



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



www.emsl.pnl.gov


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- 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

Simple Example

3B_1 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; 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
 - *energies*,
 - *gradients* and
 - *second derivatives*
- ◆ finite *symmetry*
- ◆ Exchange-Correlation functionals for
 - *Closed*-Shell systems and *Open*-Shell systems

Exchange-Correlation Functionals



- Pure 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

Local Basis (Gaussian Basis Set)



Memory requirements

- Largest quantities are the density, Fock, overlap, 1-electron matrices
- Memory needed $O(N^2)$
 - ◆ Replicated data $O(N^2)$ per node
 - ◆ Distributed data $O(N^2)$ for whole calculation

Computational Complexity

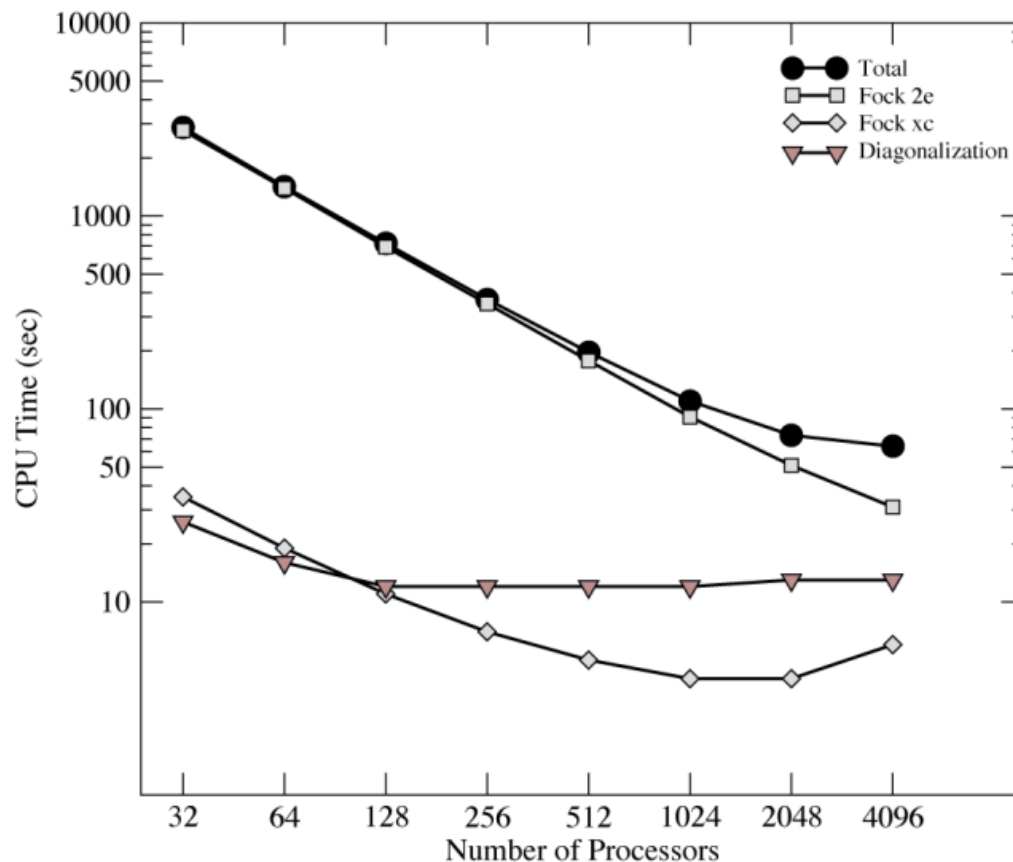
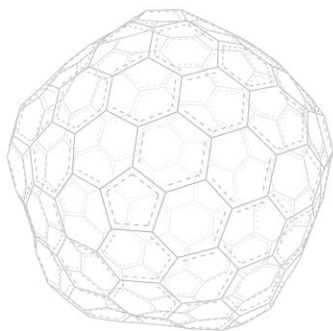
- Main cost is the evaluation of the 2-electron integrals
 - ◆ Takes $O(N^2)$ - $O(N^4)$ work
 - ◆ $O(N^4)$ for small-medium systems
 - ◆ $O(N^2)$ in the large N limit
 - Schwarz screening,...
 - ◆ For large N the linear algebra becomes dominant at $O(N^3)$
 - Matrix multiplication, diagonalization

Phys. Chem. Chem. Phys. 12, 6896 (2010)

Gaussian based HF/DFT → Finite systems (molecules, clusters, nanostructures)

- Functionality
 - ◆ Exhaustive list of exchange-correlation functionals
 - Traditional xc functionals
 - Wide range of hybrid functionals (B3LYP, PBE0, BeckeH&H...)
 - HF Exchange
 - Meta-GGA functionals
 - Minnesota functionals (M05, M06)
 - SIC and OEP
 - Range separated functionals (CAMB3LYP, LC-PBE0, BNL,...)
 - DFT + D implementation (long-range empirical vdW)
 - Double hybrid functionals
 - ◆ Spin-orbit DFT
 - ECP, ZORA, DK
 - ◆ Constrained DFT
 - ◆ TDDFT for excited states → Optical spectroscopy
 - ◆ Various properties (NMR, Linear response,...)
- System sizes: ~150 atoms, 1500-2000 basis functions are routine

- Calculation on C_{240}
 - ◆ PBE0 functional, 6-31G*
 - ◆ Direct integral evaluation
 - ◆ Size 3600 basis functions
- Timings for different components of the Kohn-Sham matrix construction
 - ◆ Fock 2e – two electron integrals
 - ◆ Fock xc – the DFT contribution
 - ◆ Diagonalization – eigensolver



- 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)

- Recent RODFT implementation

```
dft
  cgmin # quadratic conv. (required)
  mult 2
  rodft
end
```

- 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

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 Vectors

```
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.movevecs output b3lyp.movevecs
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 2 s6 1.05  
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

- ...

Detailed documentation information available on
www.nwchem-sw.org

- 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"  
  ne library "DZVP (DFT orbital)"  
end
```

```
basis "cd basis"  
  ne library "DGauss A1 DFT 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-Kowles 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)
```

- Addition quadrature choices, e.g.,

```
dft; grid eumac medium; end
```

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


- Controlling accuracy
 - Density < **tol_rho** (10-10) are screened
 - e.g., **tolerances tol_rho 1.d-12**
 - 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!

- *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 **h1_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>`

Excited State Calculations with TDDFT

Casida Formulation

Perturbed density \rightarrow first-order correction

Linear response approach \rightarrow frequency domain

Cannot be used to describe excitations in intense fields

- Working equations have $M = N_{\text{occ}} * N_{\text{virt}}$ solutions
- Dimension \rightarrow tetradic ($M * M$)
- Every root \rightarrow 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

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

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

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

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

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

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
  roots 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

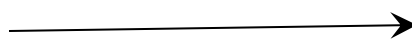
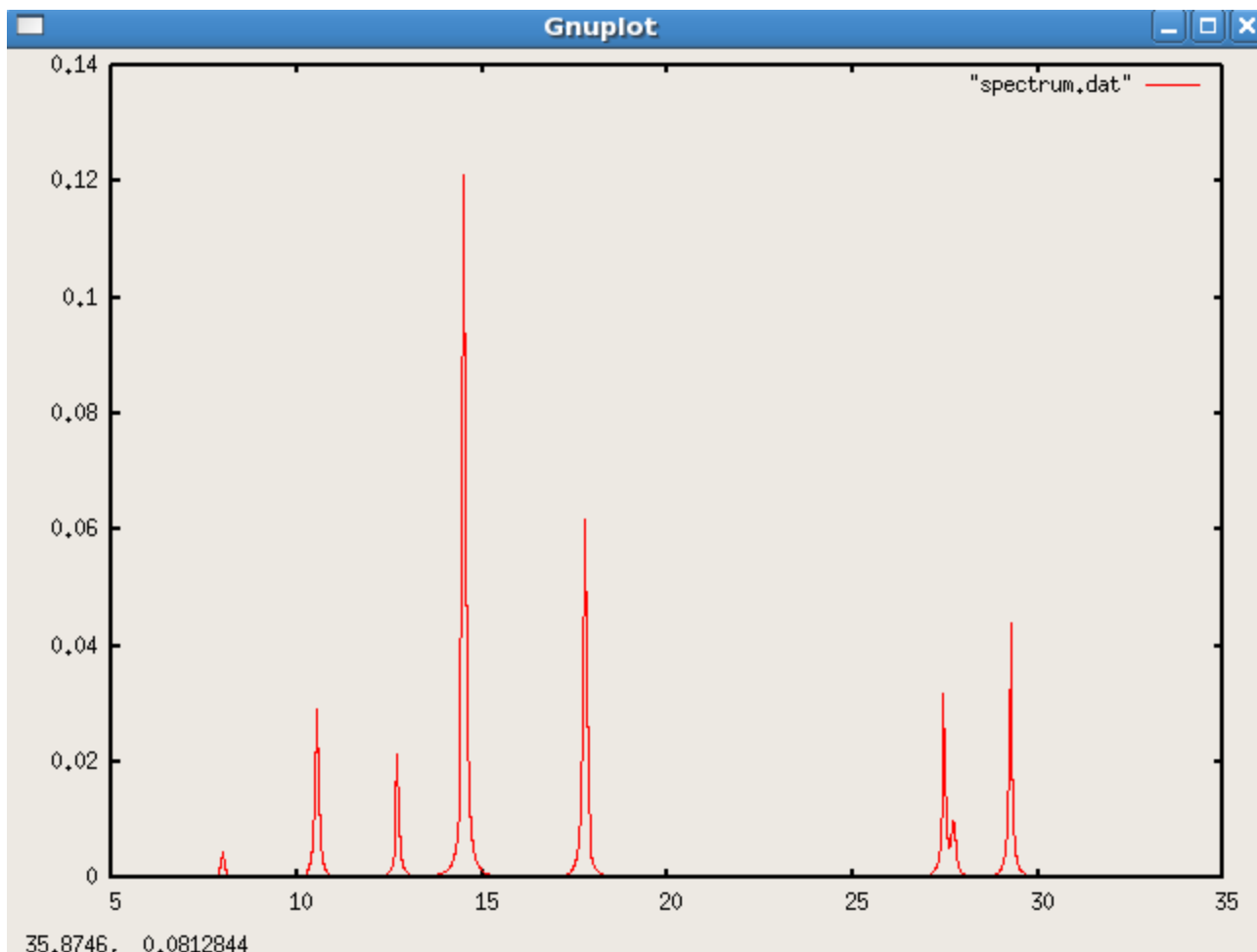
Occ. 5 b2 --- Virt. 6 a1 -1.00002 X

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

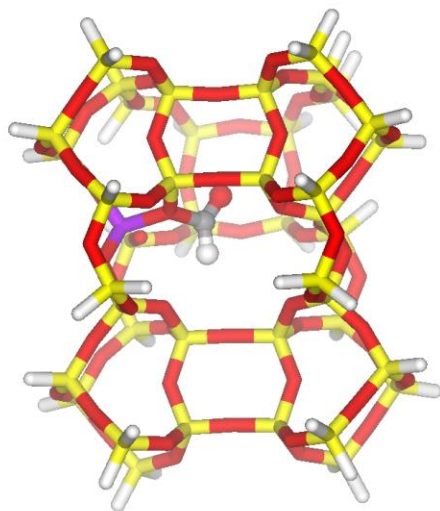
Occ. 5 b2 --- Virt. 7 b1 -0.99936 X

Excited State Spectrum

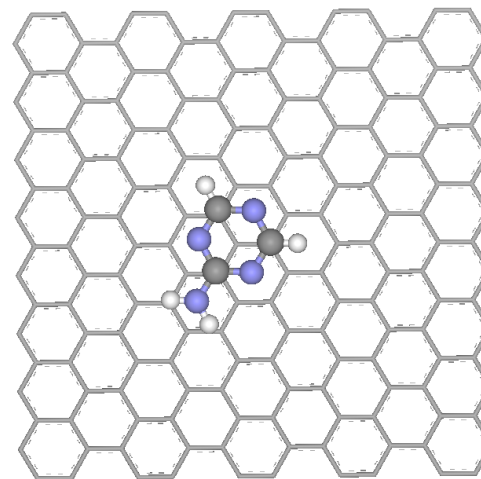


Energy (eV)

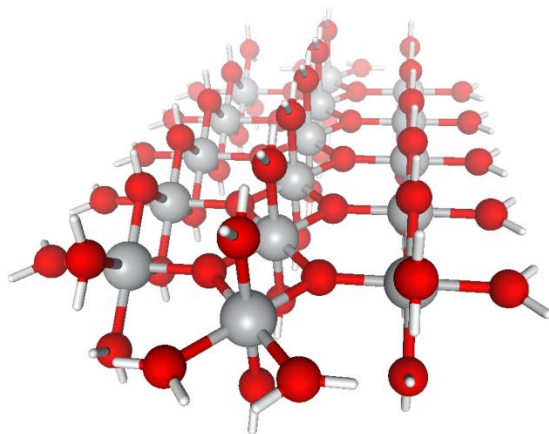
Recent Applications (1)



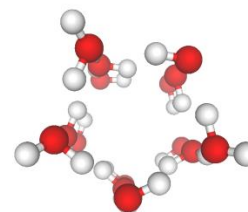
Formyl cation bound to a Bronsted acid site in a zeolite cavity



Adsorption of aminotriazines on graphene using dispersion corrected DFT

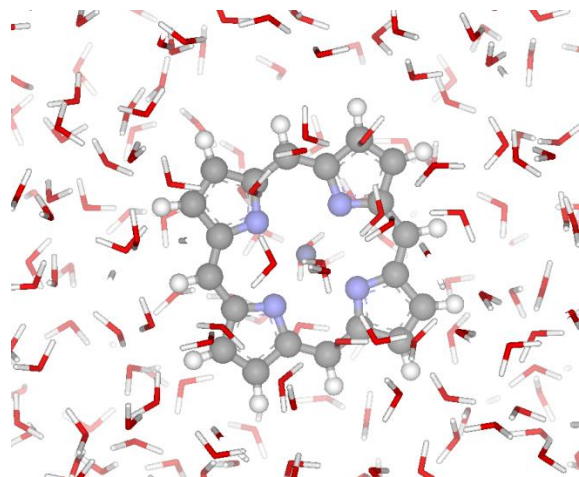


Ground & Excited state properties of pure and N-doped TiO₂ rutile

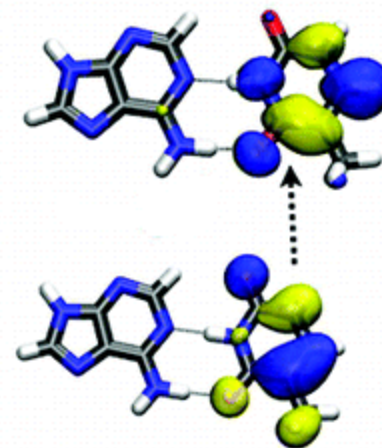


Dipole polarizabilities of water clusters

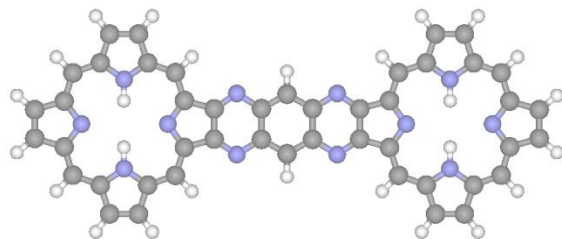
Recent Applications (2)



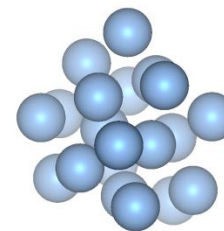
Charge transfer excitations in zinc porphyrin in aqueous solution



Correct lowest excitation in the Adenine-Thymine base pair using range-separated functionals



Excitations energies in the oligoporphyrin dimer



Optical properties of silver clusters

Tutorial exercises

=====

hf-dft

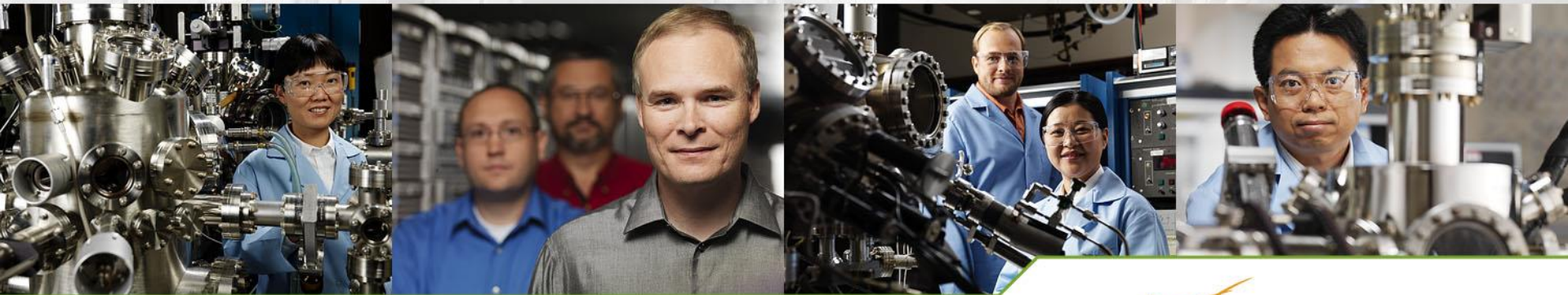
- b3lyp:** Shows how to perform a single point energy, geometry optimization and frequency calculation
- combined:** Shows how to perform single point energy calculations with various exchange-correlation functionals
- restart:** Shows how to restart a calculation
- files:** Shows how to use the scratch and permanent directories
- multiplicity:** Shows how to set the multiplicity in a calculation
- convergence:** Shows how to specify other useful keywords in the dft block
- ecp:** Shows how to use effective core potentials (ECP)
- direct:** Shows how to perform direct calculations
- densityfitting:** Shows how to use charge density fitting basis sets
- sodft:** Shows how to perform calculation with a spin-orbit ecp
- explicitbasis:** Shows how to specify the basis explicitly
- multiplestructures:** Shows how to specify multiple structures
- multiplebasis:** Shows how to specify multiple basis sets

tddft

h2o, 2h2o, ethane, butane

properties

Questions?



EXTRA MATERIAL

Hartree-Fock & Density Functional Theory I



- The energy expression is derived from a single determinant wave function approximation

- Replace the exchange with a exchange-correlation functional to go from Hartree-Fock → DFT

- Implemented using various basis set approaches
 - ▶ Plane waves
 - ▶ Gaussian functions
 - ▶ Slater functions
 - ▶ Numerical atomic orbitals
 - ▶ Wavelets
 - ▶ Mixed basis sets
 - ▶ ...

Hartree-Fock & Density Functional Theory II

Local Basis

$$\varphi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}(\mathbf{r})$$

$$E = \sum_{\mu\nu} F_{\mu\nu} D_{\mu\nu} + \sum_i \varepsilon_i \sum_j \left(\sum_{\mu\nu} C_{\mu i}^* S_{\mu\nu} C_{\nu j} - \delta_{ij} \right)$$

$$D_{\mu\nu} = \sum_{i \in \{occ\}} C_{\mu i}^* C_{\nu i}$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} + G_{\mu\nu}^J + \alpha G_{\mu\nu}^K + \beta G_{\mu\nu}^{X-DFT} + \gamma G_{\mu\nu}^{C-DFT}$$

$$G_{\mu\nu}^J = \sum_{\sigma\tau} (\mu\nu | \sigma\tau) D_{\sigma\tau}$$

$$G_{\mu\nu}^K = -\frac{1}{2} \sum_{\sigma\tau} (\mu\tau | \sigma\nu) D_{\sigma\tau}$$

$$G_{\mu\nu}^{y-DFT} = \int \sum_{\xi \in \{\rho_{\alpha}, \rho_{\beta}, |\nabla\rho_{\alpha}|, |\nabla\rho_{\beta}|, \nabla\rho_{\alpha} \cdot \nabla\rho_{\beta}, \dots\}} \frac{\partial f^y}{\partial \xi} \frac{\partial \xi}{\partial D_{\mu\nu}} d\vec{r}$$

- Minimize energy with respect to $C_{\mu i}$ and ε_i
- Gives
 - ◆ The total energy E
 - ◆ The molecular orbitals $C_{\mu i}$
 - ◆ The orbital energies ε_i