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

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Hartree-Fock

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

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- 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)

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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

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Simple Example

$^3B_1$ 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
  - *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

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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

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

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

NWChem: Gaussian Basis HF/DFT

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

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NWChem: Gaussian DFT Scaling

- 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
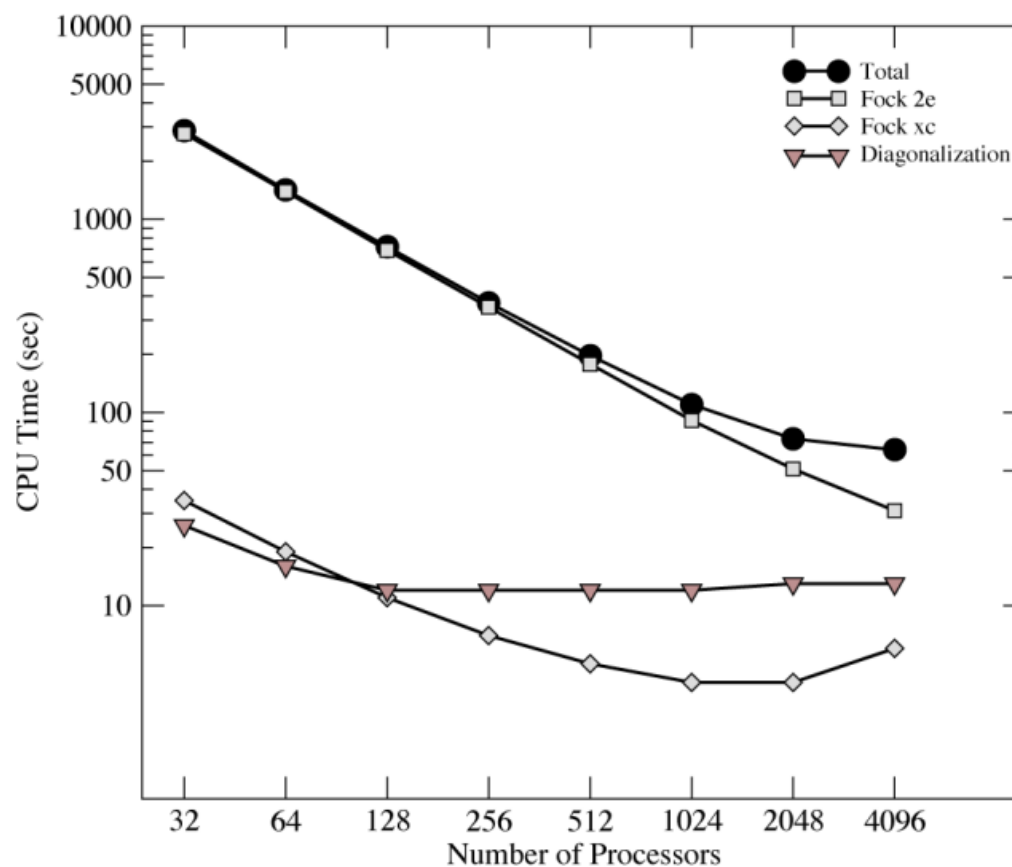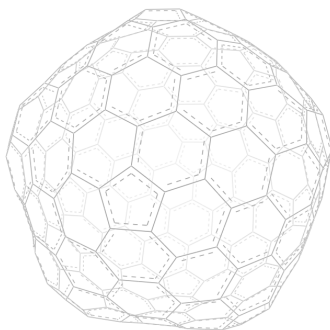
Input

- 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)

- Recent RODFT implementation

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

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**

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EMSL

```
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
```

EMSL

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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
```

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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 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.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 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)

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

- …

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

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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"
   ne library "DZVP (DFT orbital)"
end

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

- Addition quadrature choices, e.g.,

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

Modifying Accuracy

- 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!**

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

Perturbed density → first-order correction

Linear response approach → frequency domain

Cannot be used to describe excitations in intense fields

- Working equations have $M = N_{occ}*N_{virt}$ solutions
- Dimension → tetradic ($M*M$)
- 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

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

$$1 = \left(X \middle| X \right) - \left(Y \middle| Y \right)$$

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

$$B_{ia,jb} = \left(ia \middle| F_H + F_{xc} \middle| jb \right)$$

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

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

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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
```
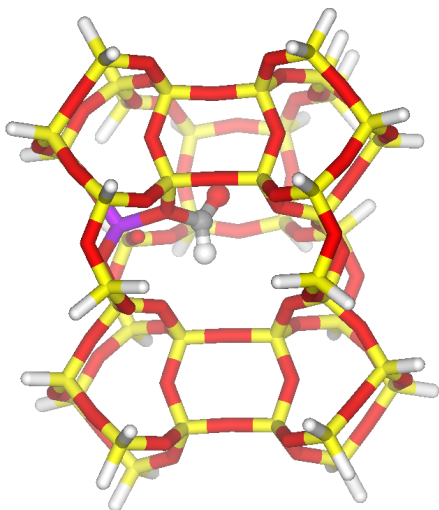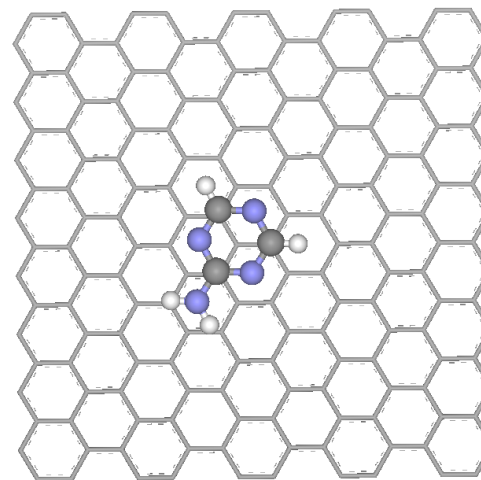
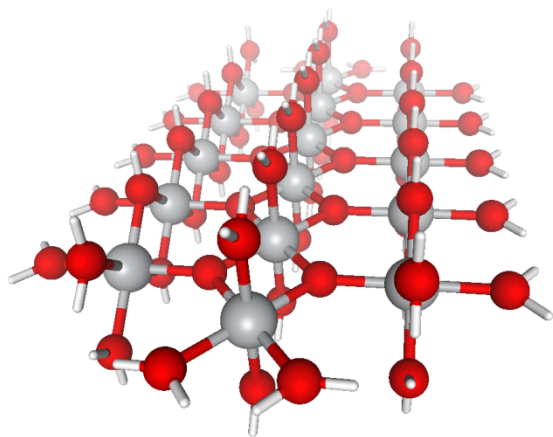# Excited State Spectrum
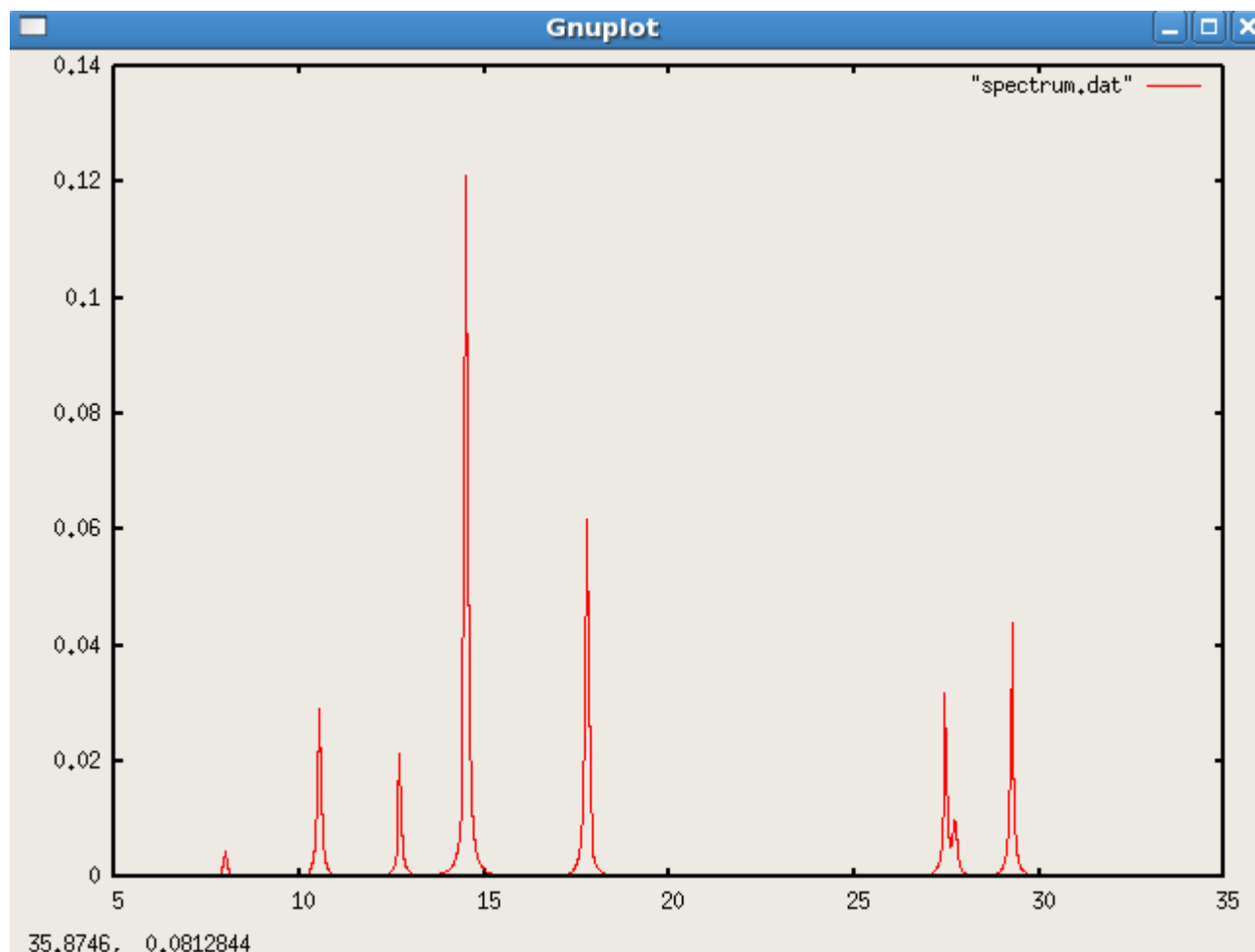
Energy (eV)

Recent Applications (1)
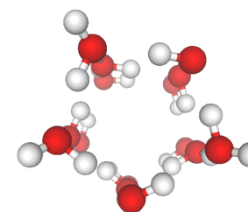
Formyl cation bound to a Bronsted acid
site in a zeolite cavity

Adsorption of aminotriazines on graphene
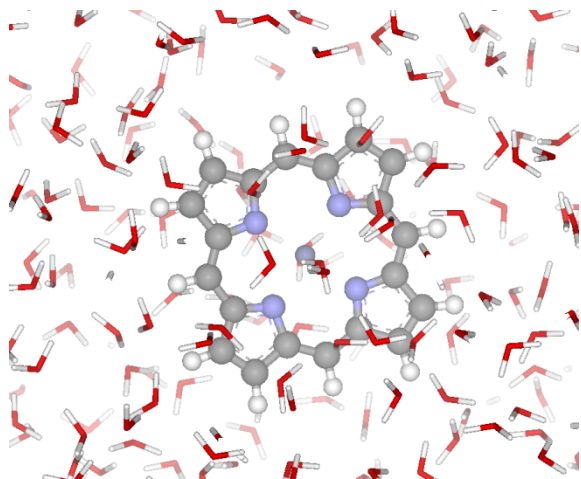using dispersion corrected DFT

Dipole polarizabilities of water clusters

Ground & Excited state properties of pure
and N-doped TiO_2 rutile

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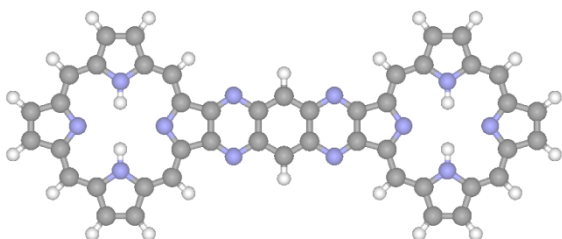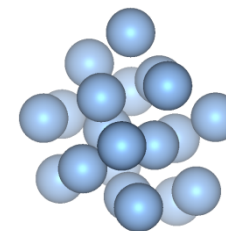
Charge transfer excitations in zinc porphyrin in aqueous solution
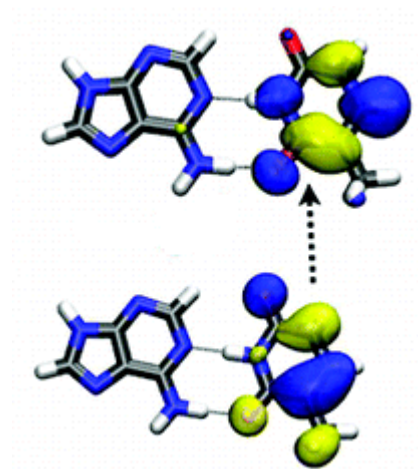
Correct lowest excitation in the Adenine-Thymine base pair using range-separated functionals

Excitations energies in the oligoporphyrin dimer

Optical properties of silver clusters

Hands-On Exercises

```
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
```
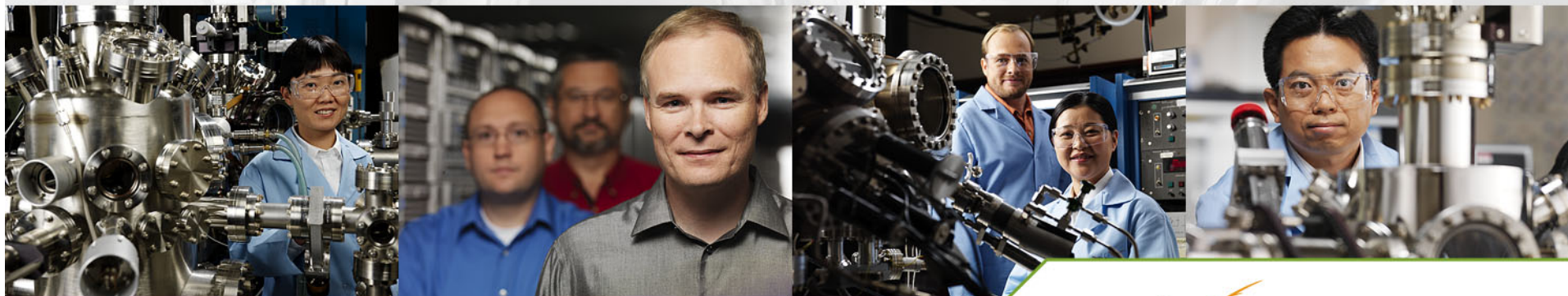
Questions?

www.**emsl**.pnl.gov

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
  - …

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

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

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

$$F_{\mu\nu} = H^{core}_{\mu\nu} + G^J_{\mu\nu} + \alpha G^K_{\mu\nu} + \beta G^{X-DFT}_{\mu\nu} + \gamma G^{C-DFT}_{\mu\nu}$$

$$G^J_{\mu\nu} = \sum_{\sigma\tau} (\mu\nu \mid \sigma\tau) D_{\sigma\tau}$$

$$G^K_{\mu\nu} = -\tfrac{1}{2} \sum_{\sigma\tau} (\mu\tau \mid \sigma\nu) D_{\sigma\tau}$$

$$G^{y-DFT}_{\mu\nu} = \int \sum_{\xi \in \{\rho_\alpha, \rho_\beta, |\nabla\rho_\alpha|, |\nabla\rho_\beta|, \nabla\rho_\alpha \bullet \nabla\rho_\beta, \ldots\}} \frac{\partial f^y}{\partial \xi} \frac{\partial \xi}{\partial D_{\mu\nu}} \mathrm{d}\mathbf{r}$$

- 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

Modern Quantum Chemistry, Ostlund & Szabo

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