Hartree-Fock

- 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
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
任务 scf optimize

scf; uhf; end
任务 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
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

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
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
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
  ```

- Unrestricted 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)

```plaintext
geometry; ne 0 0 0; end
basis; ne library cc-pvdz; end
```

- 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](https://bse.pnl.gov/bse/portal)
Changing the exchange-correlation

```plaintext
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

... 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**

```plaintext
dft
  grid fine
  convergence energy 1e-08
  xc b3lyp #B3LYP
  mult 1
end
```

**TRIPLET**

```plaintext
dft
  odft
  grid fine
  convergence energy 1e-08
  xc b3lyp #B3LYP
  mult 3
end
```
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 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

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
```
echo
start silane

permanent_dir /home/yourname/silane/b3lyp
scratch_dir /scratch

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. 27 1787 (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

Other Capabilities

- **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 $N^4 \rightarrow N^3$)

```plaintext
game; ne 0 0 0; end

basis "ao basis"
  ne library "DZVP (DFT orbital)"
end

basis "cd basis"
  ne library "DGauss Al DFT Coulomb Fitting"
end

task dft
```
Effective Core Potentials

- Reduces the cost of calculation for heavy elements
  - Additional input field required to define potential

```plaintext
gameometry; 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)

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:
  ```plaintext
  convergence lshift 0.1 damp 40 diis 5
  ```
- When invoked can be by iteration count
  ```plaintext
  convergence ncydp 5
  ```
- or by change in total energy
  ```plaintext
  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
Time-Dependent DFT

Casida Formulation

Perturbed density → first-order correction
Linear response approach → frequency domain

Working equations have $M = N_{\text{occ}} N_{\text{virt}}$ solutions
Dimension → tetradic $(M \times M)$
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


Cannot be used to describe excitations in intense fields
Excited State Calculations with TDDFT

gamma
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)

<table>
<thead>
<tr>
<th>Transition Moments</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.00000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>-0.26890</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>0.00000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Transition Moments

Dipole Oscillator Strength

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

Root 2 singlet a2 0.369097477 a.u. (10.0436576 eV)

<table>
<thead>
<tr>
<th>Transition Moments</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.00000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>0.00000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>0.00000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Transition Moments

Dipole Oscillator Strength

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$_2$ 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
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**
EXTRA MATERIAL
The energy expression is derived from a single determinant wave function approximation.

Replace the exchange with an 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

\[ \varphi_i = \sum_\mu C_{\mu i} \phi_\mu (r) \]

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

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

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

\[ G^J_{\mu \nu} = \sum_{\sigma \tau} (\mu \nu | \sigma \tau) D_{\sigma \tau} \]

\[ G^K_{\mu \nu} = -\frac{1}{2} \sum_{\sigma \tau} (\mu \tau | \sigma \nu) D_{\sigma \tau} \]

\[ G^{Y\text{-DFT}}_{\mu \nu} = \int \sum_{\xi \in \{ \rho_\alpha \rho_\beta | \rho_\alpha \rho_\beta \}} \frac{\partial f^{\gamma}}{\partial \xi} \frac{\partial \xi}{\partial D_{\mu \nu}} dr \]

- 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 \( \varepsilon_i \)

*Modern Quantum Chemistry, Ostlund & Szabo*