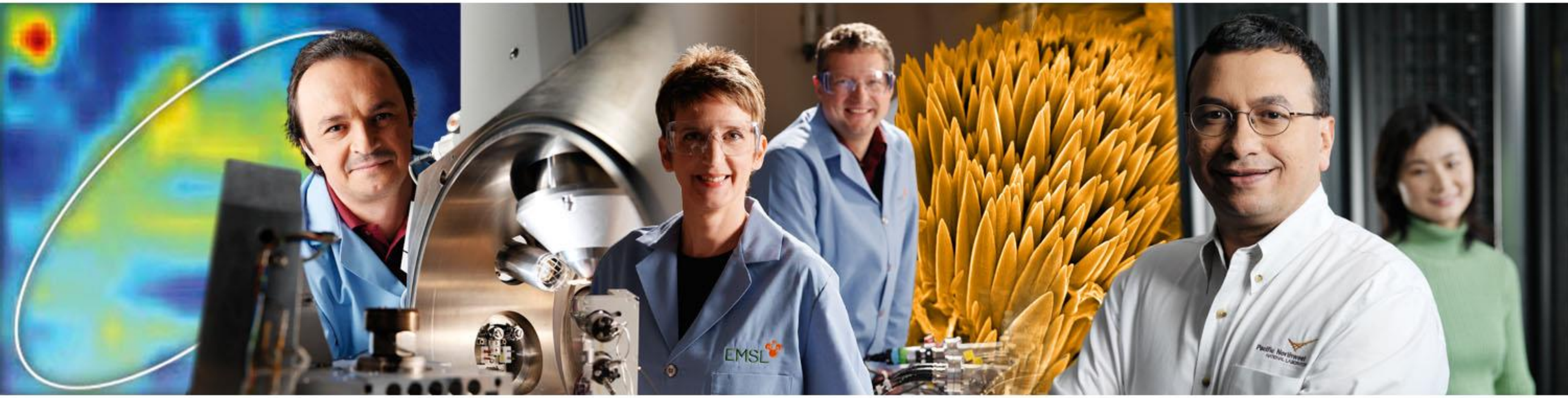
EMSL

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



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U.S. DEPARTMENT OF ENERGY

Hartree-Fock

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

Hartree-Fock Functionality

- 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)

Input

- 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

CH_2 molecule

$^3B_1$ CH_2 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; triplet; end  #default is ROHF
task scf optimize
```

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

Density-Functional Theory

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

DFT Functionality in a nutshell

- *Gaussian function*-based DFT (aka LCAO)
    - *energies*,
    - *gradients* and
    - *second derivatives*
- finite *symmetry*

- Exchange-Correlation functionals for
    - Closed-Shell systems and Open-Shell systems

Exchange-Correlation Functionals

- 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

Input

- 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

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
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
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…

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

...
```

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)

Other Capabilities

- Charge density fitting (Dunlap scheme)
  - 4-center, 2-electron Coulomb integrals → 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

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
```

Grid Options

- 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)

Modifying Accuracy

- Controlling accuracy
  - **Schwarz screening is invoked for density*integral < 10-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!**

Convergence

- *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
```

Fractional occupation of MOs

- The `SMEAR` keyword is useful in cases wit 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>`

Excited State Calculations with TDDFT

Time-Dependent DFT

Casida Formulation

Cannot be used to describe excitations in intense fields

Perturbed density → first-order correction

Linear response approach → frequency domain

- Working equations have N_{occ}*N_{virt} solutions
- Dimension → tetradic (N^2*N^2)
- Every root → cost of a HF or hybrid DFT calculation
- Note that the vectors are normalized but differently so than your usual wavefunction
- The orbital energy difference is a main term in the excitation energy
- In the case of pure DFT with large molecules most of the integrals involving F_{XC} vanish as this is a local kernel

$$\begin{pmatrix} A & B \\ B^{*} & A^{*} \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix}$$

$$1 = (X|X) - (Y|Y)$$

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ia|F_H + F_{xc}|jb)$$

$$B_{ia,jb} = (ia|F_H + F_{xc}|jb)$$

$$F_{xc}(r_1, r_2) = \frac{\partial^2 f}{\partial\rho(r_1)\,\partial\rho(r_2)}$$

Time-Dependent Density Functional Theory, Marques et al, Springer 2006

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
```

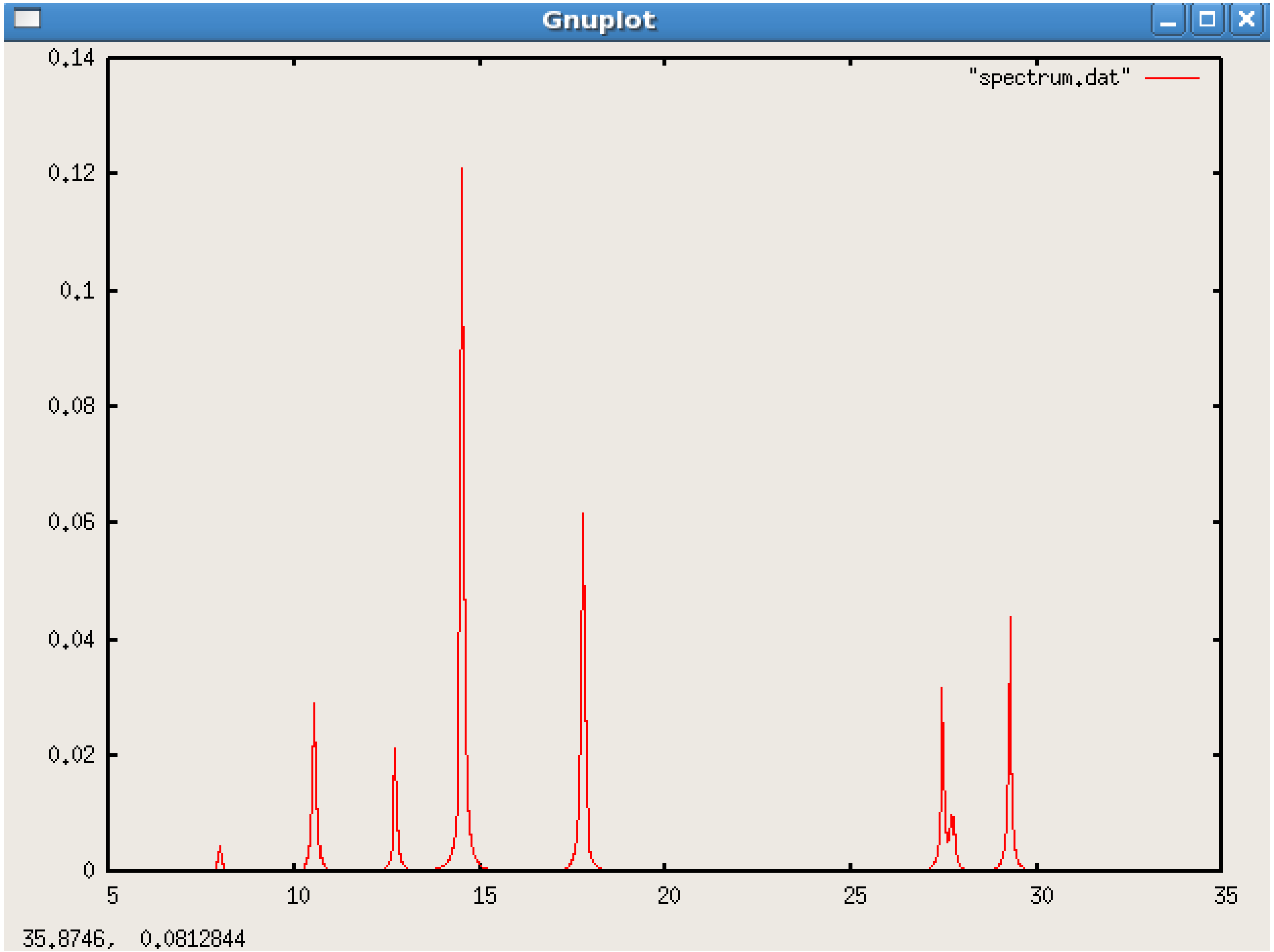
Excited State Sample Output

```
 ----------------------------------------------------------
  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
```

Excited State Spectrum



Energy (eV)