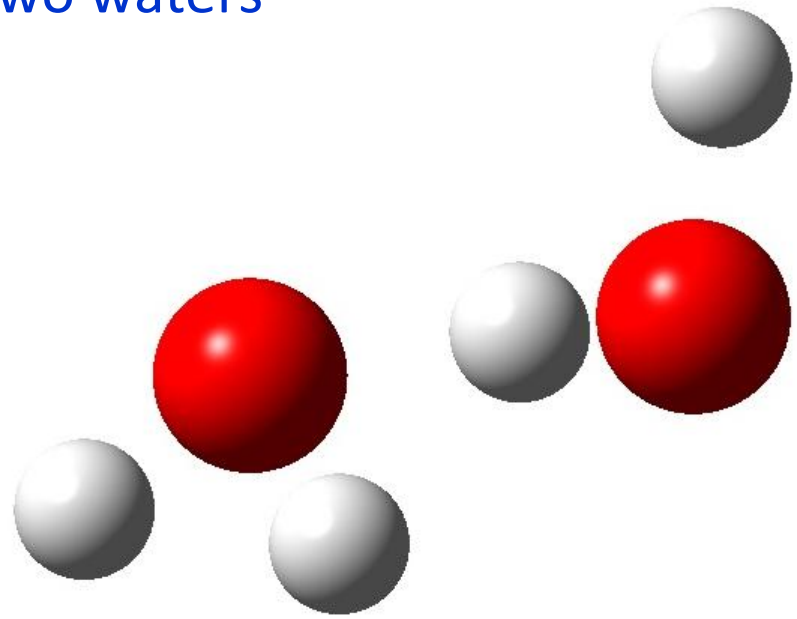
Intermolecular Interaction: Super Molecule Approximation

Super Molecule Approximation

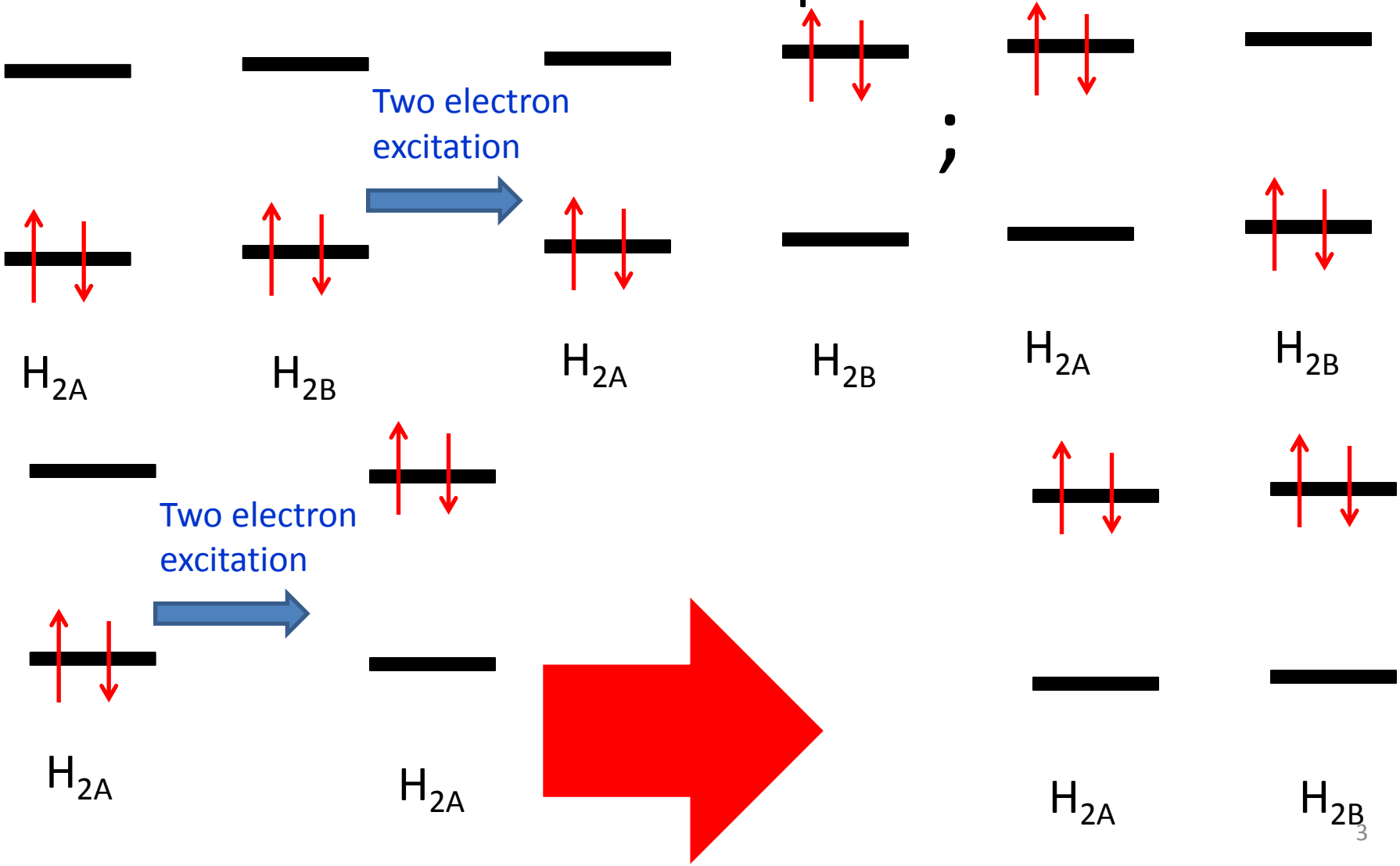
To obtain the interaction between two waters perform calculation of two waters



Two things to be careful

Size Consistancy

- Consider H2…H2 with CISD infinite far away result for H2…H2 is not equal to 2 H2!!



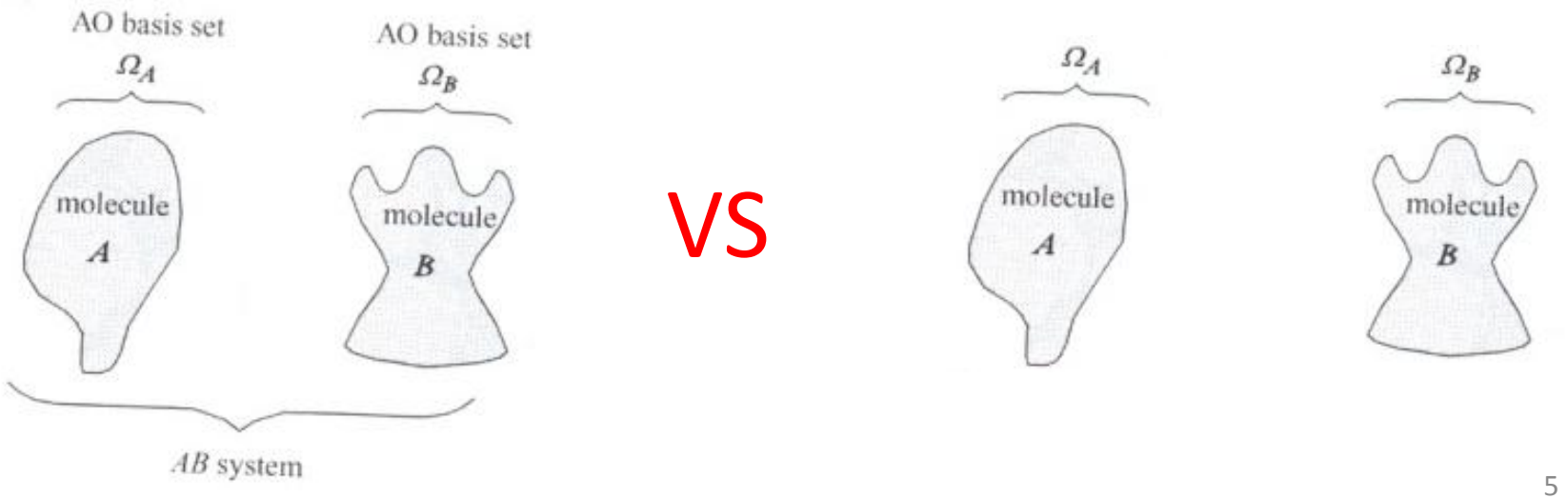
Size Consistent Methods

- HF
- MP2
- CCSD

$$CCSD = \exp^{T_1+T_2} D_0$$

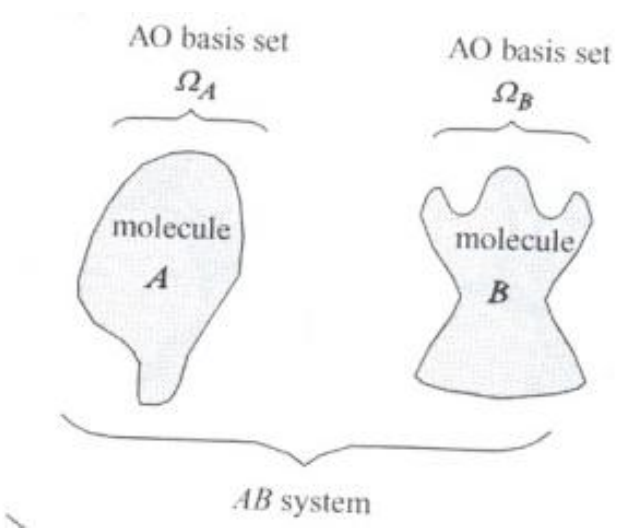
$$= T_1 D_0 + T_2 D_0 + \frac{1}{2}\left[T_1 T_1 D_0 + T_2 T_2 D_0 + T_1 T_2 D_0\right]$$

Basis Set Super Position Error

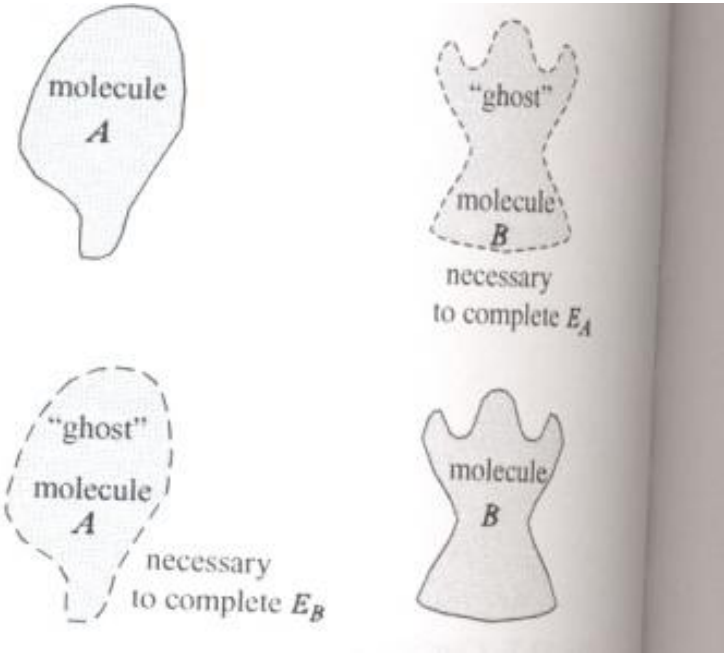


Counter Poise Correction

- Boys Lanbardi method:



VS



BSSE big for small basis sets

Gaussian CP Input

140.109.112.238:22 - Tera Term VT

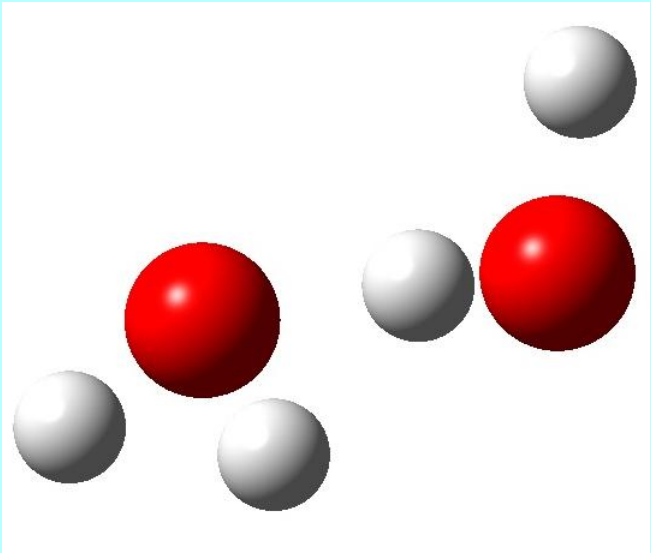
File Edit Setup Control Window Resize Help

```
%Nproc=8
%mem=12Gb
# B3LYP/STO-3G scf=(tight,maxcycle=200) CounterPoise=2
# pop=min opt=(maxcycle=100,tight,calcall) IOP(1/11=1,99/14=1)

TITLE

0  1 0  1   0   1
O1  0.0  0.0  0.0,1
O2  1,  RO1O2,2
H3, 1,  RO1H3,  2,  AO2O1H2,1
H4, 2,  RO2H4,  1,  AO1O2H4,  3,  DH3O1O2H4,0,2
H5, 2,  RO2H5,  1,  AO1O2H5,  3,  DH3O1O2H5,0,2
H6, 1,  RO1H6,  3,  AH3O1H6,  2,  DO2H3O1H6,0,1

 RO1O2=2.88716553
 RO1H3=0.96411241
 RO2H4=0.96581719
 RO2H5=0.96581719
 RO1H6=0.97337138
 AO2O1H2=110.30402085
 AO1O2H4=111.82487859
 AO1O2H5=111.82487859
 AH3O1H6=105.9829422
 DH3O1O2H4=120.58376085
 DH3O1O2H5=-120.58376085
 DO2H3O1H6=0.
```



h2oh2obsse.com lines 1-29/29 (END)

G09 CP output 1

```
140.109.112.238:22 - Tera Term VT
File  Edit  Setup  Control  Window  Resize  Help
        NMat0=    1 NMatS0=    1 NMatT0=    0 NMatD0=    1 NMtDS0=    0 NMtDT0=    0
        IlCent=           4 NGrid=           0.
Petite list used in FoFCou.
Initial guess orbital symmetries:
      Occupied  (A') (A') (A') (A') (A") (A') (A') (A') (A') (A")
      Virtual   (A') (A') (A") (A') (A') (A") (A') (A') (A') (A")
                (A') (A') (A") (A') (A') (A') (A") (A") (A') (A')
                (A') (A') (A') (A') (A") (A") (A') (A') (A") (A')
                (A') (A') (A") (A') (A") (A') (A") (A") (A') (A")
                (A') (A') (A') (A') (A") (A') (A') (A')
The electronic state of the initial guess is 1-A'.
Requested convergence on RMS density matrix=1.00D-08 within 200 cycles.
Requested convergence on MAX density matrix=1.00D-06.
Requested convergence on                energy=1.00D-06.
No special actions if energy rises.
Keep R1 ints in memory in canonical form, NReq=2444600.
Integral accuracy reduced to 1.0D-05 until final iterations.
Initial convergence to 1.0D-05 achieved.  Increase integral accuracy.
SCF Done:  E(RB3LYP) =  -152.877717698     A.U. after   11 cycles
           Convg  =    0.8255D-08             -V/T =  2.0093
Range of M.O.s used for correlation:     1    58
NBasis=    58 NAE=    10 NBE=    10 NFC=     0 NFV=     0
NROrb=     58 NOA=    10 NOB=    10 NVA=    48 NVB=    48
Symmetrizing basis deriv contribution to polar:
IMax=3 JMax=2 DiffMx= 0.00D+00
G2DrvN: will do     7 centers at a time, making    1 passes doing MaxLOS=2.
Calling FoFCou, ICntrl=  3107 FMM=F IlCent=   0 AccDes= 0.00D+00.
FoFDir/FoFCou used for L=0 through L=2.
End of G2Drv Frequency-dependent properties file   721 does not exist.
a63/h2oh2obsse.log lines 305-333/2952 9%
```

G09 CP output2

```
140.109.112.238.22 - Tera Term VT
File  Edit  Setup  Control  Window  Resize  Help
                (A') (A") (A') (A") (A") (A') (A') (A") (A") (A')
                (A') (A') (A') (A") (A') (A') (A') (A") (A') (A')
                (A') (A") (A')
 The electronic state of the initial guess is 1-A'.
 Requested convergence on RMS density matrix=1.00D-08 within 200 cycles.
 Requested convergence on MAX density matrix=1.00D-06.
 Requested convergence on                energy=1.00D-06.
 No special actions if energy rises.
 Keep R1 ints in memory in canonical form, NReq=2444600.
 Integral accuracy reduced to 1.0D-05 until final iterations.
 Initial convergence to 1.0D-05 achieved.  Increase integral accuracy.
 SCF Done:  E(RB3LYP) =  -76.4342897524     A.U. after    9 cycles
            Convg  =    0.7734D-08             -V/T =  2.0094
 Range of M.O.s used for correlation:     1    58
 NBasis=    58 NAE=     5 NBE=     5 NFC=     0 NFV=     0
 NROrb=     58 NOA=     5 NOB=     5 NVA=    53 NVB=    53
 Symmetrizing basis deriv contribution to polar:
 IMax=3 JMax=2 DiffMx= 0.00D+00
 G2DrvN: will do     7 centers at a time, making    1 passes doing MaxLOS=2.
 Calling FoFCou, ICntrl=  3107 FMM=F IlCent=   0 AccDes= 0.00D+00.
 FoFDir/FoFCou used for L=0 through L=2.
 End of G2Drv Frequency-dependent properties file   721 does not exist.
 End of G2Drv Frequency-dependent properties file   722 does not exist.
          IDoAtm=111111
          Differentiating once with respect to electric field.
                with respect to dipole field.
          Differentiating once with respect to nuclear coordinates.
          Keep R1 ints in memory in canonical form, NReq=2286689.
          There are    18 degrees of freedom in the 1st order CPHF.  IDoFFX=4.
a63/h2oh2obsse.log lines 479-507/2952 15%
```

G09 CP output3

140.109.112.238:22 - Tera Term VT

File Edit Setup Control Window Resize Help

```
No special actions if energy rises.
Keep R1 ints in memory in canonical form, NReq=2444600.
Integral accuracy reduced to 1.0D-05 until final iterations.
Initial convergence to 1.0D-05 achieved.  Increase integral accuracy.
SCF Done:  E(RB3LYP) =  -76.4350853742     A.U. after   10 cycles
           Convg  =    0.2372D-08             -V/T =  2.0094
Range of M.O.s used for correlation:     1    58
NBasis=    58 NAE=     5 NBE=     5 NFC=     0 NFV=     0
NROrb=     58 NOA=     5 NOB=     5 NVA=    53 NVB=    53
Symmetrizing basis deriv contribution to polar:
IMax=3 JMax=2 DiffMx= 0.00D+00
G2DrvN: will do     7 centers at a time, making    1 passes doing MaxLOS=2.
Calling FoFCou, ICntrl=  3107 FMM=F IlCent=   0 AccDes= 0.00D+00.
FoFDir/FoFCou used for L=0 through L=2.
End of G2Drv Frequency-dependent properties file   721 does not exist.
End of G2Drv Frequency-dependent properties file   722 does not exist.
         IDoAtm=111111
         Differentiating once with respect to electric field.
               with respect to dipole field.
         Differentiating once with respect to nuclear coordinates.
         Keep R1 ints in memory in canonical form, NReq=2286689.
         There are    18 degrees of freedom in the 1st order CPHF.  IDoFFX=4.
    18 vectors produced by pass  0 Test12= 1.47D-15 5.56D-09 XBig12= 3.76D+00 1.15D+00.
AX will form    18 AO Fock derivatives at one time.
    18 vectors produced by pass  1 Test12= 1.47D-15 5.56D-09 XBig12= 2.96D-01 1.75D-01.
    18 vectors produced by pass  2 Test12= 1.47D-15 5.56D-09 XBig12= 1.17D-03 1.09D-02.
    18 vectors produced by pass  3 Test12= 1.47D-15 5.56D-09 XBig12= 9.28D-07 2.18D-04.
    10 vectors produced by pass  4 Test12= 1.47D-15 5.56D-09 XBig12= 2.03D-10 4.32D-06.
     3 vectors produced by pass  5 Test12= 1.47D-15 5.56D-09 XBig12= 5.71D-14 7.61D-08.
```

G09 CP output4

```
140.109.112.238:22 - Tera Term VT
File  Edit  Setup  Control  Window  Resize  Help
 Harris functional with IExCor=  402 diagonalized for initial guess.
 ExpMin= 8.45D-02 ExpMax= 5.48D+03 ExpMxC= 8.25D+02 IAcc=2 IRadAn=         0 AccDes= 0.00D+00
 HarFok:  IExCor=  402 AccDes= 0.00D+00 IRadAn=         0 IDoV= 1
 ScaDFX=  1.000000  1.000000  1.000000  1.000000
 FoFCou: FMM=F IPFlag=           0 FMFlag=      100000 FMFlgl=           0
         NFxFlg=           0 DoJE=T BraDBF=F KetDBF=T FulRan=T
         Omega=  0.000000  0.000000  1.000000  0.000000  0.000000 ICntrl=     500 IOpCl=  0
         NMat0=    1 NMatS0=    1 NMatT0=    0 NMatD0=    1 NMtDS0=    0 NMtDT0=    0
         IlCent=           4 NGrid=           0.
 Petite list used in FoFCou.
 Initial guess orbital symmetries:
       Occupied  (A') (A') (A') (A') (A")
       Virtual   (A') (A') (A') (A") (A') (A') (A') (A') (A") (A')
                 (A') (A') (A") (A') (A") (A') (A') (A') (A") (A")
                 (A') (A') (A') (A')
 The electronic state of the initial guess is 1-A'.
 Requested convergence on RMS density matrix=1.00D-08 within 200 cycles.
 Requested convergence on MAX density matrix=1.00D-06.
 Requested convergence on                energy=1.00D-06.
 No special actions if energy rises.
 Keep R1 ints in memory in canonical form, NReq=1023578.
 Integral accuracy reduced to 1.0D-05 until final iterations.
 Initial convergence to 1.0D-05 achieved.  Increase integral accuracy.
 SCF Done:  E(RB3LYP) =  -76.4339805694     A.U. after   10 cycles
            Convg  =    0.6861D-08             -V/T =  2.0094
 Range of M.O.s used for correlation:     1    29
 NBasis=    29 NAE=     5 NBE=     5 NFC=     0 NFV=     0
 NROrb=     29 NOA=     5 NOB=     5 NVA=    24 NVB=    24
 Symmetrizing basis deriv contribution to polar:
a63/h2oh2obsse.log lines 798-826/2952 25%
```

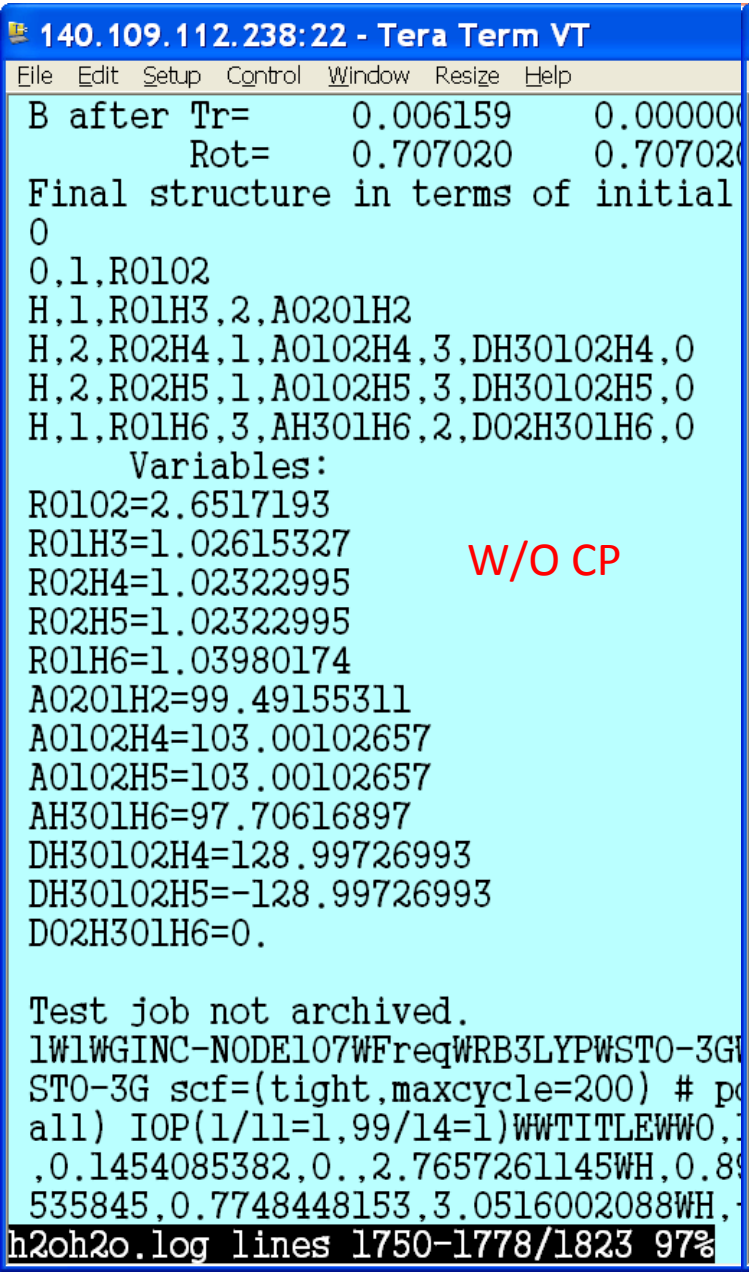
G09 CP Output 5

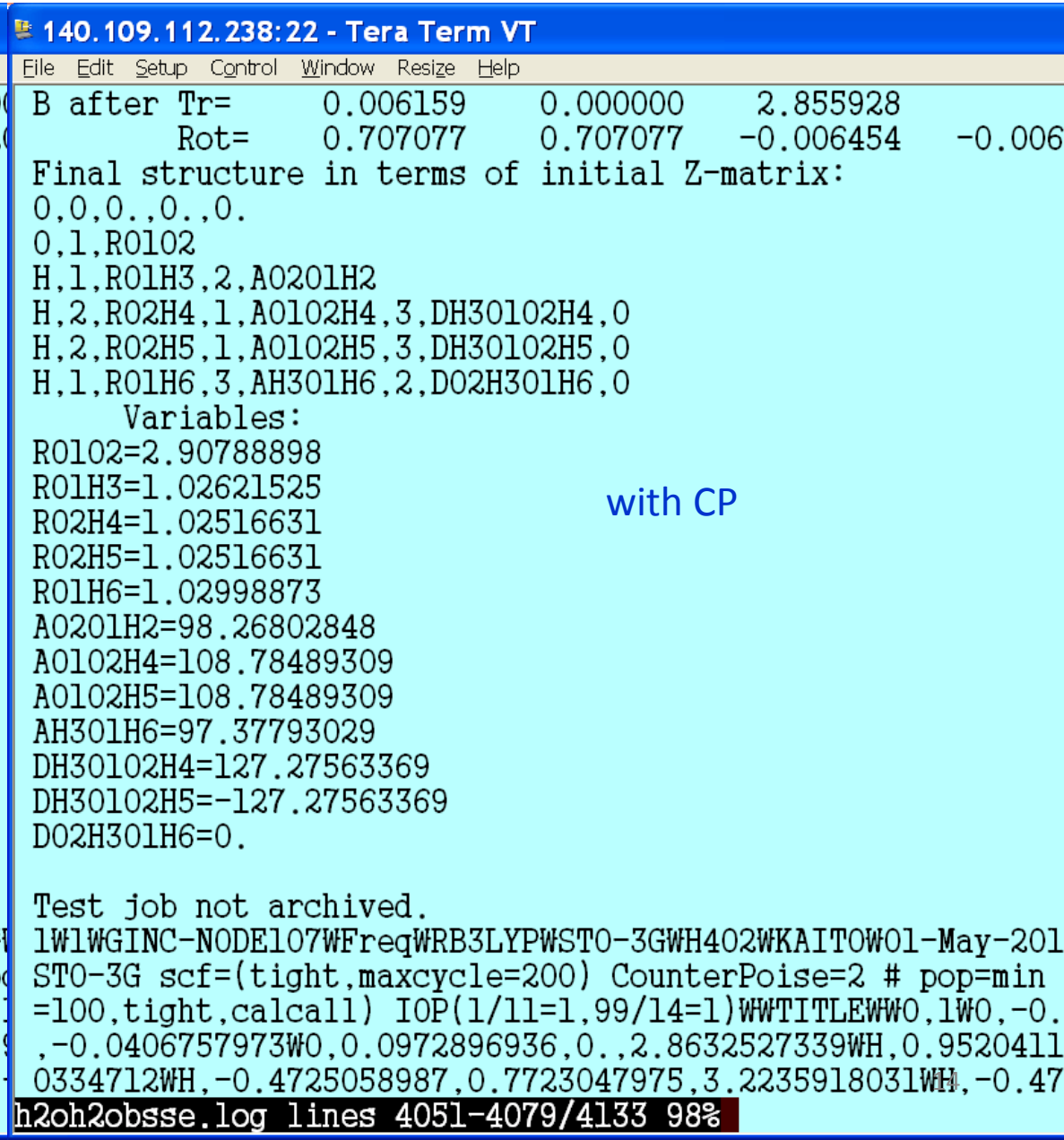
```
File  Edit  Setup  Control  Window  Resize  Help
        NMat0=    1 NMatS0=    1 NMatT0=    0 NMatD0=    1 NMtDS0=    0 NMtDT0=    0
        IlCent=           4 NGrid=           0.
Petite list used in FoFCou.
Initial guess orbital symmetries:
      Occupied  (A') (A') (A") (A') (A')
      Virtual   (A') (A") (A') (A') (A") (A') (A") (A') (A') (A")
                (A') (A') (A") (A') (A') (A') (A") (A") (A") (A')
                (A') (A') (A") (A')
The electronic state of the initial guess is 1-A'.
Requested convergence on RMS density matrix=1.00D-08 within 200 cycles.
Requested convergence on MAX density matrix=1.00D-06.
Requested convergence on                energy=1.00D-06.
No special actions if energy rises.
Keep R1 ints in memory in canonical form, NReq=1023578.
Integral accuracy reduced to 1.0D-05 until final iterations.
Initial convergence to 1.0D-05 achieved.  Increase integral accuracy.
SCF Done:  E(RB3LYP) =  -76.4340436903     A.U. after   11 cycles
           Convg  =    0.2148D-08             -V/T =  2.0093
Range of M.O.s used for correlation:     1    29
NBasis=    29 NAE=     5 NBE=     5 NFC=     0 NFV=     0
NROrb=     29 NOA=     5 NOB=     5 NVA=    24 NVB=    24
Symmetrizing basis deriv contribution to polar:
IMax=3 JMax=2 DiffMx= 0.00D+00
G2DrvN: will do     4 centers at a time, making    1 passes doing MaxLOS=2.
Calling FoFCou, ICntrl=  3107 FMM=F IlCent=   0 AccDes= 0.00D+00.
FoFDir/FoFCou used for L=0 through L=2.
End of G2Drv Frequency-dependent properties file   721 does not exist.
End of G2Drv Frequency-dependent properties file   722 does not exist.
         IDoAtm=010110
a63/h2oh2obsse.log lines 958-986/2952 30%
```

G09 CP output 6

```
File  Edit  Setup  Control  Window  Resize  Help
 XXX=              0.7498  YYY=             22.5927  ZZZ=              0.0000  XYY=             -5.5874
 XXY=              9.2561  XXZ=              0.0000  XZZ=             -0.6970  YZZ=              5.4362
 YYZ=              0.0000  XYZ=              0.0000
Hexadecapole moment (field-independent basis, Debye-Ang**3):
XXXX=            -8.0777 YYYY=           -79.0708 ZZZZ=            -6.4989 XXXY=             -0.9957
XXXZ=             0.0000 YYYX=             8.9559 YYYZ=             0.0000 ZZZX=              0.0000
ZZZY=             0.0000 XXYY=           -15.3346 XXZZ=            -2.1796 YYZZ=             -9.0910
XXYZ=             0.0000 YYXZ=             0.0000 ZZXY=             1.3695
N-N= 9.109290856459D+00 E-N=-1.985116560294D+02  KE= 7.572912647887D+01
Symmetry A'    KE= 7.212155936992D+01
Symmetry A"    KE= 3.607567108950D+00
 Exact polarizability:   6.614  -0.048   6.638   0.000   0.000   7.868
Approx polarizability:   7.333   0.402   7.139   0.000   0.000   9.711
Calling FoFJK, ICntrl=    100127 FMM=F ISym2X=1 IlCent= 0 IOpClX= 0 NMat=1 NMatS=1 NMatT=0.
***** Axes restored to original set *****
Cartesian Forces:  Max     0.001082144 RMS     0.000365181
Counterpoise: corrected energy =    -152.876366830967
Counterpoise: BSSE energy =       0.001350866952
Rotating derivatives to standard orientation.
***** Axes restored to original set *****
-------------------------------------------------------------------
Center     Atomic                   Forces (Hartrees/Bohr)
Number     Number              X              Y              Z
-------------------------------------------------------------------
     1        8           0.000007243    0.000000000   -0.000394080
     2        8          -0.000229675    0.000000000    0.001361959
     3        1          -0.000100064    0.000000000   -0.000005053
     4        1           0.000099739    0.000182663   -0.000192429
     5        1           0.000099739   -0.000182663   -0.000192429
a63/h2oh2obsse.log lines 1074-1102/2952 34%
```

Optimized Geometry CP





Excited Electronic States Calculation

Method for Excited States

- Use more than one slater determinant
  - CISD: Configuration Interaction Singles and Doubles
  - CCSD: Coupled Cluster Singles and Doubles
  - MCSCF: Multiconfigurational Self Consistent Field
  - MR-CISD: Multireference CISD
- CAS MP2
  - MP2,3,4: Mollar Plesset perturbation theory
- Equation of Motion CCSD
- Time Dependent DFT (TD-B3LYP)

Molecular Dynamics

Molecular Dynamics Simulation

For electrons we have to solve the quantum Schroedinger Equation
For nuclei we only consider that they move classically

Force on nuclei can be obtained from potential derivative

Initial Condition:

For example for harmonic oscillator

$$V(x) = \frac{1}{2} k \left(x - x_{eq}\right)^2$$

$$-\frac{dV}{dx} = -k\left(x - x_{eq}\right)$$

Method of Propagation1

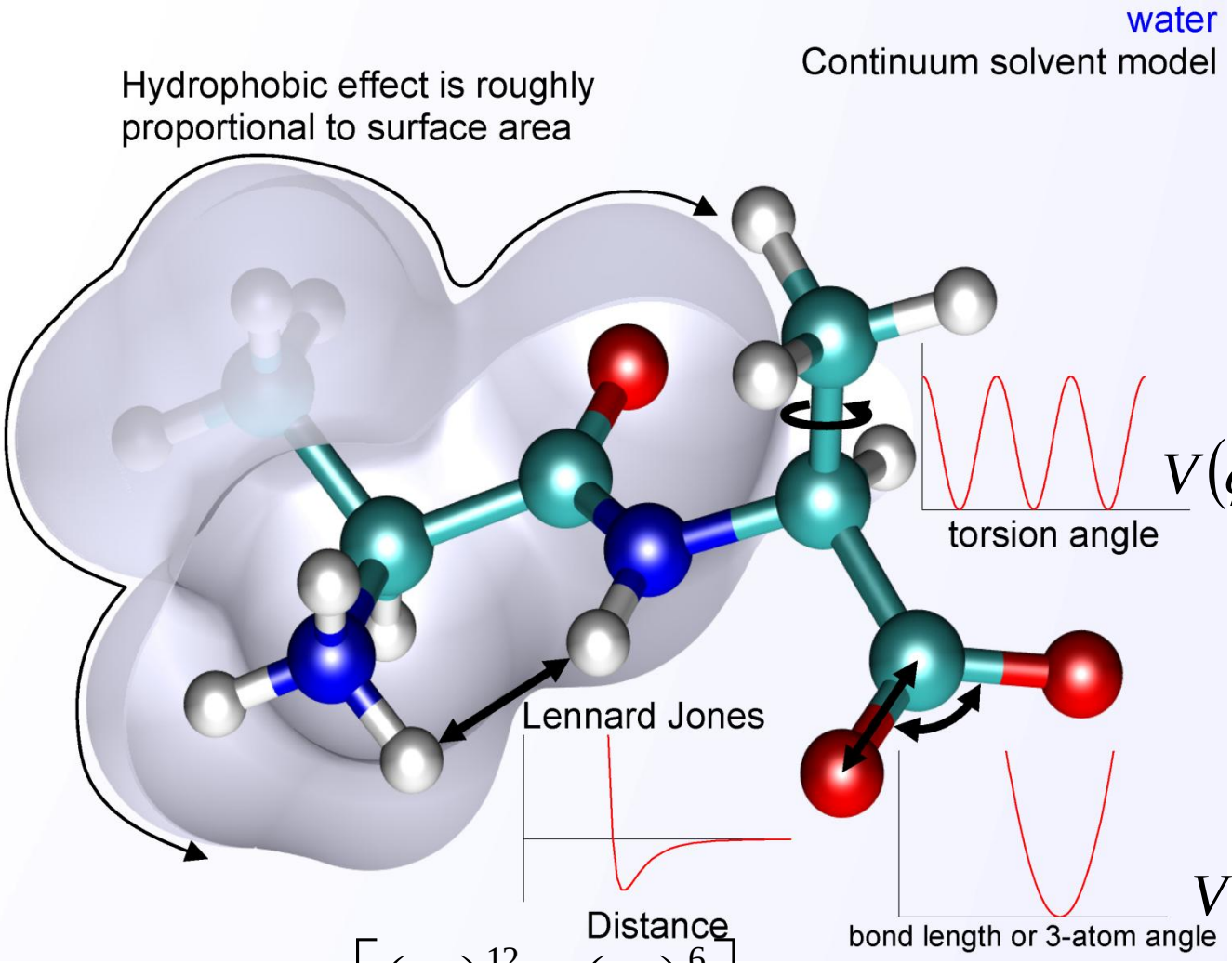
Goal:

$$\frac{dx}{dt} = f(x,t); \quad x(t_0) = x_0 \rightarrow x(t_{final}) \text{ in time step } \Delta t$$

- Euler method (first order method take gradient)

- 4th order Runge-Kutta propagation : add up contribution along the way

Types of Force Fields used in Molecular Mechanics



$$V(\phi) = V_0 \cos(a\phi)$$

$$V(x) = \frac{1}{2} k\left(x - x_{eq}\right)^2$$

$$V(x) = 4\varepsilon\left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6}\right]$$

Wikipedia “Molecular Mechanics”

On the fly simulation

At every time step solve the electronic Schrodinger equation

Good Points
1.Accurate
2.Can describe reaction
3.Do not have to worry about fitting problems

Bad Points
1.Computational time is great so can only be used for short time propagation
2.Can not perform detailed analysis

Gaussian 09 BOMD input

140.109.112.238:22 - Tera Term VT

File Edit Setup Control Window Resize Help

```
%nproc=2
%mem=2Gb
%chk=/lustre/lwork/scratch/kaito/watl0-3.chk
# B3LYP/6-31+G(d,p)
# pop=min units=au SCF=tight nosymm maxdisk=4Gb
# BOMD(Maxpoints=1000,stepsize=1000,ReadMWvelocity,ReadStop)

trajectory calculation

0  1
O1   -0.863964985562D-01 -0.465751539278D-33 -0.524452197259D-01
H2   -0.240504743927D+00  0.568982937356D-32  0.153669402428D+01
H3    0.189541778845D+01  0.335720196411D-32 -0.813279591197D+00

0
 0.543857995191400D+13, 0.230208768635600D-17, 0.143083506622000D+14,
-0.239948954079300D+14, 0.154458636218000D-17,-0.314144625994200D+14,
-0.162146179720623D+15,-0.186620915654356D-17, 0.375559408901498D+14,

kaito@master:/lustre/lwork/kaito/kaito/G09/h2o/traj/traj10-3>
```

G09 BOMD output 1

140.109.112.238:22 - Tera Term VT

File Edit Setup Control Window Resize Help

```
    0.00000000D+00     0.00000000D+00     0.00000000D+00     0.00000000D+00
    0.00000000D+00
Get start point for trajectory     1

Start point information
Time (fs)      0.000000
EKin =        0.0157313; EPot =     -76.3945963; ETot =     -76.3788650 A.U.
Angular momentum (instantaneous)
  JX = -0.1533484188D-30  JY =  0.8873643111D+00  JZ = -0.2143161482D-30
Jtot =  0.8873643111D+00 H-BAR;  J (Quantum Number) =  0.5185359202D+00
Total energy  -7.637887D+01 A.U.
Total angular momentum   8.873643D-01 h-bar
Cartesian coordinates: (bohr)
I=    1 X=  -1.022737453426D-01 Y=   0.000000000000D+00 Z=  -4.634981756906D-02
I=    2 X=  -2.563819907134D-01 Y=   0.000000000000D+00 Z=   1.542789426437D+00
I=    3 X=   1.879540541664D+00 Y=   0.000000000000D+00 Z=  -8.071841890402D-01
MW cartesian velocity: (sqrt(amu)*bohr/sec)
I=    1 X=   5.438579951914D+12 Y=   0.000000000000D+00 Z=   1.430835066220D+13
I=    2 X=  -2.399489540793D+13 Y=   0.000000000000D+00 Z=  -3.141446259942D+13
I=    3 X=  -1.621461797206D+14 Y=   0.000000000000D+00 Z=   3.755594089015D+13
TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ


TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ-TRJ
Trajectory Number     1    Step Number     2

Eigenvalues of Mass-weighted Force Constants in hartree/(bohr**2*amu):
    0.1403037lD-01     0.16647825D+00     0.12873862D+01     0.00000000D+00
    0.00000000D+00     0.00000000D+00     0.00000000D+00     0.00000000D+00
test.log.gz lines 313-341/164078 0%
```

G09 BOMD output 2

140.109.112.238:22 - Tera Term VT

File Edit Setup Control Window Resize Help

```
     0.00000000D+00

 Summary information for step      2
 Time (fs)      0.000000
 EKin =       0.0157313; EPot =     -76.3945963; ETot =     -76.3788650 A.U.
 Angular momentum (instantaneous)
   JX = -0.1533484188D-30  JY =  0.8873643111D+00  JZ = -0.2143161482D-30
 Jtot =  0.8873643111D+00 H-BAR;  J (Quantum Number) =  0.5185359202D+00
 Total energy  -7.637887D+01 A.U.
 Total angular momentum   8.873643D-01 h-bar
 Cartesian coordinates: (bohr)
 I=    1 X=  -1.022737453426D-01 Y=   0.000000000000D+00 Z=  -4.634981756906D-02
 I=    2 X=  -2.563819907134D-01 Y=   0.000000000000D+00 Z=   1.542789426437D+00
 I=    3 X=   1.879540541664D+00 Y=   0.000000000000D+00 Z=  -8.071841890402D-01
 MW cartesian velocity: (sqrt(amu)*bohr/sec)
 I=    1 X=   5.438579951914D+12 Y=   0.000000000000D+00 Z=   1.430835066220D+13
 I=    2 X=  -2.399489540793D+13 Y=   0.000000000000D+00 Z=  -3.141446259942D+13
 I=    3 X=  -1.621461797206D+14 Y=   0.000000000000D+00 Z=   3.755594089015D+13
 Next step-size   0.1000000000D+00 sqrt(amu)*bohr
 Do projection in prediction step
 Use Bulirsch-Stoer Integration Method First
 Energy from last cycle -0.7637886505D+02 A.U.
 Energy from this cycle -0.7637886890D+02 A.U.
 Predict stepsize   0.1000000000D+00 sqrt(amu)*bohr
 Time increment   0.5203919673D+00 femtosec

 Predicted information for step      3
 Time (fs)      0.520392
 EKin =       0.0264695; EPot =     -76.4053384; ETot =     -76.3788689 A.U.
test.log.gz lines 342-370/164078 0%
```