

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



# 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

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

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

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

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

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

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

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

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

# Hartree-Fock & Density Functional Theory III Exchange-Correlation Functionals



- Pure Hartree-Fock
- 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

# Hartree-Fock & Density Functional Theory IV

## 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

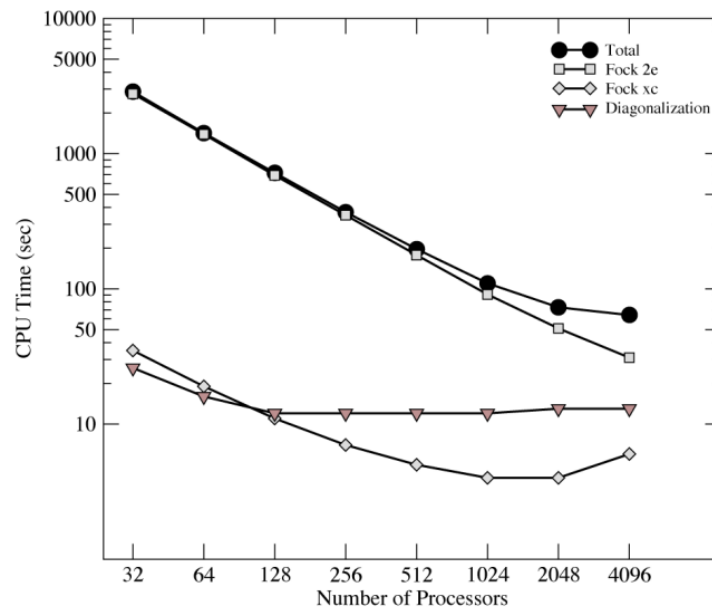
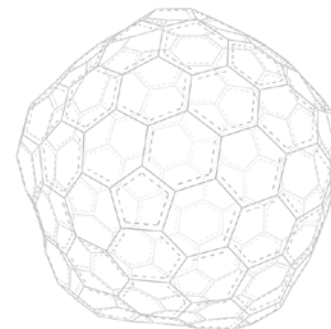
- Main cost is the evaluation of the 2-electron integrals
  - ◆ Takes  $O(N^2)$ - $O(N^4)$  work
  - ◆  $O(N^4)$  for small-medium systems
  - ◆  $O(N^2)$  in the large N limit
    - Schwarz screening, ...
  - ◆ For large N the linear algebra becomes dominant at  $O(N^3)$ 
    - Matrix multiplication, 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 – eigenvector solver
- Scalability limited by diagonalization
- Can be improved with diagonalization free approaches



# 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 #BP
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 xfine
  convergence energy 1e-08
  xc b3lyp #B3LYP
  mult 1
end
```

## TRIPLET

```
dft
  odft
  grid xfine
  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 xfine
  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 → 3-center integrals ( $N^3$ )
  - ▶ Very fast for traditional DFT (pure density based functionals)
  
- 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](http://www.nwchem-sw.org)

# 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  $N_{\text{occ}}^* N_{\text{virt}}$  solutions
- Dimension  $\rightarrow$  tetradic ( $N^2 \times N^2$ )
- 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



```
start tddft_h2o
echo

title "TDDFT H2O B3LYP/6-31G**"

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

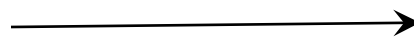
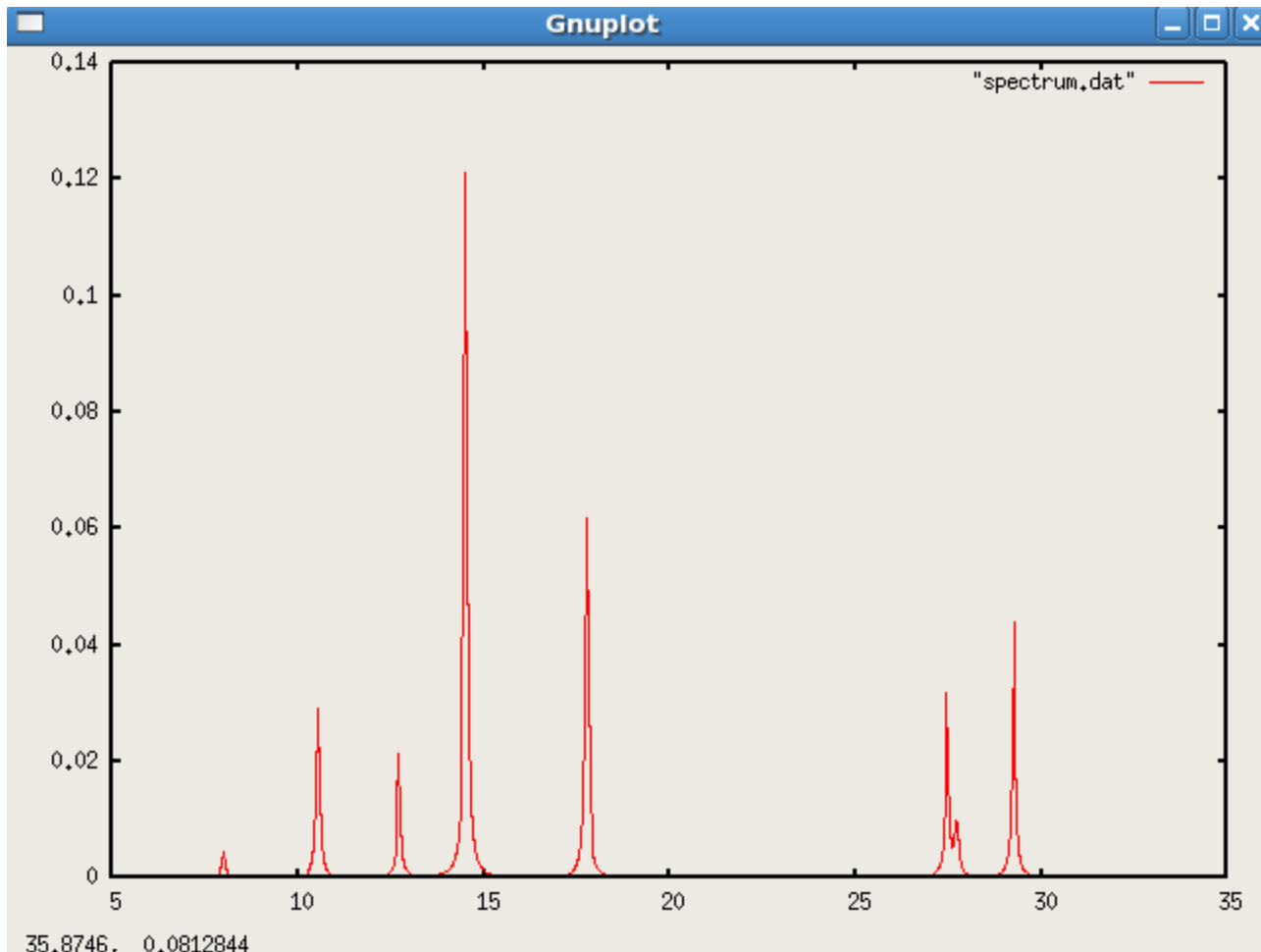
Occ. 5 b2 --- Virt. 6 a1 -1.00002 X  
-----

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

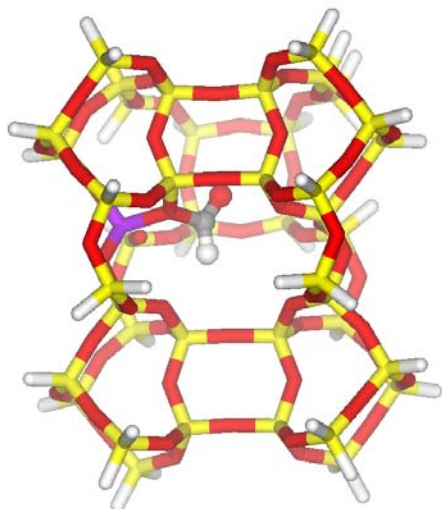
Occ. 5 b2 --- Virt. 7 b1 -0.99936 X

# Excited State Spectrum

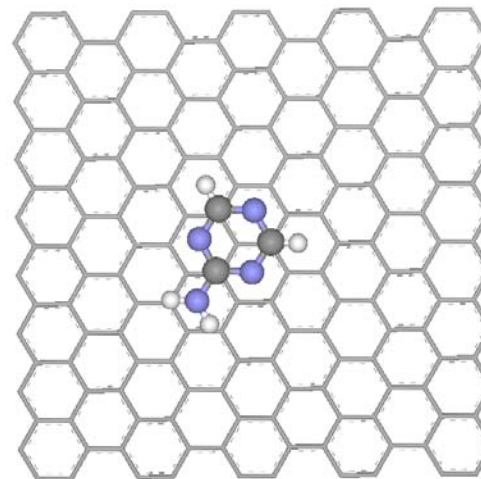


Energy (eV)

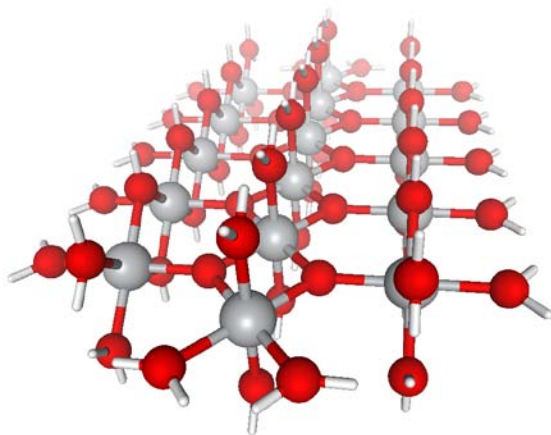
# Recent Applications (1)



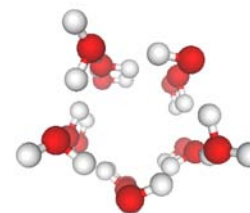
Formyl cation bound to a Bronsted acid site in a zeolite cavity



Adsorption of aminotriazines on graphene using dispersion corrected DFT

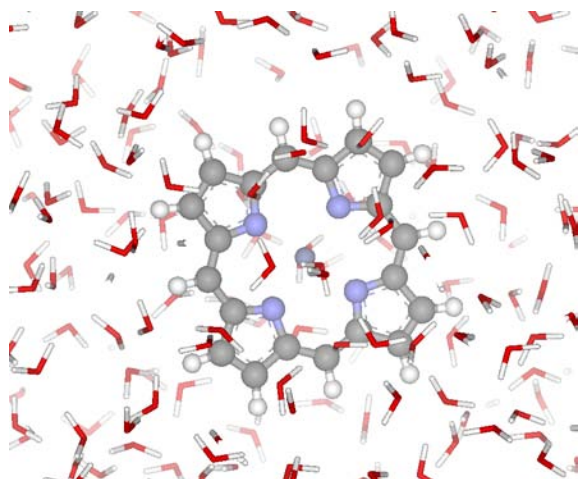


Ground & Excited state properties of pure and N-doped TiO<sub>2</sub> rutile

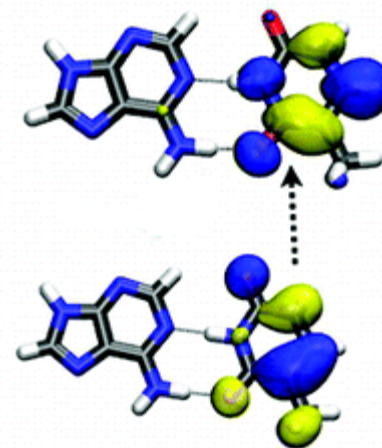


Dipole polarizabilities of water clusters

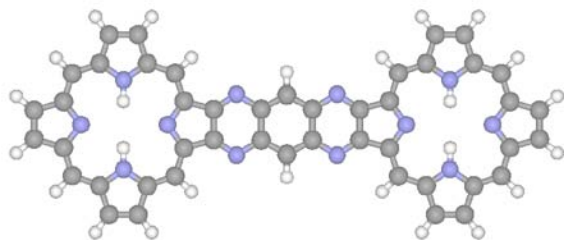
# Recent Applications (2)



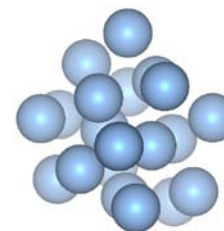
Charge transfer excitations in zinc porphyrin in aqueous solution



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**

h<sub>2</sub>o, 2h<sub>2</sub>o, ethane, butane

**properties**

# Questions?

