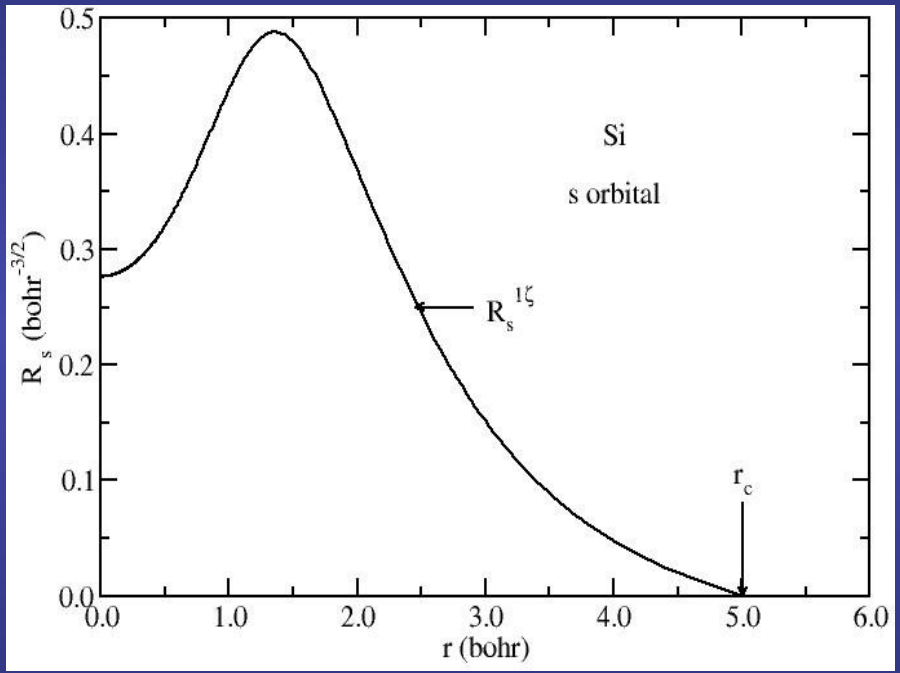
Exercises on basis set generation

Convergence of the basis set with size



Javier Junquera

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Most important reference followed in this lecture

phys. stat. sol. (b) **215**, 809 (1999)

Subject classification: 71.15.Mb; 71.15.Fv; 71.24.+q; S1.3; S5; S5.11

Linear-Scaling ab-initio Calculations for Large and Complex Systems

E. ARTACHO[1]) (a), D. SÁNCHEZ-PORTAL (b), P. ORDEJÓN (c), A. GARCÍA (d), and J. M. SOLER (e)

PHYSICAL REVIEW B, VOLUME 64, 235111

Numerical atomic orbitals for linear-scaling calculations

Javier Junquera,[1] Óscar Paz,[1] Daniel Sánchez-Portal,[2,3] and Emilio Artacho[4]

PHYSICAL REVIEW B **66**, 205101 (2002)

Systematic generation of finite-range atomic basis sets for linear-scaling calculations

Eduardo Anglada,[1,2] José M. Soler,[1] Javier Junquera,[3] and Emilio Artacho[4]

Bulk Si, a semiconductor that crystallizes in the diamond structure

Go to the directory with the exercise on the default basis set

Inspect the input file, Si.default.fdf

More information at the Siesta web page http://www.icmab.es/siesta and follow the link Documentations, Manual

```
SystemName          Bulk Silicon
SystemLabel         Si
NumberOfSpecies     1
NumberOfAtoms       2

%block ChemicalSpeciesLabel
  1  14  Si
%endblock ChemicalSpeciesLabel

LatticeConstant      5.43 Ang # We start from the experimental lattice constant
%block LatticeVectors
  0.00  0.50  0.50
  0.50  0.00  0.50
  0.50  0.50  0.00
%endblock LatticeVectors

AtomicCoordinatesFormat   Fractional
%block AtomicCoordinatesAndAtomicSpecies
  0.00  0.00  0.00        1
  0.25  0.25  0.25        1
%endblock AtomicCoordinatesAndAtomicSpecies

%block kgrid_Monkhorst_Pack
   6  0  0  0.5
   0  6  0  0.5
   0  0  6  0.5
%endblock kgrid_Monkhorst_Pack
```

As starting point, we assume the theoretical lattice constant of bulk Si

FCC lattice

Two atoms in the basis

Sampling in k in the first Brillouin zone to achieve self-consistency

For each basis set, a relaxation of the unit cell is performed

Variables to control the Conjugate Gradient minimization

```
#
# Molecular dynamics and relaxations
#

MD.TypeOfRun       CG                # We are going to perform a
                                     #   Conjugate-Gradient minimization
MD.VariableCell    .true.            # Is the lattice relaxed together with
                                     #   the atomic coordinates?
MD.NumCGsteps      50                # Number of CG minimization steps for
                                     #   cell optimization
MD.MaxStressTol    0.0010 eV/Ang**3  # Tolerance in the maximum
                                     #   stress in a MD.VariableCell CG optimi.

%block GeometryConstraints           # Constraints impossed on
   position    1    2                #   the atomic positions
   stress      4    5    6           #   the shear stresses
%endblock GeometryConstraints
```

Two constraints in the minimization:

- the position of the atoms in the unit cell

- the shear stresses are nullified to fix the angles between the unit cell lattice vectors to 60°, typical of a fcc lattice

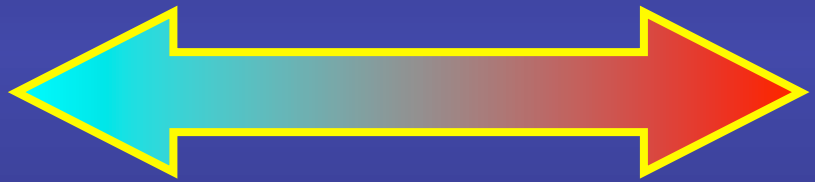
Size (number of basis set per atom)

Depending on the required accuracy and

available computational power

Quick exploratory calculations

Highly converged calculations



Minimal basis set

(single-ζ; SZ)

Multiple-ζ

+

Polarization

+

Diffuse orbitals

+ Basis optimization

The size of the basis size can be controlled easily by the user: PAO.Basis Size

Simply use the tag PAO.BasisSize. It admits four different values

SZ	Single-zeta (Single-ζ)
DZ	Double-zeta (Double-ζ)
SZP	Single-zeta plus polarization
DZP	Double-zeta plus polarization

Default: DZP (see exercise “Default”)

More complete basis set requires the explicit use of the block PAO.Basis

Relax the lattice constant and compute the energy for the different basis set sizes

Run the code for bulk Si with the default basis set

siesta < Si.sz.fdf > Si.sz.out	Single-zeta (Single-ζ, SZ)
siesta < Si.dz.fdf > Si.dz.out	Double-zeta (Double-ζ, DZ)
siesta < Si.szp.fdf > Si.szp.out	Single-zeta plus polarization (SZP)
siesta < Si.dzp.fdf > Si.dzp.out	Double-zeta plus polarization (DZP)

The numbers in this exercise have been obtained with siesta-3.0-b, compiled with the g95 compiler and double precision in the grid.

Numbers might change slightly depending on the platform, compiler and compilation flags

Relax the lattice constant and compute the energy for the different basis set sizes

Edit the output files and analyze the size of the basis set.

To understand the block PAO.Basis, see the exercise “Default”

```
PAO.BasisSize        SZ     # Single-Zeta basis set
                            # One radial parts for the s-shell (=> 1 orbitals)
                            # One radial parts for the p-shell (=> 3 orbitals)
                            #                                  ----------------
                            #                                  4 orbitals/Si atom

atom: Total number of Sankey-type orbitals:  4

%block PAO.Basis                 # Define Basis set
Si                    2                   # Species label, number of l-shells
 n=3   0   1                         # n, l, Nzeta
   5.007
   1.000
 n=3   1   1                         # n, l, Nzeta
   6.271
   1.000
%endblock PAO.Basis
```

```
PAO.BasisSize        DZ     # Double-Zeta basis set
                            # Two radial parts for the s-shell (=> 2 orbitals)
                            # Two radial parts for the p-shell (=> 6 orbitals)
                            #                                  ----------------
                            #                                  8 orbitals/Si atom

atom: Total number of Sankey-type orbitals:  8

%block PAO.Basis                 # Define Basis set
Si                    2                   # Species label, number of l-shells
 n=3   0   2                         # n, l, Nzeta
   5.007      4.419
   1.000      1.000
 n=3   1   2                         # n, l, Nzeta
   6.271      5.007
   1.000      1.000
%endblock PAO.Basis
```

```
PAO.BasisSize        SZP    # Single-Zeta plus polarization basis set
                            # One radial parts for the s-shell (=> 1 orbitals)
                            # One radial parts for the p-shell (=> 3 orbitals)
                            # One radial parts for the d-shell (=> 5 orbitals)
                            #                                  ----------------
                            #                                  9 orbitals/Si atom

atom: Total number of Sankey-type orbitals:  9

%block PAO.Basis                 # Define Basis set
Si                    2                   # Species label, number of l-shells
 n=3   0   1                         # n, l, Nzeta
   5.007
   1.000
 n=3   1   1 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   6.271
   1.000
%endblock PAO.Basis
```

DEFAULT

```
PAO.BasisSize        DZP    # Double-Zeta plus polarization basis set
                            # Two radial parts for the s-shell (=> 2 orbitals)
                            # Two radial parts for the p-shell (=> 6 orbitals)
                            # One radial parts for the d-shell (=> 5 orbitals)
                            #                                  ----------------
                            #                                  13 orbitals/Si atom

atom: Total number of Sankey-type orbitals: 13

%block PAO.Basis                 # Define Basis set
Si                    2                   # Species label, number of l-shells
 n=3   0   2                         # n, l, Nzeta
   5.007      4.419
   1.000      1.000
 n=3   1   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   6.271      5.007
   1.000      1.000
%endblock PAO.Basis
```

Study the structural and energetic properties as a function of the size of the basis size

Inspect the output files and search for the relaxed structure and Kohn-Sham energy

```
siesta: Program's energy decomposition (eV):
siesta: Ebs     =       -75.650988
siesta: Eions   =       380.802124
siesta: Ena     =       115.349306
siesta: Ekin    =        81.916758
siesta: Enl     =        29.311909
siesta: DEna    =         3.716705
siesta: DUscf   =         0.267046
siesta: DUext   =         0.000000
siesta: Exc     =       -65.238641
siesta: eta*DQ  =         0.000000
siesta: Emadel  =         0.000000
siesta: Emeta   =         0.000000
siesta: Emolmec =         0.000000
siesta: Ekinion =         0.000000
siesta: Eharris =      -215.479042
siesta: Etot    =      -215.479041
siesta: FreeEng =      -215.479041
```

We are interested in this number

Study the structural and energetic properties as a function of the size of the basis size

Inspect the output files and search for the relaxed structure and Kohn-Sham energy

SZ

```
outcoor: Relaxed atomic coordinates (fractional):
    0.00000000    0.00000000    0.00000000   1       1  Si
    0.25000000    0.25000000    0.25000000   1       2  Si

outcell: Unit cell vectors (Ang):
        0.000000    2.770221    2.770221
        2.770221    0.000000    2.770221
        2.770221    2.770221    0.000000

outcell: Cell vector modules (Ang)   :    3.917684    3.917684    3.917684
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     42.5180

siesta: Etot    =      -213.983341
```

DZ

```
outcoor: Relaxed atomic coordinates (fractional):
    0.00000000    0.00000000    0.00000000   1       1  Si
    0.25000000    0.25000000    0.25000000   1       2  Si

outcell: Unit cell vectors (Ang):
        0.000000    2.736750    2.736750
        2.736750    0.000000    2.736750
        2.736750    2.736750    0.000000

outcell: Cell vector modules (Ang)   :    3.870349    3.870349    3.870349
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     40.9954

siesta: Etot    =      -214.545956
```

SZP

```
outcoor: Relaxed atomic coordinates (fractional):
    0.00000000    0.00000000    0.00000000   1       1  Si
    0.25000000    0.25000000    0.25000000   1       2  Si

outcell: Unit cell vectors (Ang):
        0.000000    2.746686    2.746686
        2.746686    0.000000    2.746686
        2.746686    2.746686    0.000000

outcell: Cell vector modules (Ang)   :    3.884400    3.884400    3.884400
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     41.4435

siesta: Etot    =      -214.640295
```

DZP

```
outcoor: Relaxed atomic coordinates (fractional):
    0.00000000    0.00000000    0.00000000   1       1  Si
    0.25000000    0.25000000    0.25000000   1       2  Si

outcell: Unit cell vectors (Ang):
        0.000000    2.705266    2.705266
        2.705266    0.000000    2.705266
        2.705266    2.705266    0.000000

outcell: Cell vector modules (Ang)   :    3.825823    3.825823    3.825823
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     39.5968

siesta: Etot    =      -215.479041
```

Study the structural and energetic properties as a function of the size of the basis size

Inspect the output files and search for the relaxed structure and Kohn-Sham energy

SZ

```
outcoor: Relaxed atomic coordinates (fractional):
    0.00000000    0.00000000    0.00000000   1       1  Si
    0.25000000    0.25000000    0.25000000   1       2  Si

outcell: Unit cell vectors (Ang):
        0.000000    2.770221    2.770221
        2.770221    0.000000    2.770221
        2.770221    2.770221    0.000000

outcell: Cell vector modules (Ang)   :    3.917684    3.917684    3.917684
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     42.5180

siesta: Etot    =      -213.983341
```

DZ

```
outcoor: Relaxed atomic coordinates (fractional):
    0.00000000    0.00000000    0.00000000   1       1  Si
    0.25000000    0.25000000    0.25000000   1       2  Si

outcell: Unit cell vectors (Ang):
        0.000000    2.736750    2.736750
        2.736750    0.000000    2.736750
        2.736750    2.736750    0.000000

outcell: Cell vector modules (Ang)   :    3.870349    3.870349    3.870349
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     40.9954

siesta: Etot    =      -214.545956
```

SZP

```
outcoor: Relaxed atomic coordinates (fractional):
    0.00000000    0.00000000    0.00000000   1       1  Si
    0.25000000    0.25000000    0.25000000   1       2  Si

outcell: Unit cell vectors (Ang):
        0.000000    2.746686    2.746686
        2.746686    0.000000    2.746686
        2.746686    2.746686    0.000000

outcell: Cell vector modules (Ang)   :    3.884400    3.884400    3.884400
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     41.4435

siesta: Etot    =      -214.640295
```

DZP

```
outcoor: Relaxed atomic coordinates (fractional):
    0.00000000    0.00000000    0.00000000   1       1  Si
    0.25000000    0.25000000    0.25000000   1       2  Si

outcell: Unit cell vectors (Ang):
        0.000000    2.705266    2.705266
        2.705266    0.000000    2.705266
        2.705266    2.705266    0.000000

outcell: Cell vector modules (Ang)   :    3.825823    3.825823    3.825823
outcell: Cell angles (23,13,12) (deg):     60.0000     60.0000     60.0000
outcell: Cell volume (Ang**3)        :     39.5968

siesta: Etot    =      -215.479041
```

Study the structural and energetic properties as a function of the size of the basis size

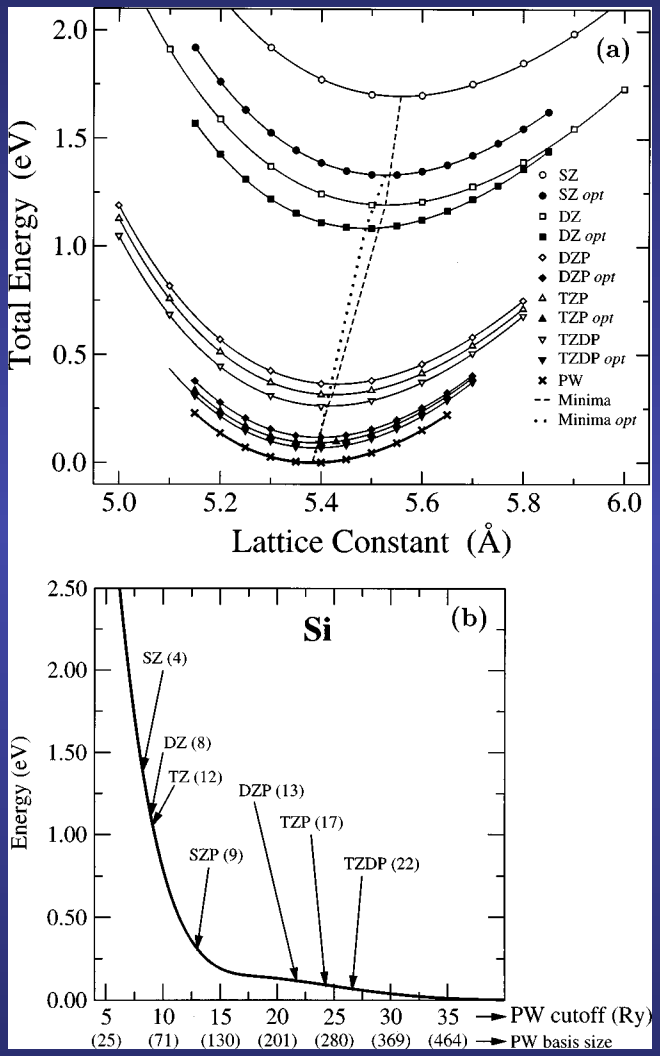
TABLE II. Basis comparisons for bulk Si. a, B, and E_c stand for lattice parameter (in Å), bulk modulus (in GPa), and cohesive energy (in eV), respectively. SZ, DZ, and TZ stand for single ζ, double ζ, and triple ζ. P stands for polarized, DP for doubly polarized. LAPW results were taken from Ref. 41, and the experimental values from Ref. 42.

	SZ	DZ	TZ	SZP	DZP	TZP	TZDP	PW	LAPW	Expt.
a	5.52	5.49	5.48	5.43	5.40	5.39	5.39	5.38	5.41	5.43
B	85	87	85	97	97	97	97	96	96	98.8
E_c	4.70	4.83	4.85	5.21	5.31	5.32	5.34	5.37	5.28	4.63

J. Junquera *et al.*, Phys. Rev. B 64, 235111 (2001)

Results in previous table have been obtained with optimized basis set, but the tendency is the same as in our example

Study the structural and energetic properties as a function of the size of the basis size



J. Junquera *et al.*,
Phys. Rev. B 64, 235111 (2001)

Nice convergence of the total energy with respect the basis set size

The problem is variational: the larger the number of orbitals in the basis set, the lower the energy

For the particular case of Si, the polarization orbitals (3d shell) are very important for convergence, more than doubling the basis.

Results in previous figures have been obtained with optimized basis set, but the tendency is the same as in our example