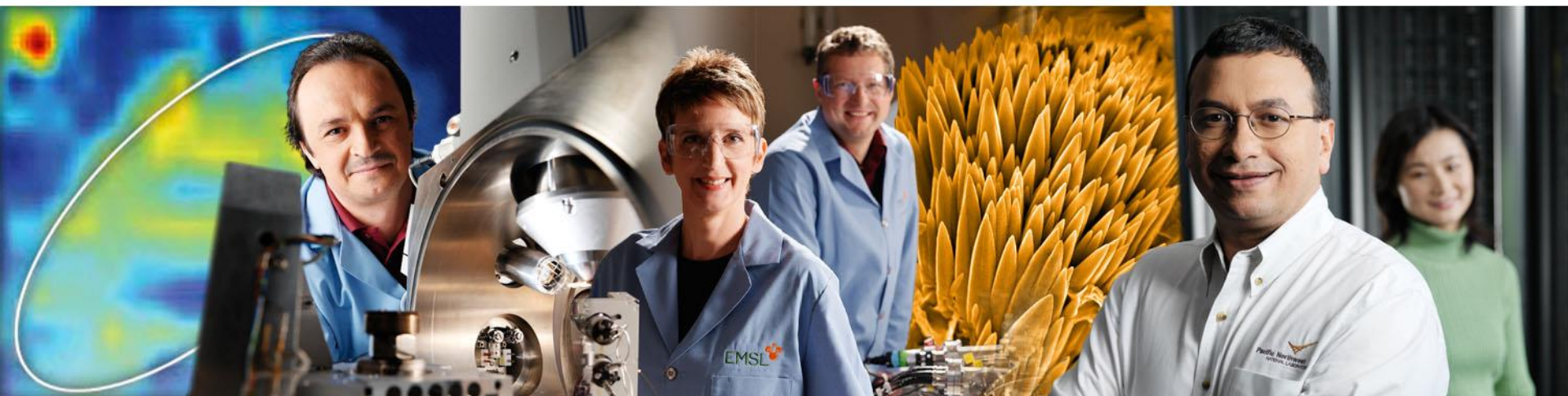


NWChem: Hartree-Fock, Density Functional Theory, Time-Dependent Density Functional Theory



- Functionality
- Input
- Wavefunctions
- Initial MO vectors
- Direct and semidirect algorithms
- Convergence, files, and restarting

- Energies and gradients
 - ◆ Closed-shell (RHF)
 - ◆ Spin-restricted, high-spin open-shell (ROHF)
 - ◆ Spin-unrestricted open-shell (UHF)
- Analytic second derivatives (RHF and UHF)
- Finite point groups
- Will be used as first step in all correlated methods (e.g. MP2, CC, etc ...)
- Resolution of the identity (energy)

- SCF input block, e.g.,

scf

triplet

uhf

end

- Defaults

- ◆ Restricted-spin wavefunction (ROHF)
- ◆ Accuracy suitable for non-floppy molecule geometry optimization
- ◆ Symmetry as defined in the geometry

³B₁ CH₂ ROHF and UHF optimizations

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

```
basis
  H library 3-21g; C library 3-21g
end
```

```
scf; sym off; triplet; end #default is ROHF
task scf optimize
```

```
scf; uhf; end
task scf optimize
```

- Functionality
- Input
- XC functionals
- Grid & Convergence options

- *Gaussian function*-based DFT (aka LCAO)
 - *energies*,
 - *gradients* and
 - *second derivatives*
- finite *symmetry*
- *Exchange-Correlation* functionals for
 - *Closed*-Shell systems and *Open*-Shell systems

- Hartree-Fock Exchange
- Traditional functionals: Density & density gradient
 - ▶ LDA, BP, BLYP, PBE, PW91,...
- Hybrid functionals: Inclusion of HF exchange
 - ▶ B3LYP, PBE0, BeckeHalfandHalf,...
- Meta functionals: Inclusion of kinetic energy
 - ▶ TPSS, PKZB, Minnesota functionals,...
- Range-separated functionals
 - ▶ CAM-B3LYP, LC-PBE0,...
- DFT + empirical dispersion (DFT+ D)
 - ▶ Based on Grimme's implementation
- Double Hybrid functionals: DFT + MP2
 - ▶ Based on Grimme's implementation

- DFT input block, e.g.,

```
dft
  mult 1
end
```

- Defaults (similar to Hartree-Fock)
 - Local density approximation (**LDA**)
 - Accuracy suitable for non-floppy molecule geometry optimization
 - Symmetry as defined in the geometry

- DFT input block, e.g.,

```
dft  
  mult 3  
end
```

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

- 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
```

- EMSL Basis Set Exchange: <https://bse.pnl.gov/bse/portal>

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...

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
```

```
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
```



```
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
```

```
...  
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
```

...

Including empirical dispersion in DFT

```
...  
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 (Dunlap scheme)
 - ▶ 4-center, 2-electron Coulomb integrals \rightarrow 3-center integrals (N^3)
 - ▶ Very fast for traditional DFT (pure density based functionals, no HF Exchange)
 - ▶ Cheaper and better parallel scaling

- Direct or on-the-fly evaluation of integrals
 - ▶ All integrals evaluated as needed
 - ▶ Useful for large systems on large numbers of processors

- Effective Core Potentials

- 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
```

- 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
```

- Numerical integration keywords and targets using Mura-Knowles radial and Lebedev angular quadratures:

```
dft; grid xcoarse; end    (1d-4 au)
dft; grid coarse; end     (1d-5 au)
dft; grid medium; end     (1d-6 au; default)
dft; grid fine; end       (1d-7 au)
dft; grid xfine; end      (1d-8 au)
dft; grid huge; end
```

- Addition quadrature choices, e.g.,

```
dft; grid eumac medium; end
dft; grid ssf lebedev 75 11; end    (= G98 fine)
```

- Controlling accuracy
 - Schwarz screening is invoked for $\text{density} \times \text{integral} < 10 - \text{accCoul}$, **accCoul** default = 10
 - e.g., **tolerances accCoul 12**
- When to change it?
 - Diffuse basis/floppy molecules
 - Changing from energy to optimizations, frequencies, etc.
 - Don't forget to increase grid accuracy too!

- *DIIS*, *level-shifting*, and *damping* are available
- Default is **DIIS** with no damping. Level-shifting is invoked when the HOMO-LUMO gap is less than **hl_tol** (default is 0.05 atomic units)
- Control of DIIS, levelshifting, and damping: **convergence**
lshift 0.1 damp 40 diis 5
- When invoked can be by iteration count
convergence ncydp 5
- or by change in total energy
**convergence ncydp 0 dampon 1d6 **
dampoff 1d-2

- The `SMEAR` keyword is useful in cases with many degenerate states near the HOMO (e.g. metallic clusters). Molecular Orbitals near the gap will be occupied with a distribution a la Fermi-Dirac corresponding to a finite temperature.
- `SMEAR <real smear default 0.001>`