse technique is tunable to create **dots**, **wires** and *nanotechnological Si structures* in a matrix of SiO<sub>2</sub>.

## What has been done (and why):

- Laser pulses of different frequencies on α-quartz have been simulated via *finite electronic temperature molecular dynamics* within the Free Energy functional (A. Alavi *et al.*, PRL 73, 2599 (1994)) formalism to check for possible creation of Si-Si bonds.
- This is supposed to reproduce what occurs when SiO<sub>2</sub> is *perturbed* as in *femto-second laser experiments*.
- Three different electronic temperatures are considered, corresponding to 3 different laser frequencies:

T[e] = 20000 K  $\hbar \omega = 1.72 \text{ eV}$ T[e] = 25000 K  $\hbar \omega = 2.16 \text{ eV}$ 

T[e] = 30000 K  $\hbar \omega = 2.59 \text{ eV}$ 

#### Simulation at $T_e$ =20000 K (1.72 eV)



### Simulation at $T_e$ =25000 K (2.16 eV)



#### Simulation at $T_e$ =30000 K (2.59 eV)





#### Ionic temperature



Electronic density of states (DOS) of the 3 systems:



Radial distribution functions for the 3 systems



T[e] (K)	T <sub>ion</sub> (K)	$D_{\rm Si}$ (cm <sup>2</sup> /s)	$D_{\rm O}~({\rm cm^{2/s}})$	Si-Si bond
20000	304+/-151	1.004 x 10 <sup>-9</sup>	1.252 x 10 <sup>-9</sup>	No
25000	367+/-102	4.100 x 10 <sup>-9</sup>	8.489 x 10 <sup>-9</sup>	Yes
30000	2870+/-220	1.415 x 10 <sup>-7</sup>	3.401 x 10 <sup>-7</sup>	Yes (but melt)

 $D_j$  is the diffusion coefficient of (j = O/Si) computed as

$$D_{j} = \frac{1}{3} \int_{0}^{\Delta t \to \infty} \left\langle \frac{1}{N_{j}} \sum_{I=1}^{N_{j}} \mathbf{v}_{I}^{j}(t) \mathbf{v}_{I}^{j}(0) \right\rangle dt$$

# Trend of the diffusion coefficient of O and Si as a function of the electronic excitation



#### Structure evolution at $T_e=25000$ K (with pbc applied): t = 1.2 ps



(\*) MB., Pasquarello, Sarnthein, Car, *Phys. Rev. Lett.* **78**, 887 (1997) Donadio, Bernasconi, MB, *Phys. Rev. Lett.* **87**, 195505 (2001)

# Final stable structure obtained at $T_e = 25000$ K with pbc (Si-Si bonds in light blue)



### Outcome of the simulations

- An electronic excitation of ~2.2 eV is able to promote Si-Si bond formation below the melting point of the material
- SiO<sub>2</sub> does not melt but a sort of *phase separation* is induced. About 20% of Si atoms form bonds with nearby Si (25% if an O vacancy is present)
- The Si-Si bonds are formed in those parts of the SiO<sub>2</sub> system where the electron excitations (higher "*hot*" filled KS states) localize
- The different diffusion coefficient of O (*fast species*) and Si (slow species) seems to play a role in the separation/reconstruction process

Related publications:

M.B., A. Oshiyama and P. L. Silvestrelli, Phys. Rev. Lett. 91, 206401 (2003)

- M.B., A. Oshiyama, P. L. Silvestrelli and K. Murakami, Appl. Phys. Lett. 86, 201910 (2005)
- M.B., A. Oshiyama, P. L. Silvestrelli and K. Murakami, *Physica B* 376, 945 (2006)