Exam 3: WebMO Computational Exercise (part 2)

You have been trained to use the WebMO software to do quantum mechanical calculations. These calculations have their limitations and as a computational chemist, it is our job to verify/test what theoretical models (HF, MP2, B3LYP, etc), as well as basic sets (3-21G, 6-31G, 6-311G+(2p,d), etc) lead to reasonable "answers." I hope that you have realized that it is relatively straightforward to determine molecular geometry. IR spectroscopy is based on bond vibrations/geometry and hence are quite accessible, although many spectroscopic properties (UV-Vis, NMR, etc) are more challenging.

As discussed in your text (Figures 15.2/15.11) we can calculate bond dissociation energies (BDE). Although there are many thermodynamic details we did not discuss, a BDE is an approximation of a bond energy. So if you have 2 hydrogen atoms do they prefer to be H-H or just 2 H• (aka H-atom, a radical) ? If you "do" the calculation, you will find that the total energy of 1 H-H is lower than 2 H•, meaning that the formation of a H-H bond is the preferred arrangement. So how do we do this calculations?... launch WebMO and follow these steps:

1) Create a new job…draw H-H…clean up, then submit an MP2/6-31G(d) job with the proper charge and multiplicity.

2) Once the job is done…view the output…measure the bond length (for table below)…scroll down to the first "window" of **Calculated Quantities** and find the MP2 Energy (enter this value in the table below).

3) Return to the Job Manager window and select a new job…draw a single H-atom…clean up, then submit an MP2/6-31G(d) job with proper charge (0) and multiplicity (doublet).

4) Once the job is done…view the output…scroll down to the first "window" of **Calculated Quantities** and find the MP2 Energy (enter this value in the table below).

5) Calculation of BDE: notice that the MP2 Energy for the H-H is lower (larger negative value) than the H-atom. If we treat this as a typical chemistry reaction:

H-H → 2 H•

then this is a "*products minus reactants*" calculation: (2 x MP2 energy for H-atom) – (MP2 energy for H-H) = BDE. No units are clearly stated in the output file, but they are in Hartree. Conversion to kJ/mol → 1 Hartree = 2625.5 kJ/mol.

Energy the values in the table below:

MP2/6-31G(d)	Bond length (angstons)	MP2 Energy (Hartree) ***5 dec. places***	MP2 Energy (kJ/mol) ***5 dec. places***	Bond Dissociation Energy (kJ/mol)
H-H				
H-atom	*na*			*na*
Li-H				
Li-atom	*na*			*Na*
Li-Li				

As you see in the table above, there are a few more compounds that I would like for you to calculate the BDE. Lithium hydride is the lightest (mw = 8 g/mol) inorganic salt. LiH is similar to the more common sodium hydride used in O-chem as a reducing agent. Does dilithium really exist? If you are a fan of Star Trek, then you are aware of the "fuel" used to power the Starship *Enterprize*. The dilithium reference in Star Trek is not Li-Li, but a more complex, fictious material. To predict whether dilithium really exists, you need to calculate the MP2 energy of the Li-Li and if it is lower (larger negative value) than 2 lithium atoms, then it does. Please do these calculations and complete the table above. By the way, theses calcs can be done using other levels of theory to get more accurate values.