# Basis Sets, SCF and DFT

**Roland Lindh**

*Department of Chemical Physics*

*Chemical Center*

*Lund University*

*Sweden*

April 18, 2006

# Overview

- Basis sets
- SCF
- DFT

# Basis Sets

- Segmented basis sets (STO-3G, 6-31G, etc.)
- Generally contracted basis sets (ANO-type)
- Cartesian v.s. Real Spherical Harmonics (6-31G family)
- Effective Core Potentials (Huzinaga)
- Pseudo Potentials

# Format of Input

```
&Seward &End
...
Basis set
BasisSetLabel
AtomLabel xyz-coordinates [Angstrom]
...
End of Basis

Basis set
...
End of Basis

End of Input
```

```
&Seward &End
...
Basis set
H.STO-3G....
H1 1.44 0.0 0.0
H2 0.0 0.0 0.0
End of Basis

Basis set
...
End of Basis

End of Input
```

# The $MOLCAS/basis_library directory

| | | | | |
|---|---|---|---|---|
| 3-21G | ANO-RCC | basistype.tbl | ECP.HW | QRPLIB |
| 4-31G | ANO-RCC.README | CC-PVDZ | ECP.PAUL | RAF-R |
| 6-31G | ANO-S | CC-PVQZ | ECP.STOLL | STO-3G |
| 6-31Gp | AUG-CC-PVDZ | CC-PVTZ | ECP.TOUL | TOULBAS |
| 6-31Gpp | AUG-CC-PVTZ | ECP | ECP.TSUC | trans.tbl |
| ANO-DK3 | AUX-CC-PVDZ | ECP.DOLG | EGP | |
| ANO-L | basis.tbl | ECP.HAY-WADT | POL | |

# Special file basis.tbl

| | |
|---|---|
| H.ANO-S-MB | H.ANO-S...1s. |
| H.ANO-S-VDZ | H.ANO-S...2s. |
| H.ANO-S-VDZP | H.ANO-S...2s1p. |
| H.ANO-S-VTZP | H.ANO-S...3s2p1d. |
| He.ANO-S-MB | He.ANO-S...1s. |
| He.ANO-S-VDZ | He.ANO-S...2s. |
| He.ANO-S-VDZP | He.ANO-S...2s1p. |
| ... | |

# Special file basistype.tbl

```
#                    1      2      3      4
# ------------    ---    ---    ---    ---
3-21G              SEG    AE_    NRH
4-31G              SEG    AE_    NRH
6-31G              SEG    AE_    NRH
6-31Gp             SEG    AE_    NRH
6-31Gpp            SEG    AE_    NRH
ANO-DK3            RAF    AE_    RH_
ANO-L              ANO    AE_    NRH
ANO-RCC            ANO    AE_    RH_
...
```

# Special file trans.tbl

```
# this file defines aliases for basis set files
# if file with basis set is not found, seward will use alias
# Format:
#Basis_name Alias(real file)
#6-31G*    6-31Gp
#
6-31G*  6-31Gp
6-31G** 6-31Gpp
```

# Notes on basis functions

- PNNL Gaussian Basis Set Order Form
- Be careful with the basis sets in relativistic calculations!
- Cartesian or Spherical Harmonic?

# SCF

- RHF
- Open-Shell RHF
- Conventional
- Direct SCF
- Semi-Direct SCF
- Parallel

# Format of Input

| | |
|---|---|
| &SCF &End | |
| UHF | For Open-Shell RHF |
| | |
| Occupation | Explicit occupation |
| ..... | Alpha orbital occupation |
| ..... | Beta orbital occupation |
| | |
| Charge | Specify total molecular charge |
| n m | used together with ZSPIN |
| | |
| AufBau | Use AufBau |
| n m | |
| | |
| End of Input | |

# Notes on SCF

- UHF has poorer convergence as compared to RHF.
- Use GuessOrb to generate starting orbitals.
- For large molecules "Core Orbitals" are very poor starting orbitals.
- For large molecules use direct or semi-direct methods.
-

# DFT

- DFT is computed with the SCF module.
- Other optimization methods might be used.
- Poorer convergence as compared to SCF.

# Format of Input

&SCF &End

.....

KSDFT

FunctionalName

.....

End of Input

# Functionals

- LDA
- BLYP
- B3LYP
- More functional to come ...

# Numerical Grids

- Standard radial grids (LOG3, Becke, MHL, and TA)
- LGM radial grid
- Angular grid Lebedev
- Standard grids: Coarse, Fine, Ultra
- Grids a la CADPAC
- Standard prunning techniques.

# More Numerical Grids ...

- Accuracy with standard grids is 1.0D-4 au.
- The heavier atom the poorer.
- Be careful! Check!
- Accurate grids are VERY expensive!

# Accuracy: H2O

```
Coarse:
      Integrated DFT Energy                          -7.5228259608
      Integrated number of electrons                  9.9985554264
      Total number of prunned grid points                 3546
Fine:
      Integrated DFT Energy                          -7.5232850369
      Integrated number of electrons                  9.9999999639
      Total number of prunned grid points                32054
```