Q1.

Ans:

(a) RHF/CC-PVDZ was performed at the given geometry. The HOMO and LUMO energies were collected by viewing orbital energies through wxMacMolPlot.
HUMO= -0.481 Ha= -13.088 eV; Ionization potential= 13.088 eV
LUMO= -0.044 Ha= -1.197 eV; Electron affinity= 1.197 eV
Yes, O_3^- is stable as electron affinity is positive.

(b) E (O_3 neutral)= -224.262570 Ha= -6102.408792 eV
E (O_3 cation)= -223.751803 Ha= -6088.510311 eV
E (O_3 anion)= -224.346811 Ha= -6104.701074 eV

Ionization potential= cation energy- neutral energy= 13.898481 eV
Electron affinity= neutral energy- anion energy= 2.292282 eV
Yes, O_3^- is stable as electron affinity is positive.

(c) Koopman theory is better for predicting IP (4% error) while it is 11% in direct method.
In EA, direct method is better (9% error) while it is 43% in Koopman's theory.

(d) Koopmans theorem should be used in calculation IP while direct method should be used in EA calculation in adiabatic computation.

2

Ans:

DEL E IN kcal/mol	RHF	MP2	CISD
CC-PVDZ	0.02259	0.0357675	-5.6355775
CC-PVTZ	0.0338	0.0847125	-9.763966264

Improvement of basis set has a significant effect.

3.

Ans:

In kcal/mol	E(Dimer)	E(H2O)	Del E
RHF/CC-PVDZ	-95,418.8548	-47,706.7247575	5.405285
MP2/CC-PVDZ	-95,668.3488	-47,831.1015325	6.145735
CISD/CC-PVDZ	-95,665.69322	-47,835.57498	-5.45674

4.

Ans:

Kcal/mol	E(OH) (ROHF)	E(H2O2)	DEL E
RHF/CC-PVDZ	-47,307.33042	-94,610.6906475	-3.9701925
MP2/ CC-PVDZ	-47,402.6093925	-94,844.1457475	38.9269625

CISD/ CC-PVDZ	-47,307.33042	-94,610.6906475	21.3770425

Yes, electron correlation does predict stronger o-o bond.

5.

Ans:

Kcal/mol	planar	pyramidal	Del E
RHF/CC-PVDZ	-35,255.611855	-35,262.820575	7.20872
MP2/ CC-PVDZ	-35,371.5544025	-35,379.8876025	8.3332
CISD/ CC-PVDZ	-35,377.7955175	-35,385.905955	8.1104375

(a) Pyramidal has larger electron correlation energy.

(b) All methods have predicted the del E inversion to be higher than experimental. Only RHF/CC-PVDZ is close to experimental value