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 your 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**)”. Larger 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:

\[
\begin{align*}
H_2 + 2 H = 2 H \\
H_2^+ = H^+ + H
\end{align*}
\]

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).