NWChem Input Basics

- Minimal input (all defaults)

```
geometry
  n    0.00 0.00 0.00
  n    0.00 0.00 1.08
end

basis
  n library cc-pvdz
end

task scf
```

- Performs a closed-shell SCF on the N_2 molecule

Geometry Input: Units

- Input can be in Angstrom or atomic units

```
geometry  # units are in angstroms
 C   0  0      0
 H   0  0.9885 -0.4329
 H   0 –0.9885  0.4329
end
```

OR

```
geometry units au  # change units to a.u.
  C   0  0      0
  H   0  1.868 -0.818
  H   0 -1.868  0.818
end
```

Geometry Input: Symmetry

- CH2 molecule with C_{2v} symmetry

```
geometry units au #input using symmetry
  C   0  0      0
  H   0  1.868 -0.818
  symmetry c2v
end
```

- C_{60} with I_h symmetry

```
geometry  #bonds = 1.4445 and 1.3945 Angstrom
    symmetry Ih
    c -1.2287651    0.0    3.3143121
end
```

Geometry Input: autosym and autoz

- By default NWChem will:
  - Attempt to find ***symmetry*** if none is specified
  - Attempt to build a ***z-matrix*** from cartesian coordinates (for the geometry optimization)
  - ***Center*** the molecule in the reference frame
  - The input below turns off these three steps (not recommended!)

```
geometry noautoz noautosym nocenter
  C   0  0      0
  H   0  0.9885 -0.4329  #Angstroms
  H   0 –0.9885  0.4329
end
```

Geometry Input: zmatrix

- Geometry can be specified using a z-matrix format

```
geometry
   zmatrix
     O
     H1 O 0.95
     H2 O 0.95 H1 108.0
   end
end
```

Geometry Input: zmatrix

- Distances and angles can be specified with variables

```
geometry
   zmatrix
     O
     H1 O doh
     H2 O doh H1 ahoh
     variables
       ahoh 108.0
     constant
       doh 0.95
   end
end
```

Geometry Input: zcoord

- Forcing internal coordinates (use with care …)

```
geometry
  Si       0.0000E+00  0.0000E+00  0.0000E+00
  H       -0.9436E+00 -0.8807E+00  0.7319E+00
  H        0.7373E+00 -0.8179E+00 -0.9932E+00
  H       -0.7835E+00  0.1038E+01 -0.7137E+00
  Si       0.1699E+01  0.1556E+01  0.1695E+01
  H        0.7715E+00  0.2377E+01  0.2511E+01
  H        0.2544E+01  0.6805E+00  0.2539E+01
  H        0.2514E+01  0.2381E+01  0.7713E+00
end

### fix the Si-Si distance to 4.0 angstroms ###
geometry adjust  # initial state
  zcoord
    bond 1 4 4.00 r constant
  end
end
```

Geometry Input: system

- Crystal lattice, used in plane wave code, for 3-D periodic systems (crystals)

```
geometry units angstroms center noautosym noautoz print
  system crystal
    lat_a 3.625d0      #diamond
    lat_b 3.625d0
    lat_c 3.625d0
    alpha 90.0d0
    beta  90.0d0
    gamma 90.0d0
  end
  C     -0.50000d0  -0.50000d0  -0.50000d0
  C      0.00000d0   0.00000d0  -0.50000d0
  C      0.00000d0  -0.50000d0   0.00000d0
  C     -0.50000d0   0.00000d0   0.00000d0
  C     -0.25000d0  -0.25000d0  -0.25000d0
  C      0.25000d0   0.25000d0  -0.25000d0
  C      0.25000d0  -0.25000d0   0.25000d0
  C     -0.25000d0   0.25000d0   0.25000d0
end
```

Basis Set Input: Using libraries

- Atoms can be defined by symbol and name

```
basis
     O library cc-pvdz
     H1 library cc-pvdz file /home/me/nwchem/libraries/
     H2 library sto-3g
end
```

- * can be used to state that all atoms in the system should be using the same basis set type

```
basis
      * library cc-pvdz
end
```

Basis Set Input: Explicit basis sets

- Basis set input can be done with exponents and coefficients

```
basis spherical
  H s
    13.0100 0.019685
    1.9620   0.137977
    0.4446   0.478148
    0.1220   0.501240
 H s
    0.1220   1.000000
 H p
    0.7270 1.000000
end
```

Basis Set Input: Explicit basis sets

- Basis Libraries and explicit input can be used together

```
basis spherical
   * library cc-pvdz
H p
   0.007270 1.000000
end
```

Task Input

- Task directive tells NWChem what it should do

```
task scf                          # default is energy
task scf energy

task dft optimize
task dft saddle
task ccsd frequencies

task pspw optimize

task md dynamics
```

Task Input

- Tasks are preformed in sequence as listed in input

```
task scf energy

task dft optimize ignore  # ignore if failed, go to next task

task dft saddle

task ccsd frequencies
```

Restarting a calculation

- To restart NWChem will need certain files, that should be saved in permanent directory

```
start ne
permanent_dir /users/me
geometry
   ne 0 0 0
end
basis
   ne library cc-pvdz
end
task scf
```

```
restart ne
permanent_dir/users/me
scf
   thresh 1e-8
end
task scf
```

Setting memory and charge keyword

- If NWChem fails with an error asking for more memory, you can set it explicitly

```
memory 2400 mb
```

- Remember, memory is per processor!
- By default, molecules have a neutral charge (0)

```
charge -1
```

Open Shell Input

- DFT input block, e.g.,

```
dft
  mult 3
end
```

- Unrestriced Open Shell Default (different from Hartree-Fock)
- RODFT is available

Minimal Input Example

- Minimal input (all defaults)

```
geometry; ne 0 0 0; end
basis; ne library cc-pvdz; end
task dft
```

- Performs a closed-shell N^4 DFT calculation using the local density approximation on the neon atom (no fitting)

Simple DFT Input Example

- Input with default DFT input (single point LDA calculation)

```
echo  # echoes the input in the output file
start silane  # name of files
title silane  # title of the calculation in output
charge 0.
geometry
   si          0.00000000     0.00000000     0.00000000
   h           0.75252170    -0.75252170     0.75252170
   h          -0.75252170     0.75252170     0.75252170
   h           0.75252170     0.75252170    -0.75252170
   h          -0.75252170    -0.75252170    -0.75252170
end
dft; mult 1;end
basis
  * library cc-pvdz
end
task dft   # specifies the task → energy by default
```

Changing the exchange-correlation

```
echo
start silane
title silane
geometry
      si          0.00000000     0.00000000     0.00000000
      h           0.75252170    -0.75252170     0.75252170
      h          -0.75252170     0.75252170     0.75252170
      h           0.75252170     0.75252170    -0.75252170
      h          -0.75252170    -0.75252170    -0.75252170
end

basis
  * library cc-pvdz
end
```

```
dft
  xc b3lyp # B3LYP
end
```

```
task dft
```

```
dft
  xc becke88 lyp #BLYP
end
```

```
dft
  xc becke88 perdew86
end
```

…

Many other combinations possible…

Important DFT keywords

xc: controls the choice of the exchange-correlation
convergence: controls the convergence (energy, density…)
grid: specifies the grid
mult: specifies the multiplicity
odft: specify open shell calculation (redundant when mult is there)
iterations: controls the number of iterations
smear: useful for degenerate states

SINGLET

```
dft
   grid fine
   convergence energy 1e-08
   xc b3lyp  #B3LYP
   mult 1
end
```

TRIPLET

```
dft
   odft
   grid fine
   convergence energy 1e-08
   xc b3lyp  #B3LYP
   mult 3
end
```

Putting it all together

```
echo
start silane
title silane

geometry
      si          0.00000000     0.00000000     0.00000000
      h           0.75252170    -0.75252170     0.75252170
      h          -0.75252170     0.75252170     0.75252170
      h           0.75252170     0.75252170    -0.75252170
      h          -0.75252170    -0.75252170    -0.75252170
end

basis
  * library cc-pvdz
end

dft
  grid fine
  convergence energy 1e-08
  xc b3lyp # B3LYP
  mult 1
end
task dft
```

Geometry Optimization

```
echo
start silane

geometry
      si          0.00000000     0.00000000     0.00000000
      h           0.75252170    -0.75252170     0.75252170
      h          -0.75252170     0.75252170     0.75252170
      h           0.75252170     0.75252170    -0.75252170
      h          -0.75252170    -0.75252170    -0.75252170
end

basis
  * library cc-pvdz
end

dft
  grid xfine
  convergence energy 1e-08
  xc b3lyp # B3LYP
  mult 1
end

task dft optimize
```

Frequencies

```
echo
start silane

geometry
  si          0.00000000     0.00000000     0.00000000
  h           0.75252170    -0.75252170     0.75252170
  h          -0.75252170     0.75252170     0.75252170
  h           0.75252170     0.75252170    -0.75252170
  h          -0.75252170    -0.75252170    -0.75252170
end

basis
  * library cc-pvdz
end

dft
  grid xfine
  convergence energy 1e-08
  xc b3lyp # B3LYP
  mult 1
end

task dft frequencies
```

Combining Calculations I

```
echo
start silane

geometry
      si          0.00000000     0.00000000     0.00000000
      h           0.75252170    -0.75252170     0.75252170
      h          -0.75252170     0.75252170     0.75252170
      h           0.75252170     0.75252170    -0.75252170
      h          -0.75252170    -0.75252170    -0.75252170
end

basis
  * library cc-pvdz
end

dft
  grid xfine
  convergence energy 1e-08
  xc b3lyp # B3LYP
  mult 1
end
task dft optimize
task dft frequencies
```

Combining Calculations II

```
geometry
  ...
end

basis
   * library cc-pvdz
end

dft
    xc b3lyp  #B3LYP
    mult 1
end

task dft optimize
task dft frequencies

dft
    odft
    xc becke88 lyp #BLYP
    mult 3
end

task dft optimize
```

Restarting Calculations

```
echo
restart silane

geometry
      si          0.00000000     0.00000000     0.00000000
      h           0.75252170    -0.75252170     0.75252170
      h          -0.75252170     0.75252170     0.75252170
      h           0.75252170     0.75252170    -0.75252170
      h          -0.75252170    -0.75252170    -0.75252170
end

basis
  * library cc-pvdz
end

dft
  grid xfine
  convergence energy 1e-08
  xc b3lyp # B3LYP
  mult 1
end

task dft
```

Restart files

- **silane.db**
- **silane.movecs**

Using Old Molecular Orbitals

```
echo
start silane

geometry
      si          0.00000000     0.00000000     0.00000000
      h           0.75252170    -0.75252170     0.75252170
      h          -0.75252170     0.75252170     0.75252170
      h           0.75252170     0.75252170    -0.75252170
      h          -0.75252170    -0.75252170    -0.75252170
end

basis
  * library cc-pvdz
end

dft
  grid xfine
  convergence energy 1e-08
  xc b3lyp # B3LYP
  mult 1
  vectors input old.movecs output b3lyp.movecs
end
task dft
```

Organizing Your Files

```
echo
start silane

permanent_dir /home/yourname/silane/b3lyp
scratch_dir /scratch

geometry
      si          0.00000000     0.00000000     0.00000000
      h           0.75252170    -0.75252170     0.75252170
      h          -0.75252170     0.75252170     0.75252170
      h           0.75252170     0.75252170    -0.75252170
      h          -0.75252170    -0.75252170    -0.75252170
end

basis
  * library cc-pvdz
end
dft
  grid xfine
  convergence energy 1e-08
  xc b3lyp  #B3LYP
  mult 1
end
task dft optimize
```

Customizing The Basis

```
...
geometry
      si          0.00000000     0.00000000     0.00000000
      h1          0.75252170    -0.75252170     0.75252170
      h2         -0.75252170     0.75252170     0.75252170
      h3          0.75252170     0.75252170    -0.75252170
      h4         -0.75252170    -0.75252170    -0.75252170
end

basis
      si library 6-31G
      h1 library h sto-3g
      h2 library h 6-31g
      h3 library h 3-21g
      h4 library h 6-31g*
end

...
```

```
...
geometry
      ...
end

basis
      ...
end
```

```
dft
 xc b3lyp
 disp vdw 4
end
task dft optimize
```

S. Grimme J. Comp. Chem. 25 1463 (2004)
S. Grimme J. Comp. Chem. 271787 (2006)

Semi-empirical hybrid DFT + MP2 Double Hybrid Functionals

```
...
geometry
      ...
end

basis
      ...
end
```

```
dft
  xc HFexch 0.53 becke88 0.47 lyp 0.73 mp2 0.27
  dftmp2 direct
  direct
  convergence energy 1e-8
  iterations 100
end
```

S. Grimme, J. Chem. Phys., 124, 034108 (2006)

Charge-Density Fitting

- Important difference between DFT and SCF
  - **Additional fitting basis set (**reduces cost from N^4 --> N^3**)**

```
geometry; ne 0 0 0; end

basis "ao basis" spherical
   ne library def2-tzvp
end

basis "cd basis"
   ne library "Weigend Coulomb Fitting"
end

task dft
```

Effective Core Potentials

- Reduces the cost of calculation for heavy elements
  - Additional input field required to define potential

```
geometry; ne 0 0 0; end

ecp spherical
  * library Stuttgart_RSC_1997_ECP
end

basis "ao basis"
   ni library "Stuttgart_RSC_1997_ECP"
end

task dft
```

Excited State Calculations with TDDFT

```
geometry
O      0.00000000      0.00000000      0.12982363
H      0.75933475      0.00000000     -0.46621158
H     -0.75933475      0.00000000     -0.46621158
end

basis
O library 6-31G**
H library 6-31G**
end

dft
  xc b3lyp
end

tddft
 nroots 10
 notriplet
end

task tddft energy
```

Excited State Sample Output

```
-----------------------------------------------------
 Root  1 singlet b2    0.294221372 a.u. (  8.0061743 eV)
 -----------------------------------------------------
    Transition Moments    X  0.00000   Y -0.26890   Z  0.00000
    Transition Moments   XX  0.00000  XY  0.00000  XZ  0.00000
    Transition Moments   YY  0.00000  YZ  0.08066  ZZ  0.00000
    Transition Moments  XXX  0.00000 XXY -0.93672 XXZ  0.00000
    Transition Moments  XYY  0.00000 XYZ  0.00000 XZZ  0.00000
    Transition Moments  YYY -1.60959 YYZ  0.00000 YZZ -0.72276
    Transition Moments  ZZZ  0.00000
    Dipole Oscillator Strength                          0.01418

    Occ.  5  b2  ---  Virt.  6  a1  -1.00002 X
 -----------------------------------------------------
 Root  2 singlet a2    0.369097477 a.u. ( 10.0436576 eV)
 -----------------------------------------------------
    Transition Moments    X  0.00000   Y  0.00000   Z  0.00000
    Transition Moments   XX  0.00000  XY  0.24936  XZ  0.00000
    Transition Moments   YY  0.00000  YZ  0.00000  ZZ  0.00000
    Transition Moments  XXX  0.00000 XXY  0.00000 XXZ  0.00000
    Transition Moments  XYY  0.00000 XYZ -0.34740 XZZ  0.00000
    Transition Moments  YYY  0.00000 YYZ  0.00000 YZZ  0.00000
    Transition Moments  ZZZ  0.00000
    Dipole Oscillator Strength                          0.00000

    Occ.  5  b2  ---  Virt.  7  b1  -0.99936 X
```