

第四章 單點計算與量化圖形

所謂單點計算是指在 Born-Oppenheimer (通常 nonrelativistic) 假設下，指定所有原子核的位置與電子數後，求解電子運動的薛丁格方程式的計算，所得的能量包含電子的動能，位能，以及原子核的靜電排斥能量，但不包含原子核的動能。其相對的能量零點為所有原子核與電子互相分離到無窮遠且為靜止狀態。 單點計算與量化圖形的產生過程大致如下：

(1) 建構 Input file (*.com, gjf)

提供分子結構，指定電子數目 (電荷)，計算理論，基底函數，其他計算選項及參數。

例如：

```
%NProcShared=4
%mem=64MW
%chk=BF3
#MP2/6-31+G(d,p) SCF=InCore Density=MP2
```

Test calculation using BF3

```
0 1
B
F 1 R1
F 1 R1 2 120.
F 1 R1 2 120. 3 180.
```

R1 = 1.3

接下來執行程式：(或由 G09W 執行)

```
hu@Hubble NCHC]$ g09 BF3.com &
[1] + Done                                     g09 BF3.com
```

```
[hu@Hubble NCHC]$ ls
BF3.chk  BF3.com  BF3.log
```

(2)檢視 Output file

```
Entering Gaussian System, Link 0=g09
Input=BF3.com
Output=BF3.log
Initial command:
/home/hu/g09/11.exe /s/hu/Gau-16489.inp -scrdir=/s/hu/
Entering Link 1 = /home/hu/g09/11.exe PID= 16490.
```

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and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Gaussian 09: EM64T-G09RevA.02 11-Jun-2009

25-Jul-2014

%NProcShared=4

Will use up to 4 processors via shared memory.

%mem=64MW

%chk=BF3

#MP2/6-31+G(d,p) SCF=InCore Density=MP2

1/30=1,38=1/1;
2/12=2,17=6,18=5,40=1/2;
3/5=1,6=6,7=111,11=9,16=1,25=1,30=1,71=1/1,2,3;
4//1;
5/5=3,38=5/2;
8/6=4,10=2/1;
9/15=1,16=-3/6;
10/5=1,13=10,20=2,30=1/2;
6/7=2,8=2,9=2,10=2,22=2/1;
99/5=1,9=1/99;

Test calculation using BF3

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

B

F	1	R1				
F	1	R1	2	120.		
F	1	R1	2	120.	3	180.
						0

Variables:

R1 1.3

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	0.000000
2	9	0	0.000000	0.000000	1.300000
3	9	0	1.125833	0.000000	-0.650000
4	9	0	-1.125833	0.000000	-0.650000

Distance matrix (angstroms):

	1	2	3	4
1 B	0.000000			
2 F	1.300000	0.000000		
3 F	1.300000	2.251666	0.000000	
4 F	1.300000	2.251666	2.251666	0.000000

Stoichiometry BF3

Framework group D3H[0(B),3C2(F)]

Deg. of freedom 1

Full point group D3H NOp 12

Largest Abelian subgroup C2V NOp 4

Largest concise Abelian subgroup C2 NOp 2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	0.000000
2	9	0	0.000000	1.300000	0.000000
3	9	0	1.125833	-0.650000	0.000000
4	9	0	-1.125833	-0.650000	0.000000

Rotational constants (GHZ): 10.4935426 10.4935426 5.2467713

Standard basis: 6-31+G(d,p) (6D, 7F)

There are 34 symmetry adapted basis functions of A1 symmetry.

There are 7 symmetry adapted basis functions of A2 symmetry.

There are 22 symmetry adapted basis functions of B1 symmetry.

There are 13 symmetry adapted basis functions of B2 symmetry.

Integral buffers will be 131072 words long.

Raffenetti 1 integral format.

Two-electron integral symmetry is turned on.

76 basis functions, 128 primitive gaussians, 76 cartesian basis functions

16 alpha electrons 16 beta electrons

nuclear repulsion energy 112.0618691461 Hartrees.

NAtoms= 4 NActive= 4 NUniq= 2 SFac= 3.00D+00 NAtFMM= 80 NAOKFM=F Big=F

One-electron integrals computed using PRISM.

NBasis= 76 RedAO= T NBF= 34 7 22 13

NBsUse= 76 1.00D-06 NBFU= 34 7 22 13

...

...

Initial guess orbital symmetries:

Occupied	(E')	(E')	(A1')	(A1')	(A1')	(E')	(E')	(A1')	(E')
	(E')	(A2")	(E')	(E')	(E")	(E")	(A2')		
Virtual	(A2")	(A1')	(E')	(E')	(A2")	(A1')	(E')	(E")	
	(E")	(A1')	(E')	(E')	(A2")	(A1')	(A2')	(E')	(E')
	(E')	(E')	(A2")	(E')	(A1')	(E")	(E")	(A1')	
	(E")	(E')	(E')	(A2")	(A1')	(A2')	(E')	(E')	
	(E')	(E")	(E')	(E")	(A1")	(E')	(E')	(A1')	(E')
	(E')	(A2")	(A1')	(A2")	(E")	(E")	(E')	(E')	(E')
	(E')	(A1')	(A1')	(A2")	(E")	(E")	(E')	(E')	(E')
	(E')	(A2")	(A1')	(A1')	(E')	(E')	(E')	(E')	(E')

The electronic state of the initial guess is 1-A1'.

Requested convergence on RMS density matrix=1.00D-08 within 128 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=5139001.

SCF Done: E(RHF) = -323.208916863 A.U. after 10 cycles
 Convg = 0.1643D-08 -V/T = 2.0026

ExpMin= 3.15D-02 ExpMax= 7.00D+03 ExpMxC= 1.05D+03 IAcc=3 IRadAn= 5 AccDes= 0.00D+00

HarFok: IExCor= 205 AccDes= 0.00D+00 IRadAn= 5 IDoV=-2

ScaDFX= 1.000000 1.000000 1.000000 1.000000

Range of M.O.s used for correlation: 5 76

NBasis= 76 NAE= 16 NBE= 16 NFC= 4 NFV= 0

NROrb= 72 NOA= 12 NOB= 12 NVA= 60 NVB= 60

**** Warning!!: The largest alpha MO coefficient is 0.11293407D+02

Fully in-core method, ICMem= 15658020.

JobTyp=1 Pass 1 fully in-core, NPsUse= 4.

Spin components of T(2) and E(2):

alpha-alpha T2 =	0.1981767387D-01	E2=	-0.8384925841D-01
alpha-beta T2 =	0.9793787105D-01	E2=	-0.4259786899D+00
beta-beta T2 =	0.1981767387D-01	E2=	-0.8384925841D-01
ANorm=	0.1066570775D+01		
E2 =	-0.5936772067D+00	EUMP2 =	-0.32380259406950D+03

...

...

Population analysis using the MP2 density.

Orbital symmetries:

Occupied	(E')	(E')	(A1')	(A1')	(A1')	(E')	(E')	(A1')	(E')
	(E')	(A2")	(E')	(E')	(E")	(E")	(A2')		
Virtual	(A1')	(A2")	(E')	(E')	(A2")	(A1')	(E')	(E')	(A1')
	(E")	(E")	(E')	(E')	(A2")	(A2')	(A1')	(E')	(E')
	(E')	(E')	(A2")	(E')	(A1')	(E")	(E")	(A1')	
	(E')	(E')	(A1')	(E")	(E")	(A2")	(A2')	(E')	(E')
	(E')	(E')	(E")	(E")	(A1")	(A1')	(E')	(E')	(E')
	(E')	(A2")	(A1')	(A2")	(E")	(E")	(E')	(E')	(E')
	(E')	(A1')	(A1')	(A2")	(E")	(E")	(E')	(E')	(E')

The electronic state is 1-A1'.

Alpha occ. eigenvalues --	-26.35738	-26.35738	-26.35736	-7.78765	-1.69774
Alpha occ. eigenvalues --	-1.65313	-1.65313	-0.86380	-0.82039	-0.82039
Alpha occ. eigenvalues --	-0.76978	-0.70503	-0.70503	-0.69072	-0.69072
Alpha occ. eigenvalues --	-0.66439				
Alpha virt. eigenvalues --	0.05156	0.06900	0.07978	0.07978	0.21533
Alpha virt. eigenvalues --	0.29519	0.29730	0.29730	0.34297	0.34333
Alpha virt. eigenvalues --	0.34333	0.36824	0.36824	0.37258	0.42644
Alpha virt. eigenvalues --	0.48588	0.48683	0.48683	0.63490	0.63490
Alpha virt. eigenvalues --	0.73378	0.93222	0.93222	1.08672	1.41390
Alpha virt. eigenvalues --	1.41390	1.74087	1.76607	1.76607	1.78347
Alpha virt. eigenvalues --	1.80467	1.80467	1.85395	1.89409	1.91239
Alpha virt. eigenvalues --	1.91239	1.97667	1.97667	2.08690	2.08690
Alpha virt. eigenvalues --	2.09410	2.14592	2.16038	2.16038	2.19248
Alpha virt. eigenvalues --	2.19248	2.25030	2.32889	2.45451	2.81503
Alpha virt. eigenvalues --	2.81503	3.30818	3.30818	3.51205	3.51205
Alpha virt. eigenvalues --	3.80449	4.16200	5.41168	5.54267	5.54267

Condensed to atoms (all electrons):

	1	2	3	4
1 B	2.836395	0.303750	0.303750	0.303750
2 F	0.303750	9.278394	-0.082346	-0.082346
3 F	0.303750	-0.082346	9.278394	-0.082346
4 F	0.303750	-0.082346	-0.082346	9.278394

Mulliken atomic charges:

	1
1 B	1.252356
2 F	-0.417452
3 F	-0.417452
4 F	-0.417452

Sum of Mulliken atomic charges = 0.00000

Mulliken charges with hydrogens summed into heavy atoms:

	1
1 B	1.252356
2 F	-0.417452
3 F	-0.417452
4 F	-0.417452

Sum of Mulliken charges with hydrogens summed into heavy atoms = 0.00000

Electronic spatial extent (au): <R**2>= 209.6544

Charge= 0.0000 electrons

Dipole moment (field-independent basis, Debye):

X=	0.0000	Y=	0.0000	Z=	0.0000 Tot=
0.0000					

Quadrupole moment (field-independent basis, Debye-Ang):

XX=	-22.3600	YY=	-22.3600	ZZ=	-18.1022
XY=	0.0000	XZ=	0.0000	YZ=	0.0000

...

...

N-N= 1.120618691461D+02 E-N=-9.945131237260D+02 KE= 3.223800929917D+02

Symmetry A1 KE= 2.037181594425D+02

Symmetry A2 KE= 6.288940396714D+00

Symmetry B1 KE= 1.009706361267D+02

Symmetry B2 KE= 1.140235702581D+01

1\1\GINC-HUBBLE\SP\RMP2-FC\6-31+G(d,p)\B1F3\HU\25-Jul-2014\0\\#MP2/6-3

```

1+G(d,p) SCF=InCore Density=MP2\\Test calculation using BF3\\0,1\\B\\F,1
,1.3\\F,1,1.3,2,120.\\F,1,1.3,2,120.,3,180.,0\\Version=EM64T-G09RevA.02\
State=1-A1'\\HF=-323.2089169\\MP2=-323.8025941\\RMSD=1.643e-09\\Dipole=0.,
0.,0.\\Quadrupole=-1.0551951,2.1103902,-1.0551951,0.,0.,0.\\PG=D03H [0(B
1),3C2(F1)]\\@

```

Sometimes the fool who rushes in gets the job done.

-- Al Bernstein

Job cpu time: 0 days 0 hours 0 minutes 10.5 seconds.

File lengths (MBytes): RWF= 5 Int= 0 D2E= 0 Chk= 1 Scr= 1

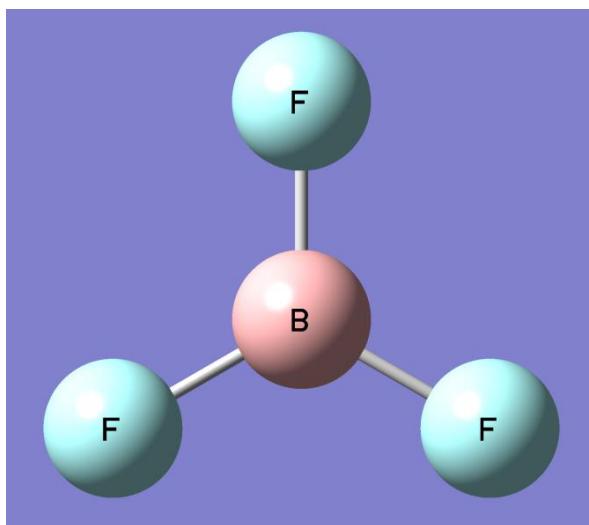
Normal termination of Gaussian 09 at Fri Jul 25 09:13:47 2014.

Atomic Units:

$$1 \text{ bohr} = a_0 = \frac{\hbar^2}{4\pi\epsilon_0 e^2 m_e} = 0.52918 \text{ \AA}$$

$$1 \text{ hartree} = h = \frac{m_e e^4}{4\epsilon_0^2 h^2} \frac{1}{n^2} = \frac{e^2}{4\pi\epsilon_0 a_0} = 627.5095 \text{ kcal/mol}$$

GaussView 可直接讀取 Gaussian 09 之 output file，並顯示基本的運算結果。

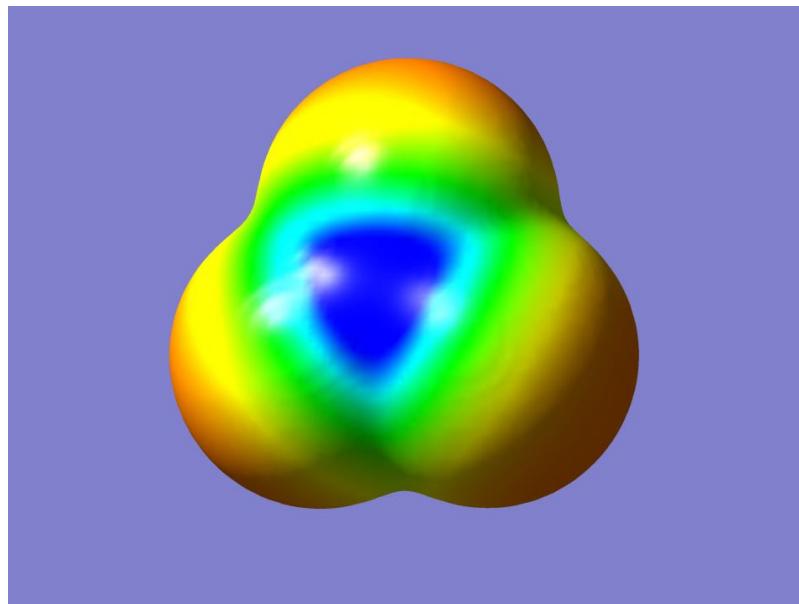


若要檢視計算所得之 orbitals, density, electrostatic potential 等波函數相關資料，需先產生 formatted formchk 檔。(GaussView 可直接讀取 G09W 之 checkpoint file)

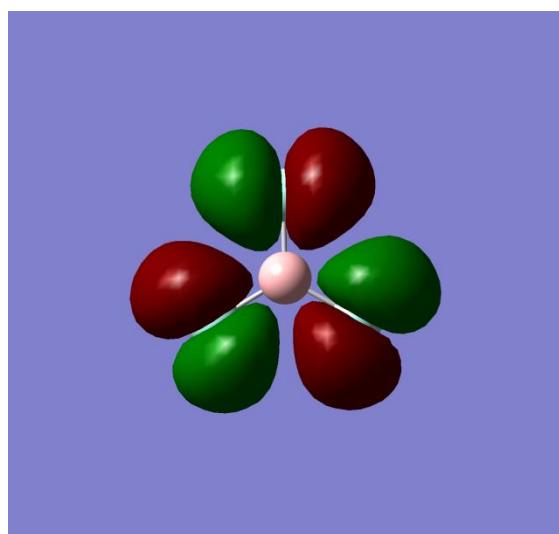
(3) 產生 Formatted checkpoint file (或者在 Route Section 加入 "FChk" keyword)

```
[hu@Hubble NCHC]$ formchk BF3.chk  
[hu@Hubble NCHC]$ ls  
BF3.chk  BF3.com  BF3.fchk  BF3.log
```

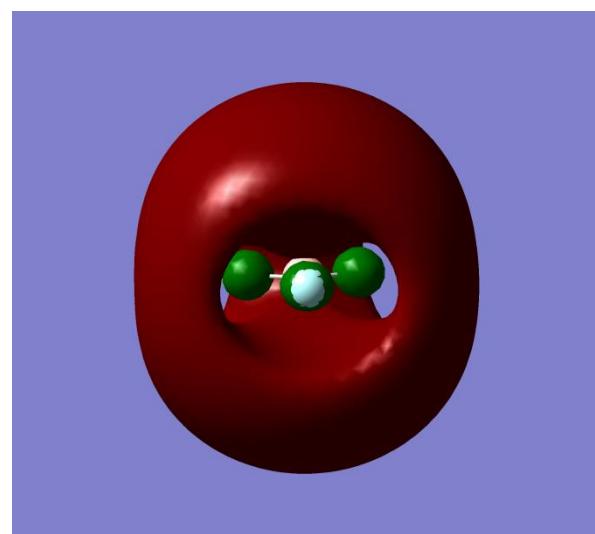
開啟 BF3.fchk, 由 Results --> Surface/Contour...



Electron Isodensity (0.0004) mapped with ESP



HOMO



LUMO

(4) 讀入非內建基底函數

雖然 Gaussian 有許多內建的基底函數，但有時候還是需要用到一些新的或 Gaussian 中沒有包含的 basis sets，最常見的情況是包含過渡金屬的計算，許多常用的基底函數不支援 3d 以後的金屬，內建可支援重金屬的基底函數通常品質也並不理想。以下是讀入 Peterson 等人於 2005 年發表的 aug-cc-pVDZ-pp basis set 計算金原子的範例：

```
#B3LYP Gen Pseudo=Read

Au atom

0 2
Au

Au      0
S    7   1.00
      38.0008000      0.0200090
      23.9725000     -0.1516790
      15.2182000      0.3639600
      5.5399900     -0.8213260
      1.3855100      0.9366410
      0.6424610      0.4235270
      0.1564960      0.0162500
S    7   1.00
      38.0008000     -0.0053040
      23.9725000      0.0463180
      15.2182000     -0.1199400
      5.5399900      0.3040620
      1.3855100     -0.4945010
      0.6424610     -0.2555160
      0.1564960      0.6091630
S    7   1.00
      38.0008000      0.0323400
      23.9725000     -0.1717620
      15.2182000      0.3395030
      5.5399900     -0.7461790
      1.3855100      1.9174980
      0.6424610     -1.1299310
      0.1564960     -1.3662840
S    1   1.00
      0.0549100      1.0000000
S    1   1.00
      0.0193000      1.0000000
P    6   1.00
      10.3092000      0.1282170
      6.6276500     -0.3537900
      1.6744700      0.5662110
      0.8011160      0.4931710
      0.3468790      0.1137750
      0.1227010      0.0025340
P    6   1.00
      10.3092000     -0.0358850
      6.6276500      0.1028900
      1.6744700     -0.2009880
      0.8011160     -0.2010450
      0.3468790      0.1165490
```

	0.1227010	0.5949690
P 6	1.00 10.3092000 6.6276500 1.6744700 0.8011160 0.3468790 0.1227010	-0.0772420 0.2226110 -0.4953530 -0.3607470 0.7100000 0.5688390
P 1	1.00 0.0424280	1.0000000
D 5	1.00 11.0027000 6.8916600 1.8080800 0.8210510 0.3441610	0.0164670 -0.0680130 0.2994920 0.4543030 0.3442240
D 5	1.00 11.0027000 6.8916600 1.8080800 0.8210510 0.3441610	-0.0236280 0.0956720 -0.5412940 -0.3955330 0.6191650
D 1	1.00 0.1297430	1.0000000
D 1	1.00 0.0489000	1.0000000
F 1	1.00 0.8919000	1.0000000
F 1	1.00 0.3789000	1.0000000

AU	0	
AU-ECP	5 60	
h-ul potential		
1		
2	1.0000000	0.0000000
s-ul potential		
2		
2	13.5232180	426.6418670
2	6.2643840	36.8006680
p-ul potential		
4		
2	11.4138670	87.0020910
2	10.3292150	174.0043700
2	5.7074240	8.8706100
2	4.8281650	17.9024380
d-ul potential		
4		
2	7.4309630	49.8836550
2	8.3219900	74.6845490
2	4.6096420	6.4862270
2	3.5115070	9.5468210
f-ul potential		
2		
2	3.0846390	8.7916400
2	3.0247430	11.6584560

指令列中 "Gen" 代表要求讀入 general basis set , Pseudo=Read 代表要輸入 Pseudo-Potential , 因為在這個 basis set 中金原子的 60 個內層電子是由 Effective Core

Potential (ECP) 所代表，只有外層 19 個電子以及 5s,5p,6s,5d,6p orbitals 是由基底函數來描述原子軌域。許多各式各樣的基底函數及 ECP 都可以由 EMSL 的網站 (<https://bse.pnl.gov/bse/portal>) 中找到並下載。

在計算中我們也可以混合基底函數，如下例 Mo(CO)₆ 分子的計算：

```
%chk=MoCO6
%mem=800MW
%NprocShared=4
#B3LYP Gen Pseudo=Read SCF=InCore OPT FREQ

Mo (CO) 6

0 1
Mo 0.0 0.0 0.0
C 2.0 0.0 0.0
C -2.0 0.0 0.0
C 0.0 2.0 0.0
C 0.0 -2.0 0.0
C 0.0 0.0 2.0
C 0.0 0.0 -2.0
O 3.2 0.0 0.0
O -3.2 0.0 0.0
O 0.0 3.2 0.0
O 0.0 -3.2 0.0
O 0.0 0.0 3.2
O 0.0 0.0 -3.2

Mo 0
LanL2DZ
*****
C,O 0
6-31G(d)
*****
Mo 0
F 1 1.00
1.043 1.00
****

Mo 0
LANL2
```

對於 C, O 我們使用 6-31G(d) basis set，對 Mo 我們使用 LANL2DZ basis set，並讀入 LANL2 ECP，另外對於 Mo 我們加上額外一組 *f* polarization functions，以平衡此混合的基底函數。通常不建議直接將較大型的基底函數如 6-311+G(d,p) 等直接與 LANL2DZ 結合，因為可能造成電子分布的不均衡，較建議直接使用 aug-cc-pVnZ-pp (n = D, T, Q) 基底函數