

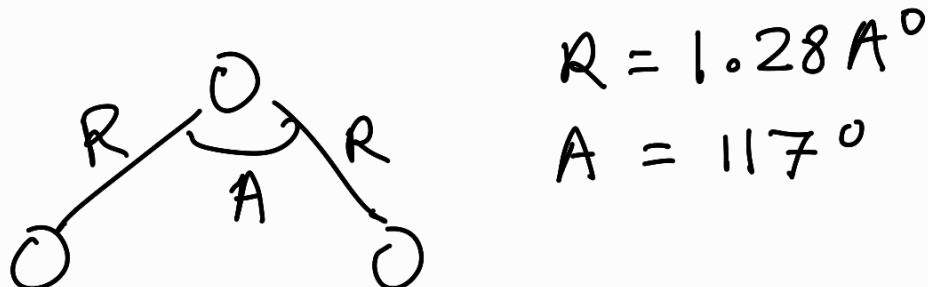
# Computational Assignment 4 X 5

Total Marks : 20

Hartree-Fock and Electron Correlation

Calculations on Simple Systems.

Q1. Consider Ozone molecule at  
the following equilib geometry.



(a) Perform RHF/cc-PVDZ calculation  
at this geometry. Apply  
Koopman's theorem and  
predict ionization potential

and electron affinity of Ozone. State the results in eV units. Is  $O_3^-$  stable?

(b) Perform ROHF/cc-pVDZ calculation on Ozone cation & anion. (Note that cation & anion can be specified using ICHARG = 1 & ICHARG = -1 in \$CONTROL card)

List the following results:

$$E(O_3 \text{ neutral, ROHF}) = \dots$$

$$E(O_3 \text{ cation, ROHF}) = \dots$$

$$E(O_3 \text{ anion, ROHF}) = \dots$$

from these results, estimate ionization potential & electron affinity of ozone directly from energy differences. State results in eV units. Is  $O_3^-$  stable?

(c) The experimental IP & EA of Ozone are 12.5 eV & 2.1 eV respectively. Compare these to computed results in (a) & (b) & discuss whether Koopman-based or direct difference methods for IP & EA

are more accurate ?

(d) If one needs to compute adiabatic IP & EA , explain which calculations needs to be done using HF method.

Q2. Consider Neon dimer .

As a rare gas dimer , it has a very shallow minimum arising from van der Waal's interaction .

Consider  $R(\text{Ne}-\text{Ne})$  to

be  $3.1 \text{ \AA}^0$ .

Estimate binding energy of  
dimer using

$$\Delta E = 2 \times E(\text{Ne}) - E(\text{Ne}_2)$$

at various levels of theories,  
RHF, MP2 & CISD using  
cc-pVDZ & cc-pVTZ basis  
sets. Build the following table

$\Delta E$  in Kcal/mol.

	RHF	MP2	CISD
CC-PVQZ	...	...	...
CC-PVTZ	...	...	...

the experimental value is

approximately 0.9 Kcal/mol.

From the above table, which

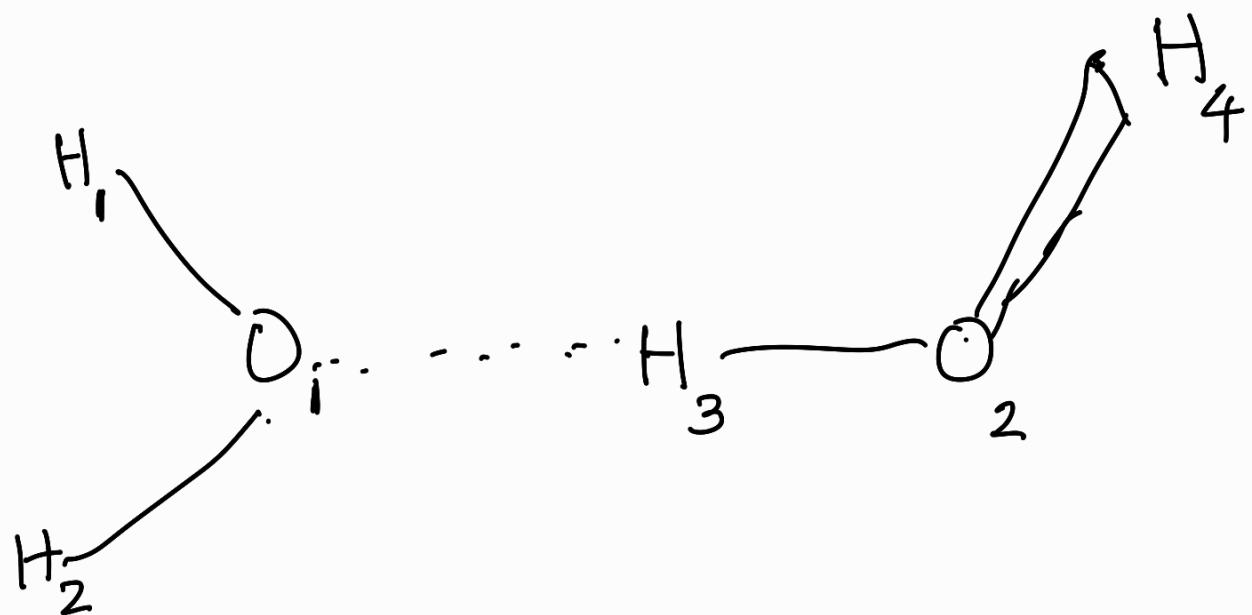
improvement (basis set or

elec corr effects) has significant

effect on bringing out closer

agreement with experimental result.

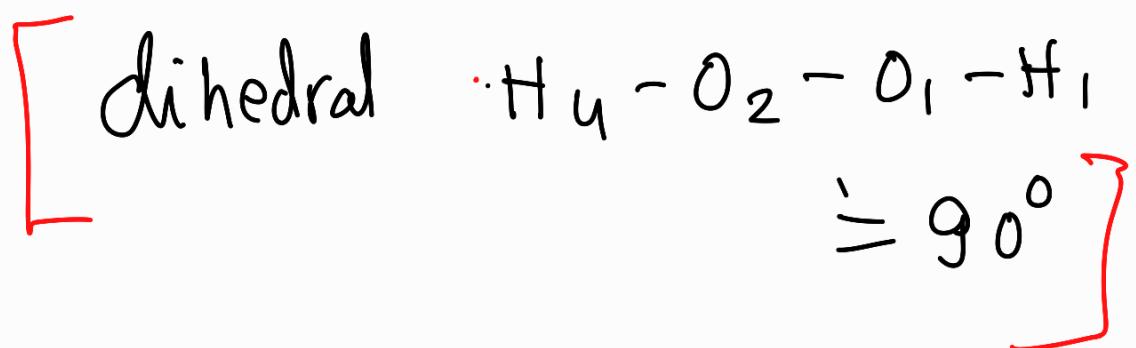
Q3. Water dimer has the following Hydrogen bonded structure.



- all OH bonds are  $0.96 \text{ \AA}^0$
- all atoms except  $\text{H}_4$  are

in a plane (of paper)

→ H<sub>u</sub> is in a plane which  
is perpendicular to the  
paper.



→  $\angle H_1-O_1-H_2 = 104.5^\circ$

$\angle H_3-O_2-H_u = 104.5$

$\angle H_1-O_1-H_3 = 127.75^\circ$

$\angle H_2-O_1-H_3 = -11-$

→ O<sub>1</sub>-H<sub>3</sub>-O<sub>2</sub> is in

Straight line.

$$\rightarrow O_1 - H_3 = 2.02 \text{ \AA}^{\circ}$$

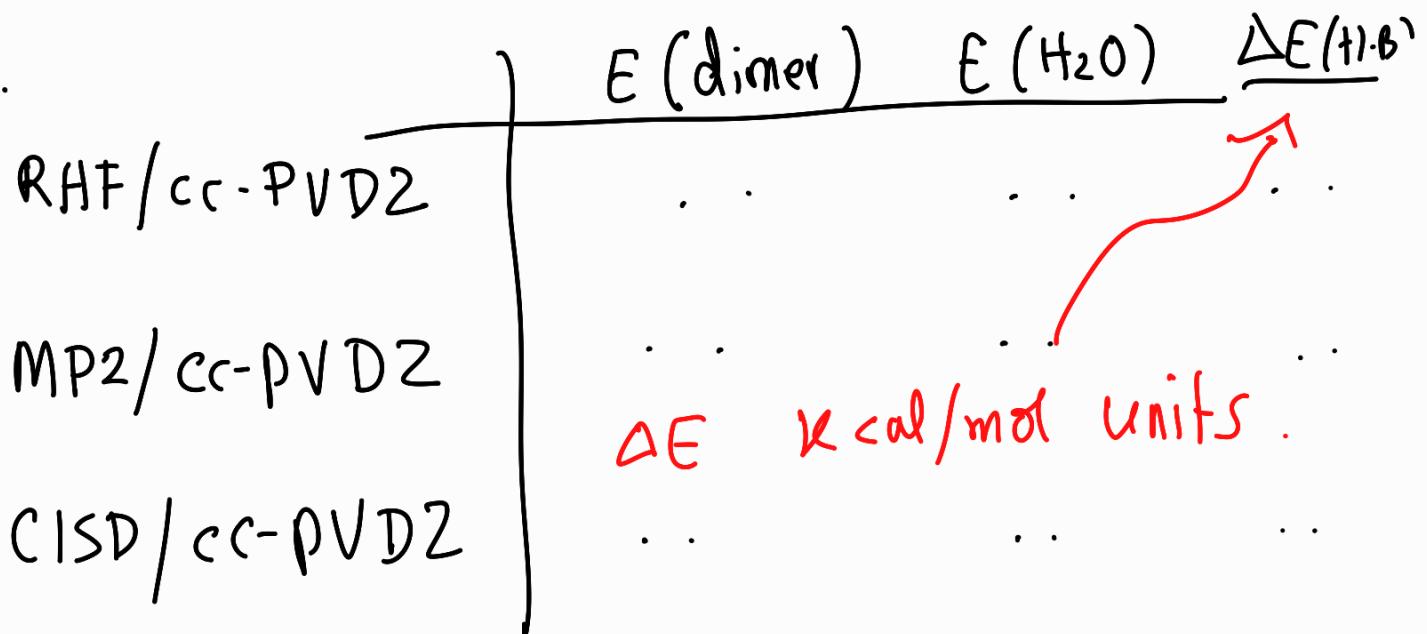
Construct Z-matrix for this  
structure & find Hydrogen  
bonding energy of  $H_2O$  dimer,  
by using

$$\Delta E(\text{Hydrogen-Bond}) = 2 \times E(H_2O) - E(H_2O\text{-dimer})$$

Compute  $\Delta E$  (Hyd-Bond) using  
(in kcal/mol units)

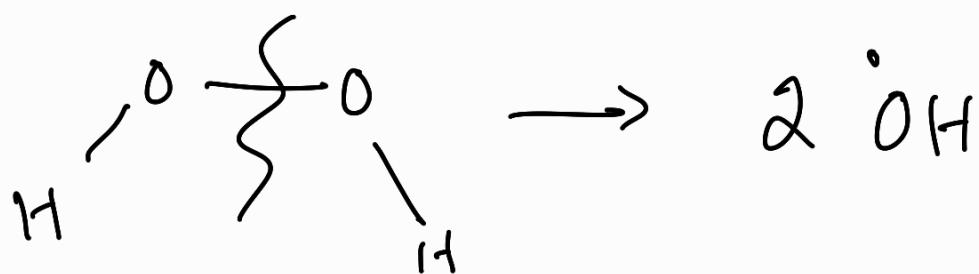
RHF / cc-PVDZ , MP2 / cc-PVDZ

and CISD / cc-PVDZ methods.



Q4. Consider the bond dissociation

energy of O-O bond  $\text{H}_2\text{O}_2$



Earlier, we noted that HF/6-31G was not able to describe it well.

$$\Delta E(\text{BDE}) = 2 \times E(\cdot\text{OH}) - E(\text{H}_2\text{O}_2)$$

Perform geometry optimization for  $\text{H}_2\text{O}_2$  &  $\cdot\text{OH}$  using cc-PVDZ basis set. At the optimized geometry, perform following calcs.

	$E(\cdot\text{OH})$	$E(\text{H}_2\text{O}_2)$	$\Delta E(\text{BDE})$
RHF/cc-PVDZ			
MP2/cc-PVDZ			
CISD/cc-PVDZ			

in kJ/mol units.

Note : 1 Hartree  $\equiv$  627.5 kcal/mol

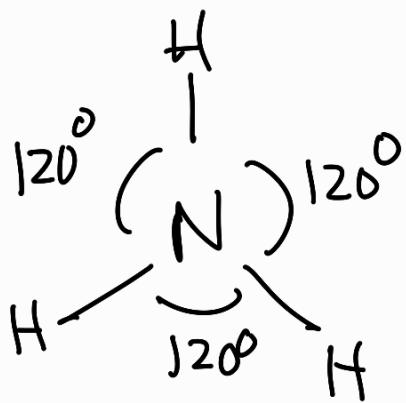
Does electron correlation predict  
Stronger O-O bond than HF?

Q5, Perform geometry optimization

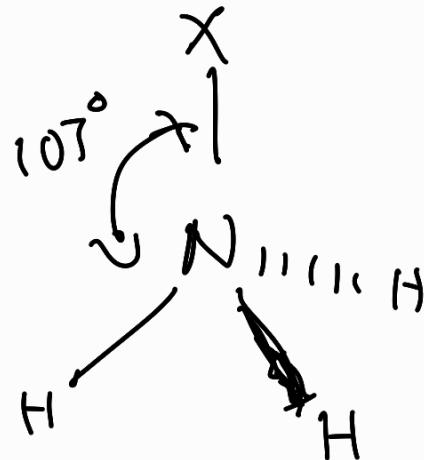
of NH<sub>3</sub> using RHF/cc-PVDZ

at planar & pyramidal geometries.

planar

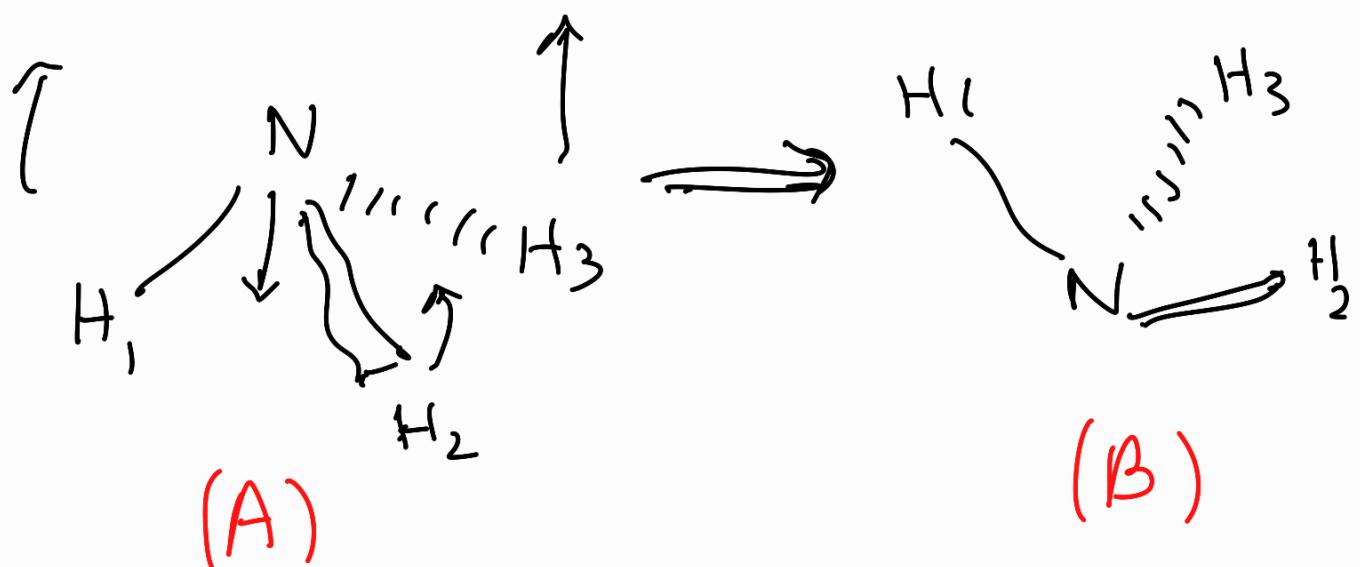


pyramidal

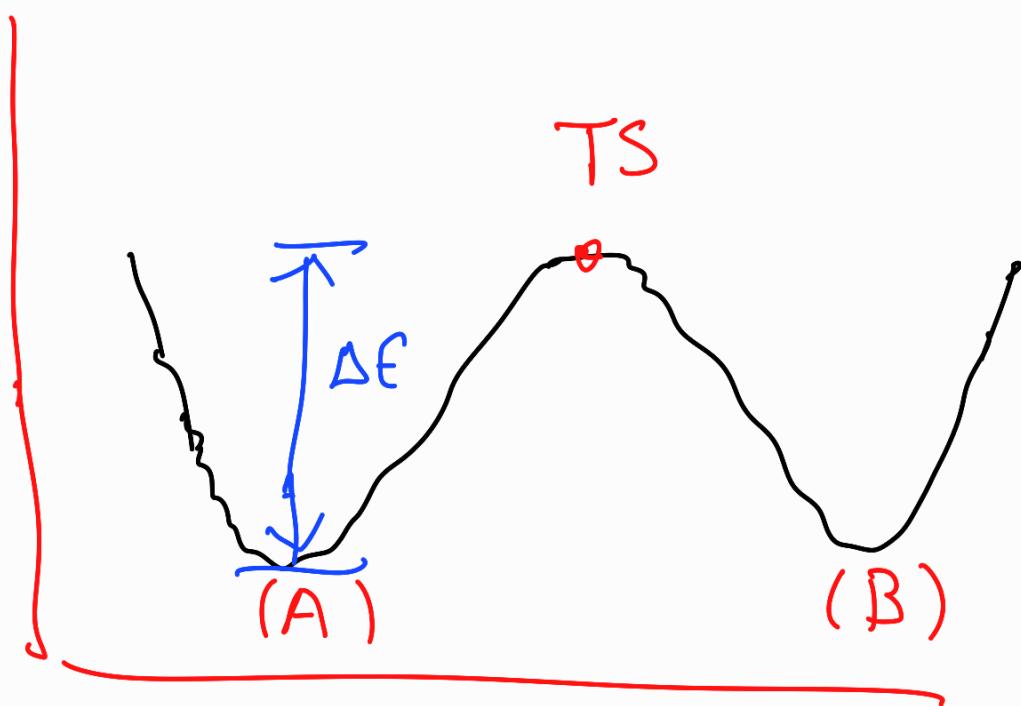


If one builds Z-matrix for above structures, then geometry optimization in .ZMAT will provide appropriate structures.

$\text{NH}_3$  is known to have an inversion barrier as follows



This leads to a double-well structure of NH<sub>3</sub>



(A) & (B) structures are pyramidal & have same energy.

The planar structure is a TS

transition state which connects them.

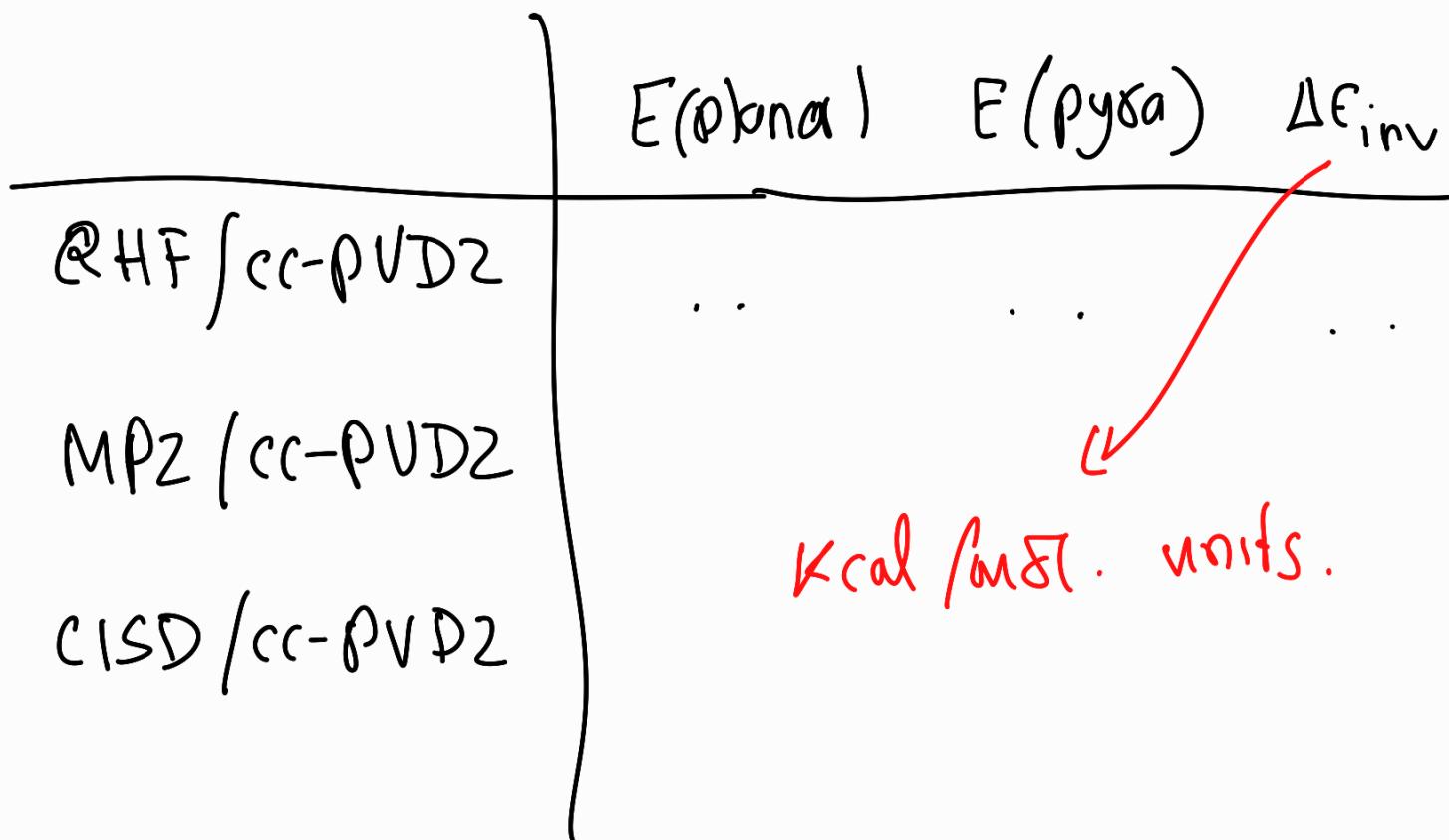
The inversion barrier in  $\text{NH}_3$   
is

$$\Delta E_{\text{inv}} = E(\text{planar}) - E(\text{pyramidal})$$

Experimental inversion barrier  
is about 5.8 kcal/mol.

Perform RHF, MP2 & CCSD  
calculations on planar & pyramidal  
structures of  $\text{NH}_3$  using cc-PVQZ  
basis set.

Build the following table.



Answer:

- (a) Which one planar / pyramidal has larger correlation energy?
- (b) Which method predicts  $\Delta E_{inv}$  closer to exp results?

## Note:

① Use of CC-PVXZ basis

sets requires

→ ISPHER = 1 in \$CONTRL

→ \$BASIS & BASIS = CCD \$END

CCD → CC-PVDZ

CCT → CC-PVTZ

CCQ → CC-PVQZ

② Performing Ne atom

Calculation, one can't  
use Z-matrix. One needs  
to use

COORD = CART in \$CONTRL

\$DATA

Neon atom calc → title

C1 → must be given

Ne 10.0 0.0 0.0 0.0

\$END

charge.

If in doubt, check Be

atom calc given in one  
of the uploaded ZSP file.

③ 1 Hartree is

$$1 \text{ Hartree} \equiv 627.5 \text{ kcal/mol}$$

$$1 \text{ Hartree} \equiv 27.211 \text{ eV}$$