Using HyperChem Professional for Geometry Optimization and Energy Calculations

Objectives: optimize geometry of H_2^+ and H_2;
calculate their energies and also the energy of the hydrogen atom;
calculate H-H bond dissociation energy in both H_2^+ and H_2;
compare them with experimental values.

Basic steps:

a) Draw your species (steps 1-5 below);
b) Set up a Molecular Orbital calculation (steps 6-7 below);
c) Optimize geometry / calculate energy (steps 8-9 below);
d) Calculate H-H bond dissociation energy in H_2^+ and H_2 (step 10 below).

Detailed instructions:

Drawing a species

1) Run HyperChem Professional program.
2) Double-click the **Draw** button (the left-most button, below "File"), the **Element table** will pop up. Choose hydrogen symbol by clicking on it.
3) Draw necessary molecule in the program main window. When you click on the black window area, an atom of a selected element appears (you can change the appearance of atoms by choosing an appropriate **Rendering** option from **Display** menu). Put two H atoms on the black area to create H_2^+ or H_2. To draw a bond, point mouse cursor on the center of one of the atoms, left-click and drag the cursor to the center of another atom, then release the mouse button. To delete an atom or a bond, right-click on it center.
4) If error message appears because of exceeding regular valence, turn on "**Allow arbitrary valence**" in the "**Edit**" menu.
5) To beautify you drawing (set all bond lengths and angles to their regular values), choose "**Add H & model build**" from the "**Build**" menu;

Setting up a calculation

6) To set up an *ab initio* calculation, click "**Setup**" button, choose "**Ab Initio…**". In the "**Ab Initio Method**" window which pops up, choose orbital **Basis Set** "**Large (6-31G**)**". Lager basis means higher precision AND slower rate of your calculation. For H_2 molecule it is affordable, to have large basis set. If your species is charged and/or has a spin multiplicity greater than 1 (one or more unpaired electrons), choose "**Options …**" button in the same window. Indicate the **Total charge**. If spin multiplicity is greater than 1, choose **Spin Paring** "**UHF**" and after that you will be able to change the multiplicity. Close the window "**An ab initio and DFT options**" by clicking "**OK**".
7) Finally, click "**Apply basis set**" in the "**Ab Initio Method**" window and then "**OK**".

Optimizing geometry / calculating energy

8) To optimize geometry of a species (H_2 or H_2^+), choose "**Compute**" menu and then "**Geometry optimization**". In the window "**Ab Initio optimization**" which will appear, click "**OK**". Wait until the optimization is complete. Look at the message in the bottom of the HyperChem window, it should contain finally the word "**YES**". In the beginning of this line you will find the energy of formation of your species from isolated nuclei and electrons **E=** … expressed in kcal/mol.
9) To calculate the energy of a single atom present on your drawing (H atom), choose "**Compute**" menu and then "**Single Point**". Wait until the calculation is complete (see message in the bottom of the HyperChem window, it should contain finally the word "**Energy=**").

Calculate H-H bond dissociation energy in H_2^+ and H_2

10) Calculate H-H bond dissociation energy in H_2^+ and H_2 as the energy of the appropriate reaction below:

$$H_2 = 2\,H$$

$$H_2^+ = H^+ + H$$

The experimental values are 109.5 kcal/mol for H_2 and 61.1 kcal/mol for H_2^+. Try to rationalize the differences between the calculated and experimental values for H_2 (two-electron system) and H_2^+ (one-electron system).