Post Hartree-Fock Theory and Property Calculation

Keywords: Many body perturbation theory, Moller-Plesset, couple cluster, configuration interaction, Post Hartree Fock

Post Hartree Fock Methods

In the last chapter, we have talked about a simple method to understand electron distribution in atoms and molecules known as Hartree-Fock (HF) theory. It is based on a particle independent model by taking all inter particle interactions into account in an average fashion, neglecting electron correlation. In this model, each electron is described by an orbital and the total wave function is given as a product of orbitals. The best set of orbitals is determined by the variational principle, i.e. the HF orbitals give the lowest energy within the restriction of the wave function being a single Slater determinant. In a sufficiently large basis set, the HF wave function is able to account for ~99% of the total energy. In order to calculate total energies of a molecular system with an accuracy of ~1 kcal/mol, it is necessary to use sophisticated methods for including electron correlation and large basis sets, which is computationally feasible only for small size systems. The difference in energy between the HF and the lowest possible energy applying a post-HF method in the given basis set is called the 'Electron Correlation' (EC) energy. Physically, it corresponds to the motion of the electrons being correlated resulting average inter particle distance to be more than that by the HF wave function.

Now we will move to examples where calculations are carried out applying post-HF electron correlated methods eg. many body perturbation theory (MBPT), couple cluster (CC) and configuration interaction (CI). At first, we take up an example to perform 'MBPT second order' calculations for geometry optimization of water molecule applying second order Moller-Plesset (MP2) correction.

Moller-Plesset (MP2)

The following INPUT is prepared for such a calculation. The input is essentially same as in case of HF calculations adding extra keyword for MP2 method.

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

$SYSTEM  TIMLIM=600.0  MWORDS=10  MEMDDI=40  $END
$CONTRL  SCFTYP=RHF  ICHARG=0  MULT=1  RUNTYP=OPTIMIZE  MPLEVL=2  COORD=ZMT  $END
$BASIS  GBASIS=N31  NGAUSS=6  NDFUNC=1  NPFUNC=1  DIFFSP=.T.  DIFFS=.T.  $END
$DATA
```

```
Water-Geometry // MP2/6-31G(d,p)
CN 1

O
H   1   roh
H   1   roh   2   ahoh

roh=1.08
ahoh=109.5
$END
********************
```

It will perform only HF calculations if MPLEVL=0 is supplied

The final optimized geometrical parameters calculated applying MP2 method with the same geometrical input parameters and basis set as in case of HF theory are as follows:

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

      ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O            8.0   0.0000000000  -0.0672610890   0.0000000000
 H            1.0   0.7661295166   0.5168495314   0.0000000000
 H            1.0  -0.7661295166   0.5168495314   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H       1    0.9634000
 H       1    0.9634000   2    105.3549308
```

These are the final geometrical parameters

```
          ---------------------
          MP2 ENERGY COMPONENTS
          ---------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

                ONE ELECTRON ENERGY =    -122.5342858206
                TWO ELECTRON ENERGY =      37.1670578500
           NUCLEAR REPULSION ENERGY =       9.1338520259
                                      ------------------
                       TOTAL ENERGY =     -76.2333759448

 ELECTRON-ELECTRON POTENTIAL ENERGY =      37.1670578500
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -198.3822671061
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       9.1338520259
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -152.0813572303
               TOTAL KINETIC ENERGY =      75.8479812854
                 VIRIAL RATIO (V/T) =       2.0050811459

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

To compare the calculated total energy of water molecule at HF and post-HF level of theory, energy components of neutral H_2O molecule based on RHF optimization adopting the atomic basis functions are given below. Note that the energy values are given in a.u. (**1 a.u. = 27.2114 eV = 627.5095 kcal/mol**).

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

          ---------------------
          RHF ENERGY COMPONENTS
          ---------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

                ONE ELECTRON ENERGY =    -123.3383142209
                TWO ELECTRON ENERGY =      37.9856765767
           NUCLEAR REPULSION ENERGY =       9.3290226296
                                      ------------------
                       TOTAL ENERGY =     -76.0236150146

 ELECTRON-ELECTRON POTENTIAL ENERGY =      37.9856765767
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -199.2027162181
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       9.3290226296
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -151.8880170118
               TOTAL KINETIC ENERGY =      75.8644019972
                 VIRIAL RATIO (V/T) =       2.0020986525

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

Thus, the calculated correlation energy of H_2O molecule at MP2 level of theory with 6-31++G(d,p) basis set is (Energy at MP2 level - Energy at HF level) = (-76.2333759448 + 76.0236150146) a.u.= -0.2097609302 a.u. = ~ -5.708 eV ~ -131.63 kcal/mol (final values are truncated according to accuracy level).

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

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

Note that for larger size systems, MP2 calculation will take significantly more time than HF procedure. Moreover, memory requirement will also be larger than HF calculation. So, one has to change the numbers given to 'SYSTEM' group in the input header. The appropriate numbers may be generated by a test run for a set of geometrical data INPUT.

So far, all calculations in the previous examples are carried out for a neutral molecule with closed shell electronic structure. We will now consider water molecule with odd number of electrons i.e. by adding an extra electron to the molecule thus making an anion and by removing an electron from the molecule thus making a cation. For such a system, Unrestricted Hartee Fock (UHF) method has to be applied in place of Restricted Hartee Fock (RHF). The following two INPUT examples are prepared to UHF calculations on water anion and water cation systems.

****

```
$SYSTEM  TIMLIM=600.0  MWORDS=10  MEMDDI=40  $END
$CONTRL  SCFTYP=UHF  ICHARG=-1  MULT=2  RUNTYP=OPTIMIZE  MPLEVL=0  COORD=ZMT  $END
$BASIS  GBASIS=N31  NGAUSS=6  NDFUNC=1  NPFUNC=1  DIFFSP=.T.  DIFFS=.T.  $END
$DATA
Water anion-Geometry // UHF/6-31G(d,p)
CN 1

O
H   1   roh
H   1   roh   2   ahoh

roh=1.08
ahoh=109.5
$END
```

****

Note the changes made for keywords 'SCFTYP', 'ICHARG' and 'MULT' in 'CONTRL' group for this negatively charged water molecule keeping rest of the input same as the neutral one. As the system is an odd electron system, one has to choose UHF for SCF calculations. The negative charge of the system is given through the keyword, 'ICHARG=-1' and multiplicity of this doublet (s=1/2, multiplicity=2s+1=2) system is supplied by keyword, 'MULT=2'. The next INPUT is meant for water cation system. Again, it's an odd electron system, thus 'SCFTYP=UHF and MULT=2' are supplied. The keyword, 'ICHARG=1' is given to consider the system as positively charged one.

****

```
$SYSTEM  TIMLIM=600.0  MWORDS=10  MEMDDI=40  $END
$CONTRL  SCFTYP=UHF  ICHARG=1  MULT=2  RUNTYP=OPTIMIZE MPLEVL=0 COORD=ZMT  $END
$BASIS  GBASIS=N31  NGAUSS=6  NDFUNC=1  NPFUNC=1  DIFFSP=.T.  DIFFS=.T.  $END
$DATA
Water anion-Geometry // UHF/6-31G(d,p)
CN 1
```

```
O
H   1   roh
H   1   roh   2   ahoh

roh=1.08
ahoh=109.5
$END

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

The final optimized geometrical parameters calculated applying UHF method with the same geometrical input parameters and basis set as in case of RHF method are as follows:

For water anion system (UHF):

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

      ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O           8.0   0.0000000000  -0.2233870621   0.0000000000
 H           1.0   0.8186920114   0.5841822048   0.0000000000
 H           1.0  -0.8186920114   0.5841822048   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   1.1499673
 H      1   1.1499673  2     90.7837318
```

These are the final geometrical parameters

```
          --------------------
          SPIN SZ   =     0.500
          S-SQUARED =     0.814
          --------------------

          ---------------------
          UHF ENERGY COMPONENTS
          ---------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

                ONE ELECTRON ENERGY =    -123.4975150138
                TWO ELECTRON ENERGY =      40.0633209235
           NUCLEAR REPULSION ENERGY =       7.6858601703
                                      ------------------
                       TOTAL ENERGY =     -75.7483339201

 ELECTRON-ELECTRON POTENTIAL ENERGY =      40.0633209235
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -199.3951512057
```

```
  NUCLEUS-NUCLEUS POTENTIAL ENERGY =        7.6858601703
                                     ------------------
            TOTAL POTENTIAL ENERGY =     -151.6459701119
              TOTAL KINETIC ENERGY =       75.8976361918
                VIRIAL RATIO (V/T) =        1.9980328469

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

For water cation system (UHF):

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

      ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O           8.0   0.0000000000  -0.2101249336   0.0000000000
 H           1.0   0.8173304842   0.3347446215   0.0000000000
 H           1.0  -0.8173304842   0.3347446215   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   0.9822993
 H      1   0.9822993  2    112.6215572
```

These are the final geometrical parameters

```
          --------------------
          SPIN SZ   =    0.500
          S-SQUARED =    0.757
          --------------------

          ---------------------
          UHF ENERGY COMPONENTS
          ---------------------

         WAVEFUNCTION NORMALIZATION =        1.0000000000

                ONE ELECTRON ENERGY =     -117.6740287680
                TWO ELECTRON ENERGY =       33.1026355691
           NUCLEAR REPULSION ENERGY =        8.9431282670
                                     ------------------
                       TOTAL ENERGY =      -75.6282649320

 ELECTRON-ELECTRON POTENTIAL ENERGY =       33.1026355691
  NUCLEUS-ELECTRON POTENTIAL ENERGY =     -193.0536141031
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =        8.9431282670
                                     ------------------
             TOTAL POTENTIAL ENERGY =     -151.0078502670
               TOTAL KINETIC ENERGY =       75.3795853351
                 VIRIAL RATIO (V/T) =        2.0032990311


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

Note the significant differences in geometrical parameters.

One has to also look into another important parameter, $\langle s_z^2 \rangle$ with the calculated equilibrium geometrical parameters in the OUTPUT file. The values are **0.814** and **0.757** for negatively and positively charged water molecule at present. As you expect, the ideal $\langle s_z^2 \rangle$ value for a **doublet** system should be **0.75**. The calculated large values are due to spin contamination that arises due to mixing of pure singlet and pure triplet states resulting artificial minima on UHF energy surface. This is a major drawback of UHF calculations. However, there are few procedures to bypass it and Restricted Open-shell Hartee Fock (ROHF) method is one such method. For a small system, one may not find any difference in CPU time to run a job under UHF and ROHF framework. However, for large system ROHF usually takes longer time compared to UHF method. Spin projection procedures are also available in some *ab initio* suit of packages to remove spin contamination from a wave function. With the same INPUT files for the negatively and positively charged water molecules with the keyword 'SCFTYP=ROHF', the following results are obtained.

For negatively charged water molecule (ROHF):

****

```
     ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O            8.0   0.0000000000  -0.1179129403   0.0000000000
 H            1.0   0.7905603808   0.5314451440   0.0000000000
 H            1.0  -0.7905603808   0.5314451440   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   1.0230599
 H      1   1.0230599  2    101.2013445
```

These are the final geometrical parameters

The calculated $\langle s_z^2 \rangle$ value for this negatively charged **doublet** system is **0.750**, the ideal one.

```
         -----------------
         ENERGY COMPONENTS
         -----------------

        WAVEFUNCTION NORMALIZATION =       1.0000000000

               ONE ELECTRON ENERGY =    -125.2055682182
               TWO ELECTRON ENERGY =      40.7697568978
          NUCLEAR REPULSION ENERGY =       8.6106770234
                                     ------------------
                      TOTAL ENERGY =     -75.8251342970

 ELECTRON-ELECTRON POTENTIAL ENERGY =      40.7697568978
```

```
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -201.3596224782
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       8.6106770234
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -151.9791885570
               TOTAL KINETIC ENERGY =      76.1540542600
                 VIRIAL RATIO (V/T) =       1.9956808608

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

For positively charged water molecule (ROHF):

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

      ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O            8.0   0.0000000000  -0.2100155167   0.0000000000
 H            1.0   0.8164757436   0.3346899131   0.0000000000
 H            1.0  -0.8164757436   0.3346899131   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   0.9814971
 H      1   0.9814971  2   112.5821473
```

These are the final geometrical parameters

Again, the calculated $<s_z^2>$ value for this positively charged **doublet** system is **0.750**, the ideal one.

```
          ------------------
          ENERGY COMPONENTS
          ------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

                ONE ELECTRON ENERGY =    -117.6894053944
                TWO ELECTRON ENERGY =      33.1150833915
           NUCLEAR REPULSION ENERGY =       8.9505117736
                                      ------------------
                       TOTAL ENERGY =     -75.6238102293

 ELECTRON-ELECTRON POTENTIAL ENERGY =      33.1150833915
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -193.0636081665
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       8.9505117736
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -150.9980130014
               TOTAL KINETIC ENERGY =      75.3742027721
                 VIRIAL RATIO (V/T) =       2.0033115767

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

Note that for charged systems, one should add diffuse functions to the chosen atomic basis functions for more accurate results. 'DIFFSP=.T. DIFFS=.T.' in INPUT ($BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=1 DIFFSP=.T. DIFFS=.T. $END is equivalent to 6-31++G**) ensures that diffuse functions are added to atomic basis functions. Now we will compare these results with the results based on post-HF MP2 results under both UHF and ROHF frameworks and considering the same INPUT except keeping MPLEVL=2 in 'CONTRL' group.

Final MP2 results on negatively charged water molecule:

UHF Framework

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

      ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O            8.0   0.0000000000  -0.0595114706   0.0000000000
 H            1.0   0.7798623454   0.5129747222   0.0000000000
 H            1.0  -0.7798623454   0.5129747222   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   0.9674325
 H      1   0.9674325   2   107.4362421


          SPIN SZ   =0.500
          S-SQUARED =0.750



          ---------------------
          MP2 ENERGY COMPONENTS
          ---------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

                ONE ELECTRON ENERGY =    -124.0815418643
                TWO ELECTRON ENERGY =      38.8259638483
           NUCLEAR REPULSION ENERGY =       9.0911379645
                                      ------------------
                       TOTAL ENERGY =     -76.1644400515

 ELECTRON-ELECTRON POTENTIAL ENERGY =      38.8259638483
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -200.0001536701
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       9.0911379645
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -152.0830518573
               TOTAL KINETIC ENERGY =      75.9186118058
                 VIRIAL RATIO (V/T) =       2.0032380498
```

****

ROHF Framework

****

```
      ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O           8.0   0.0000000001  -0.0866386393   0.0000000000
 H           1.0   0.7599569624   0.5265383065   0.0000000000
 H           1.0  -0.7599569625   0.5265383066   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   0.9764838
 H      1   0.9764838  2   102.2028330


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


          ---------------------
          MP2 ENERGY COMPONENTS
          ---------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

                ONE ELECTRON ENERGY =    -124.2678996698
                TWO ELECTRON ENERGY =      39.0499185082
           NUCLEAR REPULSION ENERGY =       9.0189017320
                                      ------------------
                       TOTAL ENERGY =     -76.1990794297

 ELECTRON-ELECTRON POTENTIAL ENERGY =      39.0499185082
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -200.1567551801
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       9.0189017320
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -152.0879349400
               TOTAL KINETIC ENERGY =      75.8888555103
                 VIRIAL RATIO (V/T) =       2.0040878719
```

****

Final MP2 results on positively charged water molecule:

UHF Framework

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

      ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O           8.0   0.0000000000  -0.0589999594   0.0000000000
 H           1.0   0.8212678720   0.5127189666   0.0000000000
 H           1.0  -0.8212678720   0.5127189666   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   1.0006715
 H      1   1.0006715  2   110.3132177


          SPIN SZ   =0.500
          S-SQUARED =0.757


          ---------------------
          MP2 ENERGY COMPONENTS
          ---------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

                ONE ELECTRON ENERGY =    -117.1910616872
                TWO ELECTRON ENERGY =      32.6322015518
           NUCLEAR REPULSION ENERGY =       8.7833252537
                                      ------------------
                       TOTAL ENERGY =     -75.7755348817

 ELECTRON-ELECTRON POTENTIAL ENERGY =      32.6322015518
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -192.5669646924
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       8.7833252537
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -151.1514378869
               TOTAL KINETIC ENERGY =      75.3759030052
                 VIRIAL RATIO (V/T) =       2.0053018519


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

ROHF Framework

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

     ***** EQUILIBRIUM GEOMETRY LOCATED *****
 COORDINATES OF ALL ATOMS ARE (ANGS)
   ATOM   CHARGE       X              Y              Z
 ------------------------------------------------------------
 O            8.0   0.0000000000  -0.0589906126   0.0000000000
 H            1.0   0.8210594088   0.5127142932   0.0000000000
 H            1.0  -0.8210594088   0.5127142932   0.0000000000

 THE CURRENT FULLY SUBSTITUTED Z-MATRIX IS
 O
 H      1   1.0004924
 H      1   1.0004924  2   110.3008942


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


          --------------------
          MP2 ENERGY COMPONENTS
          --------------------

         WAVEFUNCTION NORMALIZATION =       1.0000000000

                ONE ELECTRON ENERGY =    -117.1942100576
                TWO ELECTRON ENERGY =      32.6344646038
           NUCLEAR REPULSION ENERGY =       8.7849216446
                                      ------------------
                       TOTAL ENERGY =     -75.7748238092

 ELECTRON-ELECTRON POTENTIAL ENERGY =      32.6344646038
  NUCLEUS-ELECTRON POTENTIAL ENERGY =    -192.5698192565
   NUCLEUS-NUCLEUS POTENTIAL ENERGY =       8.7849216446
                                      ------------------
             TOTAL POTENTIAL ENERGY =    -151.1504330081
               TOTAL KINETIC ENERGY =      75.3756091989
                 VIRIAL RATIO (V/T) =       2.0052963368

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

As the total energy of neutral, negatively and positively charged water molecule have been calculated electron affinity (EA) and ionization potential (IP) of H2O molecule can be calculated applying following relations.

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

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

The calculated EA and IP values of H_2O molecule under gas phase isolated condition at different levels of theory are tabulated below for comparison.

Calculated Parameter	**Theoretical Method**			
	HF		**Post HF (MP2)**	
	RHF/UHF	**RHF/ROHF**	**RHF/UHF**	**RHF/ROHF**
EA (eV)	**7.49**	**5.40**	**1.87**	**0.93**
IP (eV)	**10.76**	**10.88**	**12.45**	**12.48**

Experimental value: EA = 1.3 eV and IP = 12.61 eV

One can see from the above Table that post-HF MP2 method is capable of predicting electron affinity (EA) and ionization potential (IP) values quite close to experimental ones. It may improve even further adopting a large atomic basis function. MP2 method typically accounts for 80–90% of the correlation energy and the third order energy correction (MP3) typically accounts for 90–95% of the correlation energy. The full fourth order energy correction (MP4) accounts for 95–98% of the correlation energy. However, computational cost increases significantly from MP2 to MP4 method. It is prescribed to perform geometry optimization at MP2 level of theory and energy of the system may be improved further by MP4 procedure. We will also discuss other post-HF methods which is capable of producing more accurate energy parameters.

Couple Cluster (CC)

Many Body Perturbation Theories (MBPT) add different types of corrections to the reference wave function to a given order (second, third or fourth as in MP2, MP3 or MP4).The idea in Coupled Cluster (CC) methods is to include all corrections of a given type to infinite order. Coupled cluster is closely connected with Moller-Plesset perturbation theory and the infinite Taylor expansion of the exponential operator ensures that the contributions from a given excitation level are included to infinite order. Perturbation theory indicates that doubles are the most important, since they are the only contributors to MP2 and MP3. At fourth order, there are contributions from singles, doubles, triples and quadruples. In the '$CONTRL' group if 'CCTYP=CCD' is used GAMESS performs a CC calculation using the coupled-cluster method with doubles which is the lowest level of approximation. Whereas for 'CCTYP=CCSD' it performs coupled-cluster calculations with singles and doubles. When, the triples contribution are evaluated by perturbation theory and added to the CCSD results it is known as CCSD(T) procedure. This is capable of predicting very accurate results accounting 99.99% correlation energy and applicable only for medium size molecules due to computational cost.

The calculated couple cluster energies with different levels of corrections along with MP2 method are listed below for comparison. The calculations are carried out with the same set of geometrical parameters of neutral H_2O molecule.

```
                    SUMMARY OF RESULTS

      REFERENCE ENERGY:       -76.0304191949
        MBPT(2) ENERGY:       -76.2333759470   CORR.E=   -0.2029567522
        CCSD    ENERGY:       -76.2412017458   CORR.E=   -0.2107825509
        CCSD(T) ENERGY:       -76.2446812103   CORR.E=   -0.2142620154
```

'`REFERENCE ENERGY`' refers to the HF energy of H_2O molecule with the same set of geometrical parameters and '`CORR.E`' refers to the calculated 'electron correlation energy' at different level of theory. This method is used mainly for single point energy calculation as it is computationally expensive.

Configuration Interaction (CI)

In this procedure, the trial wave function is written as a linear combination of determinants. Determinants that are singly, doubly, triply, etc. excited relative to the HF configuration and the energy is minimized under the constraint that the total CI wave function is normalized. The excited Slater determinants are generated by removing electrons from occupied orbitals, and placing them in virtual orbitals. The number of excited Slater Determinants increases factorially with the number of electrons and basis functions. This is the best possible wave function within the limitations of the basis set, i.e. it recovers 100% of the electron correlation in the given basis. However, even for a system like H_2O molecule (18 electrons) with a 6-31G* basis set it is impossible to solve. In order to develop a computationally tractable model, the number of excited determinants in the CI expansion must be reduced. Truncating the excitation level to one (known as CI singles or CIS) does not give any improvement over the HF result. The lowest CI level that gives an improvement over the HF result is to include only doubly excited states, yielding the CI with doubles. Compared with the number of doubly excited determinants, there are relatively few singly excited determinants and including these gives the CISD (CI singles and doubles) method. This is a method commonly used for small to medium sized molecules.

Summary

In this chapter, discussions on post-HF method, MP2 are made and calculated results are compared with HF method both for closed and open shell systems. Calculated results on EA and IP are also compared with available experimental data. Discussions on CC and CI method are also made with reference to accuracy of results and computational cost.