The SIESTA program

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ICMAB

CECAM-Siesta Tutorial -- June 2007

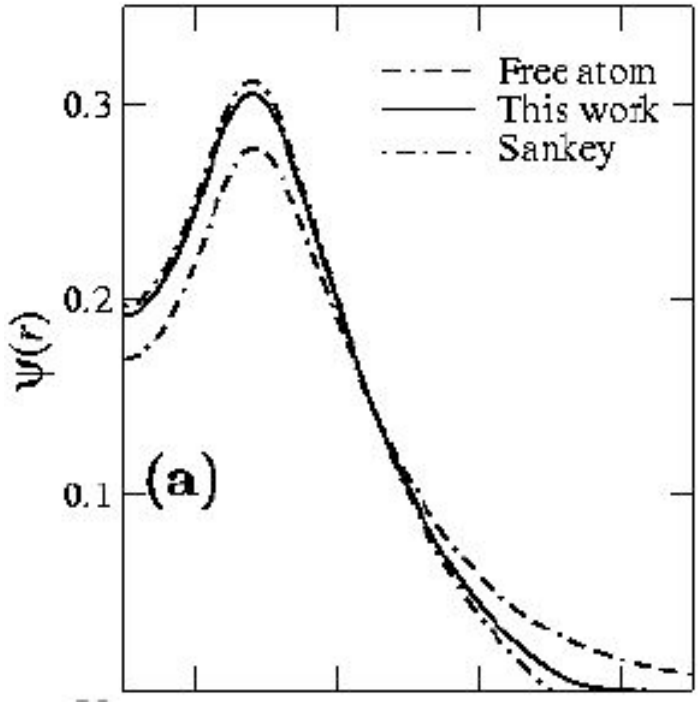
Basis set: Atomic orbitals

s

p

d

f

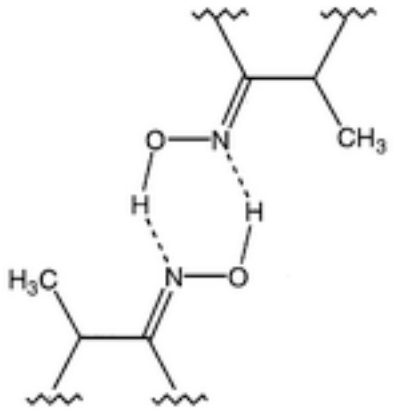


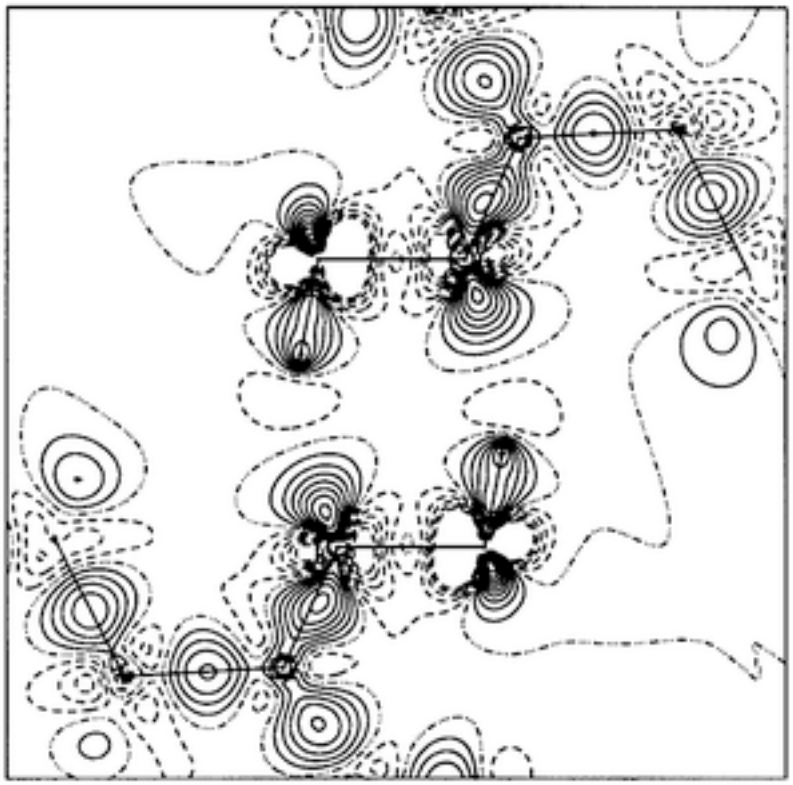
SIESTA: Strictly localized

(zero beyond cut-off radius)

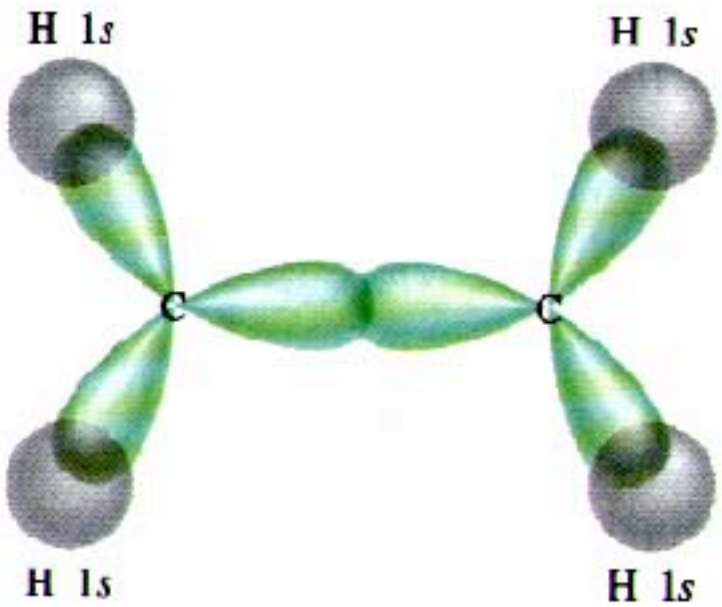
Why atomic orbitals?

- "Atoms" are a very good first approximation.
- Most of the language of the chemical bond is based on atomic orbitals.
- The size of the basis is relatively small.

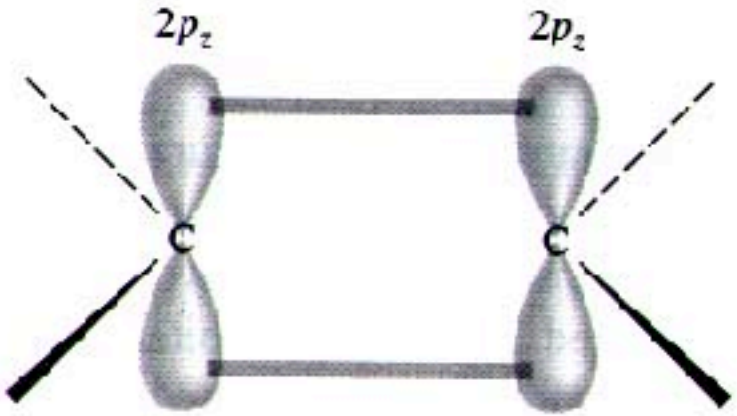


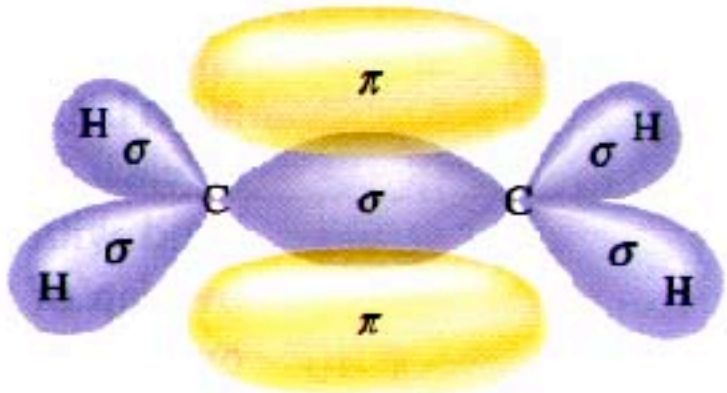


Most crystallographic analyses are done by using superpositions of atomic charges

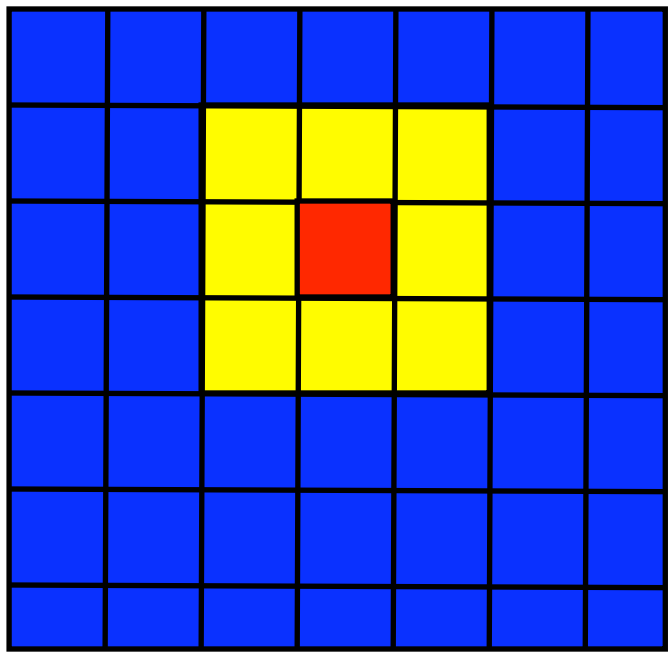


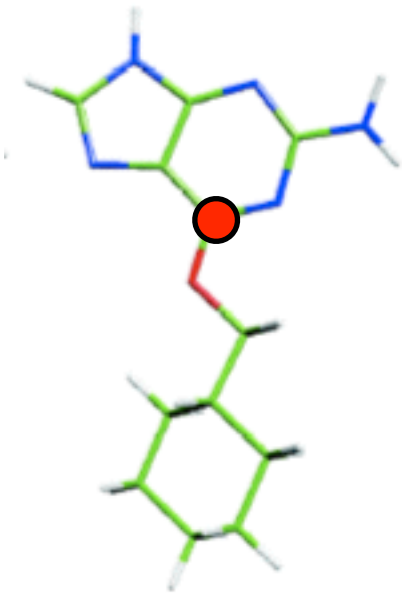
(a)



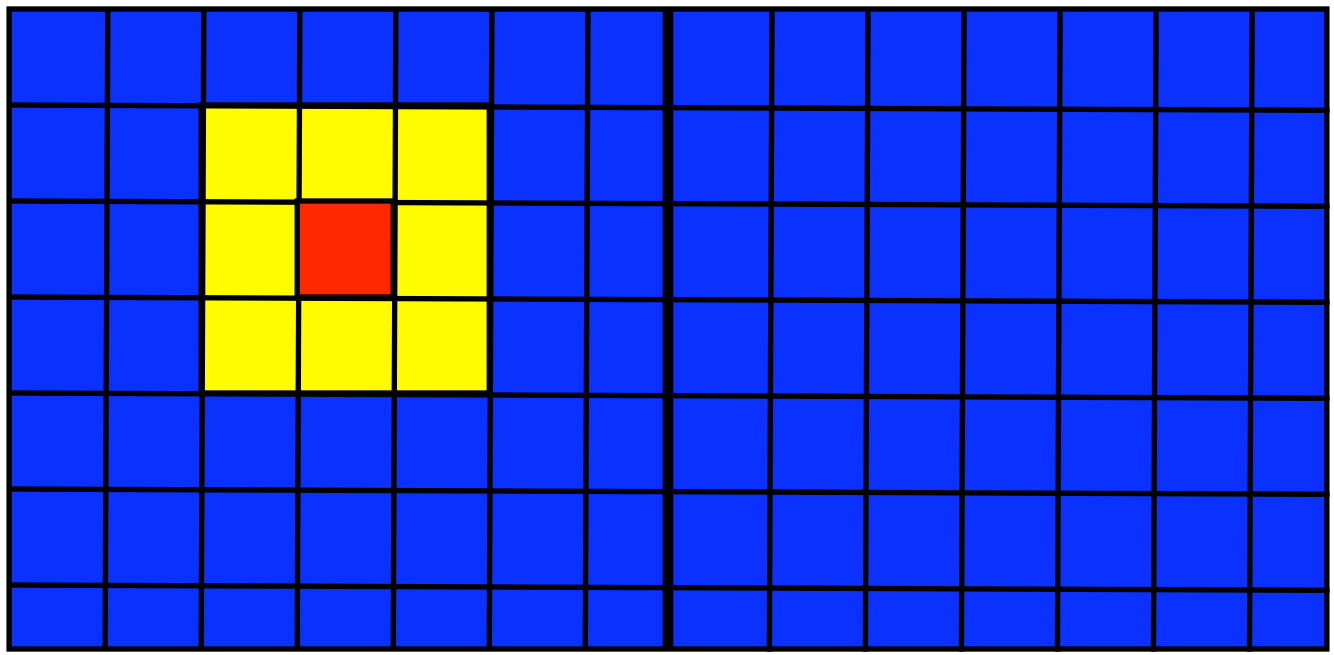


Chemical near-sightedness





Locality is key to Order-N scaling



``Divide and conquer'' W. Yang, Phys. Rev. Lett. 66, 1438 (1992)

``Nearsightedness'' W. Kohn, Phys. Rev. Lett. 76, 3168 (1996)

Basis Size

Depending on the required accuracy and

available computational power

Quick and dirty calculations

Highly converged calculations

Minimal basis set

(single- ζ; SZ)

Complete multiple-ζ

+

Polarization

+

Diffuse orbitals

+ Basis Optimization

Kohn-Sham eqns in a Plane Wave Basis (1)

Bloch's Theorem (k in 1st BZ) ⇒

$$\phi_{i,\bar{k}}(\bar{r}) = e^{i\bar{k}\bar{r}} u_i(\bar{r})$$

$u_i(r)$ periodic ⇒ expanded in reciprocal lattice vectors {G} (Fourier Transform)

$$\phi_{i,\bar{k}}(\mathbf{r}) = \sum_{\bar{G},\frac{\hbar^2}{2m}|\bar{G}+k|^2 \le E_{cut}} c_{i,\bar{G}+\bar{k}} e^{i(\bar{G}+\bar{k})\cdot r}$$

Uniform convergence with E_{cut} !!!

Kohn-Sham equations

$$\begin{aligned}\varepsilon_i c_{i,\bar{k}+\bar{G}} &= \left(\frac{\hbar^2}{2m}|\mathbf{G}+\bar{k}|^2\right) c_{i,\bar{k}+\bar{G}} + \sum_{\bar{G}'} V_H(\bar{G}-\bar{G}') c_{i,\bar{k}+\bar{G}'} \\ &+ \sum_{\bar{G}'} \left[V_{XC}(\bar{G}-\bar{G}') + V_{e-ion}(\bar{k}+\bar{G},\bar{k}+\bar{G}')\right] c_{i,\bar{k}+\bar{G}'}\end{aligned}$$

$$V_H = \frac{4\pi}{\Omega_c}\frac{n(\bar{G})}{|\bar{G}|^2}$$

$$n(\bar{G}) = \sum_{i,\bar{k},\bar{G}'} c^*_{i,\bar{k}+\bar{G}}\, c_{i,\bar{k}+\bar{G}+\bar{G}'}$$

V_H easy to calculate in reciprocal space

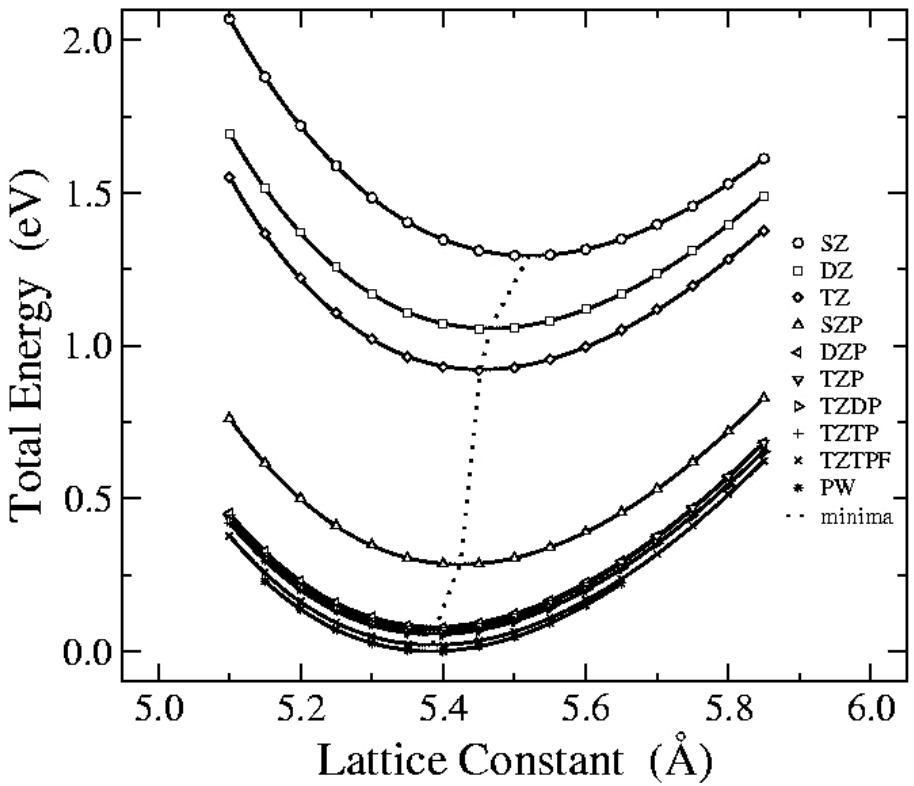
Ω_c = unit cell volume

(we need twice the number of PWs to describe n(r) than $\phi_{i,k}(r)$)

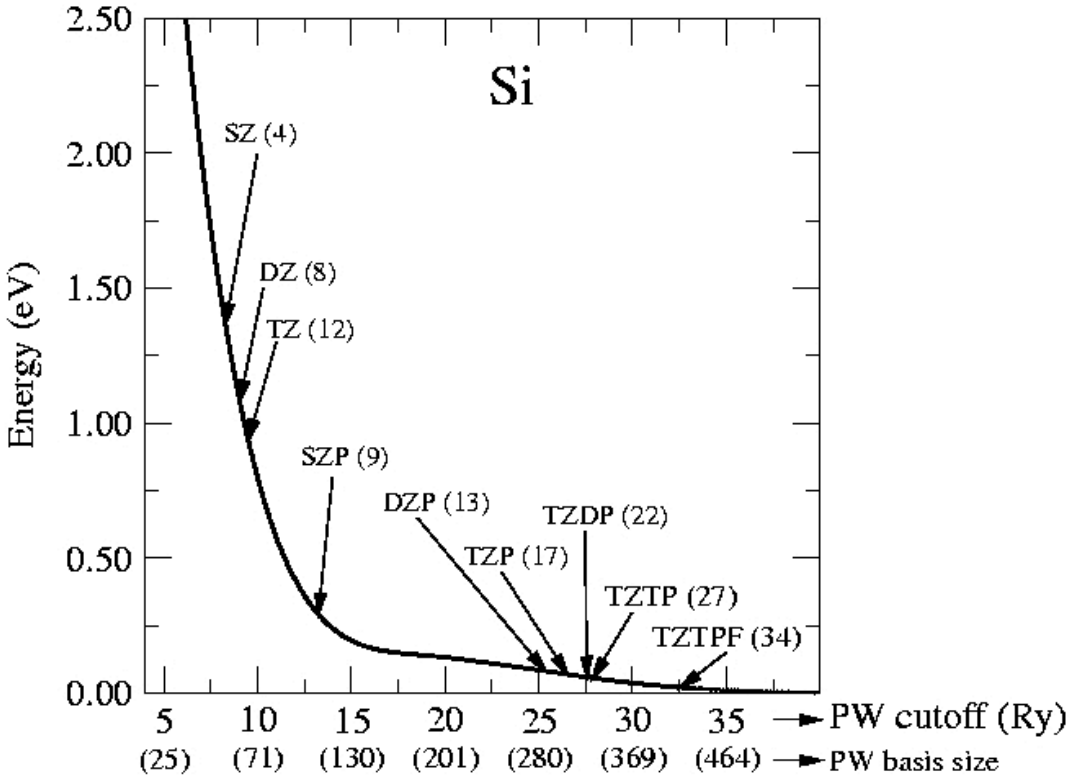
Convergence of the basis set

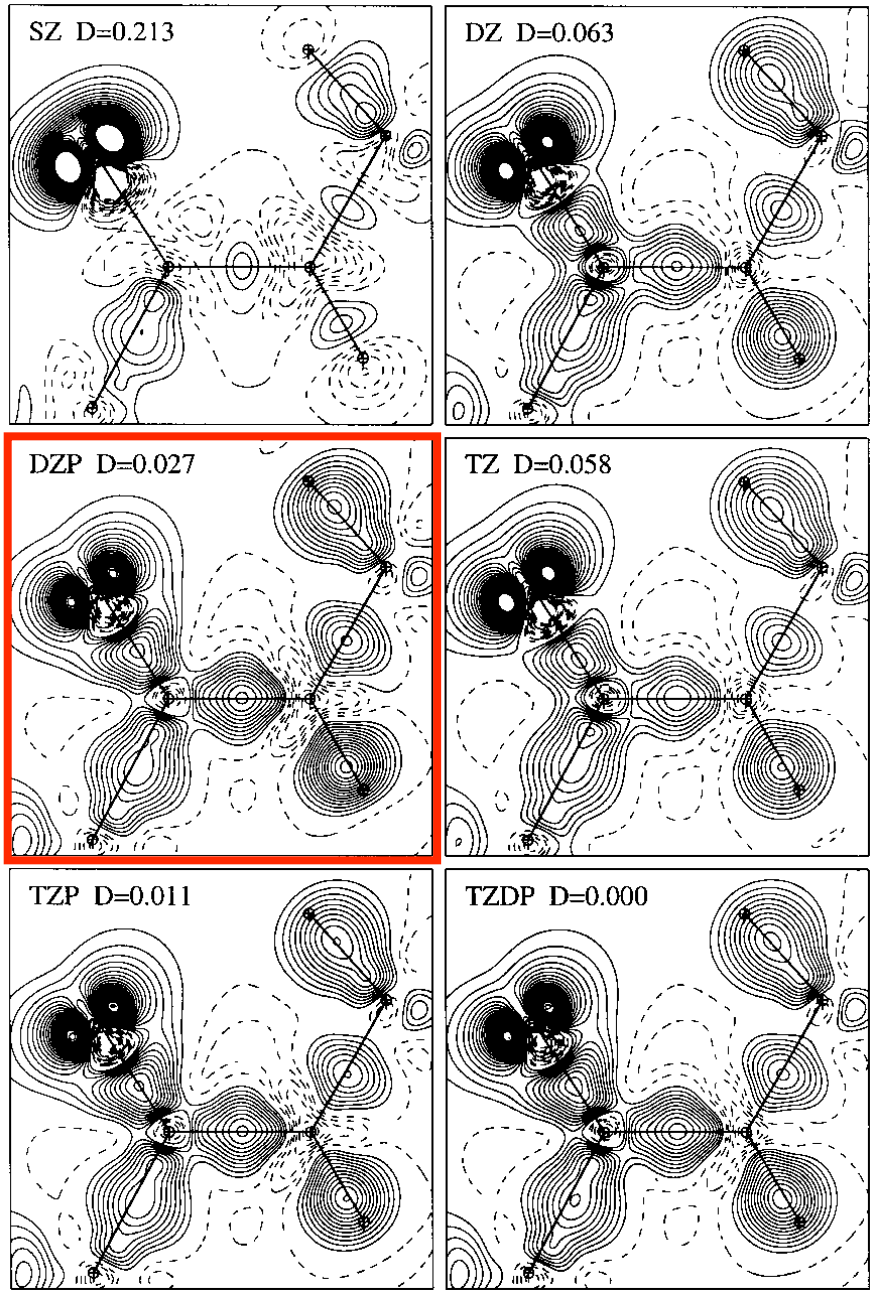
Bulk Si

Cohesion curves



PW and NAO convergence



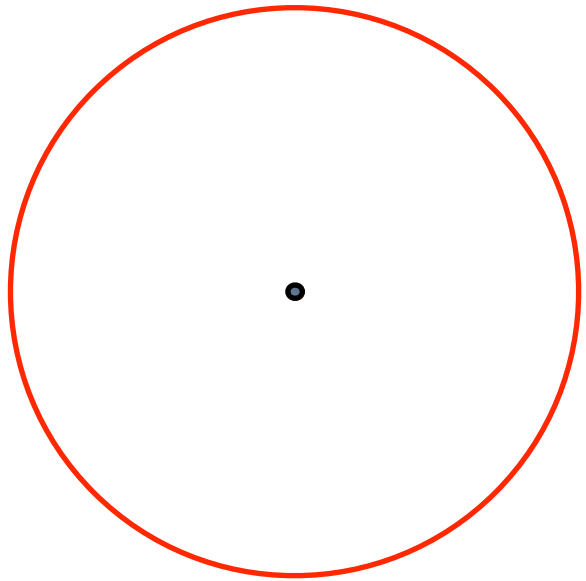


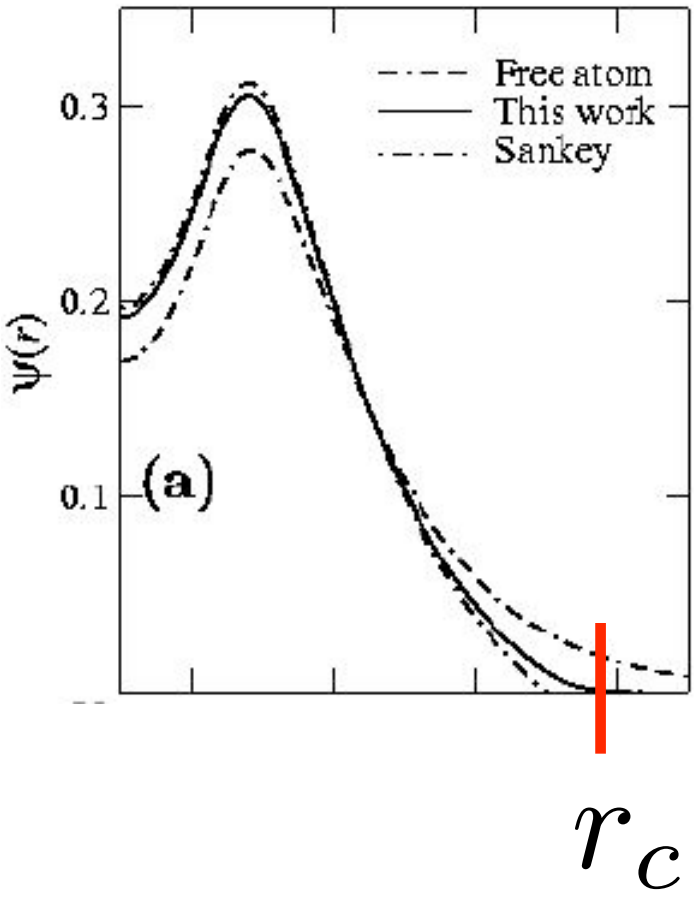
Deformation charge density in peptide bond in Crambine

DZP Basis Set is adequate

Fernandez-Serra et al, Sol. St. Comm. 116 (2000) 395

The most important parameter is the range of the orbital



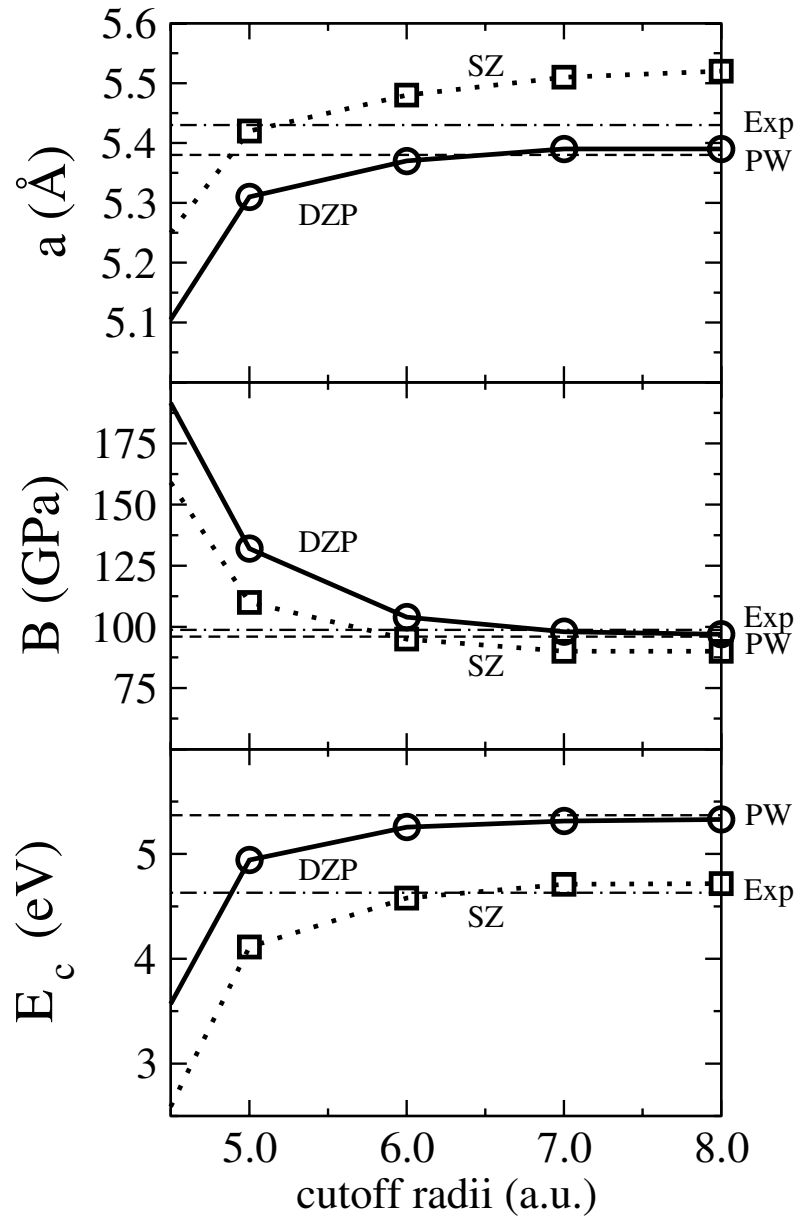


Confinement == Increase in kinetic energy

Convergence with the range

bulk Si

equal *s*, *p* orbitals radii



J. Soler *et al*, J. Phys: Condens. Matter, **14**, 2745 (2002)

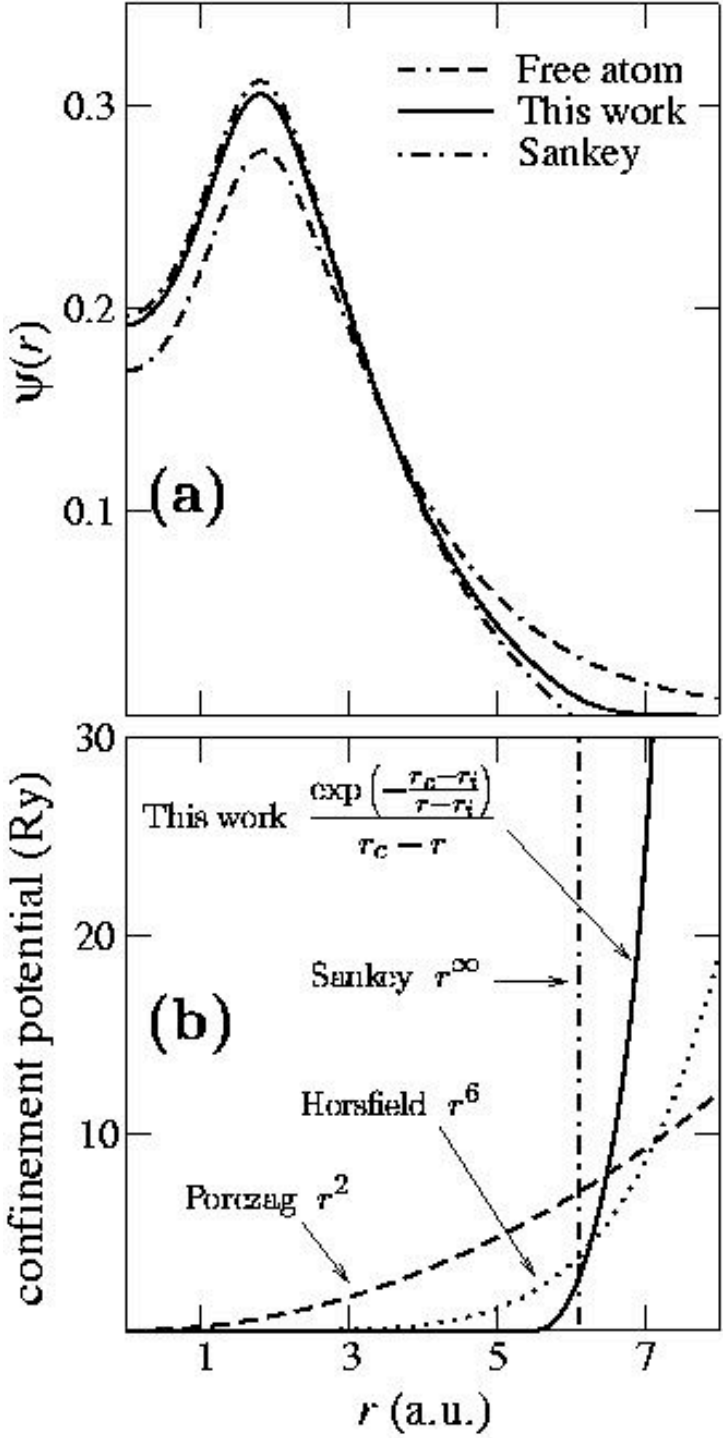
Soft confinement

(J. Junquera *et al*, Phys. Rev. B **64**, 235111 (01))

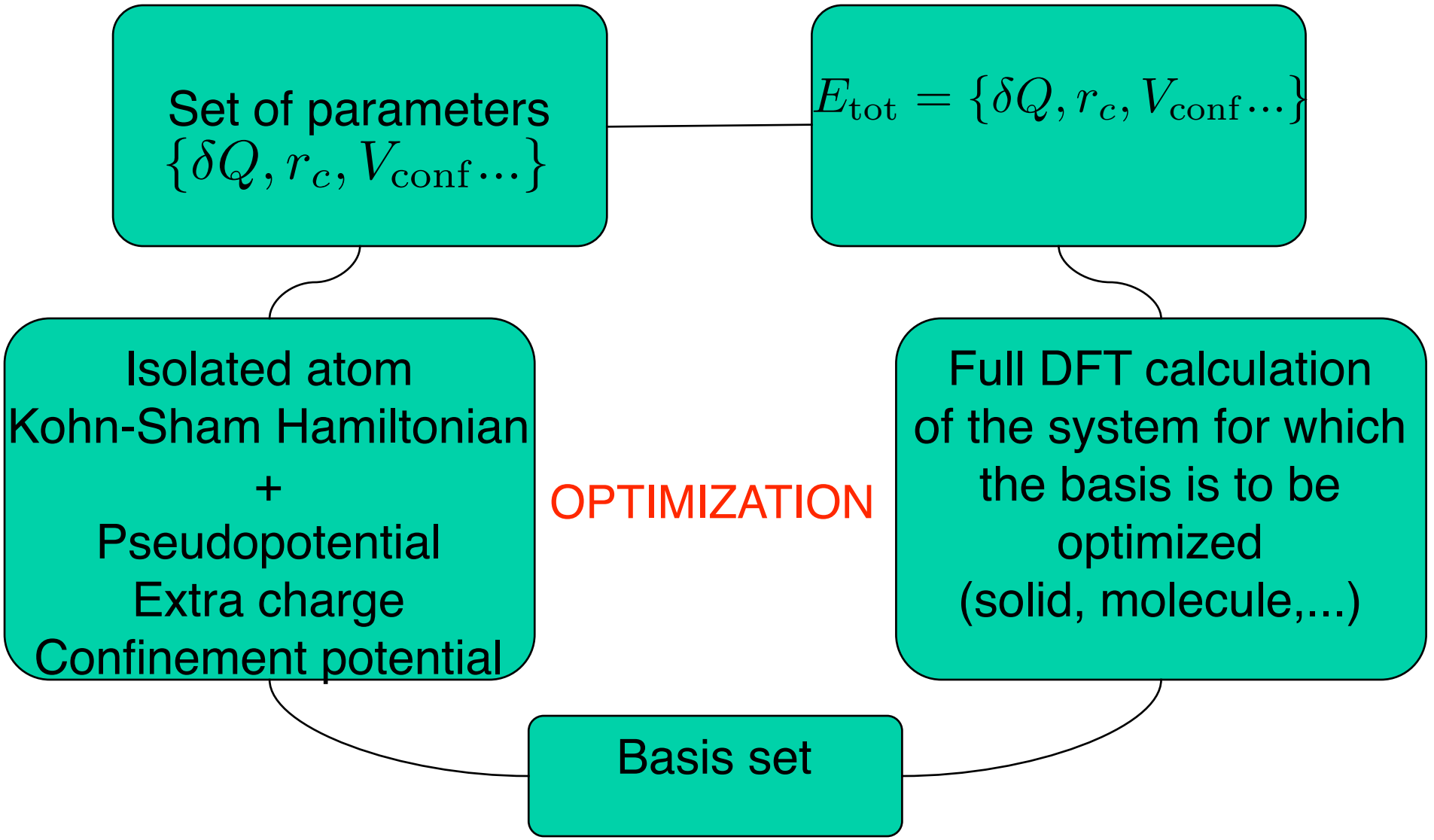
Shape of the optimal **3*s*** orbital of Mg in MgO for different schemes

Corresponding optimal confinement potential

- Better variational basis sets
- Removes the discontinuity of the derivative

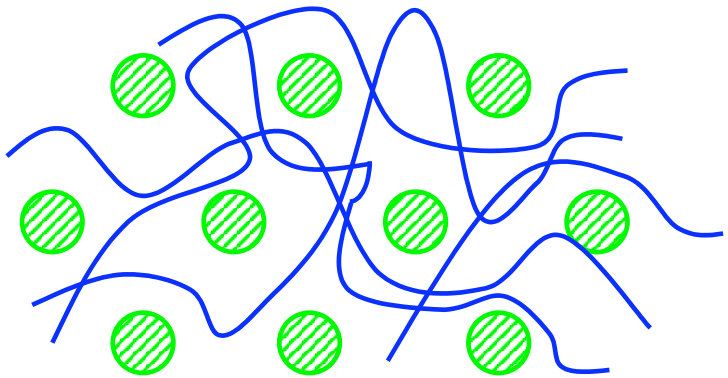


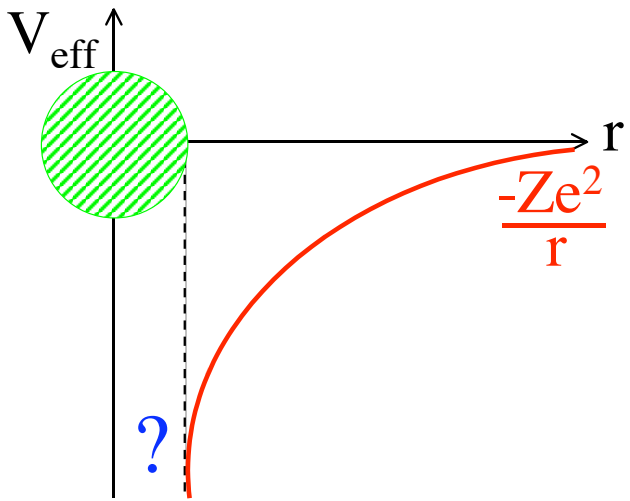
Optimization Procedure



Technical details

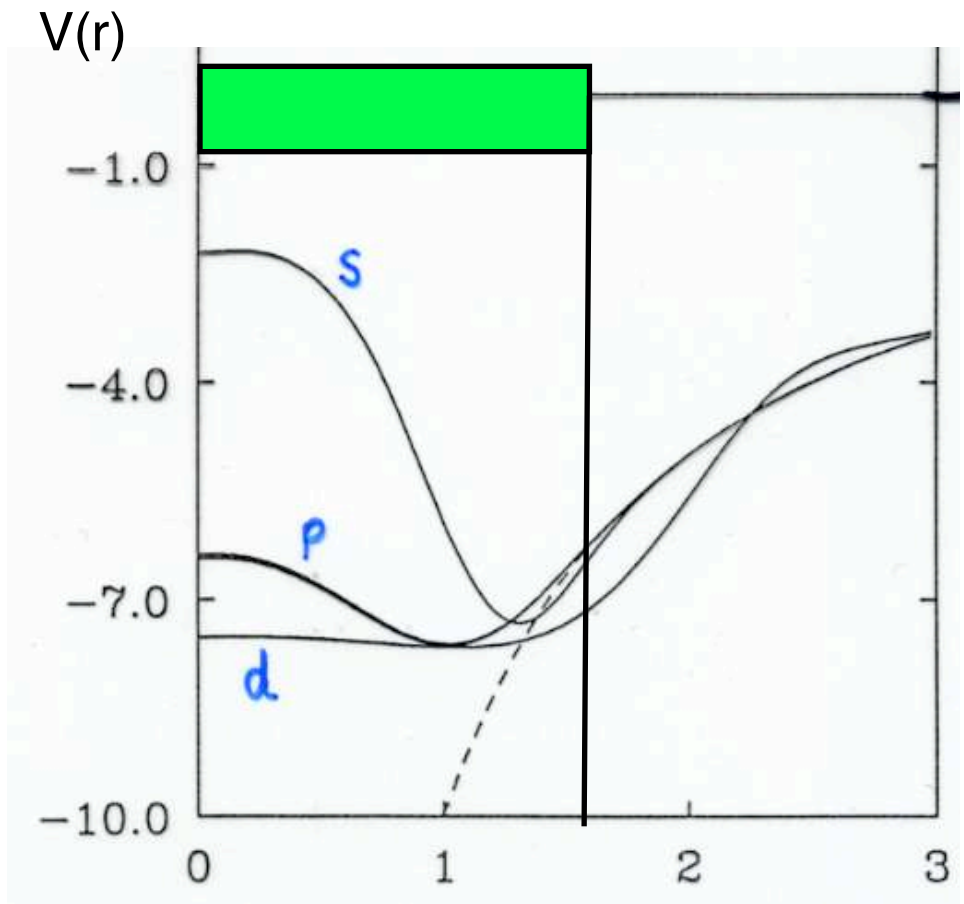
The internal electrons do not participate in the chemical bond





Effective potential for valence electrons

Pseudopotential



Norm-conserving pseudopotentials in Kleinman-Bylander form

$$\hat{V}^{PS} = V_{local}(r) + \hat{V}^{KB}$$

$$\hat{V}^{KB} = \sum_{l=0}^{l_{max}^{KB}} \sum_{m=-l}^{l} \sum_{n=1}^{N_l^{KB}} |\chi_{lmn}^{KB}\rangle v_{ln}^{KB} \langle \chi_{lmn}^{KB}|$$

$$v_{ln}^{KB} = \langle \varphi_{ln} | \delta V_l(r) | \varphi_{ln} \rangle$$

The pseudopotential is used to construct the pseudoatomic orbitals

$$\left(-\frac{1}{2r} \frac{\mathrm{d}^2}{\mathrm{d}r^2} r + \frac{l(l+1)}{2r^2} + V_l(r) \right) \phi_l(r) = (\epsilon_l + \delta\epsilon_l)\phi_l(r)$$

$$\psi_i(\boldsymbol{r}) = \sum_\mu \phi_\mu(\boldsymbol{r}) c_{\mu i},$$

$$\sum_{\nu\beta} (H^{\alpha\beta}_{\mu\nu} - E_i S_{\mu\nu}\delta^{\alpha\beta}) c^{\beta}_{\nu i} = 0$$

Generalized eigenvalue problem

$$H^{\alpha\beta}_{\mu\nu} = \langle \phi_\mu | \hat{T} + \hat{V}^{KB} + V^{NA}(\boldsymbol{r}) + \delta V^{H}(\boldsymbol{r}) + V^{\alpha\beta}_{XC}(\boldsymbol{r}) | \phi_\nu \rangle$$

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$$

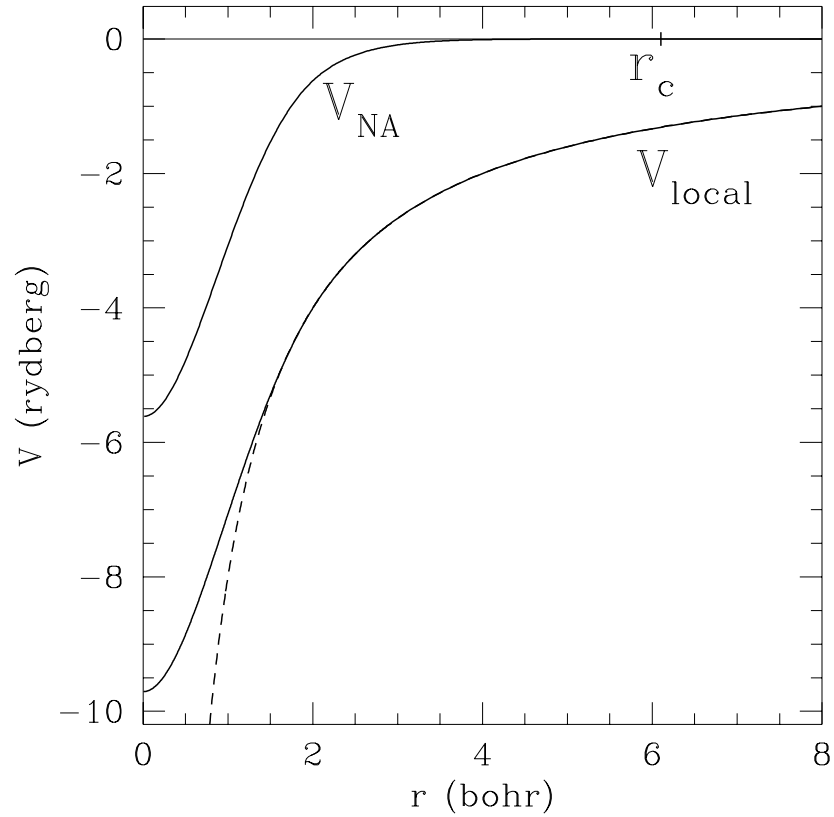
$$\rho(\boldsymbol{r}) = \sum_{\mu\nu} \rho_{\mu\nu} \phi^*_\nu(\boldsymbol{r}) \phi_\mu(\boldsymbol{r})$$

$$E^{BS} = \sum_i n_i \langle \psi_i | \hat{H} | \psi_i \rangle = \sum_{\mu\nu} H_{\mu\nu}\rho_{\nu\mu} = \mathrm{Tr}(H\rho)$$

$$\rho_{\mu\nu} = \sum_i c_{\mu i} n_i c_{i\nu}$$

Density matrix

$$H = T + V_{ion}(r) + V_{nl} + V_H(r) + V_{xc}(r)$$



$$\mathbf{V_{na}(r) = V_{ion}(r) + V_H[\rho_{atoms}(r)]}$$

Neutral-atom potential

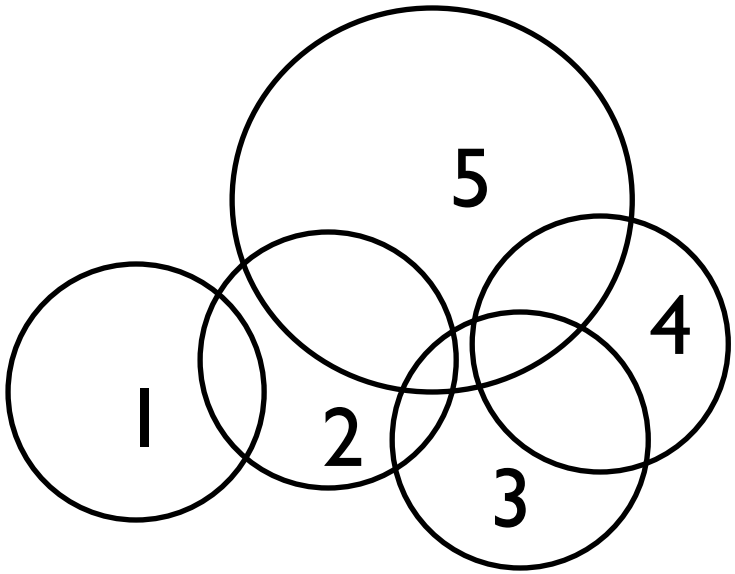
$$\mathbf{\delta V_H(r) = V_H[\rho_{SCF}(r)] - V_H[\rho_{atoms}(r)]}$$

$$\mathbf{H = T + V_{nl} + V_{na}(r) + \delta V_H\,(r) + V_{xc}(r)}$$

Two-center integrals

Grid integrals

Sparsity



1 with 1 and 2

2 with 1,2,3, and 5

3 with 2,3,4, and 5

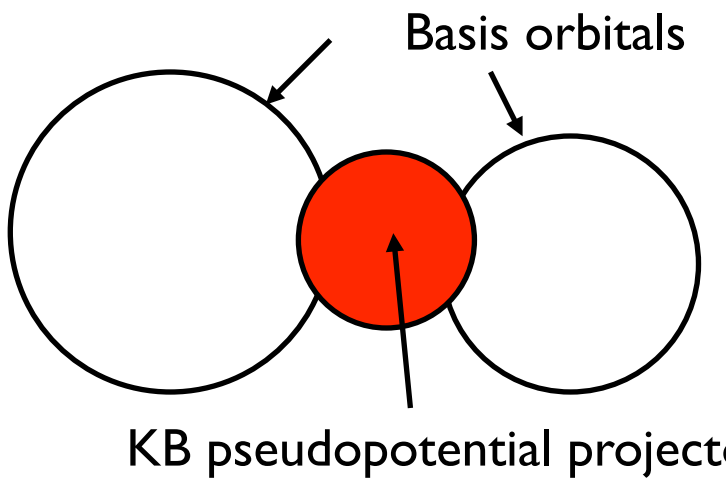
4 with 3,4 and 5

5 with 2,3,4, and 5

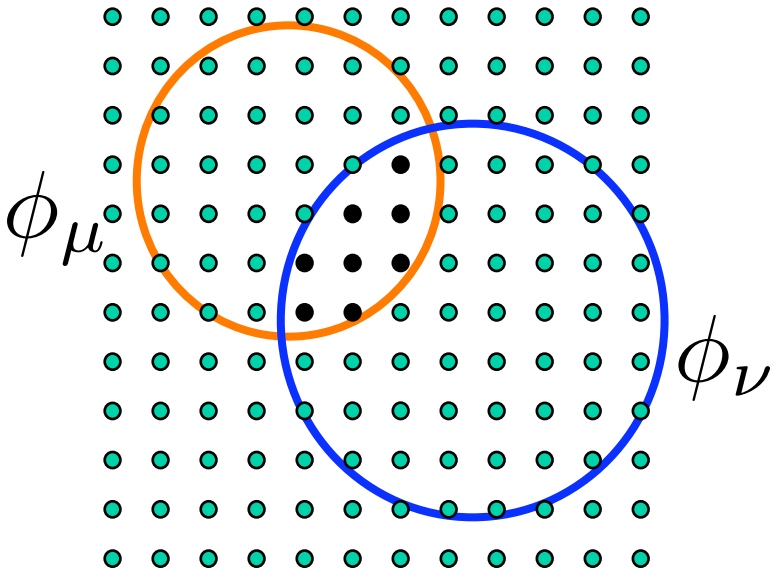
$S_{\mu\nu}$ and $H_{\mu\nu}$ are sparse

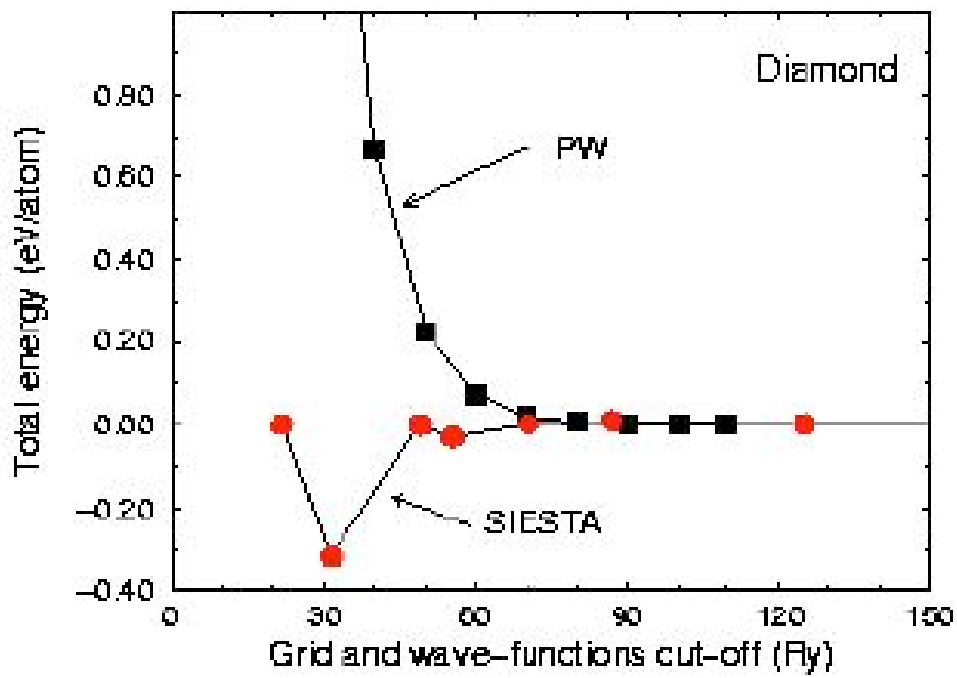
$\rho\mu\nu$ is not strictly sparse but only a sparse subset is needed

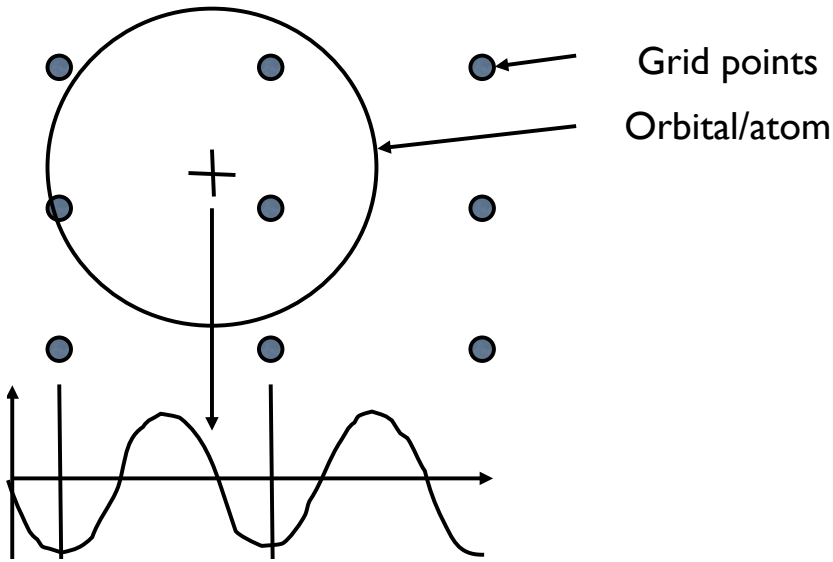
Non-overlap interactions



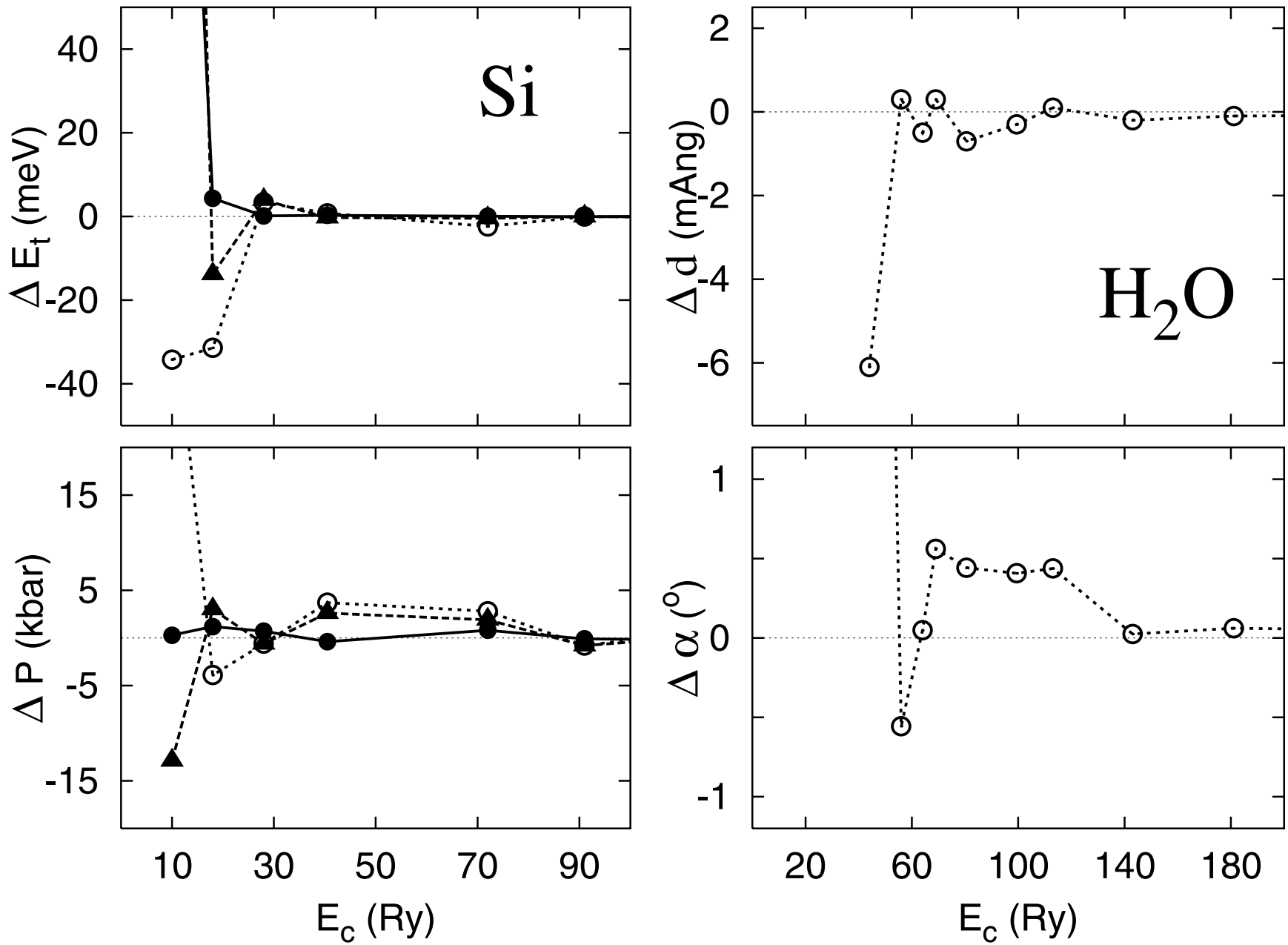
Real-Space Grid







Eggbox effect

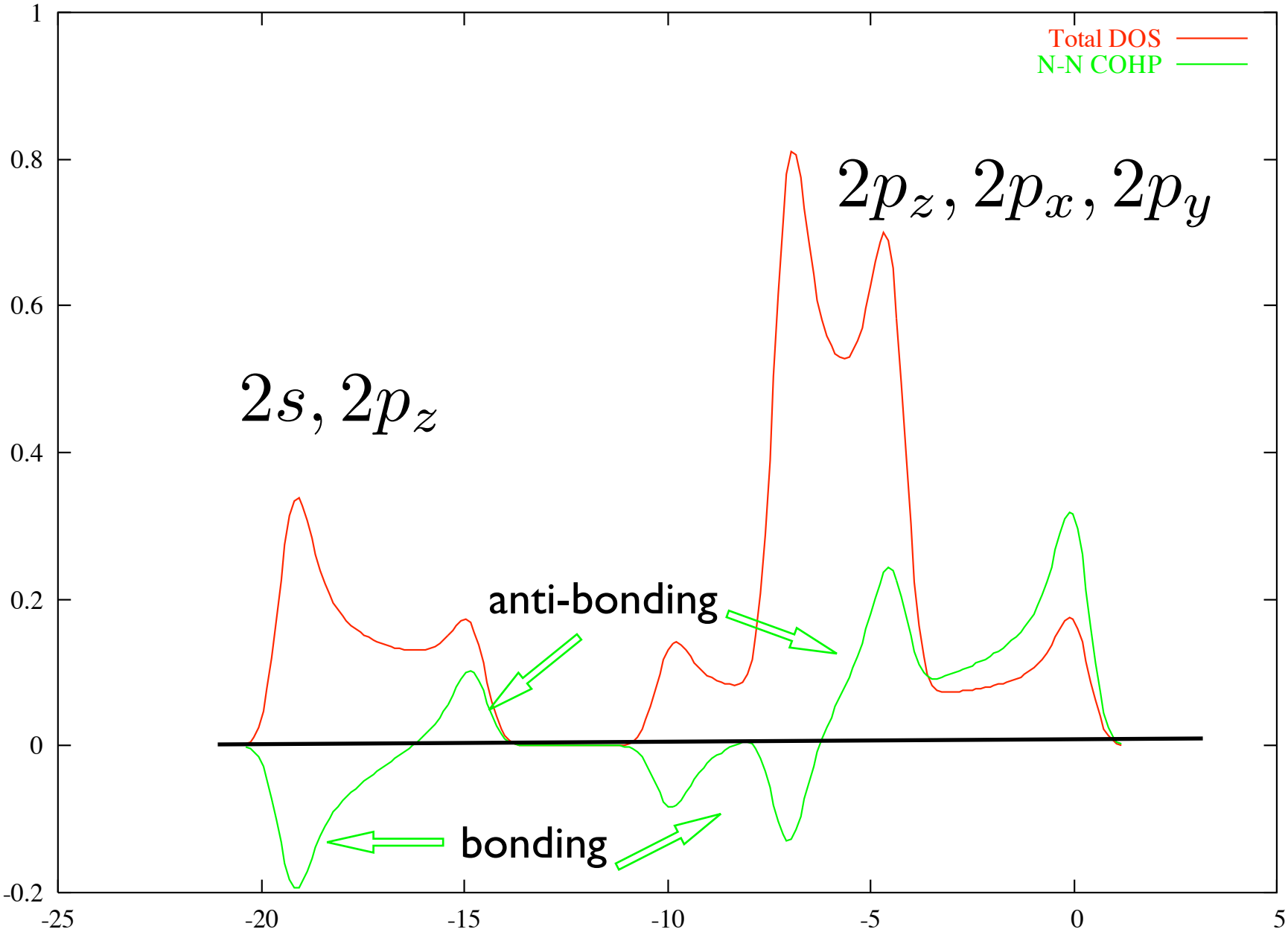

Si
H_2O
ΔE_t (meV)
Δd (mAng)
ΔP (kbar)
$\Delta \alpha$ (^{o})
E_c (Ry)
E_c (Ry)
40
20
0
-20
-40
2
0
-2
-4
-6
15
5
-5
-15
1
0
-1
10
30
50
70
90
20
60
100
140
180

FEATURES

Electronic structure

- Bands (including (non-collinear) spin polarization)
- Mulliken population analysis, (partial) density of states. Soon: COOP and COHP curves.
- Berry-phase polarization calculations

COHP curves: Bonding analysis



Molecular Dynamics and relaxation

- NVE ensemble dynamics
- NVT dynamics with Nose thermostat
- NVE dynamics with Parrinello-Rahman barostat
- NVT dynamics with thermostat/barostat
- Anneals to specified p and T
- Relaxation (with constraints) of atomic coordinates and cell parameters

Parallel SIESTA

- Standard mode:
  - Parallel diagonalization and grid operations.
  - Needs good communication among nodes.
  - Uses SCALAPACK
- Parallel over k-points mode:
  - Very efficient (operations are trivially parallel)

FDF Input file

```
# This is a comment

NumberOfSpecies         1
number-of-atoms         2

LatticeConstant     5.43 Ang      # Note units

%block LatticeVectors
  0.000  0.500  0.500
  0.500  0.000  0.500
  0.500  0.500  0.000
%endblock LatticeVectors

%block ChemicalSpeciesLabel
  1  14  Si              # Species number, Z, Symbol
%endblock ChemicalSpeciesLabel
```

FDF

- Data can be given in any order
- Some data can be omitted and will be assigned default values
- Syntax: ‘data label’ followed by its value

Character string:	SystemLabel	h2o
Integer:	NumberOfAtoms	3
Real:	PAO.SplitNorm	0.15
Logical:	SpinPolarized	.false.
Physical magnitudes	LatticeConstant	5.43 Ang

FDF

- Labels are case insensitive. Characters -_. are ignored

  LatticeConstant is equivalent to lattice-constant

- Text following # are comments
- Logical values: T , .true. , true , yes

  F , .false. , false , no

- Character strings, NOT in apostrophes
- Complex data structures: blocks

  %block label

  …

  %endblock label

FDF

- Physical magnitudes: followed by their units.

  Many physical units are recognized for each magnitude

  (Length: m, cm, nm, Ang, bohr)

  Automatic conversion to the ones internally required.

- You may 'include' other FDF files or redirect the search to another file:

```
lattice-vectors < cell.fdf
```

Lattice Vectors

LatticeConstant: real length to define the scale of the lattice vectors

```
LatticeConstant       5.43 Ang
```

LatticeParameters: Crystallographic way

```
%block LatticeParameters
    1.0  1.0  1.0  60.  60.  60.
%endblock LatticeParameters
```

LatticeVectors: read as a matrix, each vector being a line

```
%block LatticeVectors
    0.0   0.5   0.5
    0.5   0.0   0.5
    0.5   0.5   0.0
%endblock LatticeVectors
```

Atomic Coordinates

AtomicCoordinatesFormat: format of the atomic positions in input:

Bohr: cartesian coordinates, in bohrs

Ang: cartesian coordinates, in Angstroms

ScaledCartesian: cartesian coordinates, units of the lattice constant

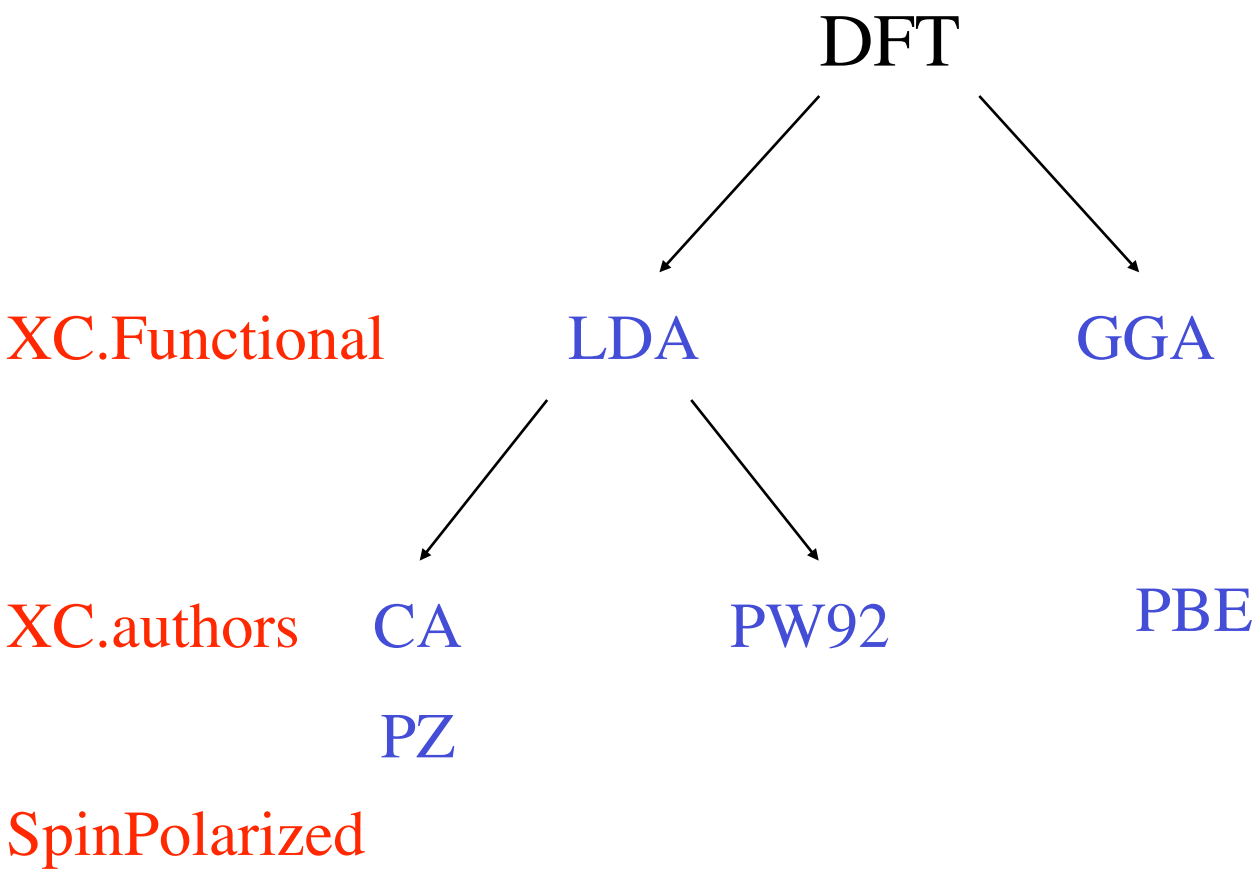
Fractional: referred to the lattice vectors

```
AtomicCoordinatesFormat      Fractional
```

AtomicCoordinatesAndAtomicSpecies:

```
%block AtomicCoordinatesAndAtomicSpecies
    0.00   0.00   0.00   1
    0.25   0.25   0.25   1
%endblock AtomicCoordinatesAndAtomicSpecies
```

Functional



DFT ≡ Density Functional Theory

LDA ≡ Local Density Approximation

GGA ≡ Generalized Gradient Approximation

CA ≡ Ceperley-Alder

PZ ≡ Perdew-Zunger

PW92 ≡ Perdew-Wang-92

PBE ≡ Perdew-Burke-Ernzerhof

Solution method

From the atomic coordinates and the unit cell

$$\left\{\vec{R}, \vec{a}\right\}$$

Order *N* operations

Hamiltonian, *H*, and Overlap, *S*, matrices

SolutionMethod diagon Order-N

k-sampling

Special set of k-points: **Accurate results** with a **few** k-points:

Baldereschi, Chadi-Cohen, Monkhorst-Pack

kgrid_cutoff:

```
kgrid_cutoff        10.0 Ang
```

kgrid_Monkhorst_Pack:

```
%block kgrid_Monkhorst_Pack
    4    0    0   0.5
    0    4    0   0.5
    0    0    4   0.5
%endblock kgrid_Monkhorst_Pack
```

The SIESTA code

http://www.uam.es/siesta

- Linear-scaling DFT
- Numerical atomic orbitals, with quality control.
- Forces and stresses for geometry optimization.
- Diverse Molecular Dynamics options.
- Capable of treating large systems with modest hardware.
- Parallelized.

J. Soler *et al*, J. Phys: Condens. Matter, **14**, 2745 (2002)
350 citations (Dec 2005)
> 600 (May 2007)

More than 800 registered users
(SIESTA is free for academic use)

More than 450 published papers
have used the program

The SIESTA Team

Emilio Artacho	*(Cambridge University)*
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Richard Martin	*(U. Illinois, Urbana)*
Javier Junquera	*(U. Cantabria, Santander)*
Daniel Sánchez-Portal	*(UPV, San Sebastián)*
Eduardo Anglada	(Nanotec)
Alberto García	*(ICMAB, Barcelona)*