

Homework set 2

1 Hartree product

Problem: Define the Hartree product

$$\Psi^{HP}(x_1, x_2, \dots, x_N) = \chi_i(x_1)\chi_j(x_2) \cdots \chi_k(x_N). \quad (1.1)$$

Consider the Hamiltonian

$$\mathcal{H}^{HP} = \sum_{i=1}^N h(i), \quad (1.2)$$

in which

$$h(i)\chi_j(x_i) = \varepsilon_j\chi_j(x_i). \quad (1.3)$$

Shown that the Hartree product (1.1) is an eigenfunction of the Hamiltonian (1.2) with an eigenvalue given by

$$E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k. \quad (1.4)$$

Solution: According to (1.3) and (1.1), we have

$$\begin{aligned} h(i)\Psi^{HP} &= \varepsilon_i\Psi^{HP}, \\ \Rightarrow \sum_{i=1}^N h(i)\Psi^{HP} &= (\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k)\Psi^{HP}, \\ \Rightarrow \mathcal{H}^{HP}\Psi^{HP} &= E\Psi^{HP}, \end{aligned}$$

where E is given by (1.4).

2 Slater determinate

Problem: Consider the Slater determinants

$$|K\rangle = |\chi_i\chi_j\rangle, \quad (2.1)$$

$$|L\rangle = |\chi_k\chi_l\rangle. \quad (2.2)$$

Show that

$$\langle K|L\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}. \quad (2.3)$$

Solution: By the definition of Slater determinate, we have

$$\begin{aligned} |K\rangle &= 2^{-1/2}(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)), \\ |L\rangle &= 2^{-1/2}(\chi_k(1)\chi_l(2) - \chi_k(2)\chi_l(1)). \end{aligned}$$

It follows that

$$\begin{aligned}
 \langle K|L \rangle &= 1/2 [\langle \chi_i(1)\chi_k(1) \rangle \langle \chi_j(2)\chi_l(2) \rangle + \langle \chi_i(2)\chi_k(2) \rangle \langle \chi_j(1)\chi_l(1) \rangle \\
 &\quad - \langle \chi_i(1)\chi_l(1) \rangle \langle \chi_j(2)\chi_k(2) \rangle - \langle \chi_j(1)\chi_k(1) \rangle \langle \chi_i(2)\chi_l(2) \rangle], \\
 &= 1/2 [\delta_{ik}\delta_{jl} + \delta_{jl}\delta_{ik} - \delta_{il}\delta_{jk} - \delta_{jk}\delta_{il}], \\
 &= \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}.
 \end{aligned}$$

Now we verify the (2.3).

3 Self-consistent procedure

Nonlinear Hartree-Fock equations

$$F(C)C = SCE \quad (3.1)$$

can be solved by a self-consistent procedure, as follows

1. An initial guess orbitals (matrix C^0) are generated;
2. Fock operator is calculated for this set of orbitals ($F^0 = F(C^0)$);
3. Fock operator is diagonalized, $F^0 C^1 = S C^1 E^1$, and new orbitals C^1 replace the orbitals C^0 from previous step;
4. Steps 2-3 are repeated until the difference between orbitals from step n and step $n + 1$ is below certain (user-specified) threshold.

Problem: As an example of a non-linear problem, consider the equation

$$5x^2 - 3x - 2 = 0. \quad (3.2)$$

We can try to find its solution ($x = -2/5, 1$) by a self-consistent procedure.

We can rewrite the equation (3.2) as

$$x * A(x) = 2, \quad A(x) := 5x - 3, \quad (3.3)$$

where $A(x)$ is a nonlinear coefficient, an analogue of the Fock operator.

Solution: The iteration scheme associated with (3.3) is shown in Algorithm 1.

Algorithm 1 Self consistent procedure with (3.3)

- 1: Initial guess x_0 .
- 2: **for** $k = 0, 1, 2, \dots$ **do**
- 3: Solve x_{k+1} from the equation

$$x_{k+1} = \frac{2}{5x_k - 3}. \quad (3.4)$$

- 4: Compute the $\Delta x = x_{k+1} - x_k$. If $|\Delta x| < \epsilon$, then stop.
 - 5: **end for**
-

The numerical results for Algorithm 1 with $x_0 = 0$ is shown in Table 1 and Fig.1. Besides, for other initial guess x_0 , it is highly possible that the numerical solution obtained by Algorithm 1 converges to $x = -0.4$ instead of $x = 1$.

In the mathematical point of view, the reason could be roughly explained as follows:

1. Assume $x_k = 1 + \delta x$, where $|\delta x| \ll 1$, then by (3.6),

$$x_{k+1} = \frac{2}{5x_k - 3} = \frac{2}{5(1 + \delta x) - 3} = \frac{2}{5\delta x + 2},$$

$$\Rightarrow |x_{k+1} - 1| = \left| \frac{5\delta x}{5\delta x + 2} \right| \approx \frac{5}{2}|\delta x|.$$

It means that the error at the $k + 1$ -th will be amplified by 2.5 times compared to the k -th step! That is why the numerical solutions do not converge to $x_e = 1$, for almost all initial guess. Fig 2 shows that even if x_0 is very closed to 1, after several iterations, x_k always diverges.

2. Assume $x_0 = -0.4 + \delta x$, where $|\delta x| \ll 1$, then by (3.6),

$$x_1 = \frac{2}{5x_0 - 3} = \frac{2}{5(-0.4 + \delta x) - 3} = \frac{2}{5\delta x - 5},$$

$$\Rightarrow |x_1 - (-0.4)| = \left| \frac{2\delta x}{5\delta x - 5} \right| \approx \frac{2}{5}|\delta x|.$$

It means that the error at $k + 1$ -th step will be reduced by 40% compared to the k -th step, which guarantees that the Algorithm 1 is convergent for the solution $x_e = -0.4$.

Table 1: Self-consistent procedure: Algorithm 1 and $x_0 = 0$

Iteration number	x	Δx	$ x - x_e $
0	0		0.4
1	-0.66666667	-0.66666667	0.26666667
2	-0.31578947	0.35087719	0.08421053
3	-0.43678161	-0.12099214	0.03678161
4	-0.38580931	0.05097230	0.01419069
5	-0.40575798	-0.01994867	0.00575798
6	-0.39770999	0.00804799	0.00229001
7	-0.40091811	-0.00320811	0.00091811
8	-0.39963309	0.00128501	0.00036691
9	-0.40014682	-0.00051372	0.00014682
10	-0.39994128	0.00020553	0.00005872
11	-0.40002349	-0.00008221	0.00002349
12	-0.39999060	0.00003288	0.00000940
13	-0.40000376	-0.00001315	0.00000376
14	-0.39999850	0.00000526	0.00000150
15	-0.40000060	-0.00000210	0.00000060
16	-0.39999976	0.00000084	0.00000024
17	-0.40000010	-0.00000034	0.00000010
18	-0.39999996	0.00000013	0.00000004
19	-0.40000002	-0.00000005	0.00000002
20	-0.39999999	0.00000002	0.00000001

Note that $x_e = -0.4$ in this table.

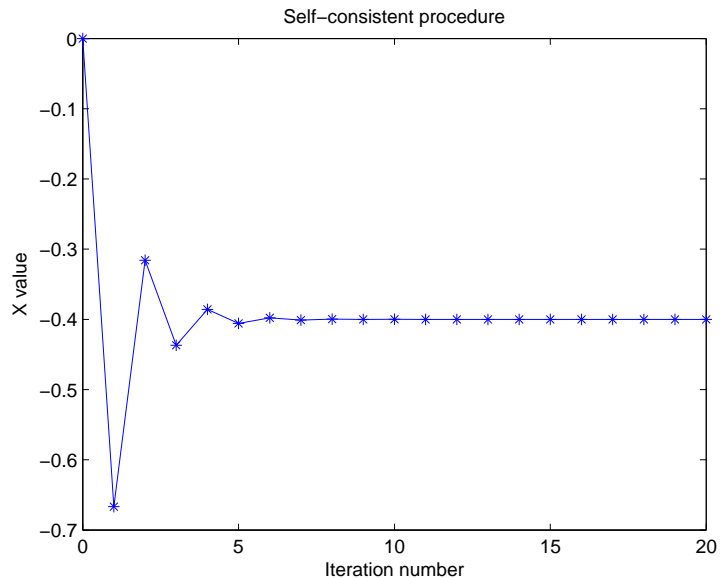


Figure 1: Self-consistent procedure: Algorithm 1 and $x_0 = 0$

In order to find the solution $x = 1$, we need to rewrite the Eq.(3.2) in other forms. For example,

$$x * A(x) = B(x), \quad A(x) := 5x + 1, \quad B(x) := 4x + 2. \quad (3.5)$$

The iteration scheme associated with (3.5) is shown in Algorithm 2.

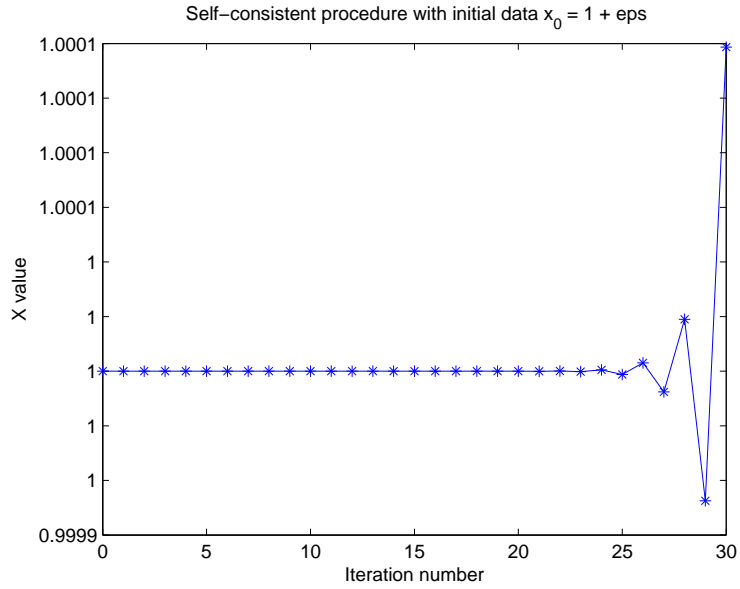
Algorithm 2 Self consistent procedure with (3.5)

- 1: Initial guess x_0 .
- 2: **for** $k = 0, 1, 2, \dots$ **do**
- 3: Solve x_{k+1} from the equation

$$x_{k+1} = \frac{4x_k + 2}{5x_k + 1}. \quad (3.6)$$

- 4: Compute the $\Delta x = x_{k+1} - x_k$. If $|\Delta x| < \epsilon$, then stop.
 - 5: **end for**
-

The numerical results for Algorithm 2 with $x_0 = 0$ is shown in Table 2 and Fig.3.

Figure 2: Self-consistent procedure: Algorithm 1 and $x_0 = 1 + \epsilon$ Table 2: Self-consistent procedure: Algorithm 2 and $x_0 = 0$

Iteration number	x	Δx	$ x - x_e $
0	0		1
1	2.00000000	2.00000000	1.00000000
2	0.90909091	-1.09090909	0.09090909
3	1.01639344	0.10730253	0.01639344
4	0.99730458	-0.01908886	0.00269542
5	1.00045025	0.00314567	0.00045025
6	0.99992499	-0.00052526	0.00007501
7	1.00001250	0.00008752	0.00001250
8	0.99999792	-0.00001459	0.00000208
9	1.00000035	0.00000243	0.00000035
10	0.99999994	-0.00000041	0.00000006
11	1.00000001	0.00000007	0.00000001
12	1.00000000	-0.00000001	0.00000000
13	1.00000000	0.00000000	0.00000000
14	1.00000000	-0.00000000	0.00000000
15	1.00000000	0.00000000	0.00000000
16	1.00000000	-0.00000000	0.00000000
17	1.00000000	0.00000000	0.00000000
18	1.00000000	-0.00000000	0.00000000
19	1.00000000	0.00000000	0.00000000
20	1.00000000	-0.00000000	0.00000000

Note that $x_e = 1$ in this table.

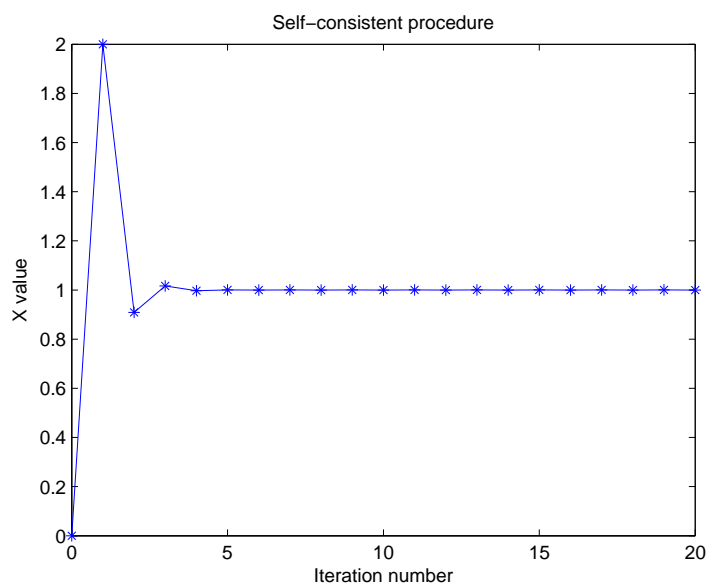


Figure 3: Self-consistent procedure: Algorithm 2 and $x_0 = 0$

Homework set 3

Notations

$$(ij|kl) = \int dr_1 dr_2 \psi_i^*(r_1) \psi_j(r_1) r_{12}^{-1} \psi_k^*(r_2) \psi_l(r_2), \quad (0.1)$$

$$\langle ij|kl \rangle = \int dr_1 dr_2 \psi_i^*(r_1) \psi_j^*(r_2) r_{12}^{-1} \psi_k(r_1) \psi_l(r_2), \quad (0.2)$$

$$J_{ij} = (ii|jj) = \langle ij|ij \rangle, \quad \text{called 'coulomb integral'} \quad (0.3)$$

$$K_{ij} = (ij|ji) = \langle ij|ji \rangle, \quad \text{called 'exchange integral'}. \quad (0.4)$$

1 Coulomb and exchange integrals

Problem: Prove the following properties of coulomb and exchange integrals:

$$J_{ii} = K_{ii}, \quad (1.1)$$

$$J_{ij}^* = J_{ij}, \quad (1.2)$$

$$K_{ij}^* = K_{ij}, \quad (1.3)$$

$$J_{ij} = J_{ji}, \quad (1.4)$$

$$K_{ij} = K_{ji}. \quad (1.5)$$

Proof. According to the notations (0.1)-(0.4), it is easy to know the following.

$$J_{ii} = (ii|ii) = K_{ii};$$

$$J_{ij}^* = (ii|jj) = J_{ij};$$

$$\begin{aligned} K_{ij}^* &= (ji|ij), \\ &= \int dr_1 dr_2 \psi_j^*(r_1) \psi_i(r_1) r_{12}^{-1} \psi_i^*(r_2) \psi_j(r_2), \\ &= \int dr_1 dr_2 \psi_j^*(r_2) \psi_i(r_2) r_{12}^{-1} \psi_i^*(r_1) \psi_j(r_1), \\ &= \int dr_1 dr_2 \psi_i^*(r_1) \psi_j(r_1) r_{12}^{-1} \psi_j^*(r_2) \psi_i(r_2), \\ &= (ij|ji) = K_{ij}; \end{aligned}$$

$$\begin{aligned}
J_{ij} &= (ii|jj), \\
&= \int dr_1 dr_2 \psi_i^*(r_1) \psi_i(r_1) r_{12}^{-1} \psi_j^*(r_2) \psi_j(r_2), \\
&= \int dr_1 dr_2 \psi_i^*(r_2) \psi_i(r_2) r_{12}^{-1} \psi_j^*(r_1) \psi_j(r_1), \\
&= \int dr_1 dr_2 \psi_j^*(r_1) \psi_j(r_1) r_{12}^{-1} \psi_i^*(r_2) \psi_i(r_2), \\
&= (jj|ii) = J_{ji};
\end{aligned}$$

$$\begin{aligned}
K_{ij} &= (ij|ji), \\
&= \int dr_1 dr_2 \psi_i^*(r_1) \psi_j(r_1) r_{12}^{-1} \psi_j^*(r_2) \psi_i(r_2), \\
&= \int dr_1 dr_2 \psi_i^*(r_2) \psi_j(r_2) r_{12}^{-1} \psi_j^*(r_1) \psi_i(r_1), \\
&= \int dr_1 dr_2 \psi_j^*(r_1) \psi_i(r_1) r_{12}^{-1} \psi_i^*(r_2) \psi_j(r_2), \\
&= (ji|ij) = K_{ji}.
\end{aligned}$$

□

2 Real spatial orbitals

Problem: Show that for real spatial orbitals,

$$K_{ij} = (ij|ij) = (ji|ji) = \langle ii|jj \rangle = \langle jj|ii \rangle. \quad (2.1)$$

Proof. For real spatial orbitals, we have

$$\begin{aligned}
K_{ij} &= \int dr_1 dr_2 \psi_i(r_1) \psi_j(r_1) r_{12}^{-1} \psi_j(r_2) \psi_i(r_2), \\
&= \int dr_1 dr_2 \psi_i(r_1) \psi_j(r_1) r_{12}^{-1} \psi_i(r_2) \psi_j(r_2) = (ij|ij), \\
&= \int dr_1 dr_2 \psi_j(r_1) \psi_i(r_1) r_{12}^{-1} \psi_j(r_2) \psi_i(r_2) = (ji|ji), \\
&= \int dr_1 dr_2 \psi_i(r_1) \psi_i(r_2) r_{12}^{-1} \psi_j(r_1) \psi_j(r_2) = \langle ii|jj \rangle, \\
&= \int dr_1 dr_2 \psi_j(r_1) \psi_j(r_2) r_{12}^{-1} \psi_i(r_1) \psi_i(r_2) = \langle jj|ii \rangle.
\end{aligned}$$

□

3 Energy determinants

Problem: Verify the energies of the determinants shown in Fig.1 by inspection.

- a. $h_{11} + h_{22} + J_{12} - K_{12}$,
- b. $h_{11} + h_{22} + J_{12}$,
- c. $2h_{11} + J_{11}$,
- d. $2h_2 + J_{22}$,
- e. $2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$,
- f. $2h_{22} + h_{11} + J_{22} + 2J_{12} - K_{12}$,
- g. $2h_{11} + 2h_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$.

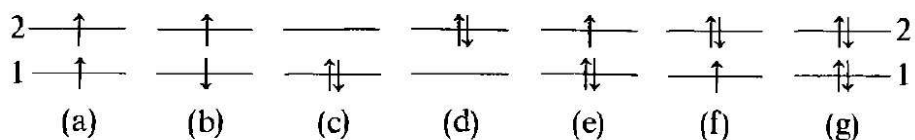


Figure 1: Energy determinants

Solution: Please see Table 1.

Table 1: Interpretation of determinantal energies

Number	one-electron	Coulomb	Exchange
a	$h_{11} + h_{22}$	J_{12}	$-K_{12}$
b	$h_{11} + h_{22}$	J_{12}	0
c	$2h_{11}$	J_{11}	0
d	$2h_2$	J_{22}	0
e	$2h_{11} + h_{22}$	$J_{11} + 2J_{12}$	$-K_{12}$
f	$2h_{22} + h_{11}$	$J_{22} + 2J_{12}$	$-K_{12}$
g	$2h_{11} + 2h_{22}$	$J_{11} + J_{22} + 4J_{12}$	$-2K_{12}$

Homework set 4

1 Basis sets

Question: Determine the total number of basis functions and primitive basis functions for STO-3G, 6-31G, 6-31G**, and 6-311(+,+)G** calculations of methane (CH_4). Write the contraction scheme in general notations for each basis (Szabo & Ostlund, chapter 3.6). Assume that pure angular momentum (5d,7f etc functions) polarization functions are used.

Answer:

- The STO-3G basis set for methane consists of one 1s orbital on each H atom and a 1s, 2s, and set of three 2p orbitals on C. See Tables 1-3 for details. The contraction scheme in general notations is $(6s3p/3s) [2s1p/1s]$.

Table 1: STO-3G: Carbon atom

	1s	2s	2p(3)	Total
No. Basis Functions	1	1	3	5
No. Gaussians for each orbital	3	3	3	
No. Primitives	3	3	9	15

Table 2: STO-3G: Hydrogen atom

	1s	Total
No. Basis Functions	1	1
No. Gaussians for each orbital	3	
No. Primitives	3	3

Table 3: STO-3G: Methane molecule

No. Basis Functions	$5 + 1 \times 4 = 9$
No. Primitives	$15 + 3 \times 4 = 27$

- The 6-31G basis set is a split valence double zeta basis set. For hydrogen atom, a split valence double zeta basis consists of two 1s orbitals, denoted 1s and 1s'. Note that for the H atom, because the 1s electron is considered the valence shell a double zeta basis set is used. For the carbon atom, a split valence double zeta basis set consists of a single 1s orbital, along with two 2s and two each of 2p_x, 2p_y, and 2p_z orbitals, denoted as 1s, 2s, 2s', 2p(3) and 2p'(3). See Tables 4-6 for details. The contraction scheme in general notations is $(10s4p/4s) [3s2p/2s]$.

Table 4: 6-31G: Carbon atom

	1s	2s	2s'	2p(3)	2p'(3)	Total
No. Basis Functions	1	1	1	3	3	9
No. Gaussians for each orbital	6	3	1	3	1	
No. Primitives	6	3	1	9	3	22

Table 5: 6-31G: Hydrogen atom

	1s	1s'	Total
No. Basis Functions	1	1	2
No. Gaussians for each orbital	3	1	
No. Primitives	3	1	4

Table 6: 6-31G: Methane molecule

No. Basis Functions	$9 + 2 \times 4 = 17$
No. Primitives	$22 + 4 \times 4 = 38$

3. The 6-31G** basis set is a split valence double zeta basis set with added polarization functions on both carbon and hydrogen atoms. For hydrogen atom, the split valence double zeta basis consists of two 1s orbitals, and extra polarization functions 2px, 2py, and 2pz orbitals, denoted 1s, 1s' and 2p(3). For the carbon atom, a split valence double zeta basis set consists of a single 1s orbital, along with two 2s and a double set of 2p orbitals, 2p(3) and 2p'(3), and extra polarization functions d(5). See Tables 7-9 for details. The contraction scheme in general notations is (10s4p1d/4s1p) [3s2p1d/2s1p].

Table 7: 6-31G**: Carbon atom

	1s	2s	2s'	2p(3)	2p'(3)	d(5)	Total
No. Basis Functions	1	1	1	3	3	5	14
No. Gaussians for each orbital	6	3	1	3	1	1	
No. Primitives	6	3	1	9	3	5	27

Table 8: 6-31G**: Hydrogen atom

	1s	1s'	2p(3)	Total
No. Basis Functions	1	1	3	5
No. Gaussians for each orbital	3	1	1	
No. Primitives	3	1	3	7

Table 9: 6-31G**: Methane molecule

No. Basis Functions	$14 + 5 \times 4 = 34$
No. Primitives	$27 + 7 \times 4 = 55$

4. The 6-311(+,+)G** basis set is a split valence triple zeta basis set with added diffuse and polarization functions on both carbon and hydrogen atoms. For hydrogen atom, the split valence triple zeta basis consists of three 1s orbitals 1s,1s',1s'', and diffuse function 2s, and extra polarization functions 2px, 2py, and 2pz orbitals, 2p(3). For the carbon atom, a split valence triple zeta basis set consists of a single 1s orbital, along with three 2s orbitals 2s,2s',2s'', and a triple set of 2p orbitals, 2p(3), 2p'(3) and 2p''(3), and diffuse functions 3s, 3p(3), and extra polarization functions 3d(5). See Tables 10-12 for details. The contraction scheme in general notations is (12s6p1d/6s1p) [5s4p1d/4s1p].

Table 10: 6-311(+,+)G**: Carbon atom

	1s	2s	2s'	2s''	2p(3)	2p'(3)	2p''(3)	3s	3p	d(5)	Total
No. Basis Functions	1	1	1	1	3	3	3	1	3	5	22
No. Gaussians for each orbital	6	3	1	1	3	1	1	1	1	1	
No. Primitives	6	3	1	1	9	3	3	1	3	5	35

Table 11: 6-311(+,+)G**: Hydrogen atom

	1s	1s'	1s''	2s	2p(3)	Total
No. Basis Functions	1	1	1	1	3	7
No. Gaussians for each orbital	3	1	1	1	1	
No. Primitives	3	1	1	1	3	9

Table 12: 6-311(+,+)G**: Methane molecule

No. Basis Functions	$22 + 7 \times 4 = 50$
No. Primitives	$35 + 9 \times 4 = 71$

2 Ethylene(C_2H_4).

Question: Below is an output from the Q-Chem electronic structure program. This output specifies a nonstandard basis set for ethylene (C_2H_4). S,P,D specify an angular momentum of the basis functions, first column gives exponents of primitive Gaussians, and second column gives contraction coefficients.

- Find diffuse functions on carbon and hydrogen (check for each angular momentum). What are their exponents?
- Find polarization functions.
- Write the contraction scheme in general notations for this basis.
- Determine the total number of basis functions and primitive basis functions for the calculations of ethylene using this basis.
- Try to name this basis.
- Find a split-valence Pople basis set which is approximately of the same quality.

```
****
H 0
S 3 1.00
  33.8700000 0.0060680
  5.0950000 0.0453080
  1.1590000 0.2028220
S 1 1.00
  0.3258000 1.0000000
S 1 1.00
  0.1027000 1.0000000
S 1 1.00
  0.0252600 1.0000000
P 1 1.00
  1.4070000 1.0000000
P 1 1.00
  0.3880000 1.0000000
****
C 0
S 8 1.00
  8236.0000000 0.0005310
  1235.0000000 0.0041080
  280.8000000 0.0210870
  79.2700000 0.0818530
  25.5900000 0.2348170
  8.9970000 0.4344010
  3.3190000 0.3461290
  0.3643000 -0.0089830
S 8 1.00
  8236.0000000 -0.0001130
  1235.0000000 -0.0008780
  280.8000000 -0.0045400
```

```

79.2700000 -0.0181330
25.5900000 -0.0557600
8.9970000 -0.1268950
3.3190000 -0.1703520
0.3643000 0.5986840
S 1 1.00
0.9059000 1.0000000
S 1 1.00
0.1285000 1.0000000
S 1 1.00
0.0440200 1.0000000
P 3 1.00
18.7100000 0.0140310
4.1330000 0.0868660
1.2000000 0.2902160
P 1 1.00
0.3827000 1.0000000
P 1 1.00
0.1209000 1.0000000
P 1 1.00
0.0356900 1.0000000
D 1 1.00
1.0970000 1.0000000
D 1 1.00
0.3180000 1.0000000
****

```

Answer:

- a) Diffusion functions for carbon is s orbital with exponent 0.04402 in primitive Gaussian and p orbital with exponent 0.1209.
Diffusion function for hydrogen is s orbital with exponent 0.02526.
- b) Polarization functions for hydrogen are two p orbitals and for carbon are two d orbitals.
- c) Contraction scheme in general notations for this basis is (19s6p2d/6s2p) [5s4p2d/4s2p].
- d) See Tables 13-15.

Table 13: New basis: Hydrogen atom

	1s	1s'	1s''	2s	2p(3)	2p'(3)	Total
No. Basis Functions	1	1	1	1	3	3	10
No. Gaussians for each orbital	3	1	1	1	1	1	
No. Primitives	3	1	1	1	3	3	12

Table 14: New basis: Carbon atom

	1s	2s	2s'	2s''	2p(3)	2p'(3)	2p''(3)	3s	3p	d(5)	d'(5)	Total
No. Basis Functions	1	1	1	1	3	3	3	1	3	5	5	27
No. Gaussians for each orbital	8	8	1	1	3	1	1	1	1	1	1	
No. Primitives	8	8	1	1	9	3	3	1	3	5	5	47

Table 15: New basis: Ethylene molecule

No. Basis Functions	$27 \times 2 + 10 \times 4 = 94$
No. Primitives	$47 \times 2 + 12 \times 4 = 142$

e) I think the name should be 8-811-311(+,+)G^{2*,2*}.

f) 8-311(+,+)G**.

PURDUE UNIVERSITY
CHM 67300
COMPUTATIONAL QUANTUM CHEMISTRY

LAB REPORT
Yingwei Wang
October 15, 2013

Lab 1

1 Summarize the results you obtained for your (neutral) molecule

User input

```
$molecule
0 1
C -3.7092889 1.8914774 -0.2589004
C -1.8236162 1.4342382 0.0611085
C -2.0064467 -0.7242650 0.1820433
C -4.1032293 -0.1872736 -0.1757624
$end
```

```
$rem
BASIS = 6-31G
EXCHANGE = HF
GUI = 2
$end
```

Equilibrium geometry

Standard Nuclear Orientation (Angstroms)				
I	Atom	X	Y	Z
1	C	1.525165	-0.122502	0.000000
2	C	0.225918	1.353707	0.000000
3	C	-1.610616	0.198575	0.000000
4	C	-0.140467	-1.429781	0.000000

Nuclear repulsion and electronic energies in Hartrees

```
Molecular Point Group          Cs    NOp = 2
Largest Abelian Subgroup       Cs    NOp = 2
Nuclear Repulsion Energy =     48.9777513471 hartrees
Hartree-Fock energy (by SCF)   = -150.5759812085
```

Harmonic vibrational frequencies– provide a sketch of each mode, write down its frequency and assignment

 Orbital Energies (a.u.) and Symmetries

Alpha MOs, Restricted

-- Occupied --

-11.461	-11.457	-11.420	-11.411	-0.930	-0.794	-0.770	-0.628
1 A'	2 A'	3 A'	4 A'	5 A'	6 A'	7 A'	8 A'
-0.403	-0.390	-0.367	-0.317				
9 A'	10 A'	11 A'	1 A''				

-- Virtual --

-0.036	-0.022	-0.004	0.075	0.094	0.104	0.186	0.207
12 A'	2 A''	3 A''	13 A'	4 A''	14 A'	15 A'	16 A'
0.692	0.701	0.703	0.728	0.736	0.775	0.786	0.834
17 A'	18 A'	5 A''	19 A'	20 A'	6 A''	7 A''	21 A'
0.859	0.871	0.882	0.913	0.918	1.102	1.156	1.305
8 A''	22 A'	23 A'	24 A'	25 A'	26 A'	27 A'	28 A'

Beta MOs, Restricted

-- Occupied --

-11.461	-11.457	-11.420	-11.411	-0.930	-0.794	-0.770	-0.628
1 A'	2 A'	3 A'	4 A'	5 A'	6 A'	7 A'	8 A'
-0.403	-0.390	-0.367	-0.317				
9 A'	10 A'	11 A'	1 A''				

-- Virtual --

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0.859	0.871	0.882	0.913	0.918	1.102	1.156	1.305
8 A''	22 A'	23 A'	24 A'	25 A'	26 A'	27 A'	28 A'

2 Now some analysis of the cation

Using frozen orbital approximation (Koopmans' theorem), determine the lowest ionization potential (IP) of the cation. The ionization potential (IP) for removing an electron from χ_c is just the negative of the orbital energy ε_c ,

$$IP = {}^{N-1} E_c - {}^N E_0 = 11.461. \quad (2.1)$$

Determine approximate excitation energy of the first electronically excited state of the cation -0.930

By looking at the corresponding molecular orbitals, predict what kind of structural changes ionization might induce in these two states.

Calculate the lowest IP as the Hartree–Fock energy difference between the neutral and the cation. Compare this so-called ΔEIP with Koopmans IP. Explain the difference

PURDUE UNIVERSITY
CHM 67300
COMPUTATIONAL QUANTUM CHEMISTRY

LAB REPORT
Yingwei Wang
October 29, 2013

Lab 2: Bond-breaking in H_2

Lab procedure

Use 6-31G** basis in this lab. In order to construct the H_2 potential energy surface, you need to run a series of calculations at different H-H separations (in Angstroms), e.g., 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5, 1.7, 2.0, 2.5, 3.0, 5.0 Angstroms.

The draw results obtained from Q-chem are listed below.

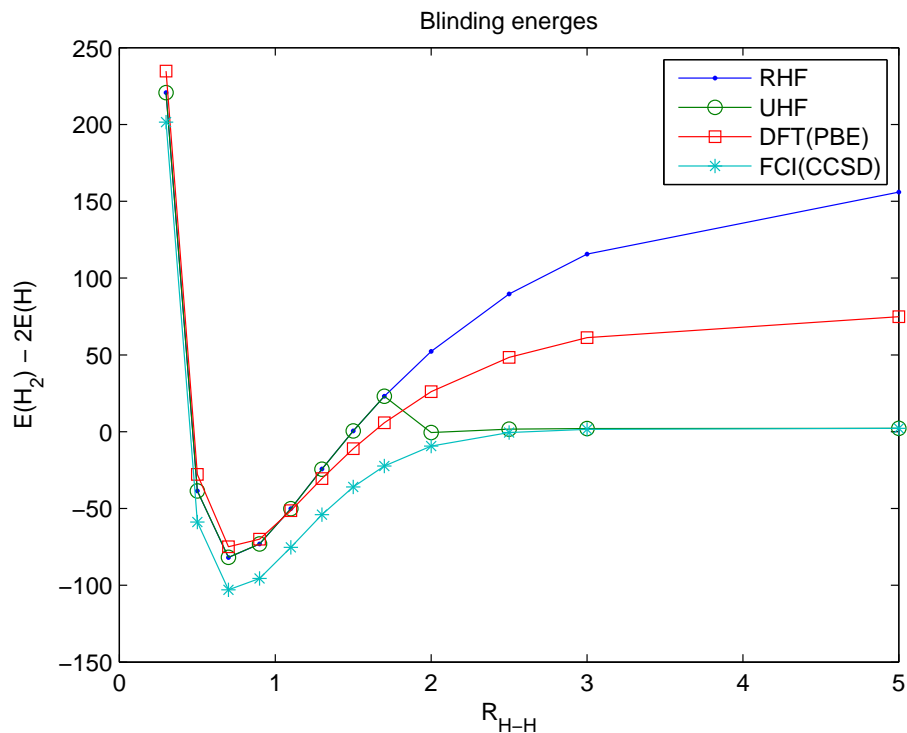
Table 1: Numerical results (total energies $E(H_2)$ in Hartree nunit)

R_{H-H}	RHF	UHF	DFT(PBE)	FCI(CCS)
0.3	-0.6482994431	-0.6482994387	-0.6258819289	-0.67875945
0.5	-1.0614822834	-1.0614751889	-1.0443843843	-1.09373008
0.7	-1.1305011820	-1.1304375436	-1.1193013192	-1.16404439
0.9	-1.1165173856	-1.1164166897	-1.1116198101	-1.15221428
1.1	-1.0799440457	-1.0798109860	-1.0819915723	-1.11992191
1.3	-1.0388109916	-1.0388638758	-1.0486477219	-1.08610950
1.5	-0.9992415372	-0.9992563112	-1.0176076594	-1.05736951
1.7	-0.9632717256	-0.9633077580	-0.9907272713	-1.03558970
2.0	-0.9167407465	-1.0009663163	-0.9585385071	-1.01486873
2.5	-0.8571393673	-0.9974193873	-0.9228514525	-1.00091065
3.0	-0.8157045814	-0.9967103756	-0.9024060795	-0.99747351
5.0	-0.7513961201	-0.9964662658	-0.8807224061	-0.99646683

1 Binding energies

Plot on the same graph the RHF, UHF, DFT, and FCI binding energies in H_2 versus the H-H distance. Use kcal/mol energy units (1 Hartree= 627.51 kcal/mol). See Fig.1.

$$E_{Binding} = E(H^2) - 2E(H).$$

Figure 1: Blinding energies in H_2

2 RHF vs. UHF

Comment on the behavior of RHF and UHF curves wrt FCI at short (around 0.7 Angstroms) and long distances.

From Fig.1, we can observe that

1. At short distance, RHF and UHF are almost the same, both of which are above the FCI curve.
2. At long distance, RHF is far away from FCI while UHF is very close to FCI.

3 S^2 from UHF

Make a table or plot of S^2 values from the UHF calculations. Explain why S^2 deteriorates when the H-H bond is stretched.

Please see Table 2 and Fig 2. The reason is that the RHF wave function is an eigenfunction of \hat{S}^2 while the UHF wave function is not.

R_{H-H}	S^2 from UHF
0.3	0.0000
0.5	0.0000
0.7	0.0001
0.9	0.0005
1.1	0.0033
1.3	0.0004
1.5	0.0003
1.7	0.0004
2.0	0.9058
2.5	0.9785
3.0	0.9954
5.0	1.0000

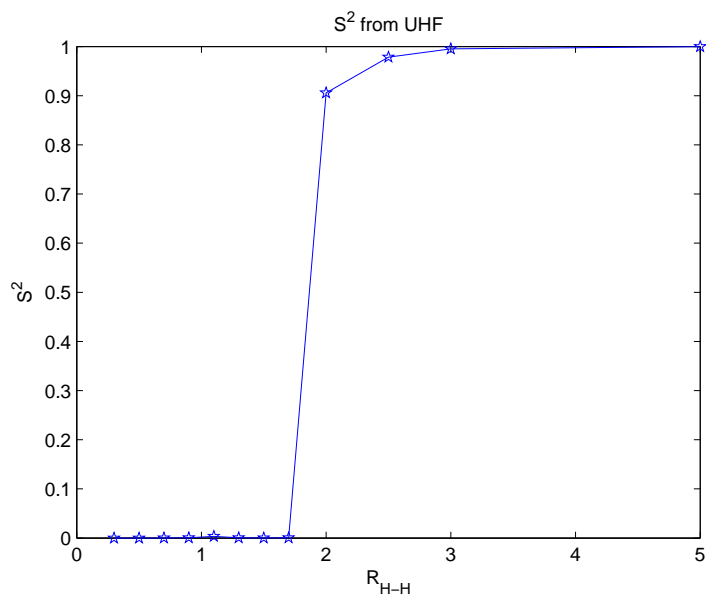


Figure 2: S^2 from UHF

4 HOMO and LUMO

Make a sketch of the first two H_2 molecular orbitals (HOMO and LUMO) from your RHF and UHF calculations at the equilibrium (0.7 Angstroms), 1.3, and 5.0 Angstroms. Comment on qualitative changes in the shape of the orbitals.

I do not know which part of the output is related to this problem.

5 Correlation energy

Difference between FCI and HF energies is the correlation energy. What is the nature of the correlation energy (dynamic vs non-dynamic) in H_2 at equilibrium? At long distances? At what distance does the non-dynamic correlation become important?

See Fig.3.

1. At equilibrium, the correlation is dynamic and the HF approximation is fine.
2. At long distance, the correlation is non-dynamic and HF approximation is bad.

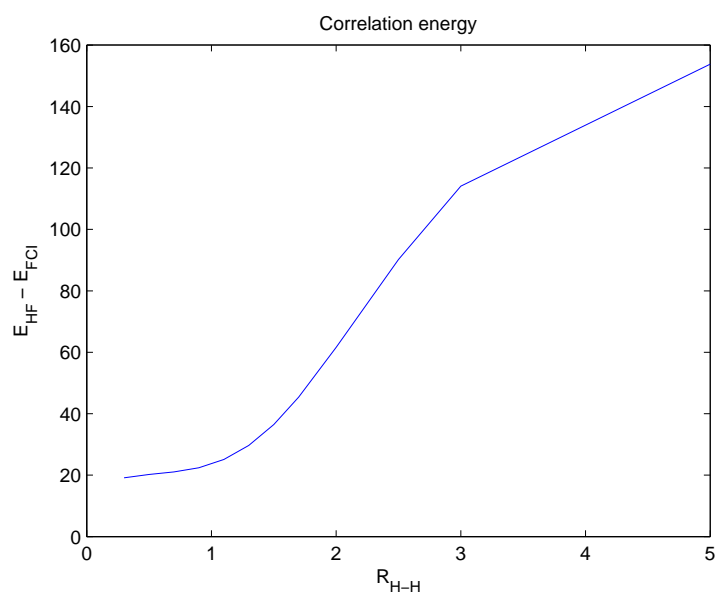


Figure 3: Correlation energies

6 DFT

Comment on the behavior of DFT at equilibrium and long distances. What is a reason of DFT failure for bond-breaking?

1. At equilibrium, the DFT is better than RHF and UHF.
2. At long distance, the DFT is worse than UHF but better than RHF.

Lab 3: Extrapolation techniques for accurate thermochemistry

Contents

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0 Lab procedure

0.1 Geometry optimization

Optimize geometry of N_2 molecule at the MP2/cc-pVDZ level and calculate the zero-point vibrational energy (ZPE).

The input file is provide as following (neglecting basis functions):

```
$comment
N_2: cc-pVDZ, for optimization
$end

$molecule
0 1
  N   -2.7391478   1.7372082   -0.0000000
  N   -2.9790021   3.1165702   -0.0000000
$end

$rem
  BASIS   =  general
  CORRELATION =  CCSD(T)
  EXCHANGE =  HF
  GUI     =  2
  JOB_TYPE =  optimization
$end

$basis
basis provided here
$end
```

The raw results obtained from Q-chem are listed below.

```
** GEOMETRY OPTIMIZATION IN DELOCALIZED INTERNAL COORDINATES **
Searching for a Minimum
Optimization Cycle:   5
                   Coordinates (Angstroms)
    ATOM           X           Y           Z
    1  N           0.000000   0.000000   -0.538684
    2  N           0.000000   0.000000    0.538684
Point Group: d*h   Number of degrees of freedom:   1
Energy is  -108.955555653
Hessian Updated using BFGS Update
1 Hessian modes will be used to form the next step
Hessian Eigenvalues:
    2.041217
Minimum Search - Taking Simple RFO Step
```

Searching for Lamda that Minimizes Along All modes

Value Taken Lamda = 0.00000000

Step Taken. Stepsize is 0.000124

	Maximum	Tolerance	Cnvgd?
Gradient	0.000254	0.000300	YES
Displacement	0.000124	0.001200	YES
Energy change	-0.000079	0.000001	NO

Distance Matrix (Angstroms)

N (1)

N (2) 1.077369

Final energy is -108.955555652652

```
*****  
** OPTIMIZATION CONVERGED **  
*****
```

Z-matrix Print:

```
$molecule  
0,1  
1 N  
2 N 1 1.077369  
$end
```

0.2 Energies calculation

N_2 molecule Using the found optimal geometry of N_2 , calculate the HF, MP2 and CCSD(T) energies in a series of the cc-pVDZ, cc-pVTZ, cc-pVQZ and quintuple-zeta cc-pV5Z bases.

The part of input file for cc-pVDZ, cc-pVTZ, cc-pVQZ is provide as following (neglecting basis functions):

```
$comment  
N_2: cc-pVDZ, cc-pVTZ, cc-pVQZ, for calculation the energy  
$end
```

```
$molecule  
0 1  
  N  0.000000  0.000000 -0.538684  
  N  0.000000  0.000000  0.538684  
$end
```

```
$rem  
BASIS = general  
CORRELATION = CCSD(T)  
EXCHANGE = HF  
GUI = 2
```

```
$end
```

```
$basis
```

```
****
```

```
$end
```

```
@@@
```

```
...
```

The input file for cc-pV5Z is provide as following (neglecting basis functions):

```
$comment
```

```
N_2: cc-pV5Z,MP2, for calculation the energy
```

```
$end
```

```
$molecule
```

```
0 1
```

```
  N  0.000000    0.000000   -0.538684
```

```
  N  0.000000    0.000000    0.538684
```

```
$end
```

```
$rem
```

```
  BASIS = general
```

```
  CORRELATION = MP2
```

```
  EXCHANGE = HF
```

```
  JOB_TYPE = sp
```

```
  mem_static = 200
```

```
$end
```

```
$basis
```

```
****
```

```
$end
```

Note that the basis sets cc-pVDZ, cc-pVTZ, cc-pVQZ and cc-pV5Z are downloaded from the online basis set library [1] (choose Gaussian94 format).

The raw results obtained from Q-chem are listed below.

```
cc-pVDZ:
```

```
SCF energy = -108.95555877
```

```
MP2 energy = -109.26018891
```

```
CCSD correlation energy = -0.30860003
```

```
CCSD total energy = -109.26415880
```

```
CCSD(T) correlation energy = -0.01131523
```

```
CCSD(T) total energy = -109.27547403
```

```
CCSD T1^2 = 0.0025 T2^2 = 0.1094.
```

cc-pVTZ:

```
SCF energy           = -108.98619427
MP2 energy           = -109.38053915
CCSD correlation energy = -0.39408464
CCSD total energy    = -109.38027892
CCSD(T) correlation energy = -0.01810667
CCSD(T) total energy = -109.39838559
CCSD T1^2 = 0.0030 T2^2 = 0.1173.
```

cc-pVQZ:

```
SCF energy           = -108.99399331
MP2 energy           = -109.44493213
CCSD correlation energy = -0.44850929
CCSD total energy    = -109.44250259
CCSD(T) correlation energy = -0.02009217
CCSD(T) total energy = -109.46259476
CCSD T1^2 = 0.0033 T2^2 = 0.1187.
```

MP2 cc-pV5Z:

```
SCF energy in the final basis set = -108.9957236721
Total energy in the final basis set = -108.9957236721
Total MP2 correlation energy = -0.4756679353 au
MP2 total energy = -109.4713916074 au
```

***N* atom** Use a series of the cc-pVDZ, cc-pVTZ, cc-pVQZ and quintuple-zeta cc-pV5Z bases to compute the energies for *N* atom.

The part of input file for cc-pVDZ, cc-pVTZ, cc-pVQZ is provide as following (neglecting basis functions):

```
$comment
N atom: cc-pVDZ, cc-pVTZ, cc-pVQZ;
multiplicity parameters: 0 4
$end

$molecule
0 4
N 0 0 0.0000000
$end

$rem
BASIS = general
CORRELATION = CCSD(T)
EXCHANGE = HF
GUI = 2
```

\$end

\$basis

\$end

The draw results obtained from Q-chem are listed below.

N atom, multiplicity 0 4

cc-pVDZ:

SCF energy	=	-54.39111456
MP2 energy	=	-54.46343781
CCSD correlation energy	=	-0.08818824
CCSD total energy	=	-54.47930280
CCSD(T) correlation energy	=	-0.00064078
CCSD(T) total energy	=	-54.47994358
CCSD T1 ²	=	0.0001
CCSD T2 ²	=	0.0300.

cc-pVTZ:

SCF energy	=	-54.40068621
MP2 energy	=	-54.50681093
CCSD correlation energy	=	-0.12181875
CCSD total energy	=	-54.52250496
CCSD(T) correlation energy	=	-0.00236823
CCSD(T) total energy	=	-54.52487319
CCSD T1 ²	=	0.0003
CCSD T2 ²	=	0.0366.

cc-pVQZ:

SCF energy	=	-54.40371796
MP2 energy	=	-54.53491025
CCSD correlation energy	=	-0.14638105
CCSD total energy	=	-54.55009901
CCSD(T) correlation energy	=	-0.00299423
CCSD(T) total energy	=	-54.55309324
CCSD T1 ²	=	0.0004
CCSD T2 ²	=	0.0377.

MP2 cc-pV5Z:

SCF energy in the final basis set	=	-54.4044415409
Total energy in the final basis set	=	-54.4044415409
Total MP2 correlation energy	=	-0.1415673099 au
MP2 total energy	=	-54.5460088509 au

1 HF energies

Estimate the basis set limits of the HF energies (i.e., complete basis set (CBS) HF energies) for N_2 and N by using the following formula:

$$E_X^{HF} = E_{CBS}^{HF} + B \exp(-AX), \quad (1.1)$$

where A and B are constants to be determined, E_X is the HF energy in cc-pVXZ basis, and E_{CBS} is the sought-for energy in the complete basis set. This extrapolation scheme requires 3 bases; use the 3-, 4-, and 5-zeta bases to obtain the CBS values (i.e., $X = 3, 4, 5$).

Solution:

For the N_2 molecule, we have this system of equations:

$$\begin{cases} -108.98619427 = E_{CBS}^{HF,N_2} + B^{N_2} \exp(-3A^{N_2}), \\ -108.99399331 = E_{CBS}^{HF,N_2} + B^{N_2} \exp(-4A^{N_2}), \\ -108.9957236721 = E_{CBS}^{HF,N_2} + B^{N_2} \exp(-5A^{N_2}). \end{cases} \quad (1.2)$$

It follows that

$$\begin{cases} A^{N_2} = 1.50566992, \\ B^{N_2} = 0.91769976, \\ E_{CBS}^{HF,N_2} = -108.99621705. \end{cases} \quad (1.3)$$

For the N atom, we have this system of equations:

$$\begin{cases} -54.26390521 = E_{CBS}^{HF,N} + B^N \exp(-3A^N), \\ -54.40371796 = E_{CBS}^{HF,N} + B^N \exp(-4A^N), \\ -54.4044415409 = E_{CBS}^{HF,N} + B^N \exp(-5A^N), \end{cases} \quad (1.4)$$

It follows that

$$\begin{cases} A^N = 8.10806828, \\ B^N = -371741.06459341, \\ E_{CBS}^{HF,N} = -54.35736569. \end{cases} \quad (1.5)$$

Note that the extrapolation results for N atom is very bad. I use another way to find the CBS result, which is

$$E_{CBS}^{HF,N} = -54.404729183627495. \quad (1.6)$$

2 Correlation and total energies

Estimate the MP2 and CCSD(T) correlation energy basis set limits (i.e., E(MP2)-E(HF), and E(CCSD(T))-E(HF)) by the following formula:

$$E_X^{corr} = E_{CBS}^{corr} + CX^{-3}, \quad (2.1)$$

where C is the coefficients, E_X and E_{CBS} are the correlation energies in the cc-pVXZ basis and in the CBS limit. This is two-point scheme, you need two basis sets to obtain CBS energies. Calculate the MP2 CBS energies using $X = 3, 4$ and $X = 4, 5$, and CCSD(T) CBS values using $X = 3, 4$.

Calculate the MP2 and CCSD(T) total energy CBS limits, which are sums of the HF CBS energies and the correlation CBS energies. Note that for MP2 you will have two different values of the CBS energies. You can refer to them as CBS(3,4) and CBS(4,5).

Solution:

For the MP2 correlation energy of N_2 molecule, we have two system of equations:

$$\begin{cases} -109.38053915 - (-108.98619427) = E_{CBS}^{MP2-corr, N_2}(3, 4) + C^{MP2-corr, N_2}(3, 4)3^{-3}, \\ -109.44493213 - (-108.99399331) = E_{CBS}^{MP2-corr, N_2}(3, 4) + C^{MP2-corr, N_2}(3, 4)4^{-3}, \end{cases} \quad (2.2)$$

and

$$\begin{cases} -109.44493213 - (-108.99399331) = E_{CBS}^{MP2-corr, N_2}(4, 5) + C^{MP2-corr, N_2}(4, 5)4^{-3}, \\ -109.4713916074 - (-108.9957236721) = E_{CBS}^{MP2-corr, N_2}(4, 5) + C^{MP2-corr, N_2}(4, 5)5^{-3}. \end{cases} \quad (2.3)$$

Solving these two systems yields that

$$\begin{cases} C^{MP2-corr, N_2}(3, 4) = 2.64308995, \\ E_{CBS}^{MP2-corr, N_2}(3, 4) = -0.49223710, \end{cases} \quad (2.4)$$

and

$$\begin{cases} C^{MP2-corr, N_2}(4, 5) = 3.24316266, \\ E_{CBS}^{MP2-corr, N_2}(4, 5) = -0.50161324. \end{cases} \quad (2.5)$$

For the CCSD(T) correlation energy of N_2 molecule, we have this system of equations:

$$\begin{cases} -109.39838559 - (-108.98619427) = E_{CBS}^{CCSD(T)-corr, N_2} + C^{CCSD(T)-corr, N_2}3^{-3}, \\ -109.46259476 - (-108.99399331) = E_{CBS}^{CCSD(T)-corr, N_2} + C^{CCSD(T)-corr, N_2}4^{-3}. \end{cases} \quad (2.6)$$

It follows that

$$\begin{cases} C^{CCSD(T)-corr, N_2} = 2.63450553, \\ E_{CBS}^{CCSD(T)-corr, N_2} = -0.50976560. \end{cases} \quad (2.7)$$

The MP2 and CCSD(T) total energy CBS limits for N_2 molecule are

$$\begin{aligned}
E_{CBS}^{MP2}(N_2)(3, 4) &= E_{CBS}^{HF, N_2} + E_{CBS}^{MP2-corr, N_2}(3, 4) \\
&= -108.99621705 - 0.49223710 = -109.48845415 \\
E_{CBS}^{MP2}(N_2)(4, 5) &= E_{CBS}^{HF, N_2} + E_{CBS}^{MP2-corr, N_2}(4, 5) \\
&= -108.99621705 - 0.50161324 = -109.49783029 \\
E_{CBS}^{CCSD(T)}(N_2) &= E_{CBS}^{HF, N_2} + E_{CBS}^{CCSD(T)-corr, N_2} \\
&= -108.99621705 - 0.50976560 = -109.50598265.
\end{aligned}$$

For the MP2 correlation energy of N atom, we have two system of equations:

$$\begin{cases} -54.50681093 - (-54.40068621) = E_{CBS}^{MP2-corr, N}(3, 4) + C^{MP2-corr, N}(3, 4)3^{-3}, \\ -54.53491025 - (-54.40371796) = E_{CBS}^{MP2-corr, N}(3, 4) + C^{MP2-corr, N}(3, 4)4^{-3}, \end{cases} \quad (2.8)$$

and

$$\begin{cases} -54.53491025 - (-54.40371796) = E_{CBS}^{MP2-corr, N}(4, 5) + C^{MP2-corr, N}(4, 5)4^{-3}, \\ -54.5460088509 - (-54.4044415409) = E_{CBS}^{MP2-corr, N}(4, 5) + C^{MP2-corr, N}(4, 5)5^{-3}. \end{cases} \quad (2.9)$$

Solving these two systems yields that

$$\begin{cases} C^{MP2-corr, N}(3, 4) = 1.17072327, \\ E_{CBS}^{MP2-corr, N}(3, 4) = -0.14948484, \end{cases} \quad (2.10)$$

and

$$\begin{cases} C^{MP2-corr, N}(4, 5) = 1.36065833, \\ E_{CBS}^{MP2-corr, N}(4, 5) = -0.15245258. \end{cases} \quad (2.11)$$

For the CCSD(T) correlation energy of N atom, we have this system of equations:

$$\begin{cases} -54.52487319 - (-54.40068621) = E_{CBS}^{CCSD(T)-corr, N} + C^{CCSD(T)-corr, N}3^{-3}, \\ -54.55309324 - (-54.40371796) = E_{CBS}^{CCSD(T)-corr, N} + C^{CCSD(T)-corr, N}4^{-3}. \end{cases} \quad (2.12)$$

It follows that

$$\begin{cases} C^{CCSD(T)-corr, N} = 1.17636168, \\ E_{CBS}^{CCSD(T)-corr, N} = -0.16775593. \end{cases} \quad (2.13)$$

The MP2 and CCSD(T) total energy CBS limits for N atom are

$$\begin{aligned}
E_{CBS}^{MP2}(N)(3, 4) &= E_{CBS}^{HF, N} + E_{CBS}^{MP2-corr, N}(3, 4) \\
&= -54.404729183627495 - 0.14948484 = -54.554214023627495, \\
E_{CBS}^{MP2}(N)(4, 5) &= E_{CBS}^{HF, N} + E_{CBS}^{MP2-corr, N}(4, 5) \\
&= -54.404729183627495 - 0.15245258 = -54.557181763627497, \\
E_{CBS}^{CCSD(T)}(N) &= E_{CBS}^{HF, N} + E_{CBS}^{CCSD(T)-corr, N} \\
&= -54.404729183627495 - 0.16775593 = -54.572485113627494.
\end{aligned}$$

3 Bond dissociation energies

Calculate the bond dissociation energies ($E_{diss} = E(N_2) - 2E(N)$) by HF, MP2, and CCSD(T) in different basis sets. Calculate CBS-estimated bond dissociation energies as a difference between CBS energies of N_2 and N :

$$E_{diss}^{CBS} = E^{CBS}(N_2) - 2E^{CBS}(N). \quad (3.1)$$

Use *kcal/mol* units for reporting bond dissociation energies. Note that $1H_{atree} = 627.51kcal/mol$.

Solution: The numerical results are shown in Table 1 and Fig.1. The experimental value of BDE in N_2 (c.f.[2]) is

$$D_0 = -225.0 \text{ kcal/mol}. \quad (3.2)$$

It tells us that the BDE obtained by CCSD(T) is in excellent agreement with the experimental value.

Table 1: Bond dissociation energies (*kcal/mol*)

Basis sets	HF	MP2	CCSD(T)
cc-pVDV	-108.76608867	-209.15742261	-198.03391679
cc-pVTV	-115.97755909	-230.24426865	-218.77459067
cc-pVQV	-117.06662780	-235.38629894	-223.64975978
cc-pV5V	-117.24433882	-238.06091950	
CBS	-117.19294101	-238.47017973 (3,4) -240.62922829 (4,5)	-226.53890540

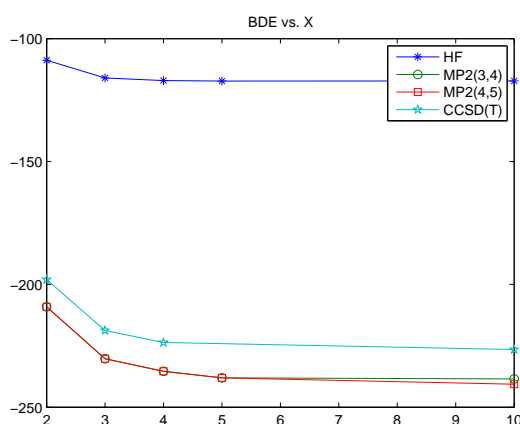


Figure 1: Bond dissociation energies versus the size of the basis set (Note that $N = 10$ means CBS)

4 Further discussion

4.1 Convergence rates

The comparison of convergence of HF, MP2, and CCSD(T) wrt basis set is shown in Fig.2. We observe that the HF energies converge faster than the correlated method energies.

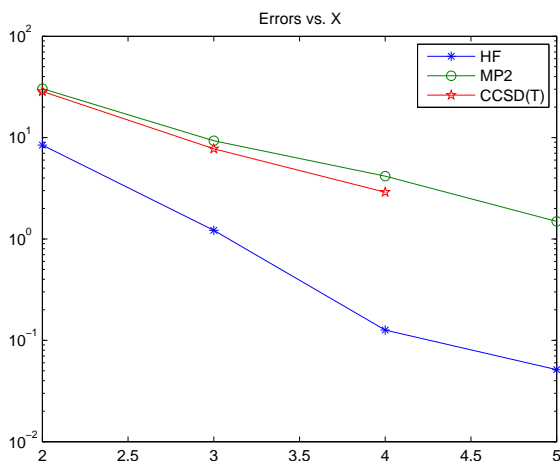


Figure 2: Convergence of HF, MP2, and CCSD(T) wrt versus the size of the basis set

4.2 MP2 CBS extrapolations

According to the numerical results shown in Table 1, we can know that the difference between $X = 3, 4$ and $X = 4, 5$ extrapolations is

$$E_{diss}^{MP2}(3, 4) - E_{diss}^{MP2}(4, 5) = 2.159048559999974,$$

which is not reliable since it is bigger than 1kcal/mol .

4.3 Accuracy and reliability

According to the numerical results shown in Table 1, and experimental value given by (3.2), we can conclude that

1. For the CBS case, the BDE predicted by CCSD(T) is the best;
2. For the cc-pVTZ basis, the BDE obtained by MP2 is the best.

4.4 Energy additivity scheme

Use the energy additivity scheme for MP2 and CCSD(T) energies:

$$E_{big}(CCSD(T)) = E_{small}(CCSD(T)) + [E_{big}(MP2) - E_{small}(MP2)]. \quad (4.1)$$

Use cc-pVTZ and cc-pVQZ bases in formula (4.1), we can get

$$\begin{aligned} E_{pVQZ}^{N_2}(CCSD(T)) &= E_{pVTZ}^{N_2}(CCSD(T)) + [E_{pVQZ}^{N_2}(MP2) - E_{pVTZ}^{N_2}(MP2)], \\ &= -109.39838559 + [-109.44493213 - (-109.38053915)], \\ &= -109.46277857. \end{aligned}$$

$$\begin{aligned} E_{pVQZ}^N(CCSD(T)) &= E_{pVTZ}^N(CCSD(T)) + [E_{pVQZ}^N(MP2) - E_{pVTZ}^N(MP2)], \\ &= -54.52487319 + [-54.53491025 - (-54.50681093)], \\ &= -54.55297251. \end{aligned}$$

The errors between exact CCSD(T)/cc-pVQZ energies and $E_{pVQZ}(CCSD(T))$ obtained by the formula (4.1) are

$$\Delta E_{pVQZ}^{N_2}(CCSD(T)) = -109.46277857 - (-109.46259476) = -1.83809999996e - 04$$

$$\Delta E_{pVQZ}^N(CCSD(T)) = -54.55297251 - (-54.55309324) = 1.207300000006e - 04.$$

It implies that the error are relatively small.

The BDE obtained by $E_{pVQZ}^{N_2}(CCSD(T))$ and $E_{pVQZ}^N(CCSD(T))$ is

$$\begin{aligned} BDE_{cc-pVQZ} &= (E_{pVQZ}^{N_2}(CCSD(T)) - E_{pVQZ}^N(CCSD(T))) \times 627.51 \\ &= -223.9166209605029 \text{ kcal/mol}, \end{aligned}$$

which is a very good result compared to the experimental value given by (3.2).

4.5 New CCSD(T) BDE values

If the CCSD(T) energies for each basis set are computed via the formula (4.1), then the BDE values are shown in Table 2. We observe that the CCSD(T) CBS BDE value is a very good result compared to the experimental value given by (3.2).

4.6 Efficiency

Based on the results shown above, the **computationally cheapest way** to achieve the targeted accuracy (i.e., 1kcal/mol) in predicting BDE of N_2 is that

1. first, calculating the energies by MP2;
2. second, obtaining CCSD(T) energies via additivity scheme (4.1);
3. third, computing the CBS values by extrapolation on HF energies and correlation energies respectively;
4. fourth, getting the BDE from (3.1).

Table 2: Bond dissociation energies for CCSD(T) obtained via additivity scheme (*kcal/mol*)

Basis sets	CCSD(T) via additivity scheme
cc-pVDV	-198.0339167937026
cc-pVTV	-219.1207628337096
cc-pVQV	-223.9166209604940
cc-pV5V	-226.3243803445530
CBS	-226.9324278234180

References

- [1] *EMSL Basis set exchange*. <https://bse.pnl.gov/bse/portal>. Last Modified: Mon,15 Jan 2007 23:47:08 GMT; Contributor: Dr. David Feller.
- [2] MATTHIAS LEIN AND GERNOT FRENKING, *Chapter 13: The nature of the chemical bond in the light of an energy decomposition analysis*, in *Theory and Applications of Computational Chemistry*, Clifford E. Dykstra, Gernot Frenking, Kwang S. Kim, and Gustavo E. Scuseria, eds., Elsevier, Amsterdam, 2005, pp. 291–372.

Lab 4: Electronic excited states of cyano radical

0 Lab procedure

Use the experimental geometry of CN: $r(\text{CN}) = 1.1718$ Angstroms. Let's use the $6 - 31 + G^*$ basis in all calculations in this lab.

0.1 EOM-EE-CCSD calculation

The input for the EOM-EE-CCSD calculation is

```
$comment
EOM-EE-CCSD for cyano radical
$end

$molecule
0 2
  N  0  0  0
  C  0  0  1.1718
$end

$rem
BASIS = 6-31+G*
CORRELATION = CCSD
EOM_EE_STATES = [2,2,2,2]
EXCHANGE = HF
GUI = 2
UNRESTRICTED = 1
JOB_TYPE = sp
print_general_basis=true
print_orbitals=99999
$end
```

The raw results obtained from Q-chem are listed below.

```
<S^2> = 1.1614
SCF energy = -92.20773976
MP2 energy = -92.44388333
```

CCSD correlation energy = -0.27643634
 CCSD total energy = -92.48417610
 CCSD $T1^2 = 0.1465$ $T2^2 = 0.1457$.

EOMEE-CCSD transition 1/A1

Total energy = -92.35485729 a.u. Excitation energy = 3.5189 eV.
 $R1^2 = 0.8693$ $R2^2 = 0.1307$ $Res^2 = 3.44e-07$

Amplitude	Transitions between orbitals			
0.8439	4 (A1) B	->	5 (A1) B	
-0.3021	4 (A1) B	->	7 (A1) B	
0.1007	1 (B2) A	->	3 (B2) A	
-0.1007	1 (B1) A	->	3 (B1) A	

Summary of significant orbitals:

Number	Type	Irrep	Energy
7	Occ Alpha	1 (B1)	-0.5218
6	Occ Alpha	1 (B2)	-0.5218
4	Occ Beta	4 (A1)	-0.6223
21	Vir Alpha	3 (B1)	0.1560
18	Vir Alpha	3 (B2)	0.1560
7	Vir Beta	5 (A1)	-0.0395
17	Vir Beta	7 (A1)	0.1263

EOMEE-CCSD transition 2/A1

Total energy = -92.20607060 a.u. Excitation energy = 7.5676 eV.
 $R1^2 = 0.8932$ $R2^2 = 0.1068$ $Res^2 = 6.58e-07$

Amplitude	Transitions between orbitals			
-0.3853	1 (B2) A	->	3 (B2) A	
-0.3853	1 (B1) A	->	3 (B1) A	
-0.2659	1 (B2) B	->	4 (B2) B	
0.2659	1 (B1) B	->	4 (B1) B	
0.2528	1 (B2) B	->	3 (B2) B	
-0.2528	1 (B1) B	->	3 (B1) B	
0.2406	1 (B2) A	->	4 (B2) A	
-0.2406	1 (B1) A	->	4 (B1) A	
-0.2267	1 (B2) A	->	2 (B2) A	
0.2267	1 (B1) A	->	2 (B1) A	
0.2125	1 (B2) B	->	2 (B2) B	
-0.2125	1 (B1) B	->	2 (B1) B	

Summary of significant orbitals:

Number	Type	Irrep	Energy
7	Occ Alpha	1 (B1)	-0.5218
6	Occ Alpha	1 (B2)	-0.5218
6	Occ Beta	1 (B1)	-0.5386
5	Occ Beta	1 (B2)	-0.5386
17	Vir Alpha	2 (B1)	0.1006
21	Vir Alpha	3 (B1)	0.1560
26	Vir Alpha	4 (B1)	0.2900
14	Vir Alpha	2 (B2)	0.1006
18	Vir Alpha	3 (B2)	0.1560
25	Vir Alpha	4 (B2)	0.2900
11	Vir Beta	2 (B1)	0.0934
21	Vir Beta	3 (B1)	0.2124
26	Vir Beta	4 (B1)	0.2757
10	Vir Beta	2 (B2)	0.0934
18	Vir Beta	3 (B2)	0.2124
25	Vir Beta	4 (B2)	0.2757

EOMEE-CCSD transition 1/A2

Total energy = -92.20607323 a.u. Excitation energy = 7.5676 eV.

R1² = 0.8932 R2² = 0.1068 Res² = 3.58e-07

Amplitude	Transitions between orbitals		
0.3853	1 (B2) A	->	3 (B1) A
-0.3853	1 (B1) A	->	3 (B2) A
-0.2659	1 (B2) B	->	4 (B1) B
-0.2659	1 (B1) B	->	4 (B2) B
0.2529	1 (B1) B	->	3 (B2) B
0.2528	1 (B2) B	->	3 (B1) B
0.2406	1 (B2) A	->	4 (B1) A
0.2406	1 (B1) A	->	4 (B2) A
-0.2267	1 (B1) A	->	2 (B2) A
-0.2267	1 (B2) A	->	2 (B1) A
0.2125	1 (B2) B	->	2 (B1) B
0.2125	1 (B1) B	->	2 (B2) B

Summary of significant orbitals:

Number	Type	Irrep	Energy
7	Occ Alpha	1 (B1)	-0.5218
6	Occ Alpha	1 (B2)	-0.5218
6	Occ Beta	1 (B1)	-0.5386

5	Occ	Beta	1 (B2)	-0.5386
17	Vir	Alpha	2 (B1)	0.1006
21	Vir	Alpha	3 (B1)	0.1560
26	Vir	Alpha	4 (B1)	0.2900
14	Vir	Alpha	2 (B2)	0.1006
18	Vir	Alpha	3 (B2)	0.1560
25	Vir	Alpha	4 (B2)	0.2900
11	Vir	Beta	2 (B1)	0.0934
21	Vir	Beta	3 (B1)	0.2124
26	Vir	Beta	4 (B1)	0.2757
10	Vir	Beta	2 (B2)	0.0934
18	Vir	Beta	3 (B2)	0.2124
25	Vir	Beta	4 (B2)	0.2757

EOMEE-CCSD transition 2/A2

Total energy = -92.17437338 a.u. Excitation energy = 8.4302 eV.

R1² = 0.9204 R2² = 0.0796 Res² = 5.23e-07

Amplitude	Transitions between orbitals			
0.4628	1 (B1) A	->	3 (B2) A	
0.4626	1 (B2) A	->	3 (B1) A	
0.2839	1 (B1) A	->	2 (B2) A	
-0.2838	1 (B2) A	->	2 (B1) A	
-0.2766	1 (B1) A	->	4 (B2) A	
0.2765	1 (B2) A	->	4 (B1) A	
-0.1726	1 (B2) B	->	4 (B1) B	
0.1724	1 (B1) B	->	4 (B2) B	
0.1690	1 (B2) B	->	3 (B1) B	
-0.1688	1 (B1) B	->	3 (B2) B	
0.1549	1 (B2) B	->	2 (B1) B	
-0.1547	1 (B1) B	->	2 (B2) B	

Summary of significant orbitals:

Number	Type	Irrep	Energy
7	Occ Alpha	1 (B1)	-0.5218
6	Occ Alpha	1 (B2)	-0.5218
6	Occ Beta	1 (B1)	-0.5386
5	Occ Beta	1 (B2)	-0.5386
17	Vir Alpha	2 (B1)	0.1006
21	Vir Alpha	3 (B1)	0.1560
26	Vir Alpha	4 (B1)	0.2900
14	Vir Alpha	2 (B2)	0.1006

18	Vir	Alpha	3 (B2)	0.1560
25	Vir	Alpha	4 (B2)	0.2900
11	Vir	Beta	2 (B1)	0.0934
21	Vir	Beta	3 (B1)	0.2124
26	Vir	Beta	4 (B1)	0.2757
10	Vir	Beta	2 (B2)	0.0934
18	Vir	Beta	3 (B2)	0.2124
25	Vir	Beta	4 (B2)	0.2757

EOMEE-CCSD transition 1/B1

Total energy = -92.42710522 a.u. Excitation energy = 1.5530 eV.

$R1^2 = 0.8937$ $R2^2 = 0.1063$ $Res^2 = 2.63e-07$

Amplitude	Transitions between orbitals			
0.8690	1 (B1) B	->	5 (A1) B	
-0.3213	1 (B1) B	->	7 (A1) B	
-0.1048	1 (B1) B	->	6 (A1) B	
-0.0753	1 (B1) B	->	9 (A1) B	

Summary of significant orbitals:

Number	Type	Irrep	Energy
6	Occ Beta	1 (B1)	-0.5386
7	Vir Beta	5 (A1)	-0.0395
14	Vir Beta	6 (A1)	0.0952
17	Vir Beta	7 (A1)	0.1263
27	Vir Beta	9 (A1)	0.3482

EOMEE-CCSD transition 2/B1

Total energy = -92.19128888 a.u. Excitation energy = 7.9699 eV.

$R1^2 = 0.9134$ $R2^2 = 0.0866$ $Res^2 = 3.17e-07$

Amplitude	Transitions between orbitals			
0.7157	5 (A1) A	->	3 (B1) A	
-0.4431	5 (A1) A	->	2 (B1) A	
0.4167	5 (A1) A	->	4 (B1) A	
-0.0858	5 (A1) A	->	6 (B1) A	

Summary of significant orbitals:

Number	Type	Irrep	Energy
5	Occ Alpha	5 (A1)	-0.5654

17	Vir	Alpha	2 (B1)	0.1006
21	Vir	Alpha	3 (B1)	0.1560
26	Vir	Alpha	4 (B1)	0.2900
32	Vir	Alpha	6 (B1)	1.2184

EOMEE-CCSD transition 1/B2

Total energy = -92.42710522 a.u. Excitation energy = 1.5530 eV.

R1² = 0.8937 R2² = 0.1063 Res² = 2.63e-07

Amplitude	Transitions between orbitals			
0.8690	1 (B2) B	->	5 (A1) B	
-0.3213	1 (B2) B	->	7 (A1) B	
-0.1048	1 (B2) B	->	6 (A1) B	
-0.0753	1 (B2) B	->	9 (A1) B	

Summary of significant orbitals:

Number	Type	Irrep	Energy
5	Occ Beta	1 (B2)	-0.5386
7	Vir Beta	5 (A1)	-0.0395
14	Vir Beta	6 (A1)	0.0952
17	Vir Beta	7 (A1)	0.1263
27	Vir Beta	9 (A1)	0.3482

EOMEE-CCSD transition 2/B2

Total energy = -92.19128888 a.u. Excitation energy = 7.9699 eV.

R1² = 0.9134 R2² = 0.0866 Res² = 3.17e-07

Amplitude	Transitions between orbitals			
-0.7157	5 (A1) A	->	3 (B2) A	
-0.4431	5 (A1) A	->	2 (B2) A	
0.4167	5 (A1) A	->	4 (B2) A	
-0.0858	5 (A1) A	->	6 (B2) A	

Summary of significant orbitals:

Number	Type	Irrep	Energy
5	Occ Alpha	5 (A1)	-0.5654
14	Vir Alpha	2 (B2)	0.1006
18	Vir Alpha	3 (B2)	0.1560
25	Vir Alpha	4 (B2)	0.2900

28 Vir Alpha 6 (B2) 1.2184

ALPHA MOLECULAR ORBITAL COEFFICIENTS

	1	2	3	4	5	6
eigenvalues:	-15.619	-11.367	-1.247	-0.744	-0.565	-0.522
	7	8	9	10	11	12
eigenvalues:	-0.522	0.076	0.100	0.101	0.101	0.156
	13	14	15	16	17	18
eigenvalues:	0.156	0.220	0.290	0.290	0.337	0.534
	19	20	21	22	23	24
eigenvalues:	0.810	0.810	0.899	1.060	1.218	1.218
	25	26	27	28	29	30
eigenvalues:	1.309	1.538	1.736	1.736	1.775	1.775
	31	32	33	34	35	36
eigenvalues:	2.233	2.233	2.681	2.869	2.869	3.256
	37	38				
eigenvalues:	4.302	4.484				

...

BETA MOLECULAR ORBITAL COEFFICIENTS

	1	2	3	4	5	6
eigenvalues:	-15.645	-11.313	-1.260	-0.622	-0.539	-0.539
	7	8	9	10	11	12
eigenvalues:	-0.039	0.093	0.093	0.095	0.126	0.212
	13	14	15	16	17	18
eigenvalues:	0.212	0.225	0.276	0.276	0.348	0.593
	19	20	21	22	23	24
eigenvalues:	0.893	0.893	0.962	1.130	1.151	1.151
	25	26	27	28	29	30
eigenvalues:	1.337	1.533	1.767	1.767	1.828	1.828
	31	32	33	34	35	36
eigenvalues:	2.232	2.232	2.735	2.900	2.900	3.278
	37	38				
eigenvalues:	4.289	4.547				

...

0.2 EOM-IP-CCSD calculation

The input for the EOM-IP-CCSD calculation is

\$comment

EOM-IP-CCSD for cyano radical

\$end

\$molecule

-1 1

```

N 0 0 0
C 0 0 1.1718

```

\$end

\$rem

```

BASIS = 6-31+G*
CORRELATION = CCSD
EOM_IP_STATES = [2,2,2,2]
EXCHANGE = HF
GUI = 2
UNRESTRICTED = 1
JOB_TYPE = sp
print_general_basis=true
print_orbitals=99999

```

\$end

The raw results obtained from Q-chem are listed below.

<S²> = 0.0000

```

SCF energy           = -92.31462822
MP2 energy           = -92.60987126
CCSD correlation energy = -0.29963068
CCSD total energy    = -92.61425890
CCSD T12 = 0.0080 T22 = 0.1235.

```

EOMIP-CCSD transition 1/A1

```

Total energy = -92.47751457 a.u.  Excitation energy = 3.7210 eV.
R12 = 0.9158  R22 = 0.0842  Res2 = 9.73e-08

```

Amplitude	Transitions between orbitals			
-0.9561	5 (A1)	A	->	infty
-0.0386	4 (A1)	A	->	infty
0.0135	3 (A1)	A	->	infty
-0.0003	2 (A1)	A	->	infty

Summary of significant orbitals:

Number	Type	Irrep	Energy
2	Occ Alpha	2 (A1)	-10.9784
3	Occ Alpha	3 (A1)	-0.9319

4	Occ	Alpha	4 (A1)	-0.3410
6	Occ	Alpha	5 (A1)	-0.1920

EOMIP-CCSD transition 2/A1

Total energy = -92.35726740 a.u. Excitation energy = 6.9931 eV.

R1² = 0.8809 R2² = 0.1191 Res² = 7.35e-08

Amplitude	Transitions between orbitals			
0.9380	4 (A1)	A	->	infty
-0.0306	5 (A1)	A	->	infty
-0.0130	3 (A1)	A	->	infty
-0.0003	2 (A1)	A	->	infty

Summary of significant orbitals:

Number	Type	Irrep	Energy
2	Occ Alpha	2 (A1)	-10.9784
3	Occ Alpha	3 (A1)	-0.9319
4	Occ Alpha	4 (A1)	-0.3410
6	Occ Alpha	5 (A1)	-0.1920

EOMIP-CCSD transition 1/A2

Total energy = -92.10080562 a.u. Excitation energy = 13.9718 eV.

R1² = 0.0000 R2² = 1.0000 Res² = 3.40e-07

Amplitude	Transitions between orbitals			
0.3271	1 (B1)	A	5 (A1) B	-> 4 (B2) B
-0.3271	5 (A1)	B	1 (B1) A	-> 4 (B2) B
0.3271	1 (B2)	A	5 (A1) B	-> 4 (B1) B
-0.3271	5 (A1)	B	1 (B2) A	-> 4 (B1) B
-0.3268	5 (A1)	A	1 (B1) B	-> 4 (B2) B
0.3268	1 (B1)	B	5 (A1) A	-> 4 (B2) B
-0.3268	5 (A1)	A	1 (B2) B	-> 4 (B1) B
0.3268	1 (B2)	B	5 (A1) A	-> 4 (B1) B
0.3267	5 (A1)	A	1 (B1) A	-> 4 (B2) A
-0.3267	1 (B1)	A	5 (A1) A	-> 4 (B2) A
0.3267	5 (A1)	A	1 (B2) A	-> 4 (B1) A
-0.3267	1 (B2)	A	5 (A1) A	-> 4 (B1) A
-0.1742	1 (B1)	A	5 (A1) B	-> 3 (B2) B
0.1742	5 (A1)	B	1 (B1) A	-> 3 (B2) B
-0.1742	1 (B2)	A	5 (A1) B	-> 3 (B1) B
0.1742	5 (A1)	B	1 (B2) A	-> 3 (B1) B

0.1740	5 (A1) A	1 (B1) B	->	3 (B2) B
-0.1740	1 (B1) B	5 (A1) A	->	3 (B2) B
0.1740	5 (A1) A	1 (B2) B	->	3 (B1) B
-0.1740	1 (B2) B	5 (A1) A	->	3 (B1) B
-0.1740	5 (A1) A	1 (B1) A	->	3 (B2) A
0.1740	1 (B1) A	5 (A1) A	->	3 (B2) A
-0.1740	5 (A1) A	1 (B2) A	->	3 (B1) A
0.1740	1 (B2) A	5 (A1) A	->	3 (B1) A
-0.1089	1 (B1) A	5 (A1) B	->	2 (B2) B
0.1089	5 (A1) B	1 (B1) A	->	2 (B2) B
-0.1089	1 (B2) A	5 (A1) B	->	2 (B1) B
0.1089	5 (A1) B	1 (B2) A	->	2 (B1) B
0.1087	5 (A1) A	1 (B1) B	->	2 (B2) B
-0.1087	1 (B1) B	5 (A1) A	->	2 (B2) B
0.1087	5 (A1) A	1 (B2) B	->	2 (B1) B
-0.1087	1 (B2) B	5 (A1) A	->	2 (B1) B
-0.1087	5 (A1) A	1 (B1) A	->	2 (B2) A
0.1087	1 (B1) A	5 (A1) A	->	2 (B2) A
-0.1087	5 (A1) A	1 (B2) A	->	2 (B1) A
0.1087	1 (B2) A	5 (A1) A	->	2 (B1) A

Summary of significant orbitals:

Number	Type	Irrep	Energy
6	Occ Alpha	5 (A1)	-0.1920
5	Occ Alpha	1 (B1)	-0.1947
7	Occ Alpha	1 (B2)	-0.1947
6	Occ Beta	5 (A1)	-0.1920
5	Occ Beta	1 (B1)	-0.1947
7	Occ Beta	1 (B2)	-0.1947
12	Vir Alpha	2 (B1)	0.2754
22	Vir Alpha	3 (B1)	0.4071
26	Vir Alpha	4 (B1)	0.5312
11	Vir Alpha	2 (B2)	0.2754
21	Vir Alpha	3 (B2)	0.4071
25	Vir Alpha	4 (B2)	0.5312
12	Vir Beta	2 (B1)	0.2754
22	Vir Beta	3 (B1)	0.4071
26	Vir Beta	4 (B1)	0.5312
11	Vir Beta	2 (B2)	0.2754
21	Vir Beta	3 (B2)	0.4071
25	Vir Beta	4 (B2)	0.5312

EOMIP-CCSD transition 2/A2

Total energy = -92.05813776 a.u. Excitation energy = 15.1328 eV.

R1² = 0.0000 R2² = 1.0000 Res² = 2.63e-07

Amplitude	Transitions between orbitals			
-0.3217	5 (A1) A	1 (B2) B	->	4 (B1) B
0.3217	1 (B2) B	5 (A1) A	->	4 (B1) B
0.3217	5 (A1) A	1 (B1) B	->	4 (B2) B
-0.3217	1 (B1) B	5 (A1) A	->	4 (B2) B
0.3216	1 (B2) A	5 (A1) B	->	4 (B1) B
-0.3216	5 (A1) B	1 (B2) A	->	4 (B1) B
-0.3216	1 (B1) A	5 (A1) B	->	4 (B2) B
0.3216	5 (A1) B	1 (B1) A	->	4 (B2) B
0.3215	5 (A1) A	1 (B2) A	->	4 (B1) A
-0.3215	1 (B2) A	5 (A1) A	->	4 (B1) A
-0.3215	5 (A1) A	1 (B1) A	->	4 (B2) A
0.3215	1 (B1) A	5 (A1) A	->	4 (B2) A
-0.1813	5 (A1) A	1 (B2) A	->	3 (B1) A
0.1813	1 (B2) A	5 (A1) A	->	3 (B1) A
0.1813	5 (A1) A	1 (B1) A	->	3 (B2) A
-0.1813	1 (B1) A	5 (A1) A	->	3 (B2) A
-0.1812	1 (B2) A	5 (A1) B	->	3 (B1) B
0.1812	5 (A1) B	1 (B2) A	->	3 (B1) B
0.1812	1 (B1) A	5 (A1) B	->	3 (B2) B
-0.1812	5 (A1) B	1 (B1) A	->	3 (B2) B
0.1812	5 (A1) A	1 (B2) B	->	3 (B1) B
-0.1812	1 (B2) B	5 (A1) A	->	3 (B1) B
-0.1812	5 (A1) A	1 (B1) B	->	3 (B2) B
0.1812	1 (B1) B	5 (A1) A	->	3 (B2) B
0.1110	5 (A1) A	1 (B2) B	->	2 (B1) B
-0.1110	1 (B2) B	5 (A1) A	->	2 (B1) B
-0.1110	5 (A1) A	1 (B1) B	->	2 (B2) B
0.1110	1 (B1) B	5 (A1) A	->	2 (B2) B
-0.1109	1 (B2) A	5 (A1) B	->	2 (B1) B
0.1109	5 (A1) B	1 (B2) A	->	2 (B1) B
0.1109	1 (B1) A	5 (A1) B	->	2 (B2) B
-0.1109	5 (A1) B	1 (B1) A	->	2 (B2) B
-0.1109	5 (A1) A	1 (B2) A	->	2 (B1) A
0.1109	1 (B2) A	5 (A1) A	->	2 (B1) A
0.1109	5 (A1) A	1 (B1) A	->	2 (B2) A
-0.1109	1 (B1) A	5 (A1) A	->	2 (B2) A

Summary of significant orbitals:

Number	Type	Irrep	Energy
6	Occ Alpha	5 (A1)	-0.1920
5	Occ Alpha	1 (B1)	-0.1947
7	Occ Alpha	1 (B2)	-0.1947
6	Occ Beta	5 (A1)	-0.1920
5	Occ Beta	1 (B1)	-0.1947
7	Occ Beta	1 (B2)	-0.1947
12	Vir Alpha	2 (B1)	0.2754
22	Vir Alpha	3 (B1)	0.4071
26	Vir Alpha	4 (B1)	0.5312
11	Vir Alpha	2 (B2)	0.2754
21	Vir Alpha	3 (B2)	0.4071
25	Vir Alpha	4 (B2)	0.5312
12	Vir Beta	2 (B1)	0.2754
22	Vir Beta	3 (B1)	0.4071
26	Vir Beta	4 (B1)	0.5312
11	Vir Beta	2 (B2)	0.2754
21	Vir Beta	3 (B2)	0.4071
25	Vir Beta	4 (B2)	0.5312

EOMIP-CCSD transition 1/B1

Total energy = -92.42730292 a.u. Excitation energy = 5.0873 eV.

R1² = 0.9334 R2² = 0.0666 Res² = 1.29e-07

Amplitude2/A2 Transitions between orbitals
 -0.9661 1 (B1) A -> infty

Summary of significant orbitals:

Number	Type	Irrep	Energy
5	Occ Alpha	1 (B1)	-0.1947

EOMIP-CCSD transition 2/B1

Total energy = -92.04147399 a.u. Excitation energy = 15.5863 eV.

R1² = 0.0003 R2² = 0.9997 Res² = 5.29e-07

Amplitude Transitions between orbitals
 0.7011 5 (A1) A 5 (A1) B -> 4 (B1) B
 -0.7011 5 (A1) B 5 (A1) A -> 4 (B1) B
 -0.3834 5 (A1) A 5 (A1) B -> 3 (B1) B
 0.3834 5 (A1) B 5 (A1) A -> 3 (B1) B
 -0.2619 5 (A1) A 5 (A1) B -> 2 (B1) B
 0.2619 5 (A1) B 5 (A1) A -> 2 (B1) B

0.2585	5 (A1) A	4 (A1) B	->	4 (B1) B
-0.2585	4 (A1) B	5 (A1) A	->	4 (B1) B
-0.2543	4 (A1) A	4 (A1) B	->	4 (B1) B
0.2543	4 (A1) B	4 (A1) A	->	4 (B1) B
0.1790	4 (A1) A	5 (A1) B	->	4 (B1) B
-0.1790	5 (A1) B	4 (A1) A	->	4 (B1) B
-0.1566	5 (A1) A	5 (A1) B	->	5 (B1) B
0.1566	5 (A1) B	5 (A1) A	->	5 (B1) B
0.1374	4 (A1) A	4 (A1) B	->	3 (B1) B
-0.1374	4 (A1) B	4 (A1) A	->	3 (B1) B
-0.1268	5 (A1) A	4 (A1) B	->	3 (B1) B
0.1268	4 (A1) B	5 (A1) A	->	3 (B1) B
-0.1046	5 (A1) A	4 (A1) B	->	2 (B1) B
0.1046	4 (A1) B	5 (A1) A	->	2 (B1) B
0.1016	4 (A1) A	4 (A1) B	->	2 (B1) B
-0.1016	4 (A1) B	4 (A1) A	->	2 (B1) B

Summary of significant orbitals:

Number	Type	Irrep	Energy
4	Occ Alpha	4 (A1)	-0.3410
6	Occ Alpha	5 (A1)	-0.1920
4	Occ Beta	4 (A1)	-0.3410
6	Occ Beta	5 (A1)	-0.1920
12	Vir Beta	2 (B1)	0.2754
22	Vir Beta	3 (B1)	0.4071
26	Vir Beta	4 (B1)	0.5312
36	Vir Beta	5 (B1)	1.1622

EOMIP-CCSD transition 1/B2

Total energy = -92.42730292 a.u. Excitation energy = 5.0873 eV.

R1² = 0.9334 R2² = 0.0666 Res² = 1.29e-07

Amplitude	Transitions between orbitals
-0.9661	1 (B2) A -> infty

Summary of significant orbitals:

Number	Type	Irrep	Energy
7	Occ Alpha	1 (B2)	-0.1947

EOMIP-CCSD transition 2/B2

Total energy = -92.04147468 a.u. Excitation energy = 15.5863 eV.

R1² = 0.0003 R2² = 0.9997 Res² = 5.39e-07

Amplitude	Transitions between orbitals			
0.7011	5 (A1) A	5 (A1) B	->	4 (B2) B
-0.7011	5 (A1) B	5 (A1) A	->	4 (B2) B
-0.3834	5 (A1) A	5 (A1) B	->	3 (B2) B
0.3834	5 (A1) B	5 (A1) A	->	3 (B2) B
-0.2619	5 (A1) A	5 (A1) B	->	2 (B2) B
0.2619	5 (A1) B	5 (A1) A	->	2 (B2) B
0.2584	5 (A1) A	4 (A1) B	->	4 (B2) B
-0.2584	4 (A1) B	5 (A1) A	->	4 (B2) B
-0.2543	4 (A1) A	4 (A1) B	->	4 (B2) B
0.2543	4 (A1) B	4 (A1) A	->	4 (B2) B
0.1791	4 (A1) A	5 (A1) B	->	4 (B2) B
-0.1791	5 (A1) B	4 (A1) A	->	4 (B2) B
0.1566	5 (A1) A	5 (A1) B	->	5 (B2) B
-0.1566	5 (A1) B	5 (A1) A	->	5 (B2) B
0.1374	4 (A1) A	4 (A1) B	->	3 (B2) B
-0.1374	4 (A1) B	4 (A1) A	->	3 (B2) B
-0.1267	5 (A1) A	4 (A1) B	->	3 (B2) B
0.1267	4 (A1) B	5 (A1) A	->	3 (B2) B
-0.1045	5 (A1) A	4 (A1) B	->	2 (B2) B
0.1045	4 (A1) B	5 (A1) A	->	2 (B2) B
0.1016	4 (A1) A	4 (A1) B	->	2 (B2) B
-0.1016	4 (A1) B	4 (A1) A	->	2 (B2) B

Summary of significant orbitals:

Number	Type	Irrep	Energy
4	Occ Alpha	4 (A1)	-0.3410
6	Occ Alpha	5 (A1)	-0.1920
4	Occ Beta	4 (A1)	-0.3410
6	Occ Beta	5 (A1)	-0.1920
11	Vir Beta	2 (B2)	0.2754
21	Vir Beta	3 (B2)	0.4071
25	Vir Beta	4 (B2)	0.5312
33	Vir Beta	5 (B2)	1.1622

ALPHA MOLECULAR ORBITAL COEFFICIENTS

	ALPHA MOLECULAR ORBITAL COEFFICIENTS					
	1	2	3	4	5	6
eigenvalues:	-15.301	-10.978	-0.932	-0.341	-0.195	-0.195

	7	8	9	10	11	12
eigenvalues:	-0.192	0.248	0.275	0.275	0.289	0.405
	13	14	15	16	17	18
eigenvalues:	0.407	0.407	0.531	0.531	0.553	0.850
	19	20	21	22	23	24
eigenvalues:	1.162	1.162	1.224	1.383	1.461	1.461
	25	26	27	28	29	30
eigenvalues:	1.618	1.818	2.084	2.084	2.136	2.136
	31	32	33	34	35	36
eigenvalues:	2.551	2.551	3.045	3.217	3.217	3.592
	37	38				
eigenvalues:	4.599	4.866				

...

	BETA MOLECULAR ORBITAL COEFFICIENTS					
	1	2	3	4	5	6
eigenvalues:	-15.301	-10.978	-0.932	-0.341	-0.195	-0.195
	7	8	9	10	11	12
eigenvalues:	-0.192	0.248	0.275	0.275	0.289	0.405
	13	14	15	16	17	18
eigenvalues:	0.407	0.407	0.531	0.531	0.553	0.850
	19	20	21	22	23	24
eigenvalues:	1.162	1.162	1.224	1.383	1.461	1.461
	25	26	27	28	29	30
eigenvalues:	1.618	1.818	2.084	2.084	2.136	2.136
	31	32	33	34	35	36
eigenvalues:	2.551	2.551	3.045	3.217	3.217	3.592
	37	38				
eigenvalues:	4.599	4.866				

...

1 MO

Draw molecular orbitals of CN.

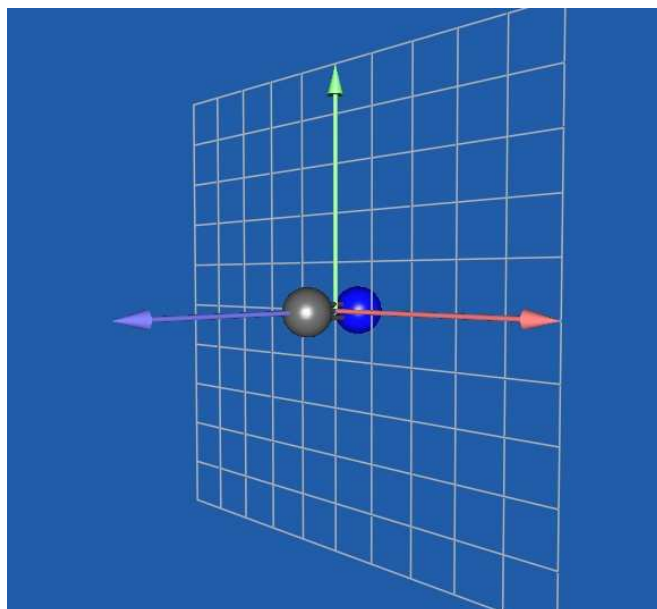


Figure 1: Molecular orbital from EOM-EE-CCSD

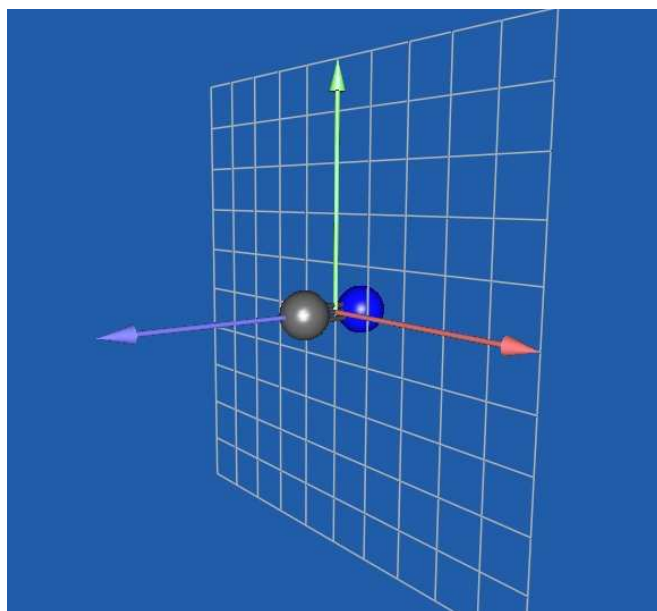


Figure 2: Molecular orbital from EOM-IP-CCSD

2 Analyze EOM-EE-CCSD output

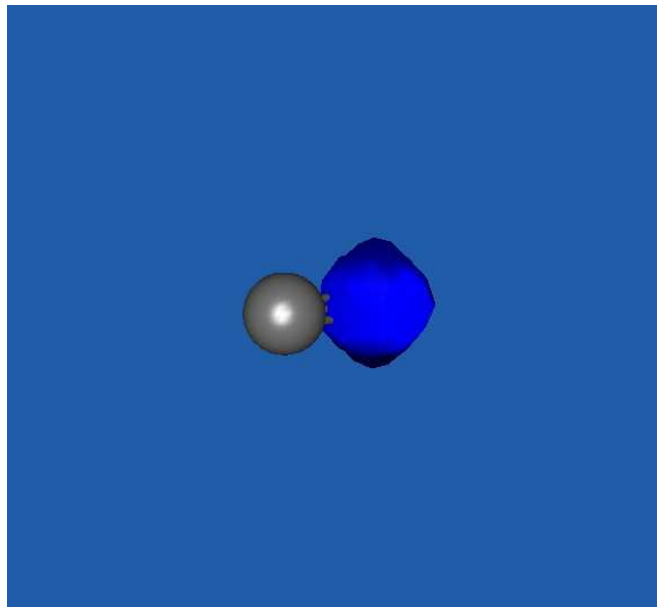


Figure 3: Surface: Alpha 1 (EOM-EE-CCSD)

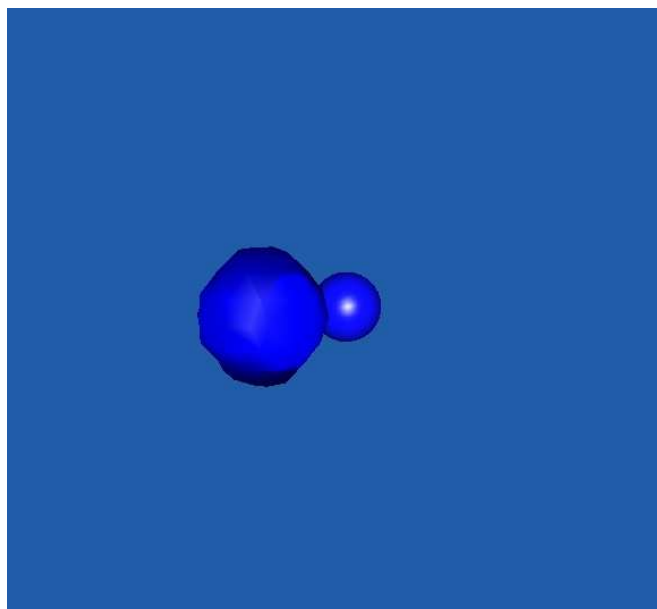


Figure 4: Surface: Alpha 2 (EOM-EE-CCSD)

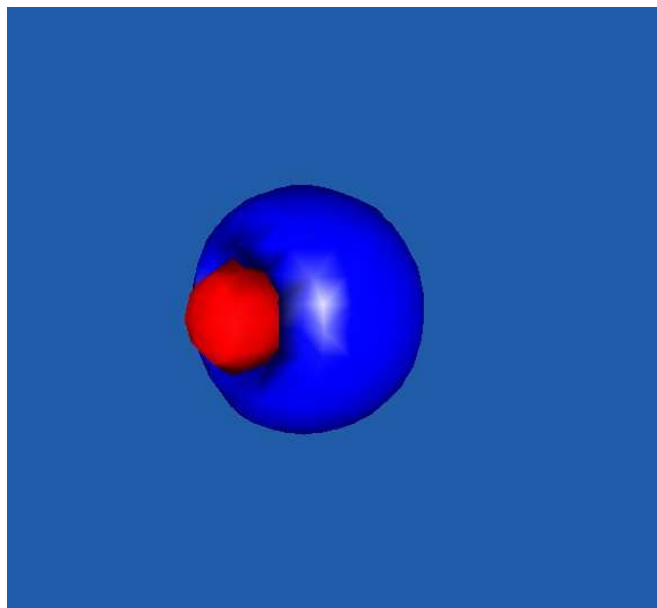


Figure 5: Surface: Alpha 3 (EOM-EE-CCSD)

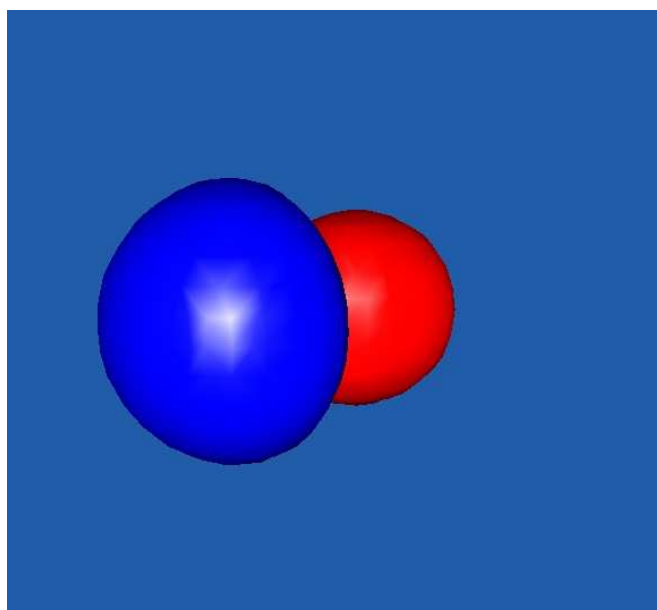


Figure 6: Surface: Alpha 4 (EOM-EE-CCSD)

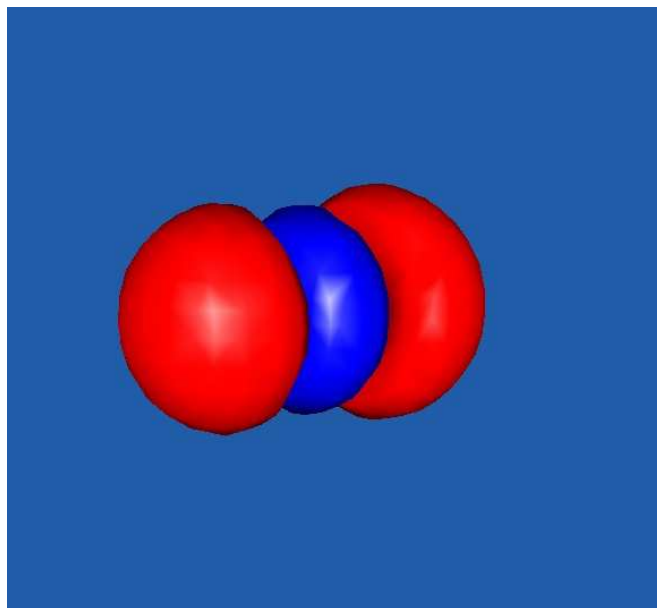


Figure 7: Surface: Alpha 5 (EOM-EE-CCSD)

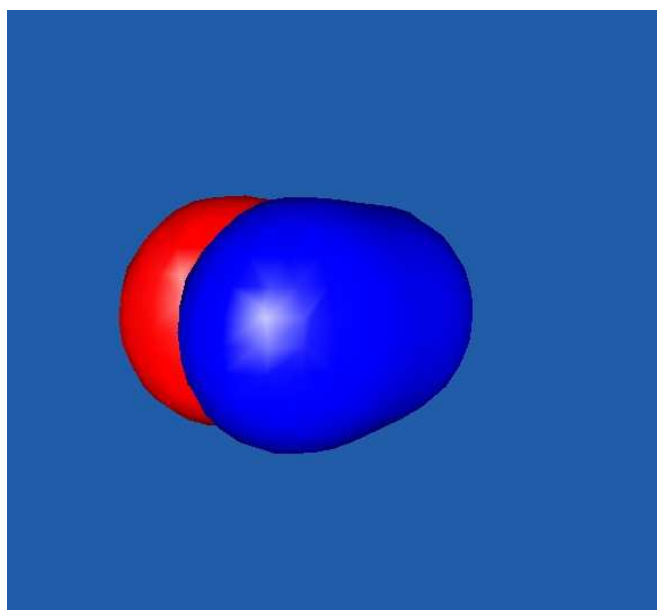


Figure 8: Surface: Alpha 6, HOMO-1 (EOM-EE-CCSD)

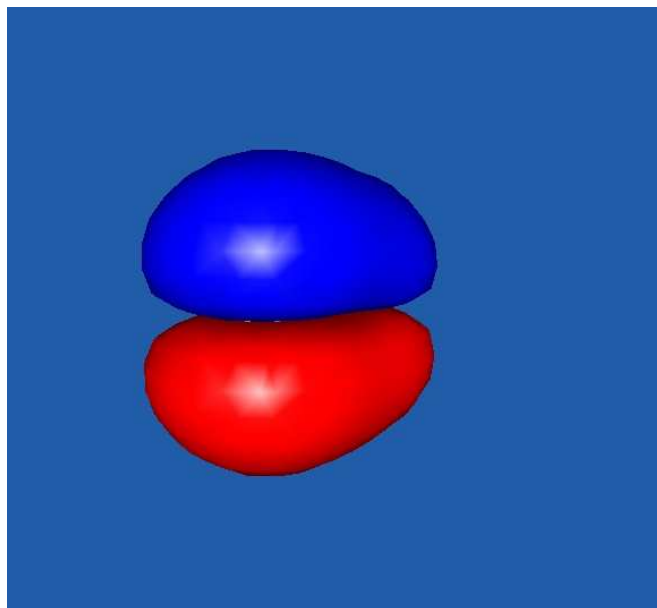


Figure 9: Surface: Alpha 7, HOMO (EOM-EE-CCSD)

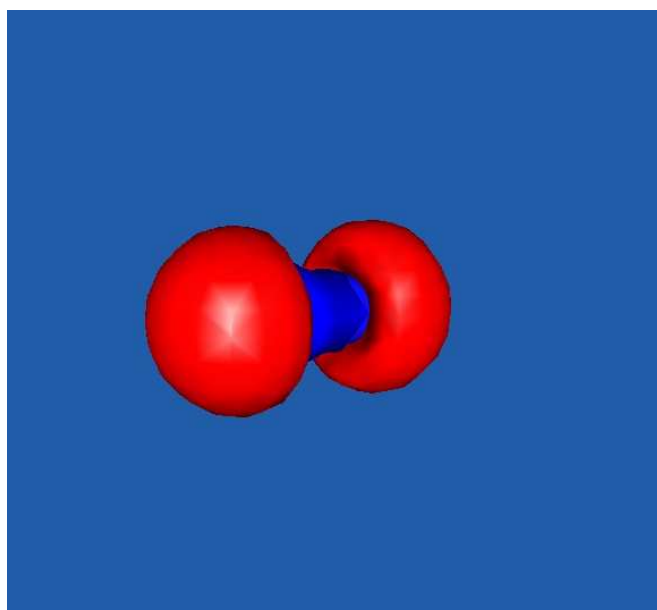


Figure 10: Surface: Alpha 8, LUMO (EOM-EE-CCSD)

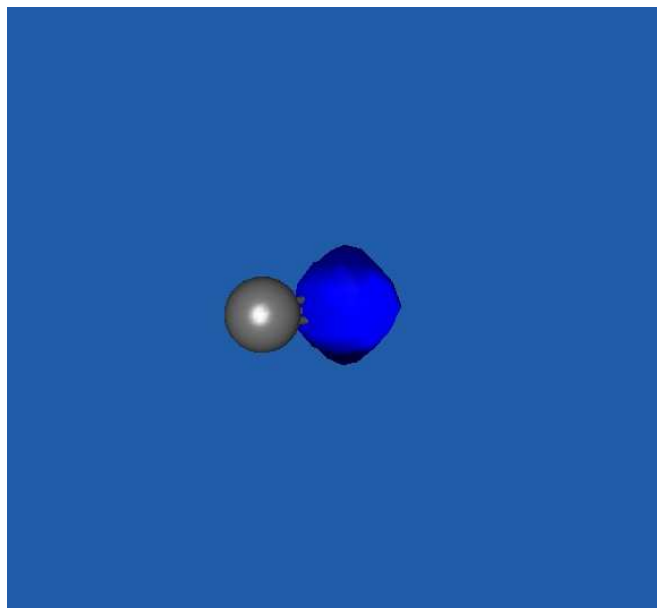


Figure 11: Surface: Beta 1 (EOM-EE-CCSD)

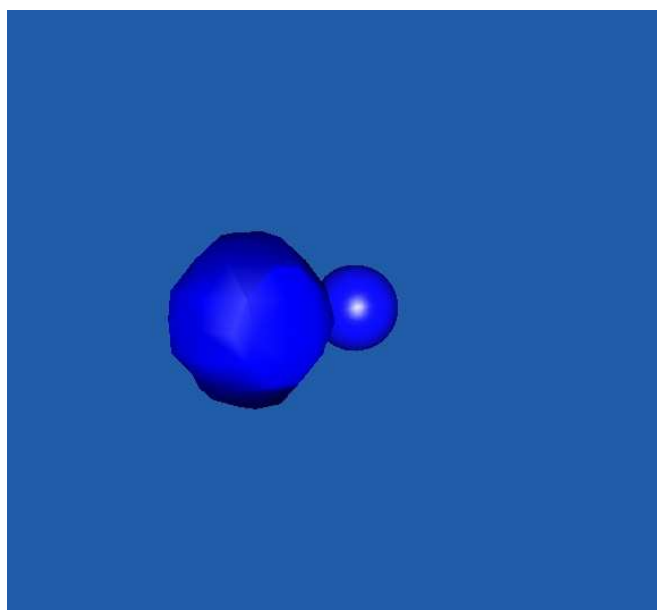


Figure 12: Surface: Beta 2 (EOM-EE-CCSD)

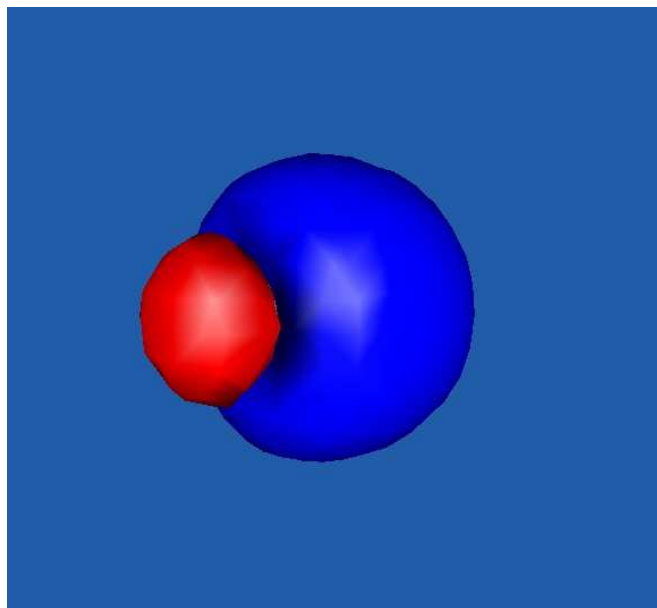


Figure 13: Surface: Beta 3 (EOM-EE-CCSD)

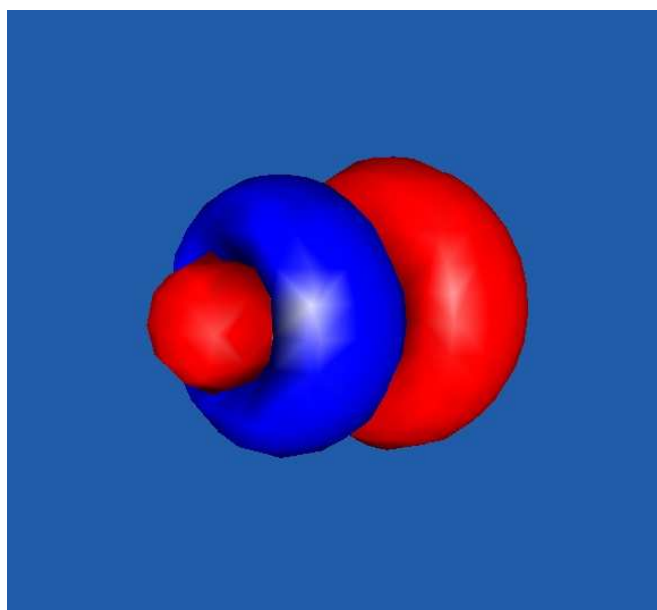


Figure 14: Surface: Beta 4 (EOM-EE-CCSD)

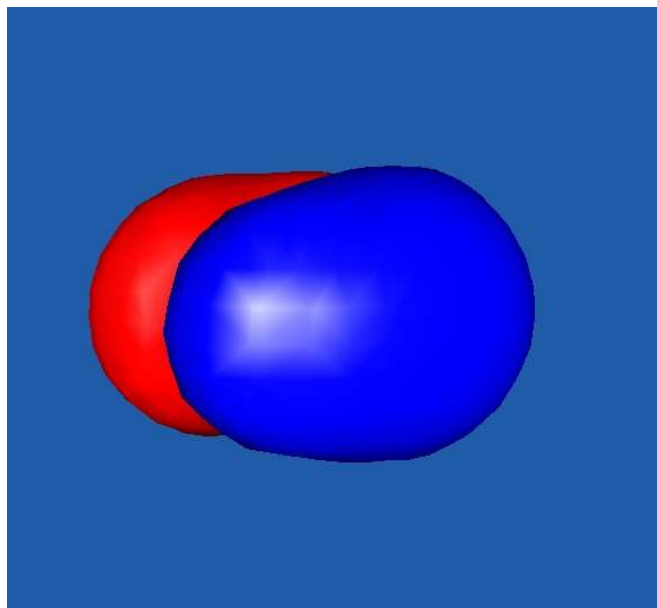


Figure 15: Surface: Beta 5, HOMO-1 (EOM-EE-CCSD)

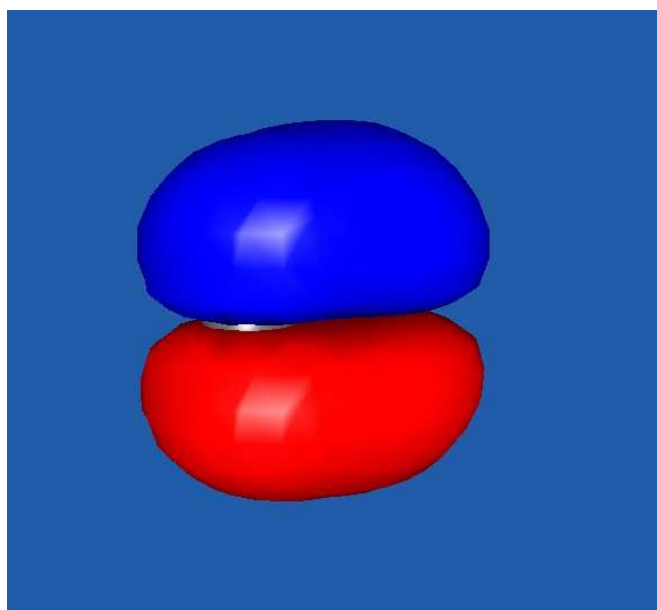


Figure 16: Surface: Beta 6, HOMO (EOM-EE-CCSD)

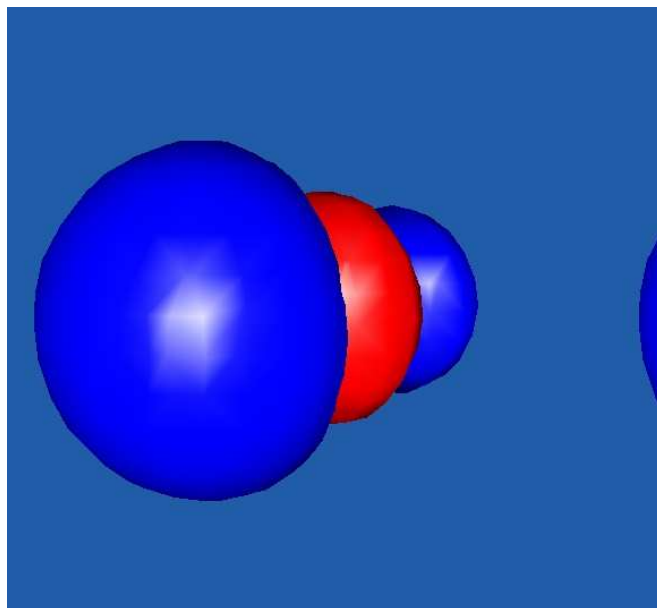


Figure 17: Surface: Beta 7, LUMO (EOM-EE-CCSD)

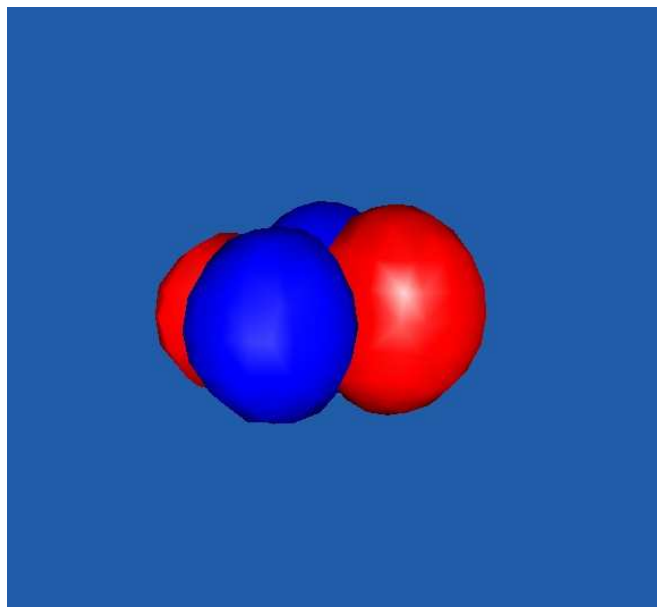


Figure 18: Surface: Beta 8, LUMO+1 (EOM-EE-CCSD)

3 Analyze EOM-IP-CCSD output

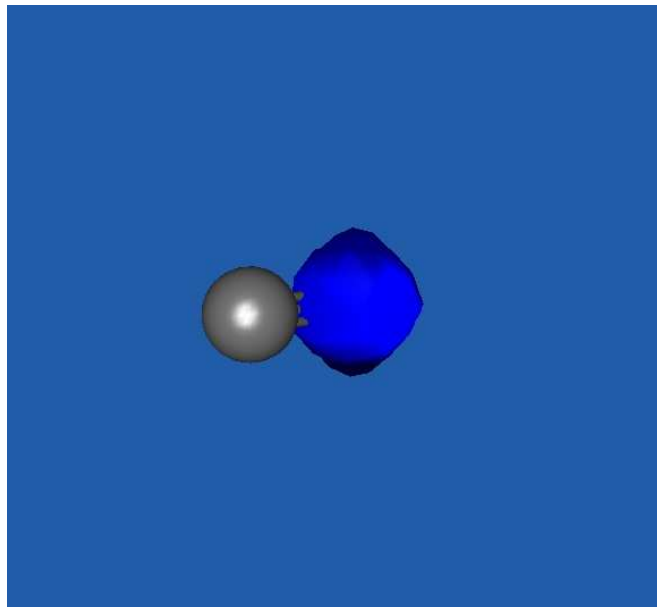


Figure 19: Surface: Alpha 1 (EOM-IP-CCSD)

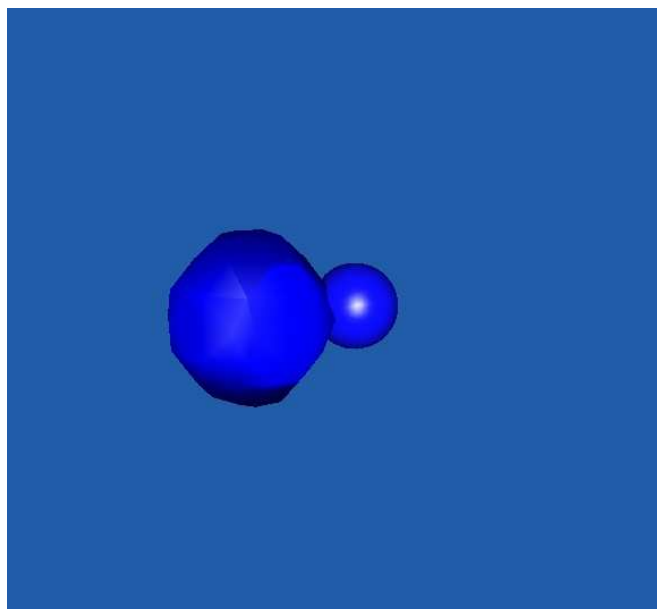


Figure 20: Surface: Alpha 2 (EOM-IP-CCSD)

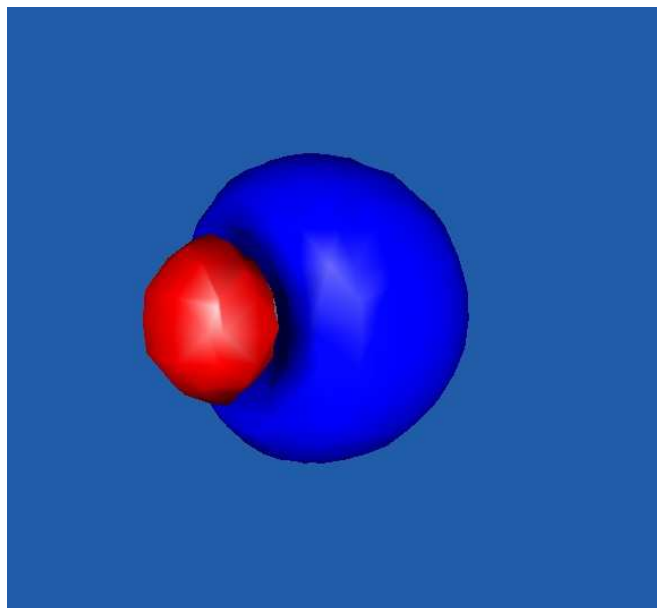


Figure 21: Surface: Alpha 3 (EOM-IP-CCSD)

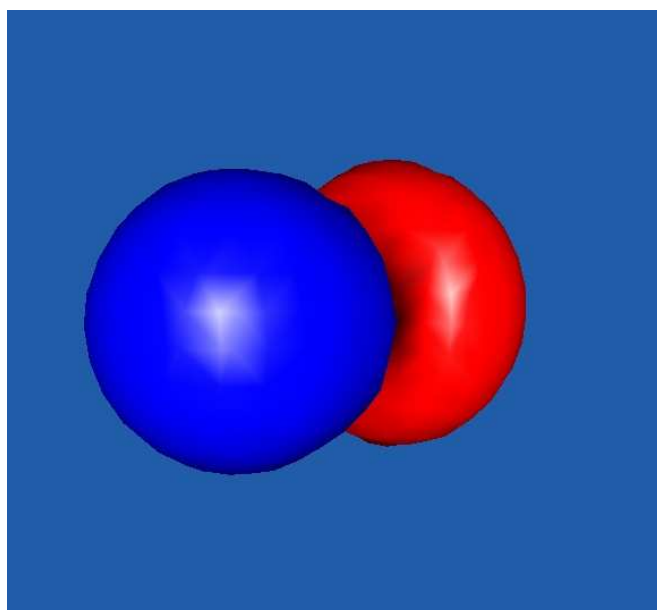


Figure 22: Surface: Alpha 4 (EOM-IP-CCSD)

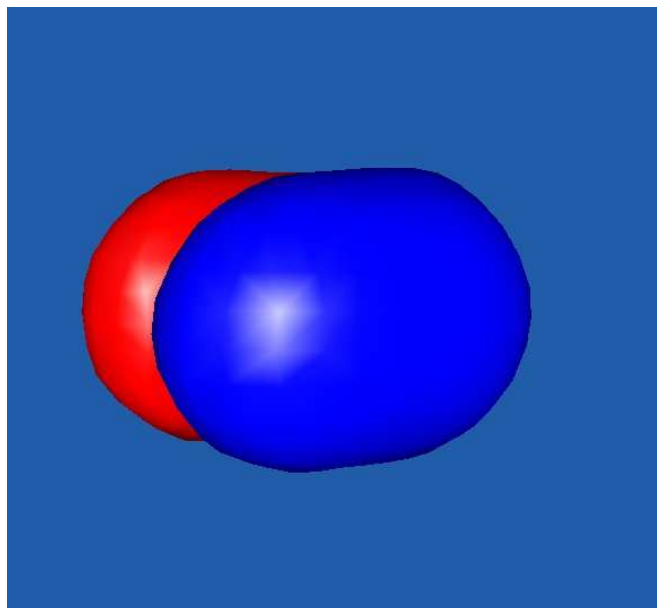


Figure 23: Surface: Alpha 5 (EOM-IP-CCSD)

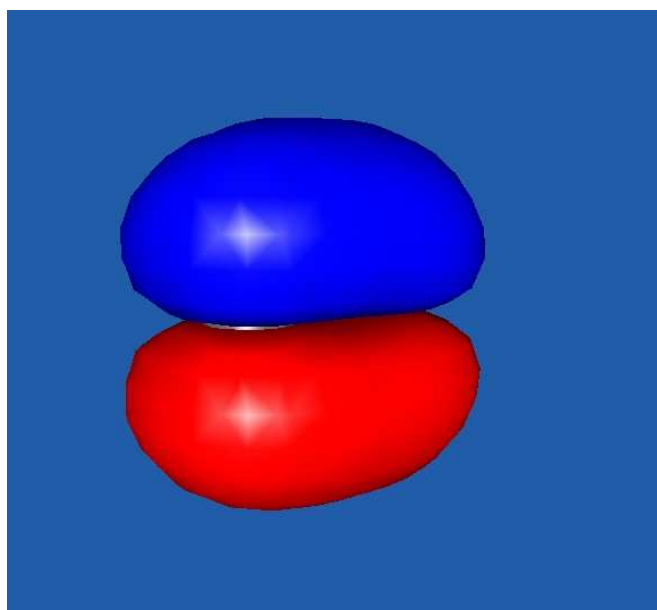


Figure 24: Surface: Alpha 6, HOMO-1 (EOM-IP-CCSD)

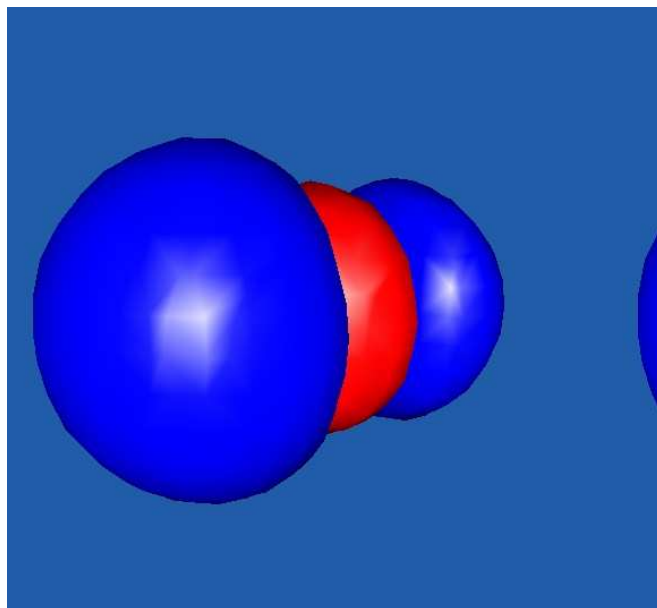


Figure 25: Surface: Alpha 7, HOMO (EOM-IP-CCSD)

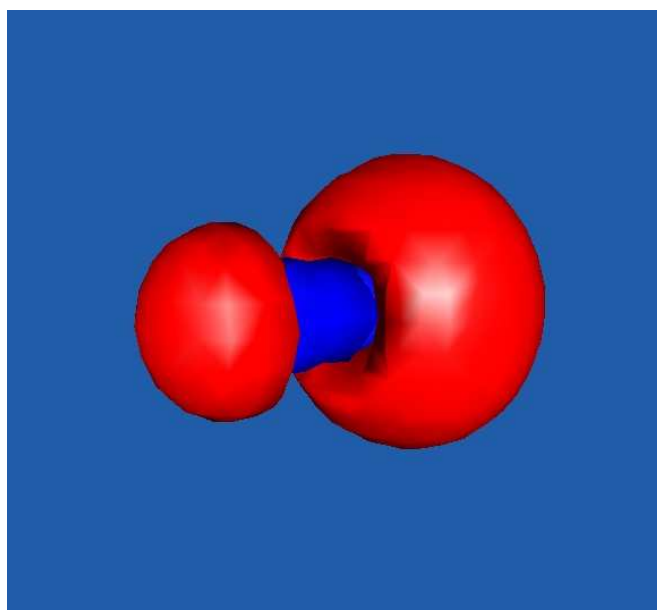


Figure 26: Surface: Alpha 8, LUMO (EOM-IP-CCSD)

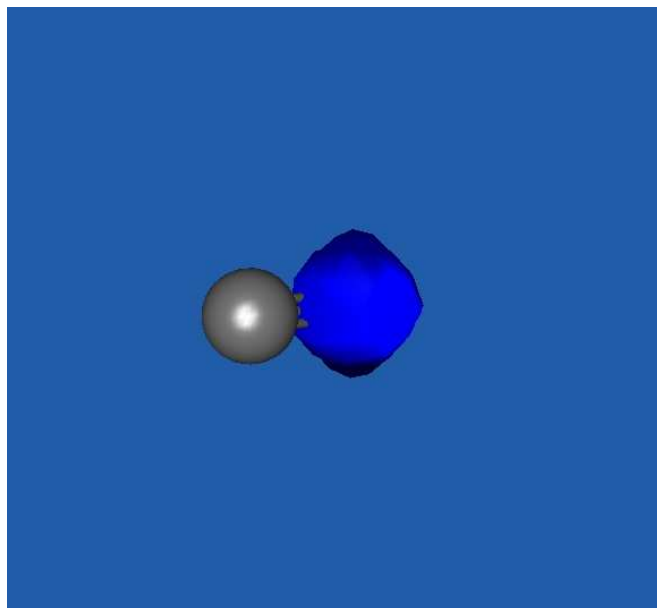


Figure 27: Surface: Beta 1 (EOM-IP-CCSD)

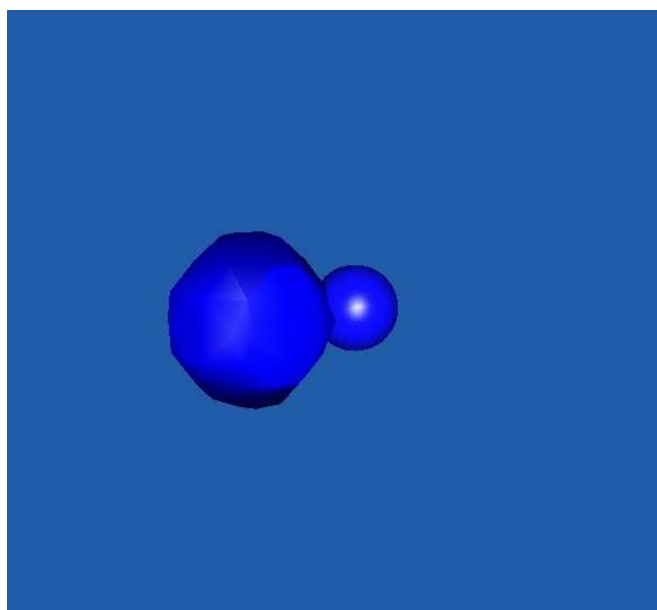


Figure 28: Surface: Beta 2 (EOM-IP-CCSD)

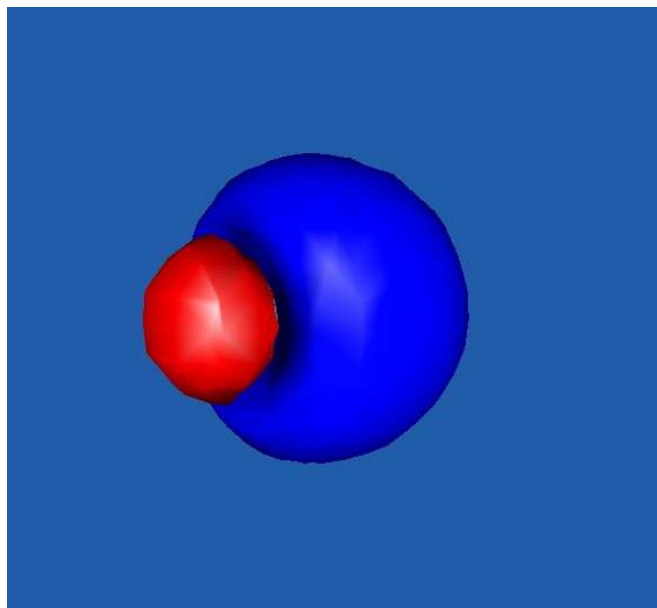


Figure 29: Surface: Beta 3 (EOM-IP-CCSD)

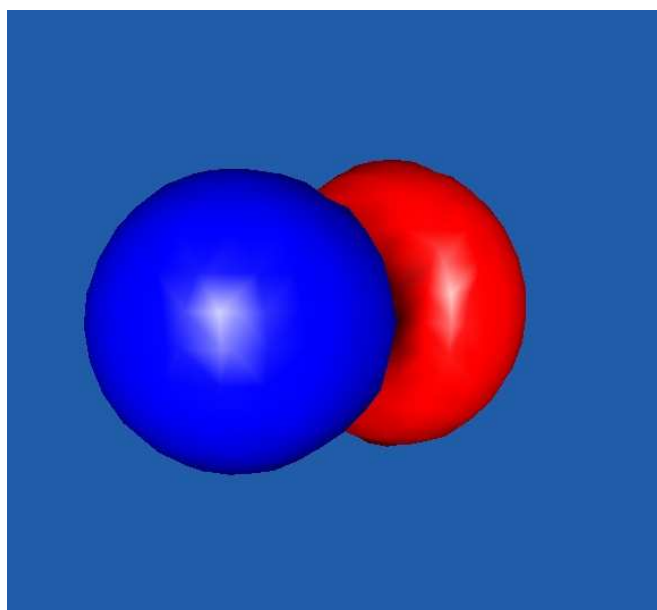


Figure 30: Surface: Beta 4 (EOM-IP-CCSD)

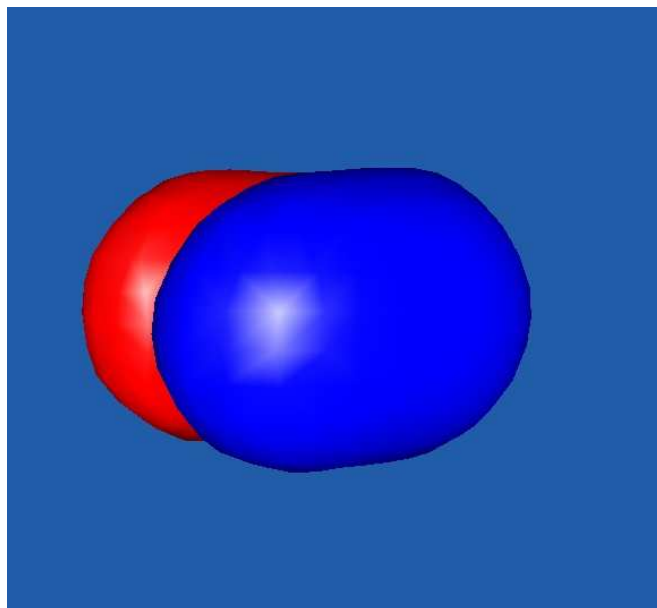


Figure 31: Surface: Beta 5 (EOM-IP-CCSD)

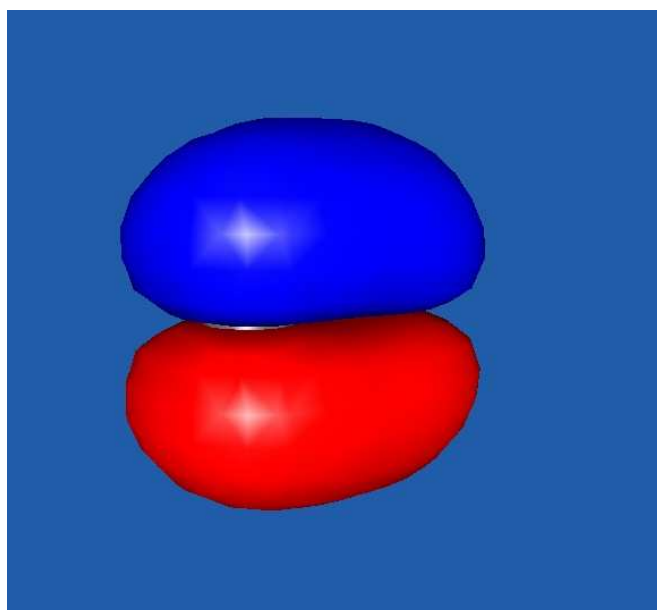


Figure 32: Surface: Beta 6, HOMO-1 (EOM-IP-CCSD)

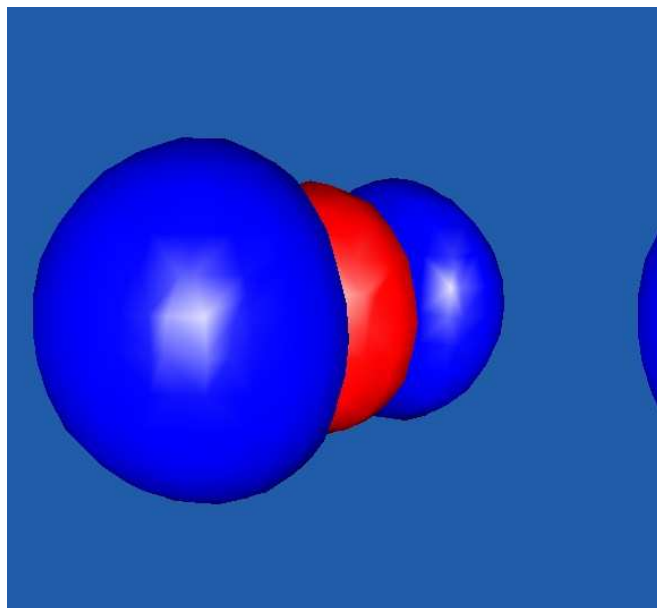


Figure 33: Surface: Beta 7, HOMO (EOM-IP-CCSD)

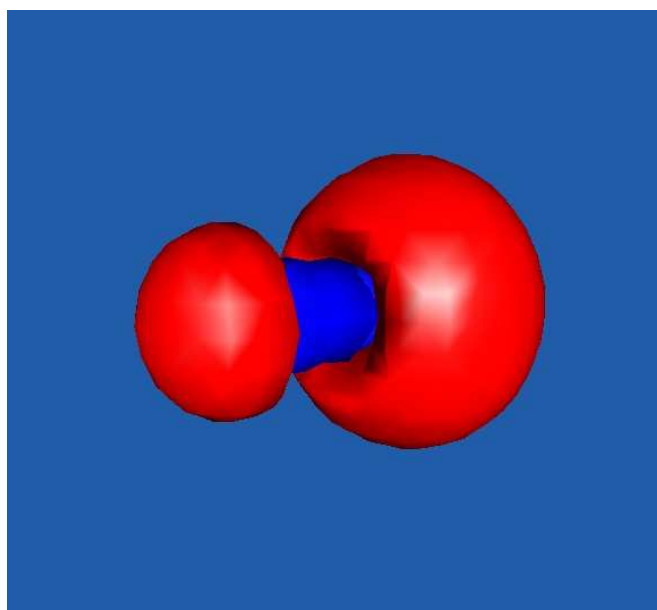


Figure 34: Surface: Beta 8, LUMO (EOM-IP-CCSD)

4 Energies

The total and excitation energies of EOM-EE-CCSD and EOM-IP-CCSD are summarized in Tables 1 and 2 respectively.

Table 1: EOM-EE-CCSD: total and excitation energies

States	Total energies (a.u)	Excitation energies (eV)	Note
1/A1	-92.35485729	3.5189	first excited state
2/A1	-92.20607060	7.5676	second excited state
1/A2	-92.20607323	7.5676	second excited state
2/A2	-92.17437338	8.4302	
1/B1	-92.42710522	1.5530	ground excited state
2/B1	-92.19128888	7.9699	
1/B2	-92.42710522	1.5530	ground excited state
2/B2	-92.19128888	7.9699	

Table 2: EOM-IP-CCSD: total and excitation energies

States	Total energies (a.u)	Excitation energies (eV)	Note
1/A1	-92.47751457	3.7210	ground state
2/A1	-92.35726740	6.9931	second excited state
1/A2	-92.10080562	13.9718	
2/A2	-92.05813776	15.1328	
1/B1	-92.42730292	5.0873	first excited state
2/B1	-92.04147399	15.5863	
1/B2	-92.42730292	5.0873	first excited state
2/B2	-92.04147468	15.5863	

5 Comparison between EOM-EE-CCSD and EOM-IP-CCSD

Why does EOM-IP-CCSD perform better than EOM-EE-CCSD ?

The reason is that the advantages of the EOM-IP method become even more important when the ionized states of the monomers feature electronic degeneracies. More precisely, the Ref.[2] says that

In cases where the difference in IEs is much larger than the coupling, EOM-IP-CCSD and EOM-EE-CCSD perform similarly. Due to the lower computational scaling, the former method is preferable. An argument can be made that just like EOM-EE-CCSD overpolarizes the states, the EOM-IPCCSD method may appreciably underpolarize the states. In the studied systems only a small degree of underpolarization has been observed. The diabatic coupling has proved to be a fairly insensitive probe of the quality of

state description. The increased polarity of EOM-EE-CCSD states is offset by lower transition dipoles and higher excitation energies. Comparison of transition dipole moments offers a better onenumber descriptor of the quality of the ground and excited state wave functions.

6 Comparison between CISD and IP-CISD

What are your expectations on the accuracy of these methods for the excited states of CN?

The method (termed IP-CISD) treats the ground and excited doublet electronic states of an N -electron system as ionizing excitations from a closed-shell $N + 1$ -electron reference state. The method is naturally spin adapted, variational, and size intensive. The computational scaling is N^5 , in contrast with the N^6 scaling of EOM-IP-CCSD.

IP-CISD structures are of similar quality as HF geometries of closed-shell molecules. Inheriting limitations of the underlying HF reference, IP-CISD systematically underestimates bond lengths and overestimates interfragment distances. Most importantly, IP-CISD correctly reproduces structural changes induced by ionization and structural differences between different ionized states.

More precisely, the Ref.[1] says that

Molecular properties such as permanent and transition dipole moments and charge distributions are reproduced very well demonstrating that IP-CISD wave functions are qualitatively correct. IEs cannot be computed by IP-CISD because of the use of uncorrelated HF description of the neutral, however, energy differences between the ionized states are of semiquantitative accuracy (errors of about 0.3 eV relative to IP-CCSD).

Our results suggest that IP-CISD is most useful as an economical alternative for geometry optimization in the ionized systems. Using IP-CISD structures, more accurate energy differences can be computed using more expensive IP-CCSD. Moreover, IP-CISD wave functions may be employed as zero-order wave functions in subsequent perturbative treatment.

References

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