TEXAS A&M HIGH PERFORMANCE RESEARCH COMPUTING

Introduction to Quantum Mechanics Short Course

Lecture 2 of 6

TEXAS A&M UNIVERSITY

Division of Research

Quantum Mechanics

Time-independent Schrödinger Equation

$$\hat{H}\psi = E\psi$$

$\hat{H}$ Hamiltonian Operator

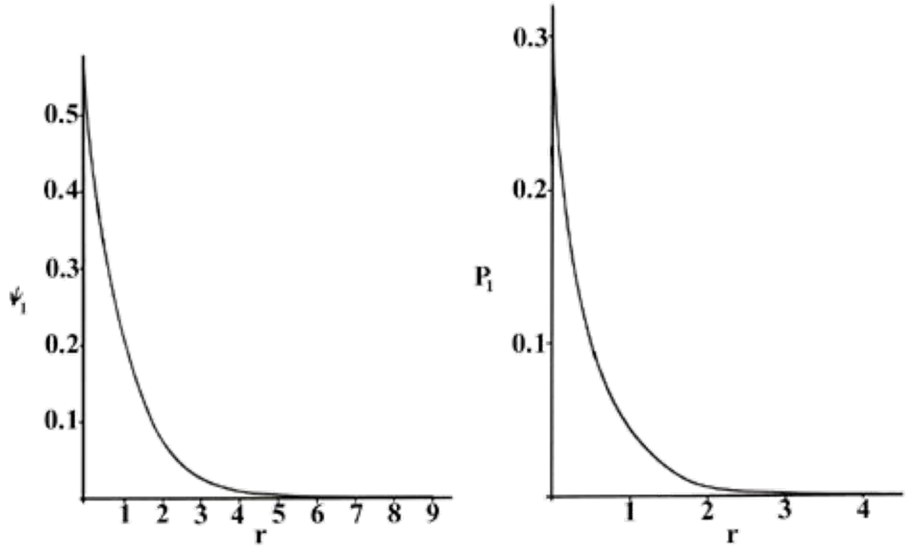
ψ Wavefunction (eigenfunction)

E Energy of the system (eigenvalue)

Linear Combination of Atomic Orbitals (LCAO)

$$\chi_i = \sum_{s=1}^{b} C_{si}\phi_s \quad where, \quad \phi_s = R_{nl}(r)Y_l^m(\theta,\phi)$$

c_i = Molecular Orbital of electron i
C_{si} = Atomic Orbital (AO) coefficient
R_{nl} = Radial component to the atomic orbital
Y_l^m = Angular component to the atomic orbital
n = principle quantum number n = 1, 2, 3,...
l = azimuthal quantum number l = 0, 1, .. n-1
m = magnetic quantum number m = -l, ... , 0, ... , l



Slater Type Orbital (STO) $\phi_s = Nr^{n-1}e^{-\varsigma r}Y_l^m(\theta,\phi)$

Gaussian Type Orbital (GTO) $\phi_s = Nr^{(2n-2-l)}e^{-\varsigma r^2}Y_l^m(\theta,\phi)$

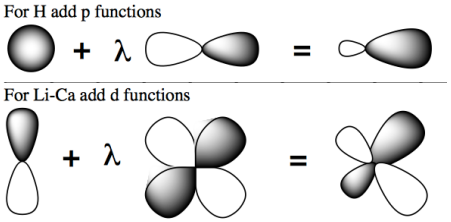
http://winter.group.shef.ac.uk/orbitron

Basis Set Terminology

- Single-ζ (SZ) Each AO is described by 1 STO
- Double-ζ (DZ) Each AO is described by 2 STO
- Triple-ζ (TZ) Each AO is described by 3 STO
- etc
- 3 GTO's are needed to adequately describe 1 STO
- Single-ζ (SZ) Each AO is described by 3 GTO
- Double-ζ (DZ) Each AO is described by 6 GTO
- Triple-ζ (TZ) Each AO is described by 9 GTO
- etc

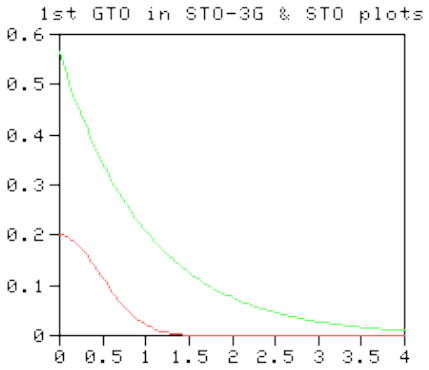
Polarization and Diffuse Functions

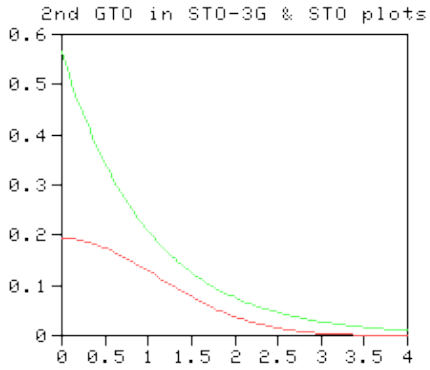
- Polarization Function – Higher angular momentum function than occupied. For example, a d function added to the C atom basis set would be a polarization function since C only has S and P orbitals occupied.
  - Important to allow the molecular orbitals to change shape.

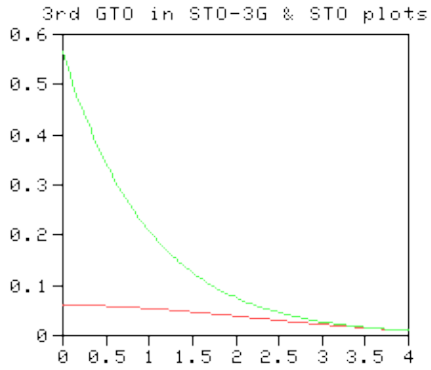


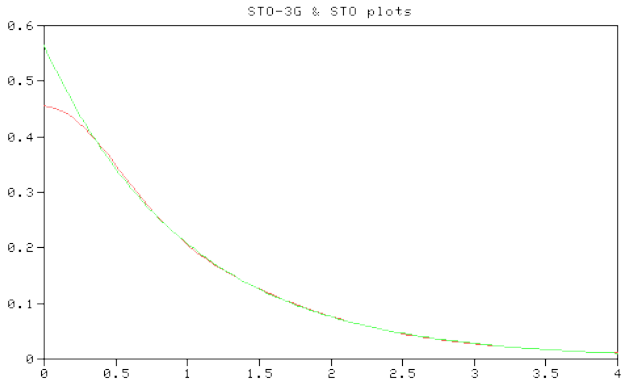
- Diffuse Function – Functions with small exponents (ζ)
  - Important for anions, NMR, excited states, and any calculation where a good description of the wavefunction far from the nucleus is important.

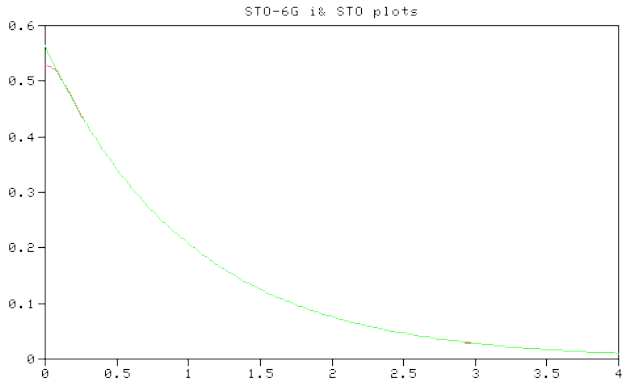
$H\psi_{1s}$ orbital plot - STO vs. GTO











http://hydra.vcp.monash.edu.au/modules/mod8/gtos.html

STO-3G for C atom

```
Standard basis: STO-3G (5D, 7F)
 1 0
S   3 1.00         .000000000000                          5 basis functions
    .7161683735E+02ζa1 .1543289673E+00ca1                 15 primitive gaussians
A   .1304509632E+02ζa2 .5353281423E+00ca2
    .3530512160E+01ζa3 .4446345422E+00ca3
SP   3 1.00         .000000000000
    .2941249355E+01ζb1 ζc1 ζd1 ζe1-.9996722919E-01cb1 .1559162750E+00 cc1 cd1 ce1
B   .6834830964E+00ζb2 ζc2 ζd2 ζe2 .3995128261E+00cb2 .6076837186E+00 cc2 cd2 ce2   } C,D,E
    .2222899159E+00ζb3 ζc3 ζd3 ζe3 .7001154689E+00cb3 .3919573931E+00 cc3 cd3 ce3
****
```

Exponent - ζ (s)(P_x, P_y, P_z) Coefficient Coefficient (P_x, P_y, P_z)

$$A\sum_{i=1}^{3} c_{ai} e^{-\zeta_{ai} r^2} + B\sum_{i=1}^{3} c_{bi} e^{-\zeta_{bi} r^2} + C\sum_{i=1}^{3} c_{ci} e^{-\zeta_{ci} r^2} + D\sum_{i=1}^{3} c_{di} e^{-\zeta_{di} r^2} + E\sum_{i=1}^{3} c_{ei} e^{-\zeta_{ei} r^2}$$

A=1

$$1(0.1543289673e^{-0.7161683735E+02r^2} + .5353281423e^{-0.1304509632E+02r^2} + 0.4446345422e^{-0.3530512160E+01r^2})$$

3-21G for C atom

```
Standard basis: 3-21G (6D, 7F)
 1 0
S   3 1.00         .000000000000
A  .1722560000E+03ζa1 .6176690738E-01ca1
   .2591090000E+02ζa2 .3587940429E+00ca2
   .5533350000E+01ζa3 .7007130837E+00ca3
SP   2 1.00         .000000000000
B  .3664980000E+01ζb1 ζc1 ζd1 ζe1-.3958951621E+00 cb1 .2364599466E+00 cc1 cd1 ce1   } C,D,E
   .7705450000E+00ζb2 ζc2 ζd2 ζe2 .1215834356E+01 cb2 .8606188057E+00 cc2 cd2 ce2   }
SP   1 1.00         .000000000000
F  .1958570000E+00ζf1 ζg1 ζh1 ζi1  .1000000000E+01 cf1 .1000000000E+01 cg1 ch2 ci1 } G,H,I
****
```

9 basis functions
15 primitive gaussians

Exponent - ζ (s)(P_x, P_y, P_z) Coefficient (s) Coefficient (P_x, P_y, P_z)

$$A\sum_{i=1}^{3} c_{ai}e^{-\varsigma_{ai}r^2} + B\sum_{i=1}^{2} c_{bi}e^{-\varsigma_{bi}r^2} + C\sum_{i=1}^{2} c_{ci}e^{-\varsigma_{ci}r^2} + D\sum_{i=1}^{2} c_{di}e^{-\varsigma_{di}r^2}$$

$$+E\sum_{i=1}^{2} c_{ei}e^{-\varsigma_{ei}r^2} + Fc_{f1}e^{-\varsigma_{f1}r^2} + Gc_{g1}e^{-\varsigma_{g1}r^2} + Hc_{h1}e^{-\varsigma_{h1}r^2} + Ic_{i1}e^{-\varsigma_{i1}r^2}$$

6-31G for C atom

```
Standard basis: 6-31G (6D, 7F)
 AO basis set in the form of general basis input:
  1 0
S   6 1.00         .000000000000
     .3047524880E+04    .1834737132E-02
     .4573695180E+03    .1403732281E-01
     .1039486850E+03    .6884262226E-01
     .2921015530E+02    .2321844432E+00
     .9286662960E+01    .4679413484E+00
     .3163926960E+01    .3623119853E+00
SP   3 1.00         .000000000000
     .7868272350E+01   -.1193324198E+00    .6899906659E-01
     .1881288540E+01   -.1608541517E+00    .3164239610E+00
     .5442492580E+00    .1143456438E+01    .7443082909E+00
SP   1 1.00         .000000000000
     .1687144782E+00    .1000000000E+01    .1000000000E+01
****
```

A

B

F

9 basis functions,
22 primitive gaussians

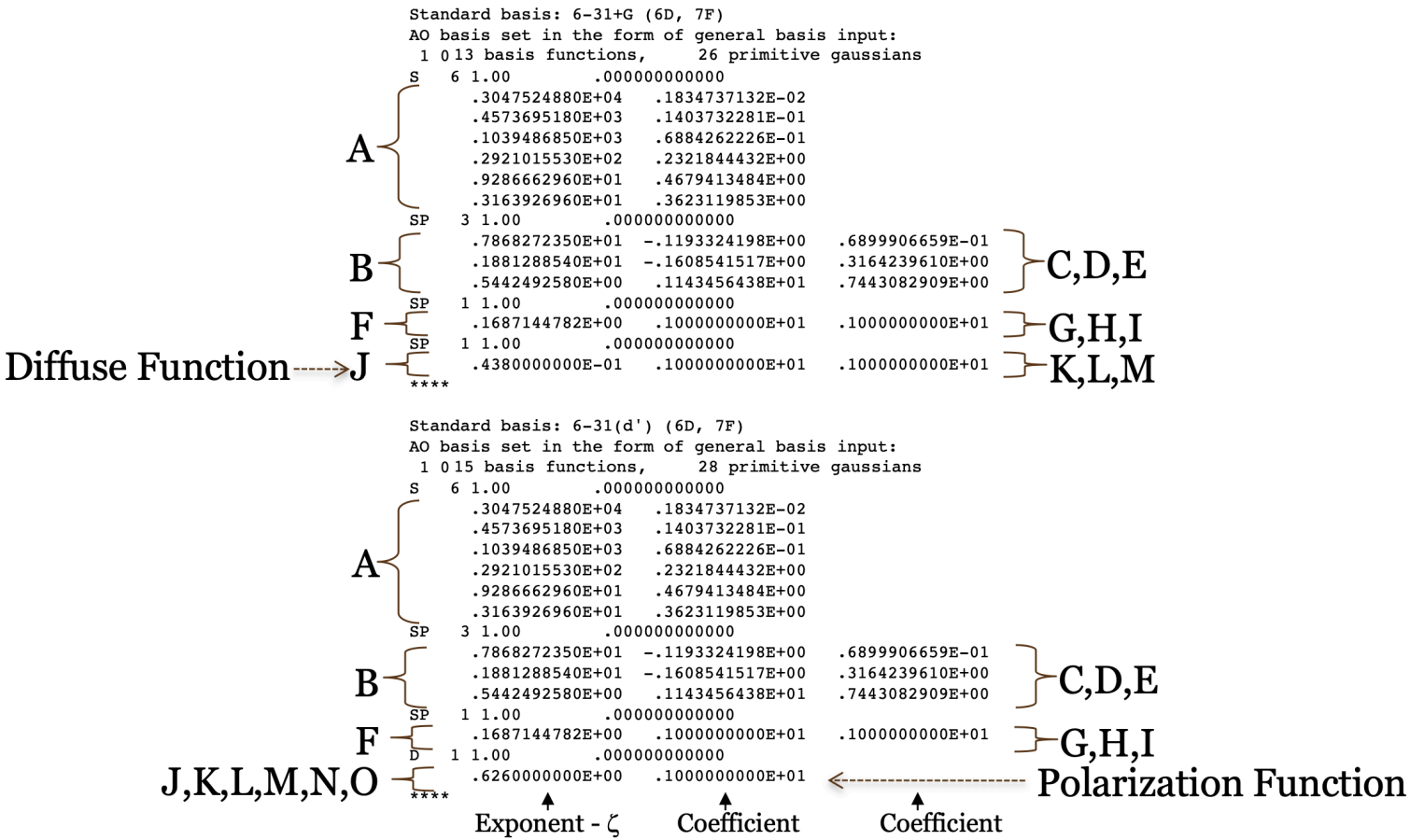
C,D,E

G,H,I

$$A\sum_{i=1}^{6} c_{ai} e^{-\varsigma_{ai} r^2} + B\sum_{i=1}^{3} c_{bi} e^{-\varsigma_{bi} r^2} + C\sum_{i=1}^{3} c_{ci} e^{-\varsigma_{ci} r^2} + D\sum_{i=1}^{3} c_{di} e^{-\varsigma_{di} r^2}$$

$$+E\sum_{i=1}^{3} c_{ei} e^{-\varsigma_{ei} r^2} + Fc_{f1} e^{-\varsigma_{f1} r^2} + Gc_{g1} e^{-\varsigma_{g1} r^2} + Hc_{h1} e^{-\varsigma_{h1} r^2} + Ic_{i1} e^{-\varsigma_{i1} r^2}$$

6-31+G and 6-31G(d') for C atom



```
AO basis set in the form of general basis input (Overlap normalization):
      1 0
S    3 1.00         0.000000000000
      0.3386500000D+02   0.2549381454D-01
  A   0.5094790000D+01   0.1903731086D+00
      0.1158790000D+01   0.8521614860D+00
S    1 1.00         0.000000000000
  B   0.3258400000D+00   0.1000000000D+01
S    1 1.00         0.000000000000
  C   0.1027410000D+00   0.1000000000D+01
S    1 1.00         0.000000000000
  D   0.3600000000D-01   0.1000000000D+01
P    1 1.00         0.000000000000
E,F,G 0.7500000000D+00   0.1000000000D+01
****
      2 0
S    3 1.00         0.000000000000
      0.3386500000D+02   0.2549381454D-01
  H   0.5094790000D+01   0.1903731086D+00
      0.1158790000D+01   0.8521614860D+00
S    1 1.00         0.000000000000
  I   0.3258400000D+00   0.1000000000D+01
S    1 1.00         0.000000000000
  J   0.1027410000D+00   0.1000000000D+01
S    1 1.00         0.000000000000
  K   0.3600000000D-01   0.1000000000D+01
P    1 1.00         0.000000000000
L,M,N 0.7500000000D+00   0.1000000000D+01
**** exponents    coefficients
```

311 split for the valence e⁻ of atom 1

6-311++G(d,p)

Diffuse function for atom 1

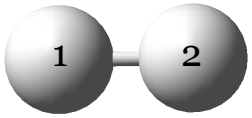
Polarization function for atom 1

311 split for the valence e⁻ of atom 2

Diffuse function for atom 2

Polarization function for atom 2

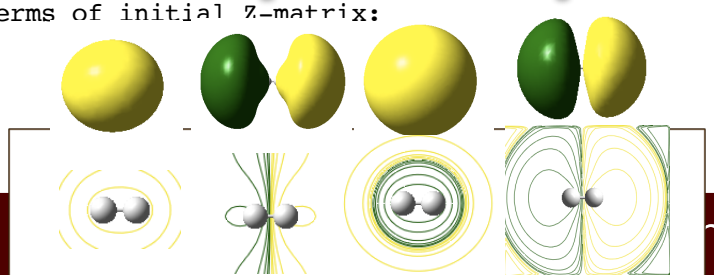
```
There are     5 symmetry adapted basis functions of AG  symmetry.
There are     0 symmetry adapted basis functions of B1G symmetry.
There are     1 symmetry adapted basis functions of B2G symmetry.
There are     1 symmetry adapted basis functions of B3G symmetry.
There are     0 symmetry adapted basis functions of AU  symmetry.
There are     5 symmetry adapted basis functions of B1U symmetry.
There are     1 symmetry adapted basis functions of B2U symmetry.
There are     1 symmetry adapted basis functions of B3U symmetry.
Integral buffers will be    131072 words long.
Raffenetti 1 integral format.
Two-electron integral symmetry is turned on.
  14 basis functions,    18 primitive gaussians,    14 cartesian basis functions
   1 alpha electrons        1 beta electrons
      nuclear repulsion energy         0.7559674408 Hartrees.
```



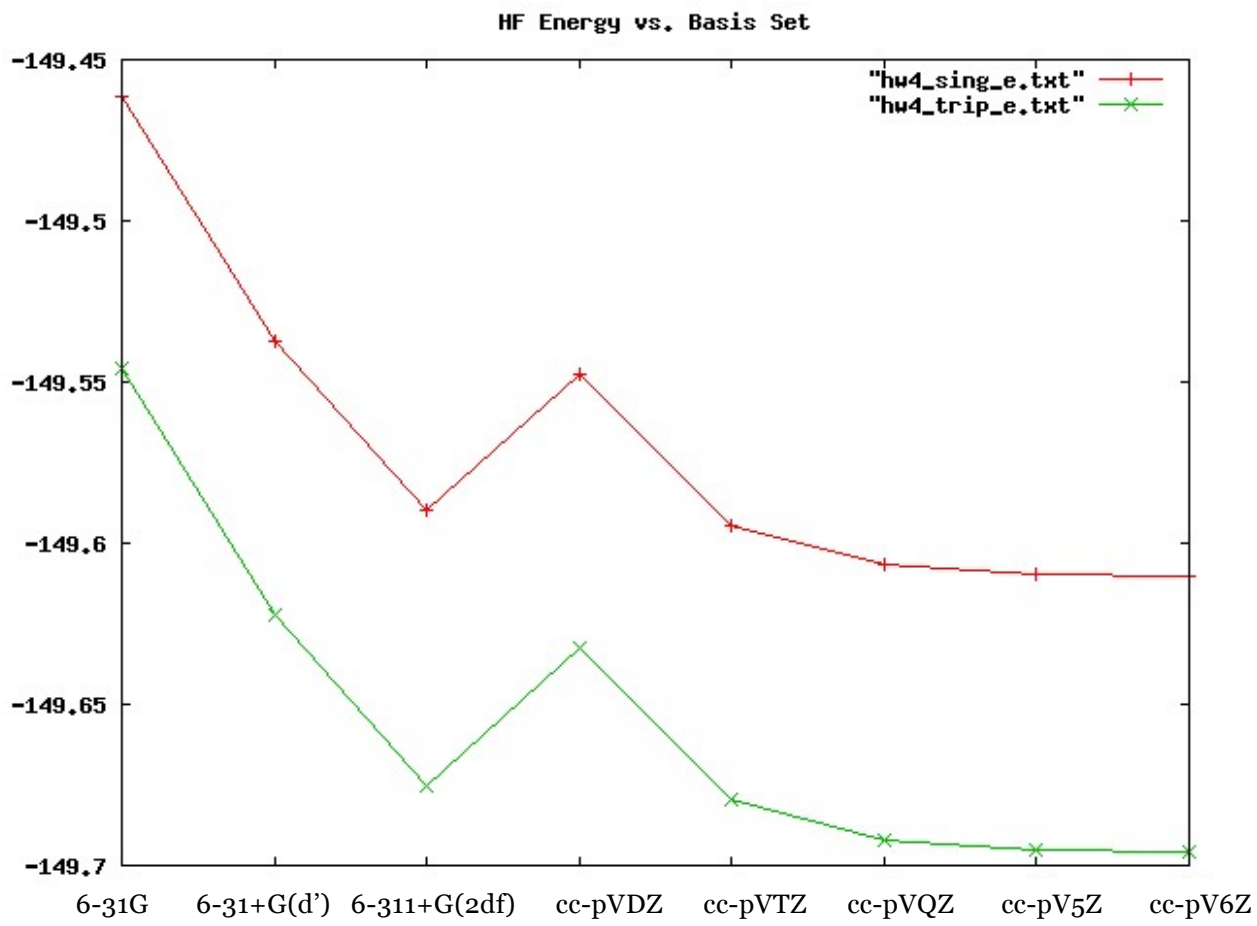
H-H starting distance
B1=0.7

```
Orbital symmetries:
       Occupied  (SGG)
       Virtual   (SGU) (SGG) (SGU) (SGG) (SGU) (PIU) (PIU) (SGG)
                 (PIG) (PIG) (SGU) (SGG) (SGU)
 The electronic state is 1-SGG.
 Alpha  occ. eigenvalues --   -0.59612
 Alpha virt. eigenvalues --    0.07148   0.07315   0.24231   0.45499   0.73347
 Alpha virt. eigenvalues --    1.33317   1.33317   1.88214   2.10212   2.10212
 Alpha virt. eigenvalues --    2.29713   2.81822   3.71362
    Molecular Orbital Coefficients:
                           1         2         3         4         5
                       (SGG)--O  (SGU)--V  (SGG)--V  (SGU)--V  (SGG)--V
     Eigenvalues --    -0.59612   0.07148   0.07315   0.24231   0.45499
   1 1   H  1S          0.18646   0.01450  -0.05296  -0.08372  -0.05201  A
   2        2S          0.28601   0.17905   0.02887   0.18299  -0.88659  B
   3        3S          0.13700  -0.56036  -0.54517  -3.37801   1.49340  C
   4        4S         -0.00402   4.33309   0.84253   3.73070  -0.66680  D
   5        5PX         0.00000   0.00000   0.00000   0.00000   0.00000  E
   6        5PY         0.00000   0.00000   0.00000   0.00000   0.00000  F
   7        5PZ        -0.02292  -0.01209   0.01158  -0.07579   0.00280  G
   8 2   H  1S          0.18646  -0.01450  -0.05296   0.08372  -0.05201  H
   9        2S          0.28601  -0.17905   0.02887  -0.18299  -0.88659  I
  10        3S          0.13700   0.56036  -0.54517   3.37801   1.49340  J
  11        4S         -0.00402  -4.33309   0.84253  -3.73070  -0.66680  K
  12        5PX         0.00000   0.00000   0.00000   0.00000   0.00000  L
  13        5PY         0.00000   0.00000   0.00000   0.00000   0.00000  M
  14        5PZ         0.02292  -0.01209  -0.01158  -0.07579  -0.00280  N
          ⋮                   ⋮         ⋮         ⋮
Final structure in terms of initial Z-matrix:
 H
 H,1,B1
      Variables:
 B1=0.73523289
```

orbitals after optimization



O_2


HF Energy vs. Basis Set
"hw4_sing_e.txt"
"hw4_trip_e.txt"
-149.45
-149.5
-149.55
-149.6
-149.65
-149.7
6-31G
6-31+G(d')
6-311+G(2df)
cc-pVDZ
cc-pVTZ
cc-pVQZ
cc-pV5Z
cc-pV6Z

Effective Core Potentials (ECP)

Assume that the core e^- are not important for reactivity and chemical properties.
Core e^- are not treated explicitly:

$$U_{ECP}(r) = \sum_i a_i r^{ni} e^{-\alpha_i r^2}$$

ECP's normally include the contraction of the inner orbitals due to relativistic effects

Large Core ECP for Pb has 78 e^- in the core and 4 e^- in the valence
Core: 1s 2s 3s 4s 5s 2p 3p 4p 5p 3d 4d 5d and 4f
Valence: 6s and 6p

Small Core ECP for Pb has 68 e^- in the core and 14 e^- in the valence
Core: 1s 2s 3s 4s 5s 2p 3p 4p 5p 3d 4d and 4f
Valence: 6s 6p and 5d

Small Core ECP for Pb has 60 e^- in the core and 22 e^- in the valence
Core: 1s 2s 3s 4s 2p 3p 4p 3d 4d and 4f
Valence: 5s 6s 5p 6p and 5d

All electron Transition Metal Basis Sets

All electron Pople-style basis sets are available for 1st row transition metals

Note:

- 6-31G* basis set is deficient
- 6-31+G* the + adds an essential p function to adequately describe the metal. It is not a diffuse function.

Basis Set Resources

- Basis Set Exchange
  - https://bse.pnl.gov/bse/portal
- Stuttgart-Cologne
  - http://www.theochem.uni-stuttgart.de/pseudopotentials/index.en.html
- Correlation Consistent Basis Sets
  - http://tyr0.chem.wsu.edu/~kipeters/basis.html

Energies

- Absolute energies are not accurate due to the approximations that are made to solve the Schrödinger equation.
- Relative energies have a cancellation of errors to give more accurate results.
- To calculate relative energies, you must use the same Hamiltonian and mathematical description of ψ (basis set):
  $\Delta H^{o}_{rxn} = H^{o}_{prod} - H^{o}_{reac}$
  - H^{o}_{prod} and H^{o}_{reac} must be calculated at the same level of theory with the same basis set.