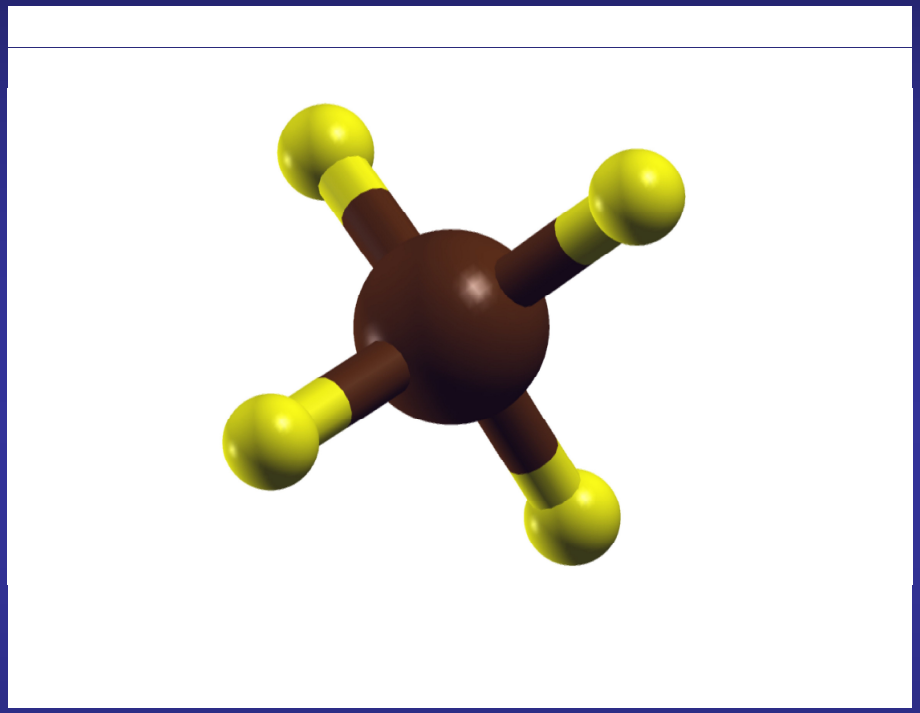
Introducing the coordinates in Z-matrix form



Objectives

study how to introduce the coordinates of a molecule in Z-matrix form

The Z-matrix provides a description of each atom in a molecule in terms of the internal coordinates

Internal coordinates:

- Species of each atom
- Distances
- Angles
- Torsion (dihedral) angles

This is particularly useful when working with molecular systems or restricted optimizations (control optimization variables)

The name arises because the Z-matrix assigns the second atom along the Z-axis from the first atom, which is at the origin.

Examples of the Z-matrix input in Siesta

%block Zmatrix

molecule

This specifies the atoms that make up each molecule and their geometry.

Examples of the Z-matrix input in Siesta

In addition, an option may be passed, that indicates the units in which distances are specified in

```
%block Zmatrix
   molecule fractional
```

```
%block Zmatrix
   molecule scaled
```

```
%block Zmatrix
   molecule
```

In the absence of such an option, the distance units are taken to be the value of "ZM.UnitsLength"

Examples of the Z-matrix input in Siesta

%block Zmatrix

molecule

Nspecie i j k r a t ifr ifa ift

Integers — Double precision — Integers

One line per each atom in the molecule

Examples of the Z-matrix input in Siesta

%block Zmatrix

molecule

Nspecie i j k r a t ifr ifa ift

One line per each atom in the molecule

Integers

Double precision

Species number of the atom

Integer flags that indicate whether r, a, and t, respectively, should be varied in a relaxation or molecular dynamics ;

0 for fixed,

1 for varying.

Examples of the Z-matrix input in Siesta

The coordinates of the first atom… the easiest one.
It will be taken as the origin

```
%block Zmatrix
  molecule
  Nspecie1   0   0   0   0.0   0.0   0.0   0   0   0
```

Species number of the atom

For the first atom, set them to 0

Cartesian coordinates

(let us take as the origin in this example)

Examples of the Z-matrix input in Siesta

The coordinates of the second atom

```
%block Zmatrix
  molecule
  Nspecie1   0   0   0   0.0   0.0   0.0   0   0   0
  Nspecie2   1   0   0   d12   0.0   0.0   0   0   0
```

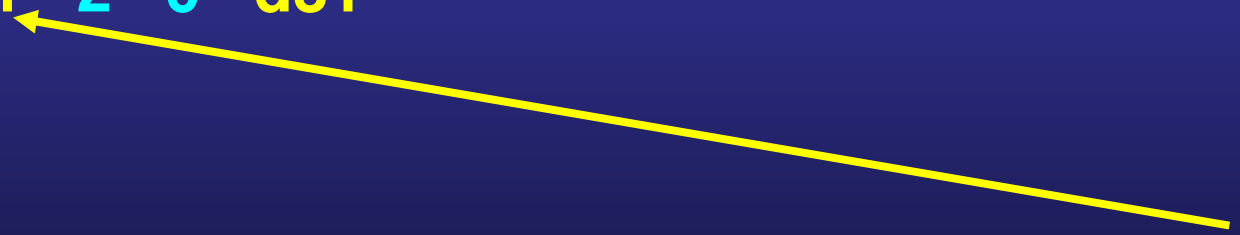
Coordinates, in spherical coordinates, of the second atom with respect to the first atom

In this particular example, this is just the distance along the z-axis of the second atom with respect to the first

Examples of the Z-matrix input in Siesta

The coordinates of the third atom

```
%block Zmatrix
  molecule
  Nspecie1   0   0   0   0.0   0.0   0.0   0   0   0
  Nspecie2   1   0   0   d12   0.0   0.0   0   0   0
  Nspecie3   1   2   0   d31
```

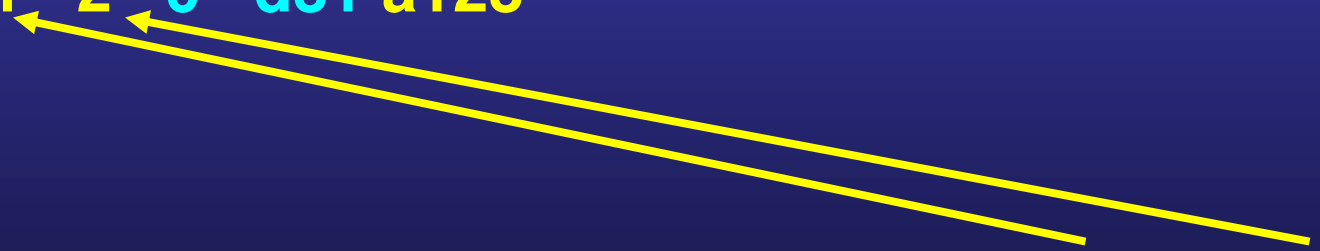


Distance of the third atom to the atom indicated in this position
(in this example, this number indicates the distance between atom 3 and atom 1)

Examples of the Z-matrix input in Siesta

The coordinates of the third atom

```
%block Zmatrix
  molecule
  Nspecie1   0   0   0   0.0   0.0   0.0   0   0   0
  Nspecie2   1   0   0   d12   0.0   0.0   0   0   0
  Nspecie3   1   2   0   d31  a123
```

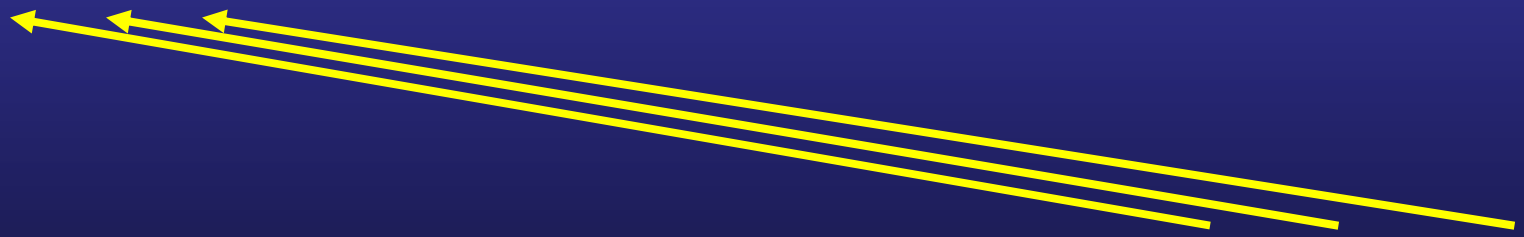


Angle made by the third atom with respect atoms indicated here and here
(in this example, this number indicates the angle formed between atoms 1, 2, and 3)

Examples of the Z-matrix input in Siesta

The coordinates of the third atom

```
%block Zmatrix
   molecule
   Nspecie1   0   0   0   0.0   0.0   0.0     0   0   0
   Nspecie2   1   0   0   d12   0.0   0.0     0   0   0
   Nspecie3   1   2   0   d31  a123  t1234    0   0   0
```



Torsional angle made by the third atom with respect atoms indicated here, here, and here
(for the third atom is defined relative to a notional atom 1 unit in the z-direction above the atom j)

Examples of the Z-matrix input in Siesta

The rest of the atoms follow the same specification:

Distance with respect atom i

Angle with respect atom j and i

Torsional angle with respect atoms k, j, and i

```
%block Zmatrix
  molecule
  Nspecie1   0   0   0   0.0   0.0   0.0     0   0   0
  Nspecie2   1   0   0   d12   0.0   0.0     0   0   0
  Nspecie3   1   2   0   d31  a123  t1234    0   0   0
  …
  NspecieX …….
%endblock Zmatrix
```

Instead of specifying a numerical value, it is possible to specify a symbol within the above geometry definitions.

Example, the water molecule

```
%block Zmatrix
   molecule fractional
   1 0 0 0   0.0 0.0 0.0 0 0 0
   2 1 0 0   HO1 90.0 37.743919 1 0 0
   2 1 2 0   HO2 HOH 90.0 1 1 0
   variables
   HO1 0.956997
   HO2 0.956997
   constant
   HOH 104.4
%endblock Zmatrix
```

Define the symbol as variables

Define the symbol as a constant

Exercise:
define the coordinates of a CH4 molecule in Z-matrix form

```
%block Zmatrix
   molecule
   1 0 0 0   0.0      0.0        0.0   0   0   0
   2 1 0 0   CH       0.0        0.0   1   0   0
   2 1 2 0   CH   109.471        0.0   1   0   0
   2 1 2 3   CH   109.471      120.0   1   0   0
   2 1 2 3   CH   109.471      240.0   1   0   0
   variables
   CH 1.089
%endblock Zmatrix
ZM.UnitsLength      Ang
ZM.UnitsAngle       Deg
```

Modify the distance CH by hand and find the equilibrium distance

Exercise:
Compute the energy for different C-H bond lengths

siesta < ch4.fdf > ch4.your_distance.Ang.out

In the present example, try from 1.05 to 1.30 Ang in steps of 0.05 Ang

```
#Atomic coordinates
AtomicCoordinatesFormat NotScaledCartesianAng
%block Zmatrix
molecule
  1 0 0 0   0.000   0.000   0.000 0 0 0
  2 1 0 0   CH      0.000   0.000 1 0 0
  2 1 2 0   CH    109.471   0.000 1 0 0
  2 1 2 3   CH    109.471 120.000 1 0 0
  2 1 2 3   CH    109.471 240.000 1 0 0
variables
    CH  1.050
%endblock Zmatrix
ZM.UnitsLength Ang
ZM.UnitsAngle deg
```

Modify this variable

Tabulate the energy as a function of the C-H bond length

grep "Total =" ch4.*.Ang.out > ch4.distance.dat

# C-H bond length (Ang)	Total energy (eV)
1.05	-213.723039
1.10	-214.557077
1.15	-214.966685
1.20	-215.039932
1.25	-214.857566
1.30	-214.473670
1.35	-213.936260

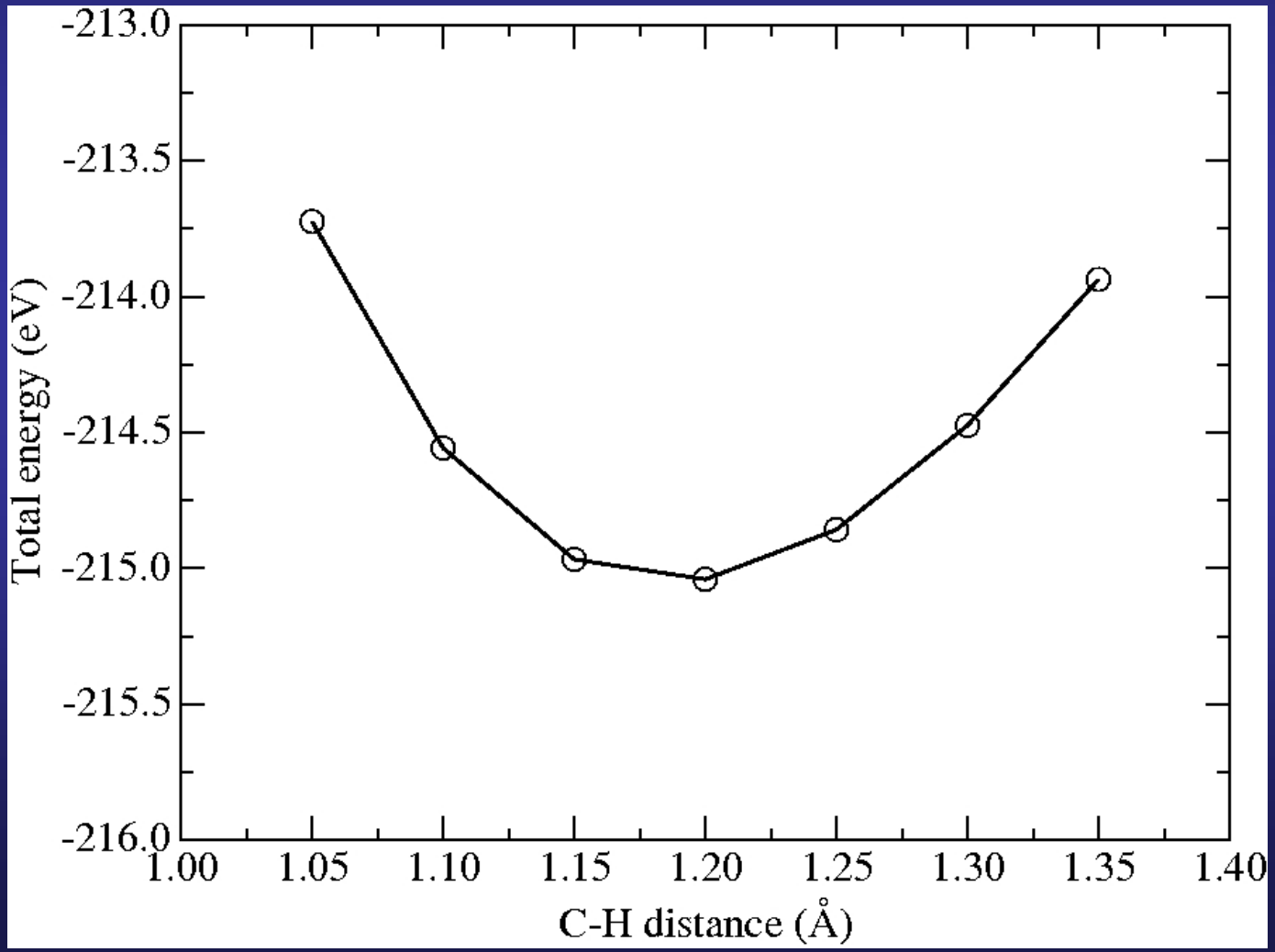
These numbers have been obtained with siesta-3.0-b, compiled with the g95 compiler and double precision in the grid.

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

Exercise:
Compute the energy for different C-H bond lengths

gnuplot

gnuplot> plot "ch4.distance.dat" using 1:2 with lines



Compare the equilibrium distance with the experimental distance of 1.09 Å

Compute the equilibrium distance by means of a Conjugate Gradient minimization: Single-ζ basis set

Edit the input file and introduce the following lines (this has been done for you in the ch4.cg.fdf file)

```
# Conjugate-gradient minimization
MD.TypeOfRun      CG              # We are going to perform a
                                  #   Conjugate Gradient (CG) minimization
MD.NumCGsteps     10              # Number of CG steps for
                                  #   coordinate optimization
ZM.ForceTolLength 0.04 eV/Ang     # Parameter that controls the convergence with
                                  # respect to forces on Z-matrix lengths
                                  #
```

siesta < ch4.cg.fdf > ch4.cg.out

Search in the output file the relaxed structure

```
outcoor: Relaxed atomic coordinates (Ang):
    0.00000000    0.00000000    0.00000000   1       1  C
    0.00000000    0.00000000    1.18749330   2       2  H
   -1.11958094   -0.00000000   -0.39582679   2       3  H
    0.55979047    0.96958554   -0.39582679   2       4  H
    0.55979047   -0.96958554   -0.39582679   2       5  H

zmatrix: Z-matrix coordinates: (Ang ; deg )
zmatrix: (Fractional coordinates have been converted to cartesian)
molecule    1 (     5 atoms)
      0.00000000      0.00000000      0.00000000
      1.18749330      0.00000000      0.00000000
      1.18749330    109.47100000      0.00000000
      1.18749330    109.47100000    120.00000000
      1.18749330    109.47100000    240.00000000
```

Here you are the equilibrium distance

Compute the equilibrium distance by means of a Conjugate Gradient minimization: Double-ζ plus polarization basis set

Edit the input file and change PAO.BasisSize to DZP
(this has been done for you in the ch4.cg.dzp.fdf file)

siesta < ch4.cg.dzp.fdf > ch4.cg.dzp.out

Search in the output file the relaxed structure and compare with the experimental value of 1.09 Å

```
outcoor: Relaxed atomic coordinates (Ang):
     0.00000000    0.00000000    0.00000000   1       1  C
     0.00000000    0.00000000    1.10911057   2       2  H
    -1.04568089   -0.00000000   -0.36969950   2       3  H
     0.52284045    0.90558622   -0.36969950   2       4  H
     0.52284045   -0.90558622   -0.36969950   2       5  H

zmatrix: Z-matrix coordinates: (Ang ; deg )
zmatrix: (Fractional coordinates have been converted to cartesian)
molecule    1 (     5 atoms)
       0.00000000      0.00000000      0.00000000
       1.10911057      0.00000000      0.00000000
       1.10911057    109.47100000      0.00000000
       1.10911057    109.47100000    120.00000000
       1.10911057    109.47100000    240.00000000
```