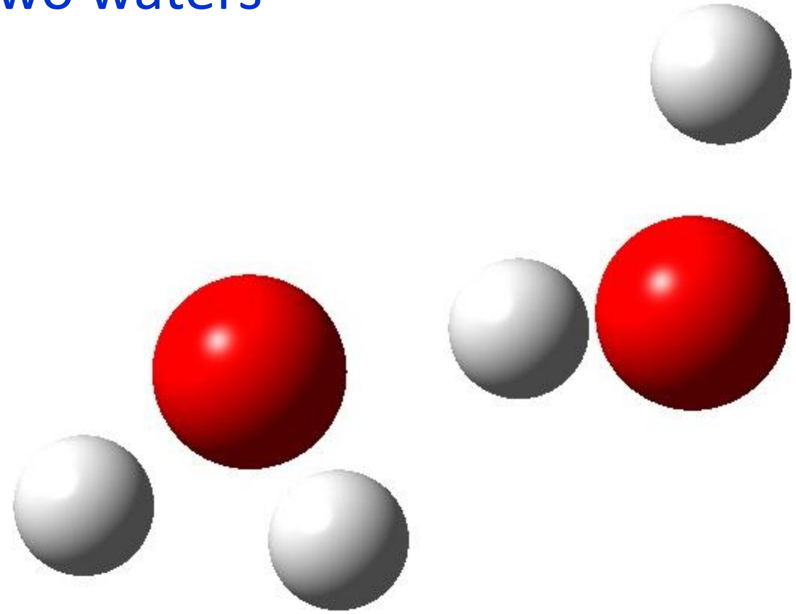
Intermolecular Interaction: Super Molecule Approximation

Super Molecule Approximation

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

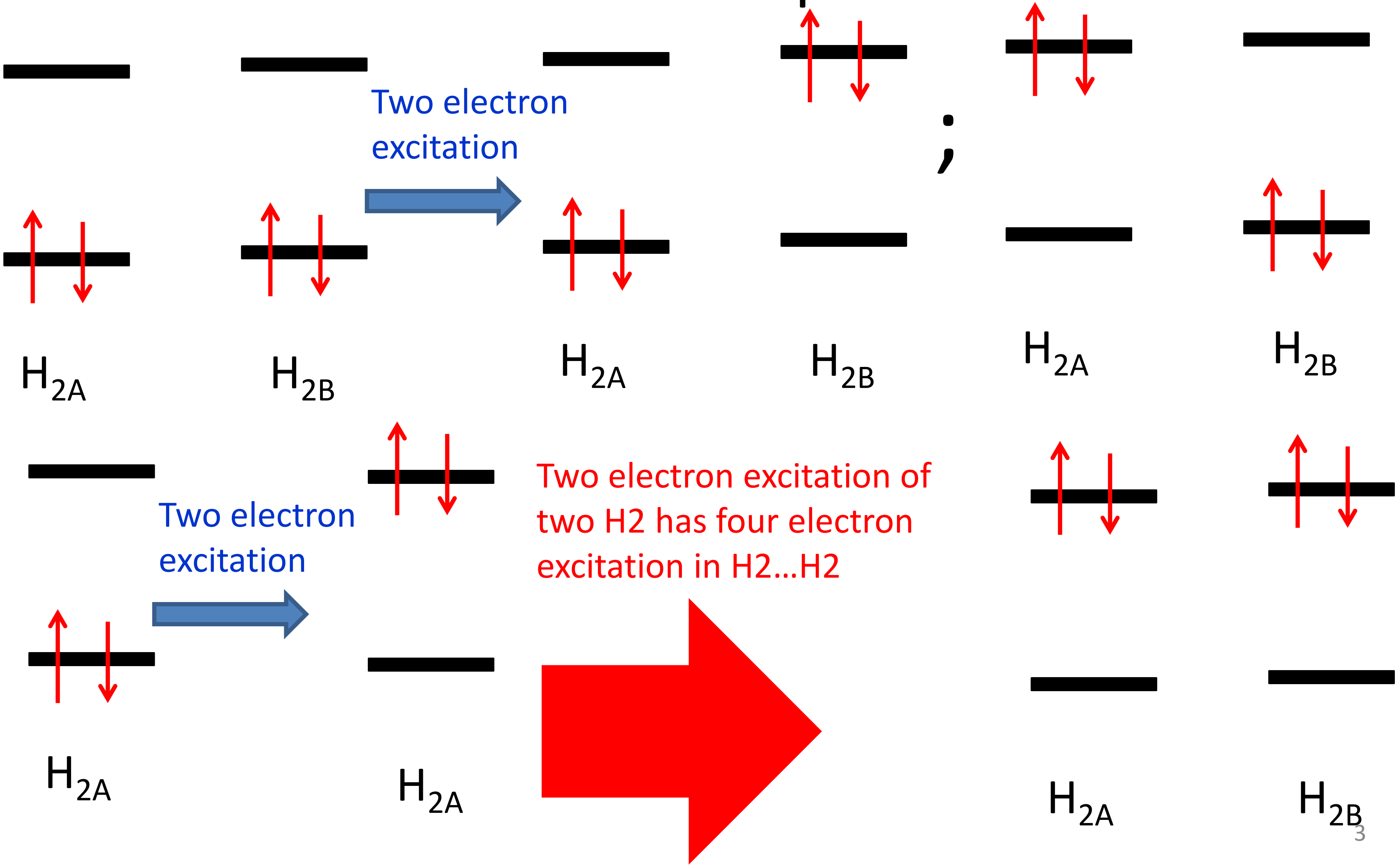


Two things to be careful

- Size Consistency
- Basis set super position error

Size Consistancy

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



Two electron excitation of two H2 has four electron excitation in H2…H2

Size Consistent Methods

- HF
- MP2
- CCSD

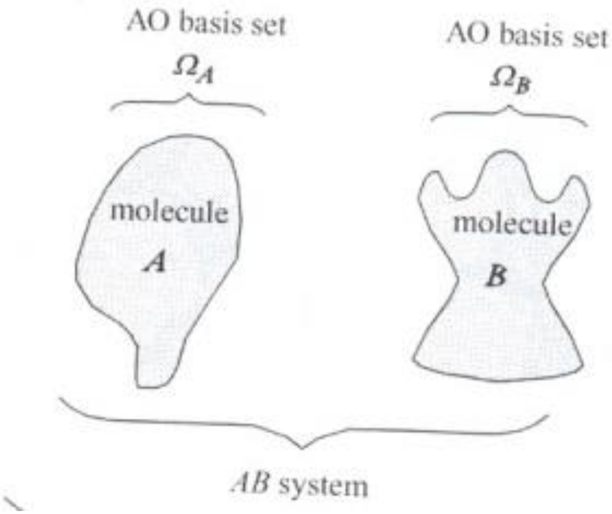
$$CCSD = \exp^{T_1+T_2} D_0$$

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

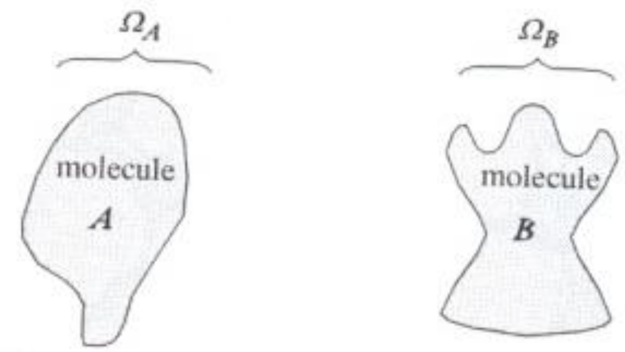
Pople et al. have defined an empirical estimation of the four electron excitation contribution MRSDCI had defined +Q so for bond dissociation and potential energy surface calculation people use MRSDCI+Q to approximately take care of the size consistancy problem

Basis Set Super Position Error

- When calculating the energy of a supermolecule we use the basis set of Molecule A and Molecule B together, when we calculate the separated products we calculate molecule A with basis of A, molecule B with basis of B

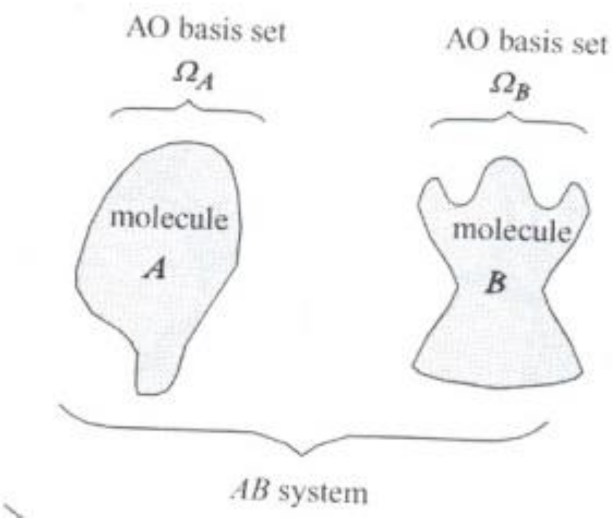


VS

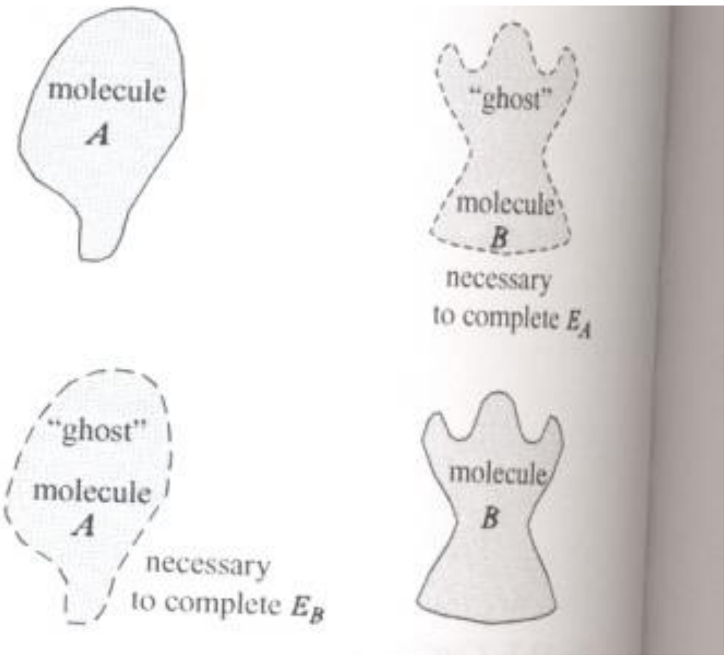


Counter Poise Correction

- Boys Lanbardi method: use ghost atoms (no charge just position to put basis)and put the basis for the respective partner in the energy calculation for molecule A and B

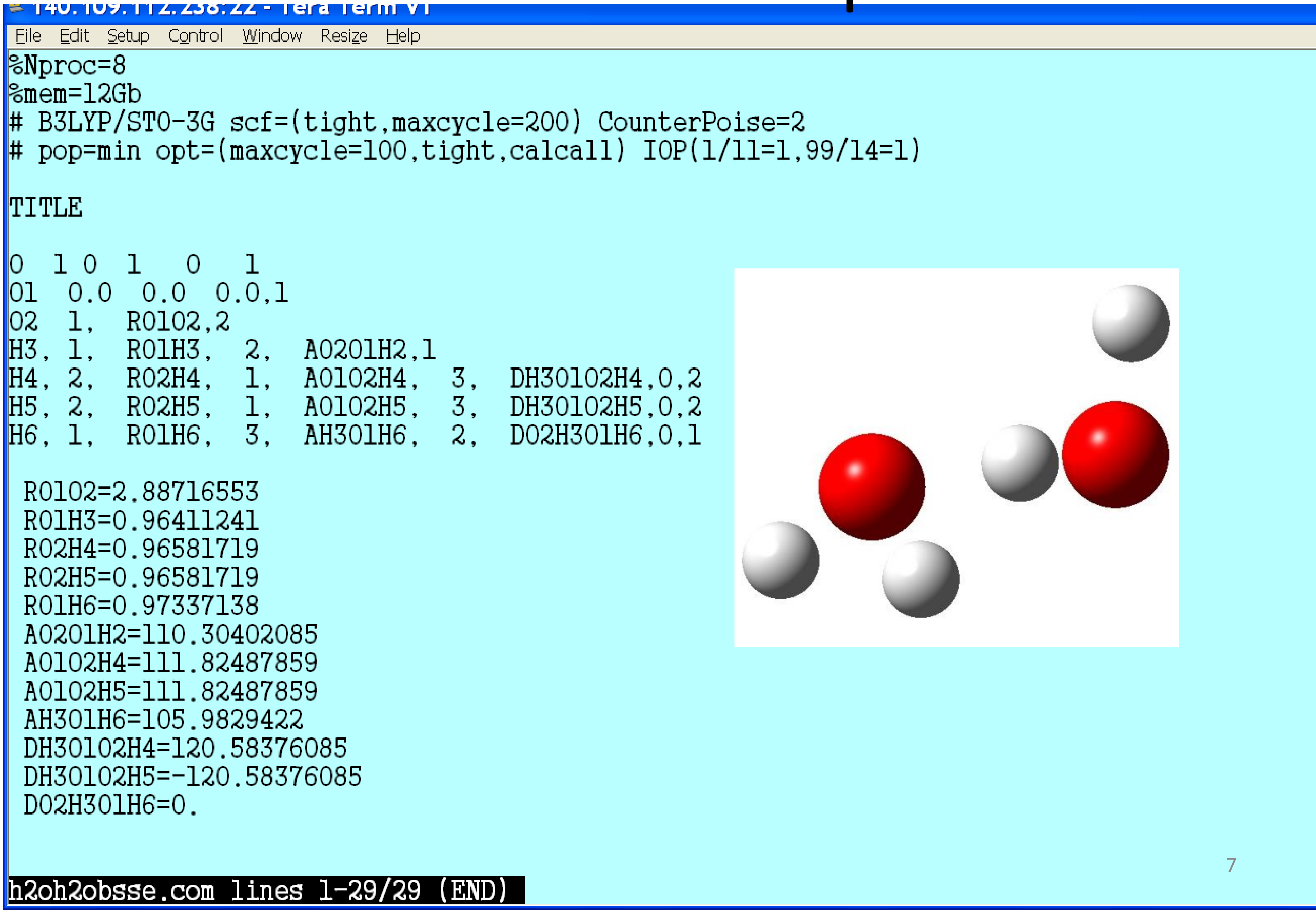


VS



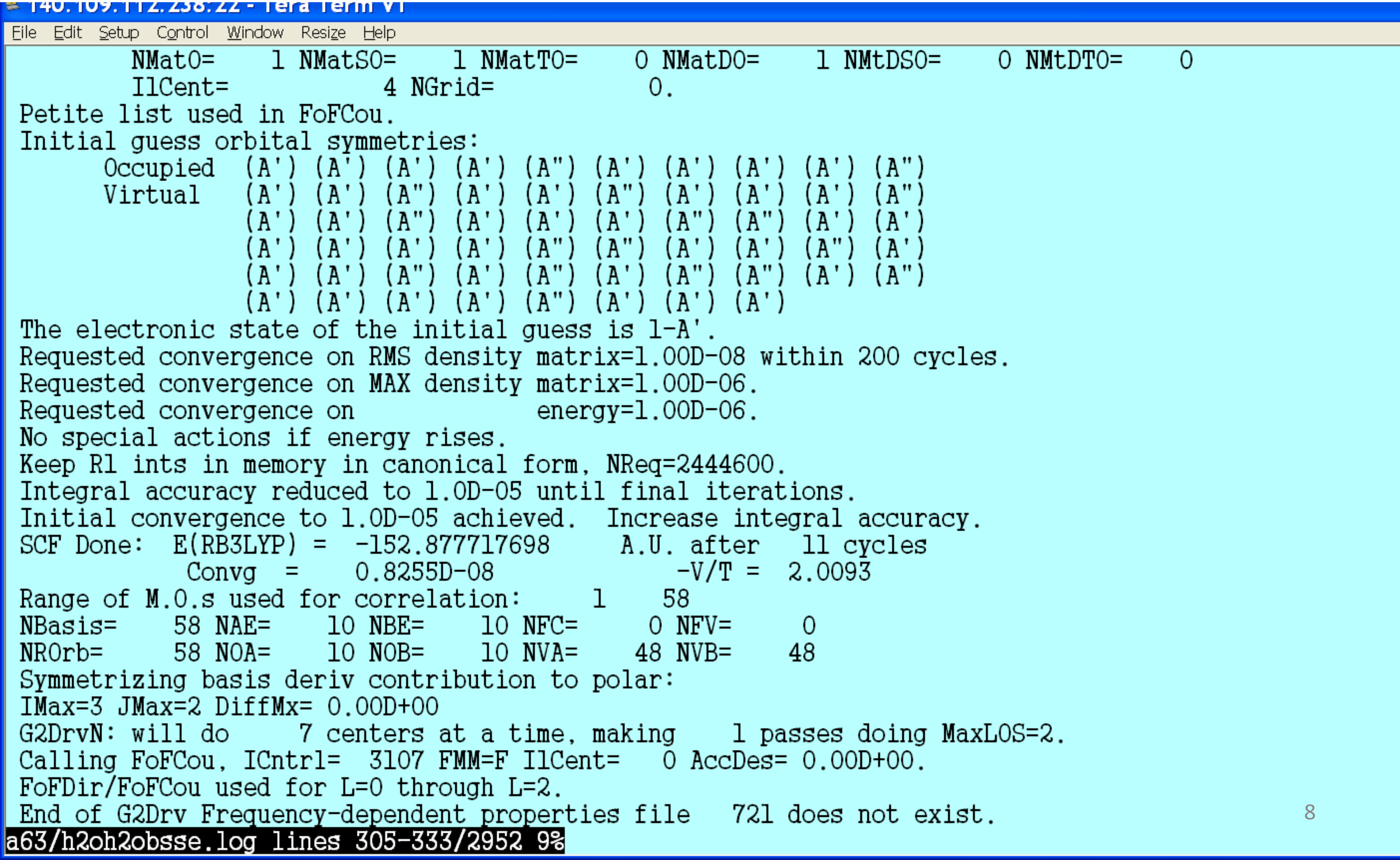
BSSE big for small basis sets

Gaussian CP Input



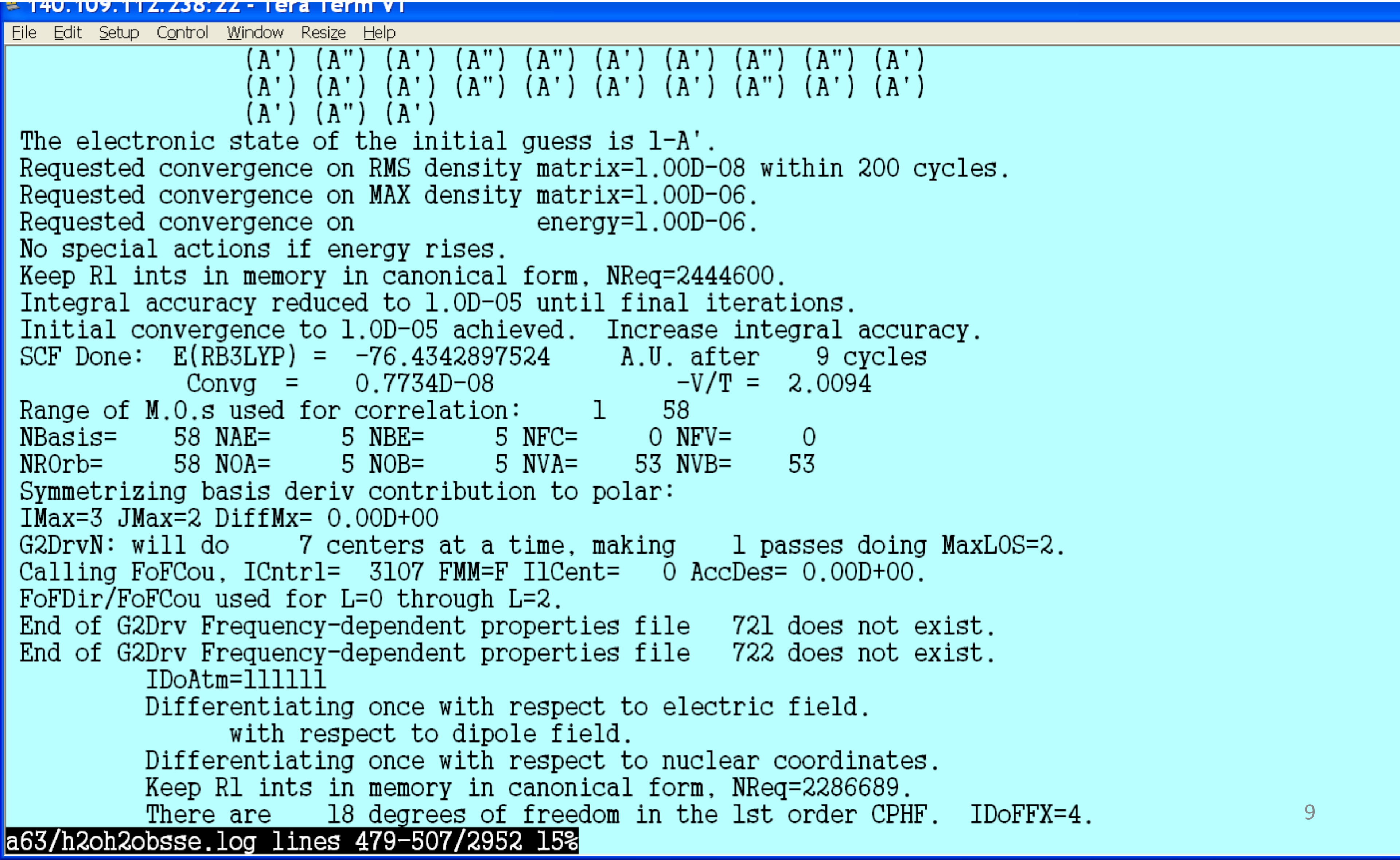
```
%Nproc=8
%mem=12Gb
# B3LYP/STO-3G scf=(tight,maxcycle=200) CounterPoise=2
# pop=min opt=(maxcycle=100,tight,calcall) IOP(1/11=1,99/14=1)

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



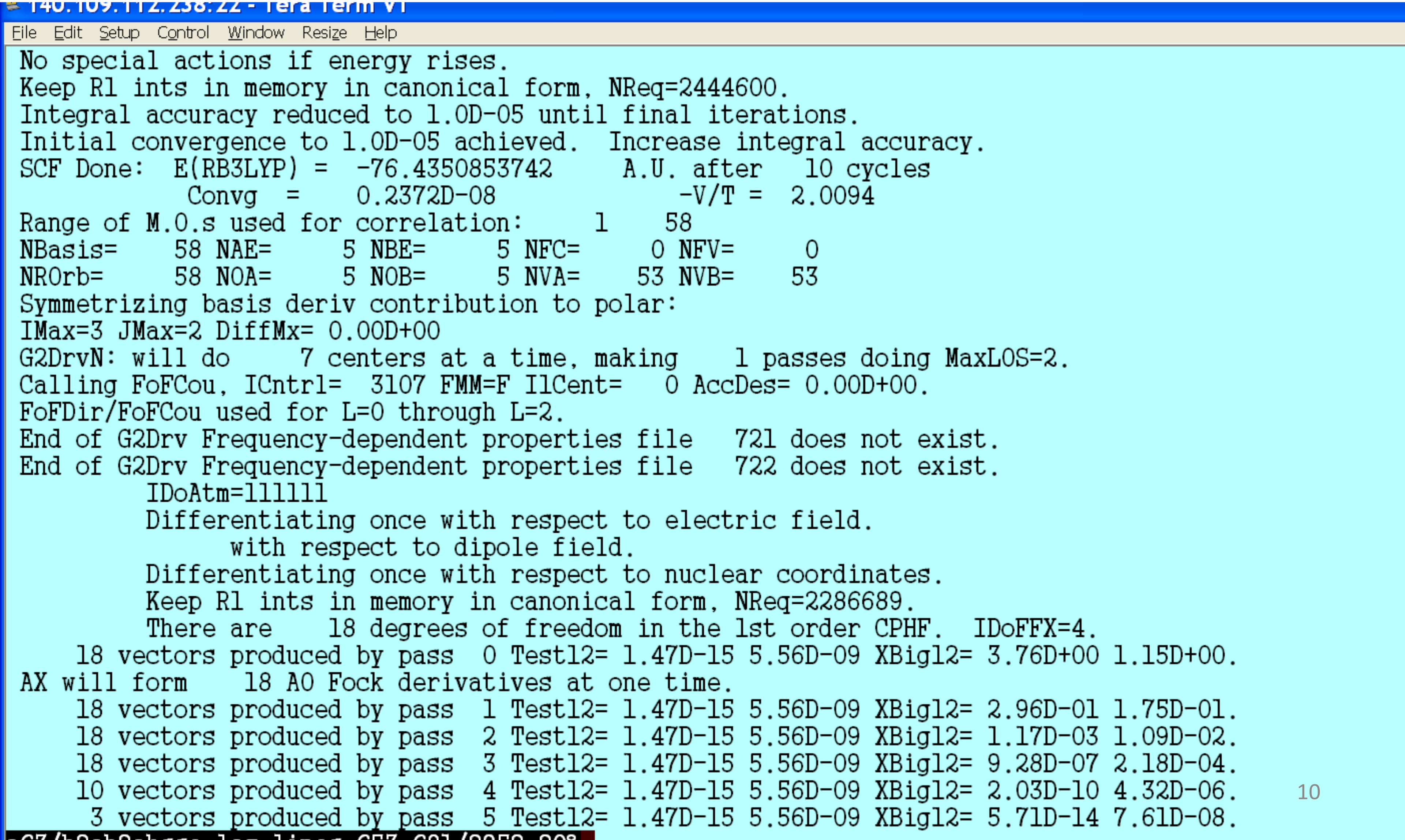
```
         NMat0=    1 NMatS0=    1 NMatT0=    0 NMatD0=    1 NMtDS0=    0 NMtDT0=    0
         I1Cent=          4 NGrid=          0.
 Petite list used in FoFCou.
 Initial guess orbital symmetries:
       Occupied  (A') (A') (A') (A') (A") (A') (A') (A') (A') (A")
       Virtual   (A') (A') (A") (A') (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 I1Cent=   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



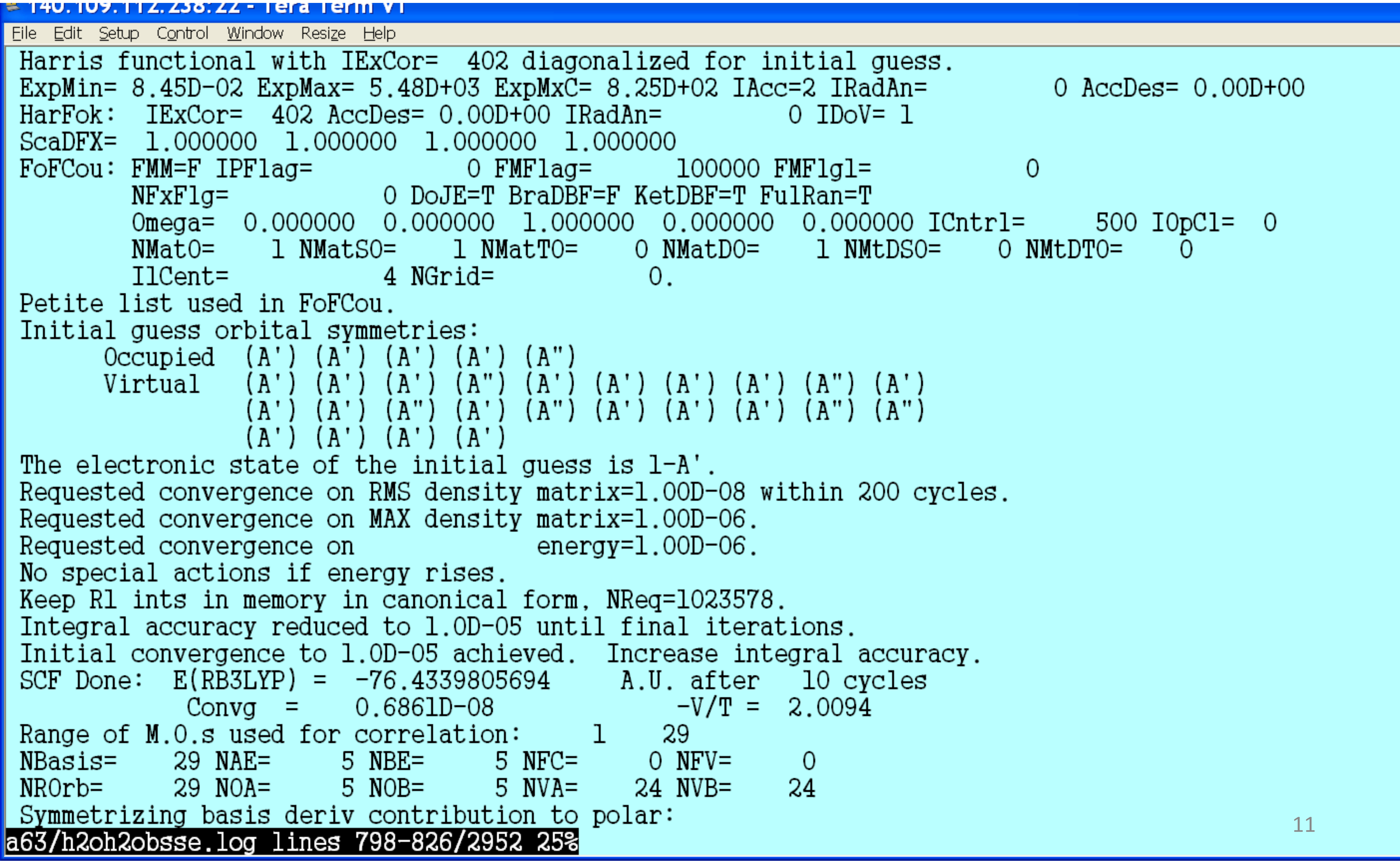
```
                 (A') (A") (A') (A") (A") (A') (A') (A") (A") (A')
                 (A') (A') (A') (A") (A') (A') (A') (A") (A') (A')
                 (A') (A") (A')
 The electronic state of the initial guess is 1-A'.
 Requested convergence on RMS density matrix=1.00D-08 within 200 cycles.
 Requested 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 I1Cent=   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



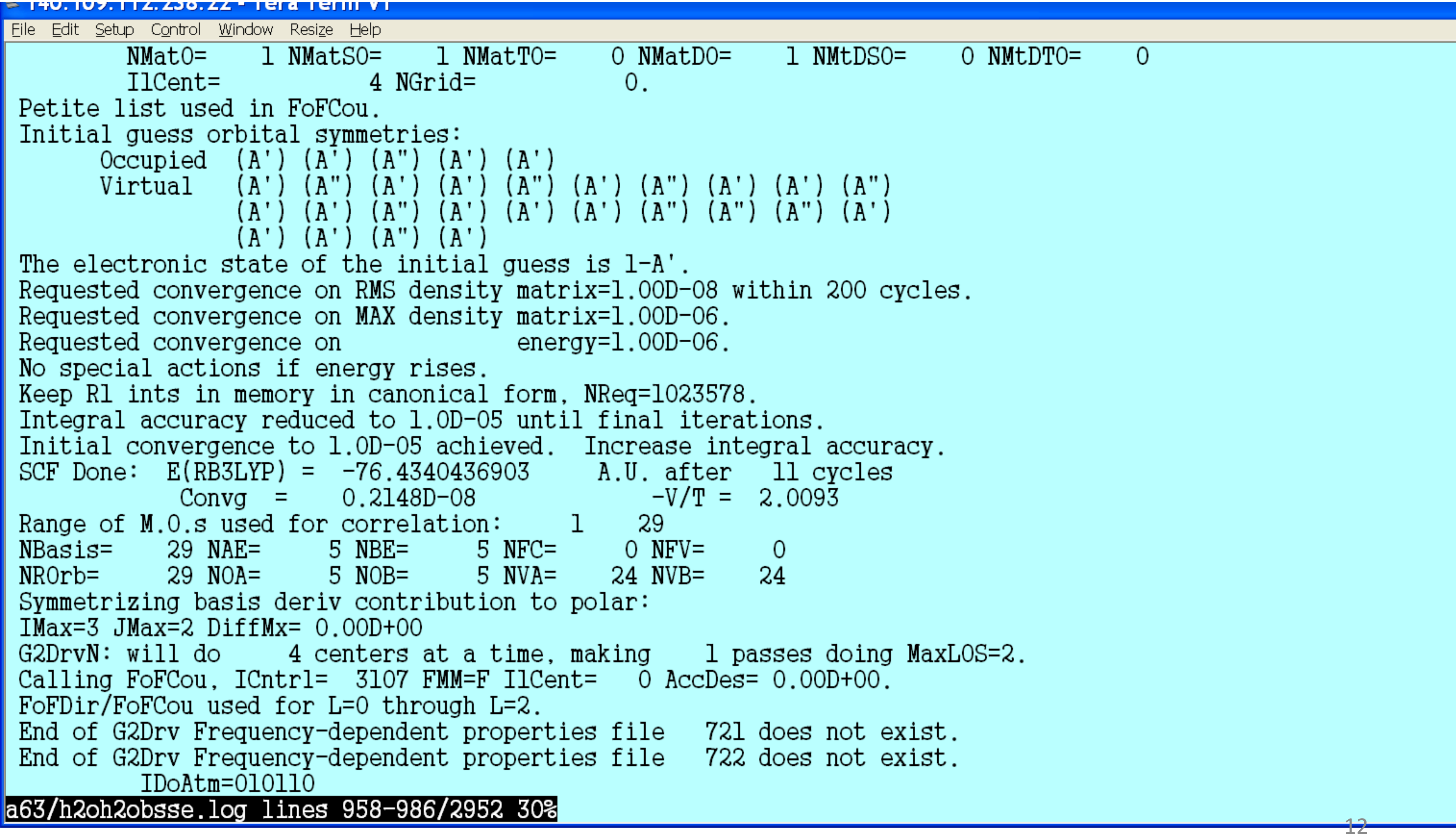
```
No special actions if energy rises.
Keep R1 ints in memory in canonical form, NReq=2444600.
Integral accuracy reduced to 1.0D-05 until final iterations.
Initial convergence to 1.0D-05 achieved.  Increase integral accuracy.
SCF Done:  E(RB3LYP) =  -76.4350853742     A.U. after   10 cycles
            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 I1Cent=   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



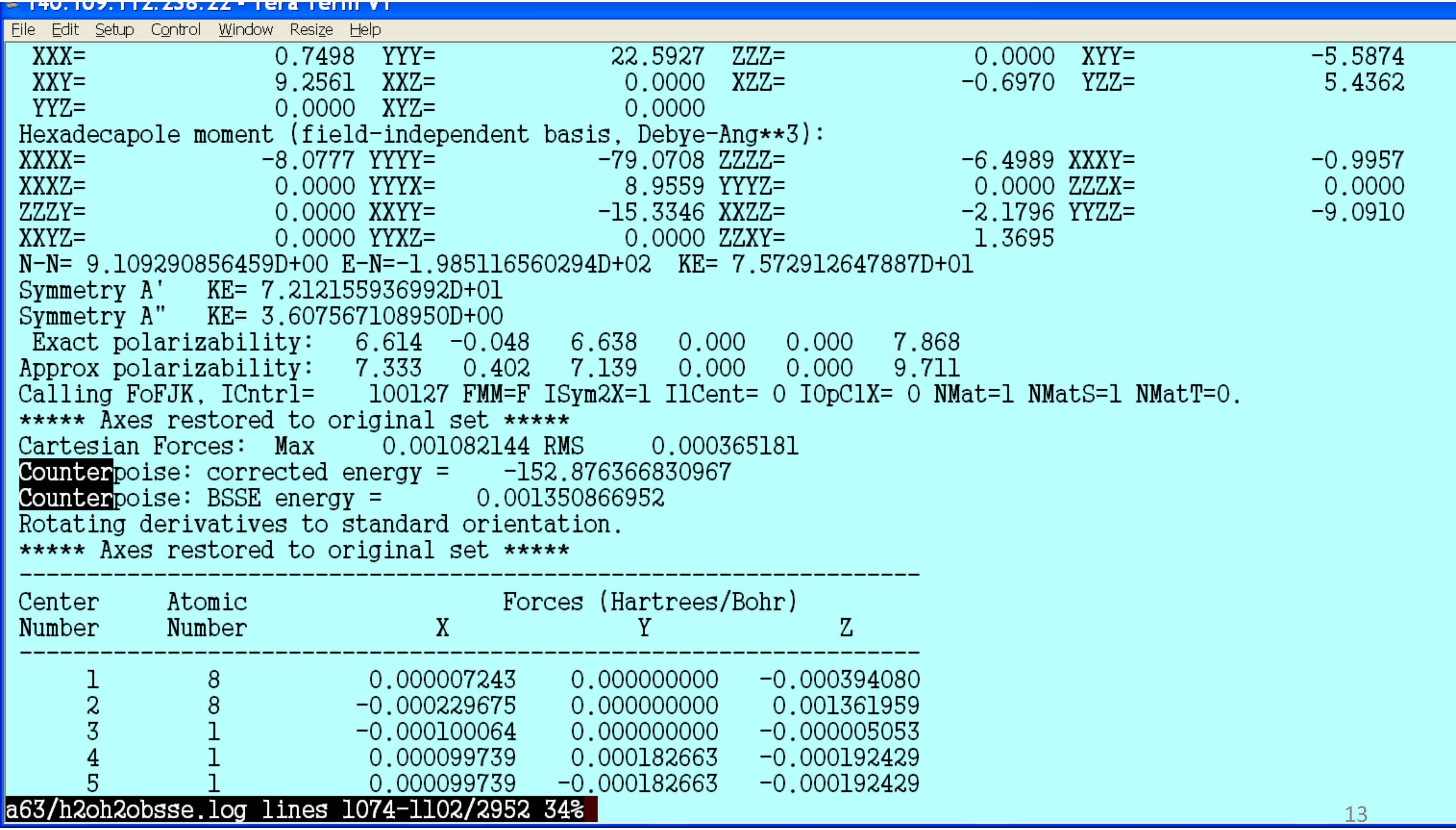
```
 Harris functional with IExCor=  402 diagonalized for initial guess.
 ExpMin= 8.45D-02 ExpMax= 5.48D+03 ExpMxC= 8.25D+02 IAcc=2 IRadAn=         0 AccDes= 0.00D+00
 HarFok:  IExCor=  402 AccDes= 0.00D+00 IRadAn=         0 IDoV= 1
 ScaDFX=  1.000000  1.000000  1.000000  1.000000
 FoFCou: FMM=F IPFlag=           0 FMFlag=      100000 FMFlg1=           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
         I1Cent=           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



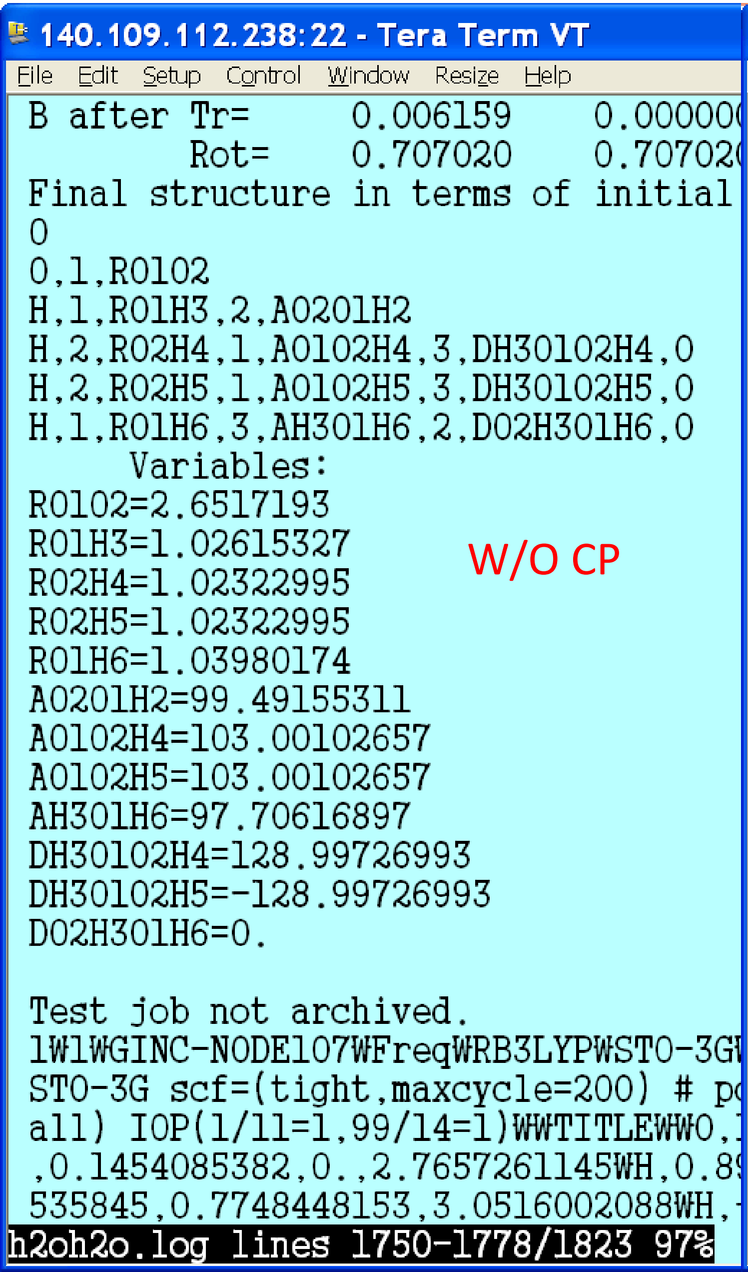
```
        NMat0=    1 NMatS0=    1 NMatT0=    0 NMatD0=    1 NMtDS0=    0 NMtDT0=    0
        IlCent=           4 NGrid=           0.
Petite list used in FoFCou.
Initial guess orbital symmetries:
      Occupied  (A') (A') (A") (A') (A')
      Virtual   (A') (A") (A') (A') (A") (A') (A") (A') (A') (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



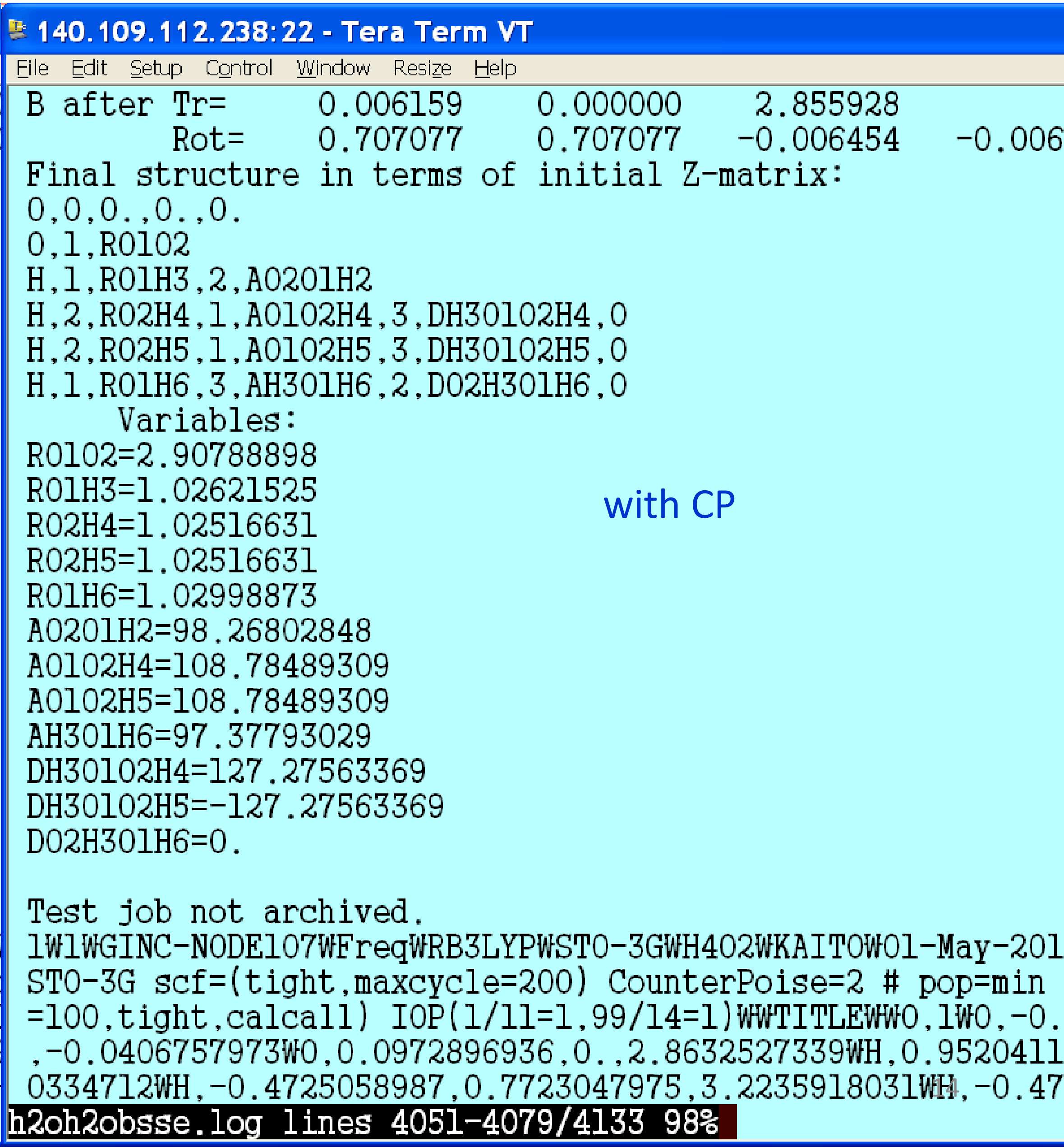
```
 XXX=              0.7498  YYY=             22.5927  ZZZ=              0.0000  XYY=             -5.5874
 XXY=              9.2561  XXZ=              0.0000  XZZ=             -0.6970  YZZ=              5.4362
 YYZ=              0.0000  XYZ=              0.0000
Hexadecapole moment (field-independent 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 I1Cent= 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



```
 B after Tr=      0.006159     0.00000
         Rot=      0.707020     0.70702
 Final structure in terms of initial
 0
 0,1,R0102
 H,1,R01H3,2,A0201H2
 H,2,R02H4,1,A0102H4,3,DH30102H4,0
 H,2,R02H5,1,A0102H5,3,DH30102H5,0
 H,1,R01H6,3,AH301H6,2,D02H301H6,0
      Variables:
 R0102=2.6517193
 R01H3=1.02615327
 R02H4=1.02322995
 R02H5=1.02322995
 R01H6=1.03980174
 A0201H2=99.49155311
 A0102H4=103.00102657
 A0102H5=103.00102657
 AH301H6=97.70616897
 DH30102H4=128.99726993
 DH30102H5=-128.99726993
 D02H301H6=0.

 Test job not archived.
 1\1\GINC-NODE107\Freq\RB3LYP\STO-3G\
 STO-3G scf=(tight,maxcycle=200) # p
 all) IOP(1/11=1,99/14=1)\\TITLE\\0,
 ,0.1454085382,0.,2.7657261145\H,0.8
 535845,0.7748448153,3.0516002088\H,
h2oh2o.log lines 1750-1778/1823 97%
```

W/O CP



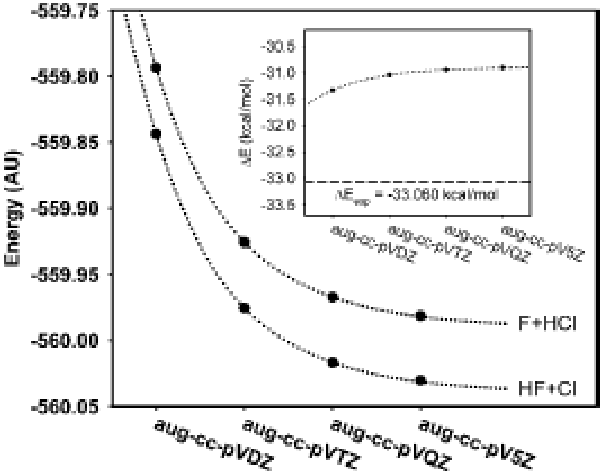
```
 B after Tr=      0.006159     0.000000     2.855928
         Rot=      0.707077     0.707077    -0.006454    -0.006
 Final structure in terms of initial Z-matrix:
 0,0,0.,0.,0.
 0,1,R0102
 H,1,R01H3,2,A0201H2
 H,2,R02H4,1,A0102H4,3,DH30102H4,0
 H,2,R02H5,1,A0102H5,3,DH30102H5,0
 H,1,R01H6,3,AH301H6,2,D02H301H6,0
      Variables:
 R0102=2.90788898
 R01H3=1.02621525
 R02H4=1.02516631
 R02H5=1.02516631
 R01H6=1.02998873
 A0201H2=98.26802848
 A0102H4=108.78489309
 A0102H5=108.78489309
 AH301H6=97.37793029
 DH30102H4=127.27563369
 DH30102H5=-127.27563369
 D02H301H6=0.

 Test job not archived.
 1\1\GINC-NODE107\Freq\RB3LYP\STO-3G\H4O2\KAITO\01-May-201
 STO-3G scf=(tight,maxcycle=200) CounterPoise=2 # pop=min
 =100,tight,calcall) IOP(1/11=1,99/14=1)\\TITLE\\0,1\0,-0.
 ,-0.0406757973\0,0.0972896936,0.,2.8632527339\H,0.9520411
 0334712\H,-0.4725058987,0.7723047975,3.2235918031\H,-0.47
h2oh2obsse.log lines 4051-4079/4133 98%
```

with CP

Dunning Correlation Consistent Basis Set

T. Dunning decided on defining the contraction coefficient and exponential coefficient to maximize electron correlation

aug-cc-pVDZ (X=2)
aug-cc-pVTZ (X=4)
aug-cc-pVQZ (X=4)
aug-cc-pV5Z (X=5)



$$E(X) = E_{CBS} + B\exp\left[-(X-1)\right] + C\exp\left[-(X-1)^2\right]$$

Density functional Theory:
Dump everything to unknown

Density Function Theory basic philosophy

- Calculate the ground state using the best electron density not the best wavefunction for n electrons

$$\rho(\boldsymbol{r}) = n \sum_{\sigma_1=}^{\pm 1/2} \int dx_2 \ldots dx_n \,|\Psi^*(x_1 \ldots x_n)\Psi(x_1 \ldots x_n)|$$

$$\int d\boldsymbol{r}\, \rho(\boldsymbol{r}) = n$$

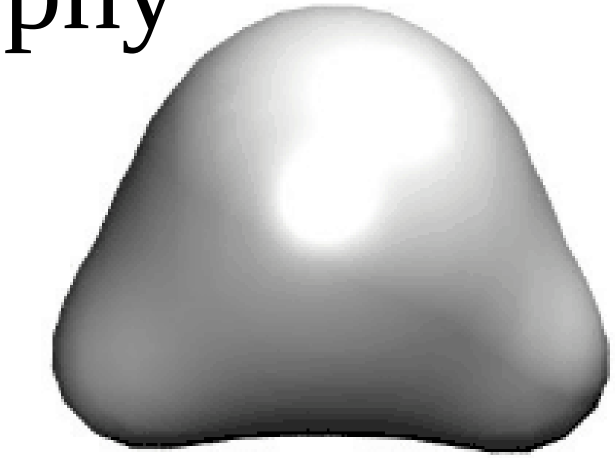
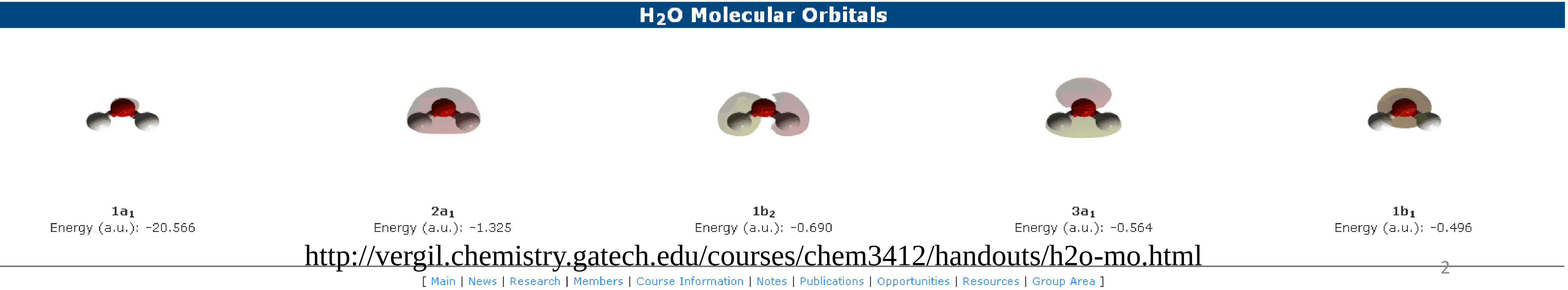


Figure 1: Total charge density for the H2O molecule, created by Waveplot, visualised by VMD.

Why?

1. Density is much easier to calculate than orbital is positive every where, only depends only on **r** not 3n coordinates



H_2O Molecular Orbitals

$1a_1$	$2a_1$	$1b_2$	$3a_1$	$1b_1$
Energy (a.u.): -20.566	Energy (a.u.): -1.325	Energy (a.u.): -0.690	Energy (a.u.): -0.564	Energy (a.u.): -0.496

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http://vergil.chemistry.gatech.edu/courses/chem3412/handouts/h2o-mo.html

Basic Idea: Hohenberg Kohn Theorem

- For a given number of electrons with external potential $v(r)$ there “exists” a functional of electron density $\rho(r)$ that

$$E_v^{HK}[\rho] \geq E_v^{HK}[\rho_0] = E_0$$

Where ρ_0 and E_0 are the EXACT GROUND STATE DENSITY AND ENERGY

- What is external potential $v(r)$???

POTENTIAL GENERATED BY NUCLEI

$$v(r_i) = \sum_{I}^{N} \frac{Z_I}{|r_{iI}|} \rightarrow V_{ext} = \sum_{i}^{n} v(r_i)$$

Minimization by density constraint

- So the ground state energy

$$E_0 = \min_{\rho, \int \rho d\tau = n} \min_{\Psi \to \rho} \langle \Psi | T + V_{ext} + V_{ele} | \Psi \rangle$$

Since the external potential only depends on sum of one electron part

$$\langle \Psi | V_{ext} | \Psi \rangle = \int v(r) \rho(r) dr$$

Then we DEFINE auxiliary functional $F^{HK}[\rho]$ so

$$F^{HK}[\rho] \equiv \langle \Psi | T + V_{ele} | \Psi \rangle$$

WE DON’T KNOW HOW IT LOOKS!! ☺

Here we are assuming that the kinetic and electron repulsion term CAN be written ONLY USING DENSITY, without wavefunction

$$E_v^{HK}[\rho] = \int v(r) \rho(r) dr + F^{HK}[\rho] \to\to E_0 = \min_{\rho, \int \rho d\tau = n} E_v^{HK}[\rho]$$

- Is it possible to construct a quantum theory based only on density?
  Yes, but we have no idea how such theory can be constructed

Kohn Sham Approximation

- Using fictitious n electron system that DO NOT INTERACT, but instead of using the nuclear external potential $v(r)$ we use a MAGICAL external potential $v_0(r)$ which can give exact ground state density ρ_0 of real system

In the KS approximation, we use one Slater determinant for the wavefunction

$$\left|\psi_1\psi_2\ldots\psi_n\right\rangle = \frac{1}{\sqrt{n!}}\begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \ldots\ldots\ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \ldots\ldots\ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_2) \\ \ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots \\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \ldots\ldots\ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_n) \end{vmatrix}$$

Kohn Sham Orbitals $\psi_i(r)$

$$\rho(\boldsymbol{r}) = \sum_{i}^{n} |\psi_i(r)|^2$$

$$\left(-\frac{1}{2}\nabla^2 + v_0\right)\psi_i = \varepsilon_i\psi_i$$

Looks similar to Hartree Fock equation!

Ground state energy

- In KS approximation we write ground state energy as

$$E_0^{KS}[\rho] = T_0 + \int v(r)\rho(r)dr + J[\rho] + E_{XC}[\rho]$$

Instead of the true kinetic energy of real system we use the KINETIC ENERGY OF THE FICTIOUS KOHN-SHAM ORBITALS

$$T_0 = \frac{1}{2}\sum_{i=1}^{n}\int \psi_i^*(r)\nabla^2\psi_i(r)$$

Second part is the true nuclei electron interaction, third is the self interaction, REPULSON OF THE ELECTRON CLOUD WITH ITSELF

$$J[\rho] = \frac{1}{2}\iint dr_1 dr_2 \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}$$

every thing we don’t know we collect and call it exchange correlation energy $E_{XC}[\rho]$ (remember it also has ignored kinetic correction)

Determination of Kohn-Sham Orbitals

- Basic idea is the same as the Hartree Fock, we want to minimize the $E_0^{KS}[\rho]$, with

$$\rho(\boldsymbol{r}) = \sum_i^n |\psi_i(r)|^2$$

So if $\psi_i(r) \to \psi_i(r) + \delta_i(r)$ then $\rho(\boldsymbol{r}) \to \rho(\boldsymbol{r}) + \delta\rho(\boldsymbol{r})$ where

$$\delta\rho(\boldsymbol{r}) = \sum_i^n |\delta_i^*(r)\psi_i(r)|^2$$

So we minimize

$$E_0^{KS}[\rho] - \sum_i^n \sum_j^n \varepsilon_{ij}\left(\langle\psi_i|\psi_j\rangle - \delta_{ij}\right)$$

Last term is from the constraint that KS orbitals are normalized and orthogonal

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}$$

Derivatives 1

$$E_0^{KS}[\rho] = T_0 + \int v(r)\rho(r)dr + J[\rho] + E_{XC}[\rho]$$

So the derivatives are

$\delta T_0 = -\frac{1}{2}\sum_{i=1}^{n}\int dr\delta_i^*(r)\nabla^2\psi_i(r)$; $\int v(r)\delta\rho(r)dr = \sum_i^n \int \delta_i^*(r)v(r)\psi_i(r)dr$

Remember the definition of using KS orbital $\delta\rho(\boldsymbol{r}) = \sum_i^n|\delta_i^*(r)\psi_i(r)|^2$

$$\delta J = \frac{1}{2}\left[\iint dr_1 dr_2 \frac{\delta\rho(r_1)\rho(r_2)}{|r_1 - r_2|} + \iint dr_1 dr_2 \frac{\rho(r_1)\delta\rho(r_2)}{|r_1 - r_2|}\right] = \iint dr_1 dr_2 \frac{\delta\rho(r_1)\rho(r_2)}{|r_1 - r_2|}$$

Remember $\rho(\boldsymbol{r}) = \sum_j^n\left|\psi_j(r)\right|^2$

$$\delta J = \iint dr_1 dr_2 \frac{\sum_i^n \delta_i^*(r_1)\psi_i(r_1)\sum_j^n \psi_j^*(r_2)\psi_j(r_2)}{|r_1 - r_2|} = \sum_i^n\sum_j^n \iint dr_1 dr_2 \frac{\delta_i^*(r_1)\psi_i(r_1)\psi_j^*(r_2)\psi_j(r_2)}{|r_1 - r_2|}$$

Here if we remember the operator for exchange in Hartree Fock

$$J_j(r_1) = \int dr_2 \frac{\psi_j^*(r_2)\psi_j(r_2)}{|r_1 - r_2|} \rightarrow \delta J = \sum_i^n\sum_j^n \int \delta_i^*(r_1)J_j(r_1)\psi_i(r_1)$$

Derivatives 2

- We don’t know how $E_{XC}[\rho]$ looks BUT ASSUME it has functional derivative

$$\delta E_{XC}[\rho] = \int dr \frac{\delta E_{XC}}{\delta\rho(r)}\delta\rho(r) = \sum_{i=1}^{n}\int dr\delta_i^*(r)\frac{\delta E_{XC}}{\delta\rho(r)}\psi_i(r)$$

- Derivative for orthogonal condition

$$\delta\langle\psi_i|\psi_j\rangle = \int dr\delta_i^*(r)\psi_i(r) + cc$$

So adding all the terms we want to solve

$$\delta\left[E_0^{KS}[\rho] - \sum_i^n\sum_j^n \varepsilon_{ij}\left(\langle\psi_i|\psi_j\rangle - \delta_{ij}\right)\right]$$

Derivative 3

$$\delta\left[E_0^{KS}[\rho]-\sum_i^n\sum_j^n\varepsilon_{ij}\left(\langle\psi_i|\psi_j\rangle-\delta_{ij}\right)\right]$$

Can be written using KS orbitals as

$$\sum_{i=1}^n\int dr\delta_i^*(r)\left[\frac{-1}{2}\nabla^2+v(r)+\sum_j^n J_j(r)+\frac{\delta E_{XC}}{\delta\rho(r)}\right]\psi_i(r)-\sum_i^n\sum_j^n\varepsilon_{ij}\int dr\delta_i^*(r)\psi_j(r)=0$$

So we have to solve

$$\left[\frac{-1}{2}\nabla^2+v(r)+\sum_j^n J_j(r)+\frac{\delta E_{XC}}{\delta\rho(r)}\right]\psi_i(r)=\sum_j^n\varepsilon_{ij}\psi_j(r)$$

Or by using canonical KS orbitals which diagonalize ε_{ij} we have KS equation

$$\left[\frac{-1}{2}\nabla^2+v(r)+\sum_j^n J_j(r)+\frac{\delta E_{XC}}{\delta\rho(r)}\right]\psi_i{}'(r)=\varepsilon_i\psi_i{}'(r)$$

Summary of Density Functional Kohn Sham Approximation

- Looking back at our derivation we said we have some magic external potential v_0 which we just have to solve for KS orbitals

$$\left(-\frac{1}{2}\nabla^2 + v_0\right)\psi_i = \varepsilon_i\psi_i$$

- After putting all the “UNKOWN” to $E_{XC}[\rho]$ and properly evaluating what we know we got Kohn Sham equation

$$\left[\frac{-1}{2}\nabla^2 + v(r) + \sum_j^n J_j(r) + \frac{\delta E_{XC}}{\delta\rho(r)}\right]\psi_i'(r) = \varepsilon_i\psi_i'(r)$$

So the magical external potential is

$$v_{XC} \equiv \frac{\delta E_{XC}}{\delta\rho(r)} \rightarrow v_0 = v(r) + \sum_j^n J_j(r) + v_{XC}$$

Remember that I still have not told you how v_{XC} looks ☺

Things to be careful when using KS equation

- People will call is “DENSITY FUNCTIONAL THEORY” or DFT when they run the KS calculation, which is really an approximation to the theory
- Since $E_{XC}[\rho]$ is unkown we have to pick an approximation. This is not an easy problem, so there are many exchange correlation functionals:

1. Local Density Approximation: $v_{XC} \sim \rho^{1/3}$
2. General Gradient Approximation: such as BLYP, PBE
   $v_{XC}[\rho] \sim \rho \quad + \nabla\rho$ add in density derivative contribution
3. Hybrid: such as B3LYP, B3PW91 $v_{XC}[\rho] \sim \rho \quad + \nabla\rho + K_j$ where the last part is Hartree Fock exchange(depends on orbital)
4. Meta: M06, M11

- Since integration of $\frac{\delta E_{XC}}{\delta\rho(r)}$ is done with numerical integration one has to be careful with the integration grid