Density Functional Theory and Property Calculation

Keywords: Density functional theory, DFT, Exchange functional, Correlation functional, Hybrid functional.

Density Functional Theory (DFT)

Density functional theory (DFT) is a quantum chemical method to study electronic structure of many electron systems. With this theory, the properties of a many-body system can be determined by using functional, i.e. function of a function, which is the spatially dependent electron density, ρ in the present case. Off late, DFT is among the most popular methods available in computational chemistry due to low computational cost and good accuracy. The basis of DFT is due to Hohenberg and Kohn who demonstrated that the ground state electronic energy can be determined completely by electron density. At present, several types of DFT functionals are available in the literature e.g., local, pure exchange, pure correlation, hybrid and long range corrected functionals. GAMESS is fairly up to date with the availability of these functionals. For large systems (with large number of total electrons), post-Hartree Fock methods (MP2, CC, CI) may not be practical as it takes more CPU time compared to the most of the DFT functionals. Let us discuss an example of INPUT file for DFT based calculation considering a popular hybrid DFT functional, namely, B3LYP for geometry optimization. The following INPUT is same as the previous examples for geometry optimization with extra keyword for DFT calculations.

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```
$SYSTEM TIMLIM=600.0 MWORDS=10 MEMDDI=40 $END
$CONTRL SCFTYP=RHF ICHARG=0 MULT=1 RUNTYP=OPTIMIZE DFTYP=B3LYP COORD=ZMT $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=1 $END
$DATA
Water-Geometry // B3LYP/6-31G(d,p)
CN 1

O
H   1   roh
H   1   roh   2   ahoh

roh=1.08
ahoh=109.5
$END
```

****

Note that in 'CONTRL' group, keyword 'DFTYP=B3LYP' is added for DFT calculations with B3LYP hybrid functional, in which B3 refers to exchange functional combining Becke + Slater + HF exchange and LYP refers to Lee-Yang-Parr correlation functional. With the same geometrical 'INPUT' parameters, the final optimized geometry and energy components of neutral H_2O molecule are as follows.

```
     ***** EQUILIBRIUM GEOMETRY LOCATED *****
COORDINATES OF ALL ATOMS ARE (ANGS)
  ATOM   CHARGE       X              Y              Z
------------------------------------------------------------
O           8.0  -0.0000000117  -0.0665358838   0.0000000000
H           1.0   0.7696177999   0.5164869335   0.0000000000
H           1.0  -0.7696177882   0.5164869242   0.0000000000

THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
O
H      1   0.9655191
H      1   0.9655191  2   105.7086105
```

These are the final geometrical parameters

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          -----------------------
          B3LYP ENERGY COMPONENTS
          -----------------------

        WAVEFUNCTION NORMALIZATION =       1.0000000000

             ONE ELECTRON ENERGY =    -122.7836354144
             TWO ELECTRON ENERGY =      37.2735602822
          NUCLEAR REPULSION ENERGY =       9.1129982681
                                    ------------------
                      TOTAL ENERGY =     -76.3970768640

ELECTRON-ELECTRON POTENTIAL ENERGY =      37.2735602822
 NUCLEUS-ELECTRON POTENTIAL ENERGY =    -198.5107433533
  NUCLEUS-NUCLEUS POTENTIAL ENERGY =       9.1129982681
                                    ------------------
            TOTAL POTENTIAL ENERGY =    -152.1241848029
              TOTAL KINETIC ENERGY =      75.7271079389
                VIRIAL RATIO (V/T) =       2.0088471479
```

Comparison of geometrical parameters of neutral H_2O obtained at different levels of theory with 6-31++G(d,p) basis set

Geometrical Parameter	Theoretical Method		
	RHF	MP2	B3LYP
rOH (Å)	0.9431015	0.9634000	0.9655191
<HOH (degree)	105.9642013	105.3549308	105.7086105

One can easily observe that equilibrium bond length and bond angle of the neutral water molecule calculated applying B3LYP DFT functional is very close to MP2 results. Computational cost in these two methods is not significantly different for such a small molecule. However, for large molecular systems the cost will be significantly different restricting application of MP2 procedure only for small systems. Let us now examine how this particular functional performs on charged (mono positive and mono negative) H_2O molecule. Final geometry and energy parameters of charged water system are as follows.

Negatively charged water molecule (ROHF reference wave function):

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```
     ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O           8.0   0.0000000552  -0.0847237491   0.0000000000
 H           1.0   0.7675735548   0.5255808371   0.0000000000
 H           1.0  -0.7675736100   0.5255808859   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   0.9806328
 H      1   0.9806330  2   103.0229530



           --------------------
           SPIN SZ   =    0.500
           S-SQUARED =    0.750
           --------------------


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           ROB3LYP ENERGY COMPONENTS
           -------------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

              ONE ELECTRON ENERGY =    -124.5237004566
              TWO ELECTRON ENERGY =      39.1748493087
       NUCLEAR REPULSION ENERGY =       8.9787602089
                                      ------------------
                     TOTAL ENERGY =     -76.3700909390

 ELECTRON-ELECTRON POTENTIAL ENERGY =      39.1748493087
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -200.2898208592
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       8.9787602089
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -152.1362113416
               TOTAL KINETIC ENERGY =      75.7661204026
                 VIRIAL RATIO (V/T) =       2.0079715120
```

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Positively charged water molecule (ROHF reference wave function):

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```
     ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O           8.0   0.0000000039  -0.0612183690   0.0000000000
 H           1.0   0.8290259972   0.5138281702   0.0000000000
 H           1.0  -0.8290260010   0.5138281727   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   1.0089413
 H      1   1.0089413  2   110.5064632


           --------------------
           SPIN SZ   =    0.500
           S-SQUARED =    0.750
           --------------------


           -------------------------
           ROB3LYP ENERGY COMPONENTS
           -------------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

               ONE ELECTRON ENERGY =    -117.3183844658
               TWO ELECTRON ENERGY =      32.6726654765
          NUCLEAR REPULSION ENERGY =       8.7109580224
                                     ------------------
                      TOTAL ENERGY =     -75.9347609669

 ELECTRON-ELECTRON POTENTIAL ENERGY =      32.6726654765
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -192.5966118012
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       8.7109580224
                                     ------------------
             TOTAL POTENTIAL ENERGY =    -151.2129883023
               TOTAL KINETIC ENERGY =      75.2782273354
                 VIRIAL RATIO (V/T) =       2.0087214279
```

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Comparison of geometrical parameters of negatively charged H_2O obtained at different levels of theory with 6-31++G(d,p) basis set

Geometrical Parameters	Theoretical Method		
	ROHF	ROMP2	ROB3LYP
rOH (Å)	1.0230599	0.9764838	**0.9806328** (0.9704752)†
<HOH (degree)	101.2013445	102.2028330	**103.0229530** (107.6046060)†

†Values in parentheses are calculated with 'UHF' reference wave function.

The above Table clearly suggests that the geometrical parameters calculated at three different levels of theory are significantly different; B3LYP results are close to MP2 results though. Moreover, DFT result on bond angle with UHF reference wave function (SCFTYP=UHF in 'CONTRL'group of INPUT file) on this open shell doublet water anion system is largely different than that with ROHF reference wave function. In the later part, results from a few other DFT functionals will also be compared with the MP2 results. Geometrical parameters calculated at three different levels of theory on mono positively charged water molecule are listed below. It is observed that HF results are quite off to MP2 results. However, geometrical parameters calculated applying B3LYP functional are very accurate compared to MP2 results. In fact the results with both the reference wave functions are pretty close.

Comparison of geometrical parameters of positively charged H_2O obtained at different levels of theory with 6-31++G(d,p) basis set

Geometrical Parameters	Theoretical Method		
	ROHF	ROMP2	ROB3LYP
rOH (Å)	0.9814971	1.0004924	**1.0089413** (1.0092708)†
<HOH (degree)	112.5821473	110.3008942	**110.5064632** (110.5123630)†

†Values in parentheses are calculated with 'UHF' reference wave function.

Before going to discuss other DFT functionals, let us discuss on calculated electron affinity (EA) and ionization potential (IP) values of H_2O molecule under gas phase isolated condition at these three different levels of theory. Calculated total energy values of neutral and charged (anion and cation) H_2O molecule at B3LYP level are supplied above (highlighted text). Applying the following definitions of EA and IP,

Electron affinity (EA) = Total energy (negatively charged) – Total energy (neutral),

Ionization potential (IP) = Total energy (positively charged) – Total energy (neutral),

the respective values are calculated at the present DFT level of theory (B3LYP) and listed in the following Table for comparison. Note that the available experimental values are 1.3 and 12.61 eV for EA and IP of water molecule in gas phase.

Comparison of calculated EA and IP values of H_2O at the three different levels of theory adopting 6-31++G(d,p) basis set

Calculated Parameters	Theoretical Method		
	ROHF	ROMP2	ROB3LYP
EA (eV)	5.40	0.93	0.73 (1.49)†
IP (eV)	10.88	12.48	11.84 (12.53)†

†Values in parentheses are calculated with 'UHF' reference wave function.

One may easily notice that B3LYP functional predicts EA and IP values which are midway between HF and post-HF MP2 values with reference ROHF wave function for the doublet open shell systems (anion and cation water molecule). When EA and IP values are calculated at B3LYP level of theory with the option in the INPUT file as SCFTYP=UHF in 'CONTRL'group for the charged open shell systems, the results are surprisingly better than MP2 and indeed very close to the experimental values.

Effect of basis functions

Note that all the above calculations are carried out adopting Gaussian type basis functions adding polarization and diffuse functions to it. There are basis sets those are able to recover correlation energy more accurately such as 'Dunning-type correlation consistent basis sets' expressed as cc-pVnZ (where n indicates level of polarization, n=D, T, Q etc for double, triple, quadruple zeta respectively). When a set of diffuse functions are augmented to it, it is denoted in literature as aug-cc-pVnZ. Let us examine the effect of basis sets on geometry and energy parameters.

The following INPUT is same as the previous example for geometry optimization of neutral water molecule applying B3LYP DFT functional with modified INPUT in 'BASIS' group.

```
********************

$SYSTEM TIMLIM=600.0 MWORDS=10 MEMDDI=40 $END
$CONTRL SCFTYP=RHF ICHARG=0 MULT=1 RUNTYP=OPTIMIZE DFTYP=B3LYP COORD=ZMT $END
#$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=1 $END
$BASIS GBASIS=ACCD $END
$DATA
Water-Geometry // B3LYP/6-31G(d,p)
CN 1

O
H   1   roh
H   1   roh   2   ahoh

roh=1.08
ahoh=109.5
$END

********************
```

Note that by putting a '#' mark at the beginning of the group, one may instruct the program GAMESS NOT to read that line. For the above written INPUT file, GAMESS is asked to run a geometry optimization job applying B3LYP DFT functional adopting 'GBASIS=ACCD' basis functions for all the atoms. GAMESS reads 'GBASIS=ACCD' as aug-cc-pVDZ basis set for all the atoms. The final optimized geometry and energy parameters calculated are as follows:

```
     ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O           8.0  -0.0000000080  -0.0706895569   0.0000000000
 H           1.0   0.7643405620   0.5185637688   0.0000000000
 H           1.0  -0.7643405539   0.5185637619   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   0.9651093
 H      1   0.9651093  2   104.7405605


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          B3LYP ENERGY COMPONENTS
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        WAVEFUNCTION NORMALIZATION =       1.0000000000

              ONE ELECTRON ENERGY =    -122.8202293135
              TWO ELECTRON ENERGY =      37.2935361107
         NUCLEAR REPULSION ENERGY =       9.1190955028
```

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                                        ------------------
                          TOTAL ENERGY =     -76.4075976999

  ELECTRON-ELECTRON POTENTIAL ENERGY =      37.2935361107
   NUCLEUS-ELECTRON POTENTIAL ENERGY =    -198.7795098581
    NUCLEUS-NUCLEUS POTENTIAL ENERGY =       9.1190955028
                                        ------------------
              TOTAL POTENTIAL ENERGY =    -152.3668782446
                TOTAL KINETIC ENERGY =      75.9592805446
                  VIRIAL RATIO (V/T) =       2.0059020722
```

Comparison of total energy and geometrical parameters of neutral H_2O calculated at B3LYP level of theory with two different basis sets

Parameter	Basis Set	
	6-31++G(d,p)	aug-cc-pVDZ
rOH (Å)	0.9655191	0.9651093
<HOH (degree)	105.7086105	104.7405605
Total Energy (au)	-76.3970768640	-76.4075976999

Note that for neutral H_2O molecule with 6-31++G(d,p) basis set, the total number of 'CARTESIAN GAUSSIAN BASIS FUNCTIONS' is 31 whereas the same is 43 when aug-cc-pVDZ basis set in considered. As a result, the computer time and disk space requirement to run the job adopting aug-cc-pVDZ basis set is much higher. So, for a very large system, one has to be careful on deciding suitable basis set compromising accuracy in result and computer time requirement. However, 'Dunning-type correlation consistent basis sets' with diffuse functions and double zeta polarization recovers more than 0.01 au extra correlation energy compared to the adopted Gaussian type basis functions in neutral water molecule. Similar calculations with negatively charged water molecule recovers more than 0.02 au extra correlation energy with Dunning-type correlation consistent basis sets + diffuse functions + double zeta polarization. However, for water cation it is calculated at ~ 0.01 au. Calculated EA and IP values of water molecule at B3LYP level of theory with this correlated basis set are 1.19 and 12.57 eV, respectively showing further improvement with respect to the experimental values.

It is worth to mention that for small size systems it is a general suggestion to use aug-cc-pVDZ basis set for geometry optimization and aug-cc-pVTZ basis set for single point energy calculation to improve energy parameters further.

Conclusions

Density functional Theory is applied to calculate structure and properties (electron affinity and ionization potential) of neutral and charged (cation and anion) water molecule. Effect of basis function on calculated properties is illustrated with example.