Optimization of Numerical Atomic Orbitals

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Atomic Orbitals

- Very efficient but they lack a systematic for convergence
- Main features:
  - Size: Number of functions with the same l
  - Range: Cutoff radius of each function
  - Shape: Position of the peak, tail.

Atomic orbitals in siesta: NAOs

- Numerical Atomic Orbitals (NAOs):

Numerical solution of the Kohn-Sham Hamiltonian for the isolated pseudoatom with the same approximations (xc, pseudos) as for the condensed system

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

$$\boxed{\phi_l(\vec{r}) = \phi(r)Y_l^m(\hat{r})}$$

NAOs: Size

Size: Number of functions with the same *l*

Quantum chemistry notation: each function is called a zeta (ζ)

Classification:

- 1 function per *l*: SZ. Very fast, but not very reliable. Very big systems.
- 2 funcitons per *l*: DZ. Fast results, moderate accuracy.
- 2 functions per *l* plus a function with *l*+1: DZP. High quality for most of the systems.

Good valence: well converged results ↔computational cost
'Standard'

Rule of thumb in Quantum Chemistry:

A basis should always be doubled before being polarized

NAOs: range and shape

For each specie:

dQ : charge per atomic specie

For each shell of valence electrons:

- First ζ:
  - Cutoff radious: r_c
  - Soft confining: r_i, V_0

$$V(r) = V_0 \frac{e^{-\frac{r_c - r_i}{r - r_i}}}{r_c - r}$$

- Multiple ζ:
  - Matching radious: r_m

Basis optimization: Procedure

Defining the basis size

- SZ: Semiquantitative results and general trends. Used in very big systems.
- DZ: “A basis should always be doubled before being polarized”
- DZP: well converged results ↔ computational cost ‘Standard’

Consider the option of moving electrons from the core to the valence “semicore”

Basis optimization: Procedure (2)
NAOs Parameters

By hand:

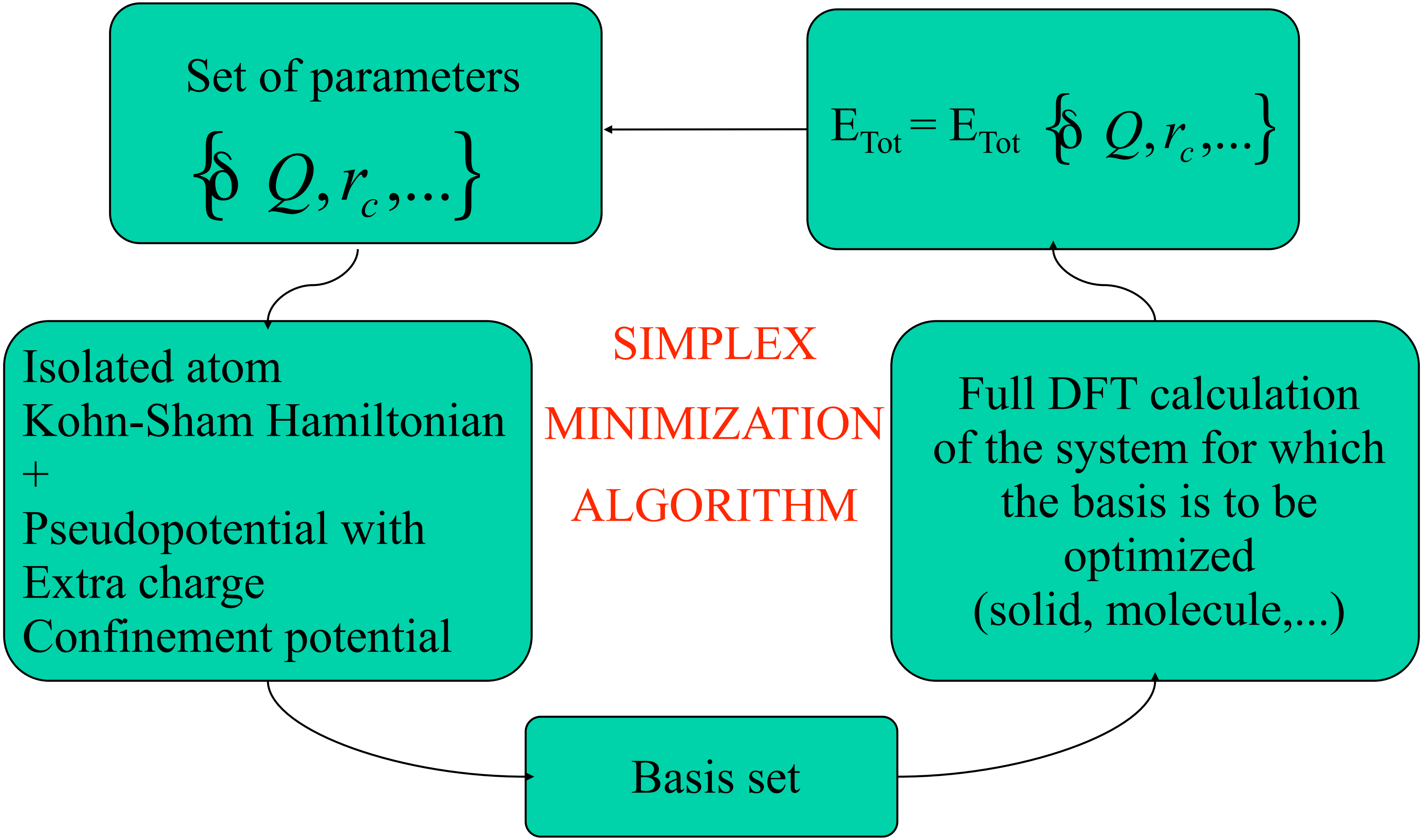
Charge (dQ): mimmic the environment

1. First ζ:
   - radious: Vary the “energy shift” until the energy is converged.
     - Use a V_0 of 150 Ryd. and a r_i up to 3/4 of r_c
2. Second and multiple z:
   - radious: Vary the “splitnorm” paremeter.

Automatic:

Using the simplex optimization procedure.

Optimization Procedure



Set of parameters

$$\{\delta Q, r_c, \ldots\}$$

$$E_{\mathrm{Tot}} = E_{\mathrm{Tot}}\{\delta Q, r_c, \ldots\}$$

Isolated atom
Kohn-Sham Hamiltonian
+
Pseudopotential with
Extra charge
Confinement potential

SIMPLEX
MINIMIZATION
ALGORITHM

Full DFT calculation
of the system for which
the basis is to be
optimized
(solid, molecule,...)

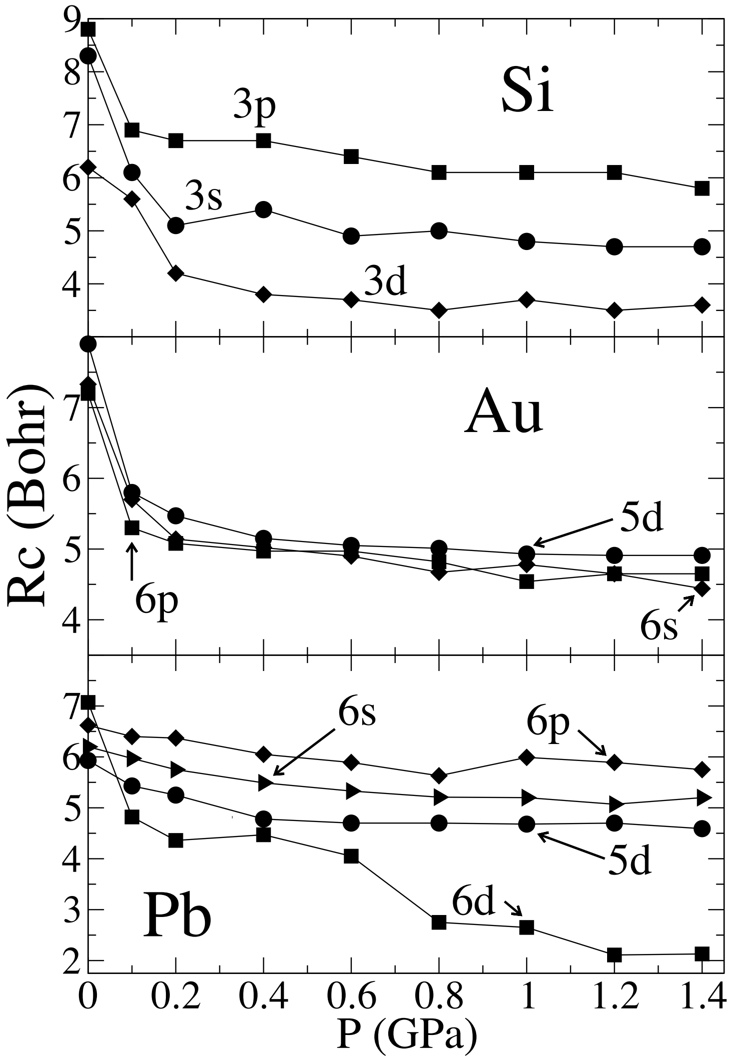
Basis set

Cutting the atomic orbitals

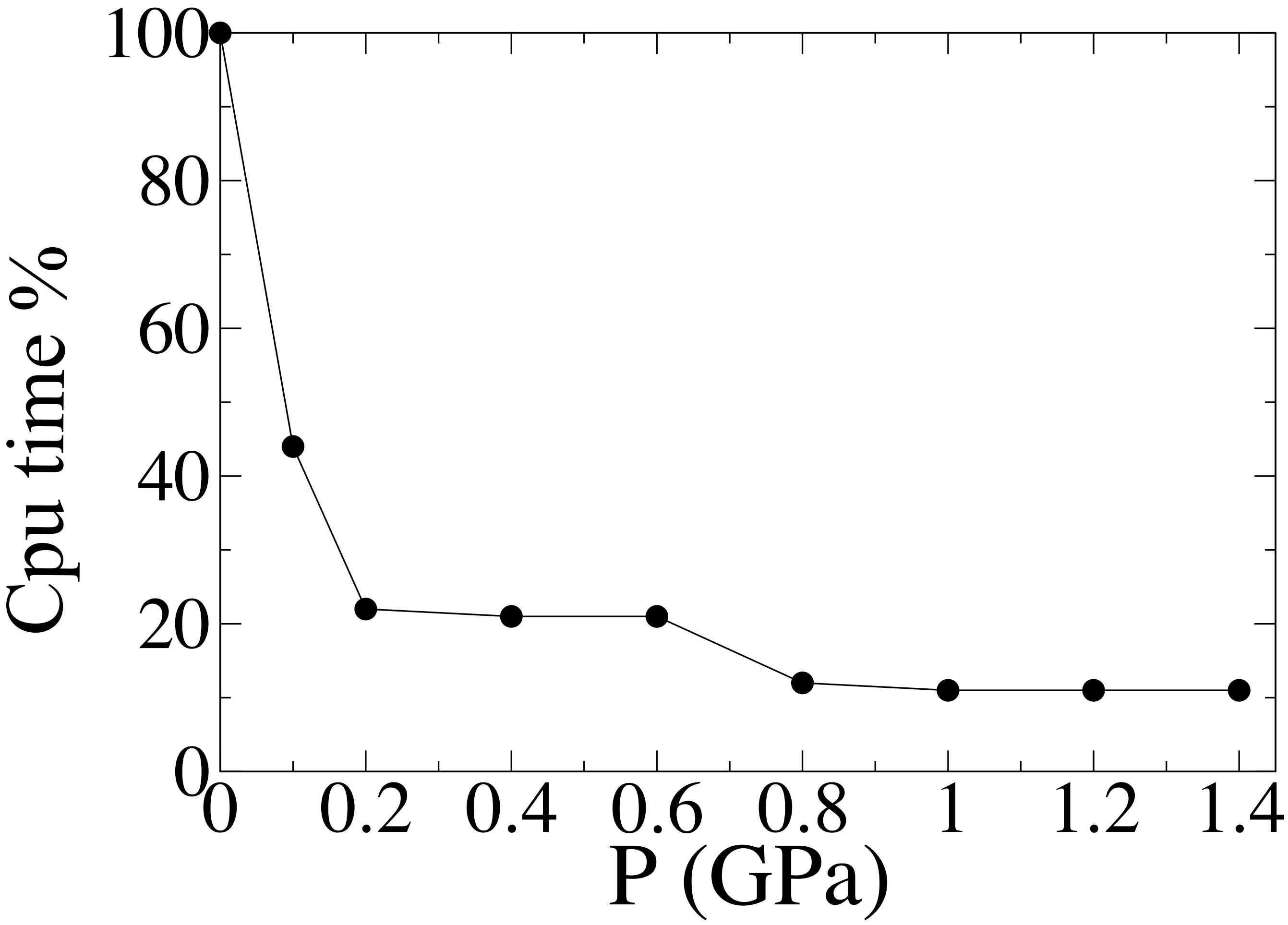
$$\mathrm{H} = \mathrm{E}_{\mathrm{Total}} + \underbrace{\mathrm{pV}}_{\text{Penalty for long range orbitals}} \qquad \left\{ \begin{array}{l} V = \sum_{l} r_c^3(l) \\ \\ \mathrm{p} \equiv \boldsymbol{pressure} \end{array} \right.$$

- Optimize the *enthalpy* in the condensed system
- Just one parameter to define all the cutoff radii: the **pressure**

Variation of the r_c



CPU time savings



Results: Bulk Silicon

	DZP		SZP		DZ		SZ		PW
	P=0	*P*=0.2	*P*=0	*P*=0.2	*P*=0	*P*=0.2	*P*=0	*P*=0.2	
E (eV)	5.36	5.30	5.13	5.10	4.30	4.28	4.06	4.03	5.40
a (Ang)	5.40	5.38	5.41	5.40	5.47	5.47	5.50	5.50	5.38
B (GPa)	97	98	98	98	85	86	91	91	96
CPU (s)	150	49	120	29	35	30	12	10	
Me. (MB)	15	8	16	8	8	8	7	6	

Results vs Pressure

		Exp	PW	P=0	0.2	0.4	0.8	1.2	1.4
Si	a	5.43	5.38	5.40	5.38	5.38	5.37	5.36	5.35
	B	99	96	97	98	100	103	107	108
	E_c	4.63	5.40	5.36	5.30	5.25	5.12	5.99	5.94
Au	a	4.08	4.05	4.06	4.06	4.05	4.02	4.00	4.00
	B	195	198	206	210	211	220	239	242
	E_c	4.13	4.36	4.04	3.96	3.95	3.80	3.77	3.66
Pb	a	4.95	4.88	4.90	4.87	4.83	4.79	4.80	4.81
	B	43	54	54	60	64	71	70	75
	E_c	2.04	3.77	3.68	3.63	3.48	3.37	3.32	3.29
MgO	a	4.21	4.10	4.11	4.10	4.10	4.11	4.09	4.06
	B	152	164	182	205	209	205	214	230
	E_c	10.30	12.39	12.18	12.10	12.00	11.86	11.92	11.66

Transferability: α-quartz

	Exp[a]	PW[b]	PW[c]	PW[d]	PW[e]	DZP
a(Å)	4.92	4.84	4.89	4.81	4.88	4.85
c(Å)	5.41	5.41	5.38	5.32	5.40	5.38
d^1_{Si-O}(Å)	1.605	1.611	1.60	1.605	-	1.611
d^1_{Si-O}(Å)	1.614	1.617	1.60	1.605	-	1.611
$\alpha_{Si-O-Si}$(deg)	143.7	140.2	-	139.0	-	140.0

Si basis set optimized in c-Si

O basis set optimized in water molecule

a Levien *et al*, Am. Mineral, **65**, 920 (1980)

b Hamann, Phys. Rev. Lett., **76**, 660 (1996)

c Sautet (using VASP, with ultrasoft pseudopotential)

d Rignanese *et al*, Phys. Rev. B, **61**, 13250 (2000)

e Liu *et al*, Phys. Rev. B, **49**, 12528 (1994) (ultrasoft pseudopotential)

System	Basis	Properties		
MgO		a (Å)	B(GPa)	E_c(eV)
	Transfer	**4.13**	**157**	**11.81**
	Opt	4.10	167	11.87
	PW	4.10	168	11.90
	Exp	4.21	152	10.30
Graphite		a (Å)	c (Å)	ΔE(meV)
	Transfer	**2.456**	**6.50**	**38**
	PW	2.457	6.72	24
	Exp	2.456	6.674	23
H_2O		$d_{O\text{-}H}$ (Å)	$\theta_{H\text{-}O\text{-}H}$(deg)	E_b(eV)
	Transfer	**0.975**	**105.0**	**12.73**
	Opt	0.972	104.5	12.94
	PW	0.967	105.1	13.10
	LAPW	0.968	103.9	11.05
	Exp	0.958	104.5	10.08

Conclusions

NAOs are very efficient, but difficult to converge.

Procedure:

1. Define the basis size (SZ, DZ, DZP)
2. Optimize the cutoff radious using the energy shift
    - Use default values of V_0 (150 Ryd) and r_{in} (3/4 of r_c)
    - Pay special attention to the r_c of polarization orbitals.
3. Consider the inclusion of core electrons in the valence (“semicore” states).

- Using the simplex method it’s possible to optimize the different parameters in an automatic way.