HW # 9

1.

Method	E_H	E_{H_2}	DE (a.u)	DE(eV)
HF/3-21G	-0.4962	-1.1229	0.1304	3.54
HF/ccpVDZ	-0.4993	-1.1287	0.1301	3.54
MP2/ccpVDZ	-0.4993	-1.1550	0.1565	4.26
B3LYP/ccpVDZ	-0.5012	-1.1733	0.1709	4.65

The experimental value of De is about 5 eV. Thus we see that the HF calculations considerably underestimate De. B3LYP and MP2 do significantly better as they include electron correlation effects.

The 2pz atomic basis functions mix into the $1\sigma_g$ orbital in the HF and B3LYP calculations.

2.

Method	E w.o. field	E with field	ΔE
HF/ccpvdz	-1.1287001	-1.1287033	-.0000032
HF/aug-cc-pvdz	-1.1287783	-1.1287815	-.0000032

With the field on μ with HF/aug-cc-pVDZ is 0.017D and the atomic charges are ± 0.0043 a.u.

$\Delta E = \frac{1}{2}\alpha\varepsilon^2$. So $\alpha = 6.4$ a.u.

3. Experimental frequencies of H_2O

harmonic	anharmonic	B3LYP
3832	3657	3727 (1.7)
1649	1595	1713 (75.8)
3943	3756	3849 (19.4)

for the calculated results, intensities are given in parentheses.

Note that the calculated frequencies if multiplied by 0.97 are in fairly good agreement with the experimental anharmonic values.