Introduction to Quantum Chemistry with Spartan

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This tutorial is designed to introduce computational chemistry using Spartan, the quantum chemistry software package. No knowledge of Spartan is assumed. Single point energy, frequencies and normal modes calculations performed on molecules of water and indole (tryptophan analogue). Calculation of proton affinity is introduced.

Estimated time to complete this tutorial is 1.5 hrs.

Outline: I. The following quantities will be computed for water and indole molecules: a) single point energy calculation, b) HOMO/LUMO, c) dipole, d) charge distribution, E) IR, NMR, and Raman spectra. II. Proton affinities calculations.

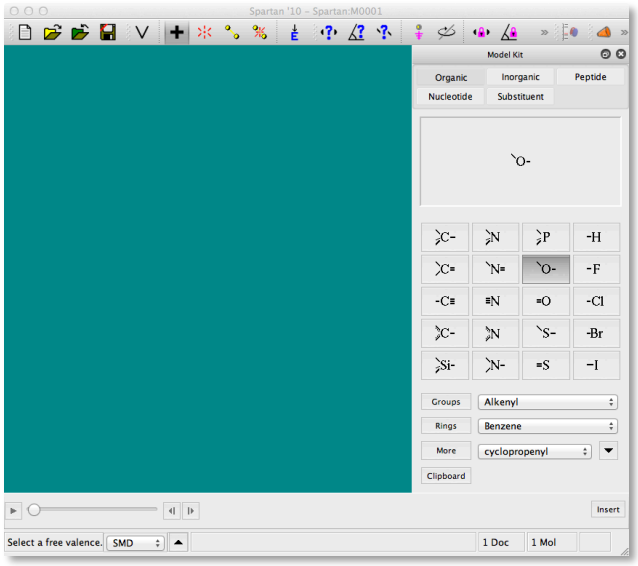
1. Software

Spartan installed in the SCS VizLab (151 Noyes Lab). Grab (iMacs VizLab) is a helpful software for preparation of images (Applications->Utilities).

2. Prepare a water molecule.

Note: this tutorial can be completed on a local computer if Spartan is installed.

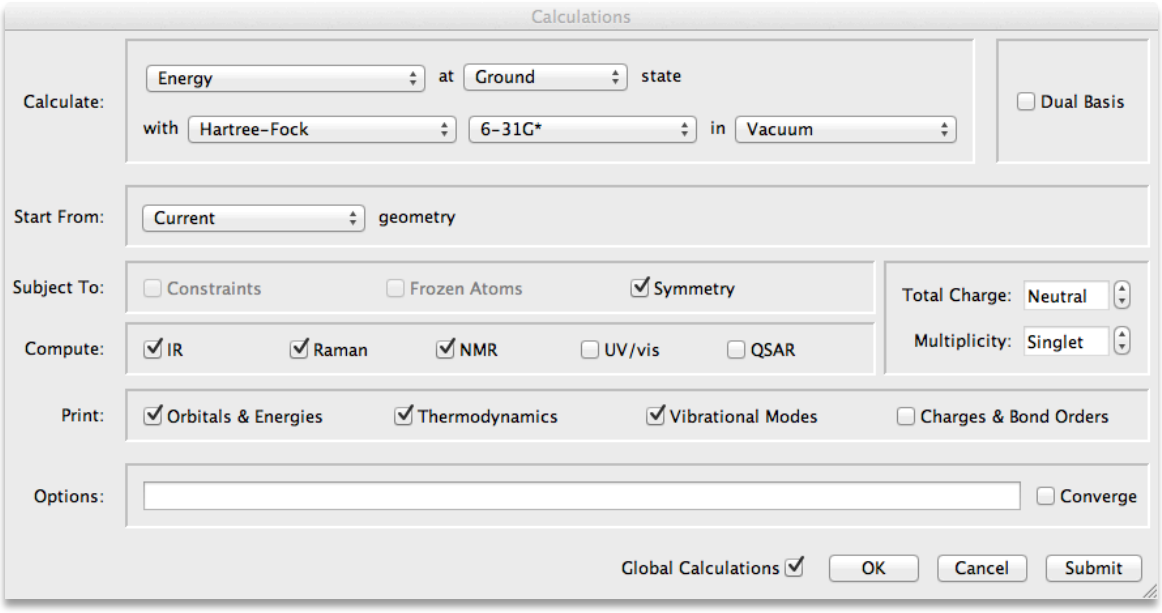
Click the Spartan button in the Application folder on the Dock. The main window of Spartan will appear. Click on the New button (Blank Sheet Icon) to open the Model Kit. Press Osp3 Oxygen button (see Figure below) and click anywhere in the main (green window). A molecule of water will appear.



Click on the View button ("V") to hide the Model Kit. Save the molecule as water.spardir.

3. Single point energy calculation: preparation

Open Calculations menu, Setup->Calculations. Set Energy at Ground State with Hartree-Fock level of theory with 6-31G* basis set. Also mark the checkboxes for IR, Raman, NMR spectra and Orbitals and Energies, Thermodynamics, and Vibrational Modes. (see Figure below).

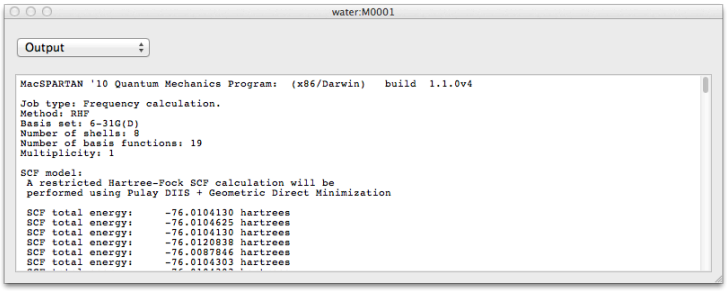


Click the Submit button. Spartan will confirm that the job "water" has started. Click OK. Open Monitor: Options->Monitor to follow the progress of the calculation. It should take 1-2 minutes to complete.

4. Single point energy calculation: analysis of results

4.1 The Output file: calculation successful

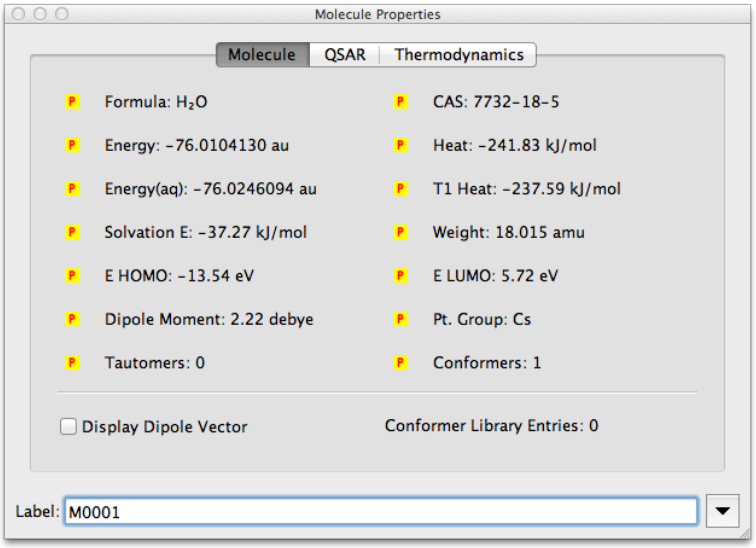
First, lets check that the calculation completed successfully. Open the Output file: Display->Output. In the file, notice the parameters of the calculation we requested are listed: Method: Restricted (all orbitals are doubly occupied) HF; Basis set: 6-31G(D) (see Figure below). Also a number of calculated quantities are listed (molecular orbitals, energies, etc.). How many atomic orbitals (basis functions) were used? How many of them are for oxygen?



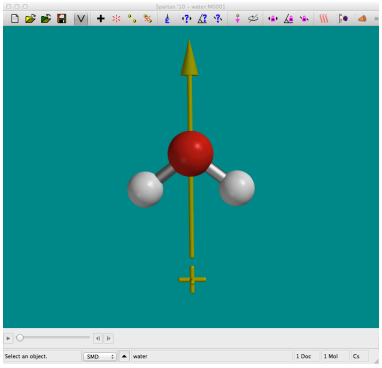
Scroll down to the end of the output file (use Cmd+F and search for “Reason for exit”) and find that the job ended due to Successful Completion. Save your work under the same name, water.spardir.

4.2 The Molecular Properties window: energies and dipole

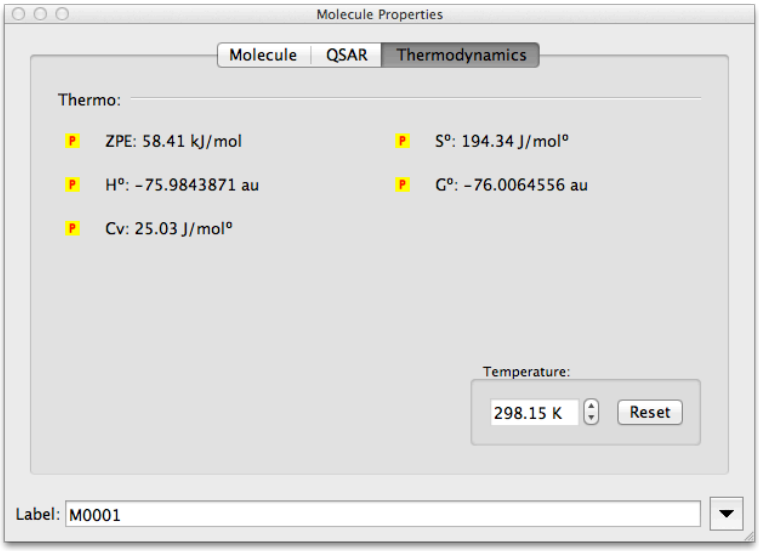
Open the Molecular Properties window: Display->Properties (see Figure below). Record the value of energy (given in a.u.,1 Hartree =627.509 kcal/mol).



Recall what contributes to the value of energy. Review the value of Dipole moment. Click the Display Dipole Vector button to display the vector.

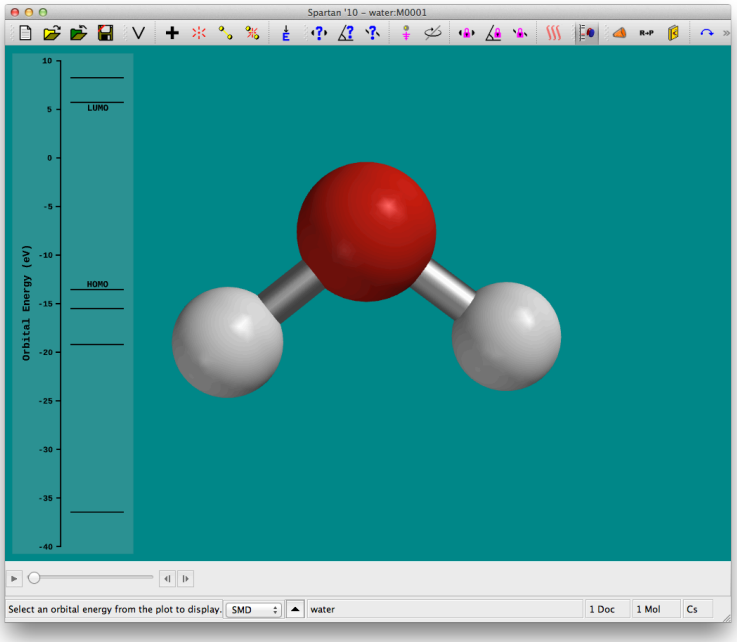


Click on the Thermodynamics button in the Molecular Properties window. Record ZPE (zero point energy) value. Note: it is given in kJ/mol (1kcal/mol =4.184 J/mol). How is this value calculated?



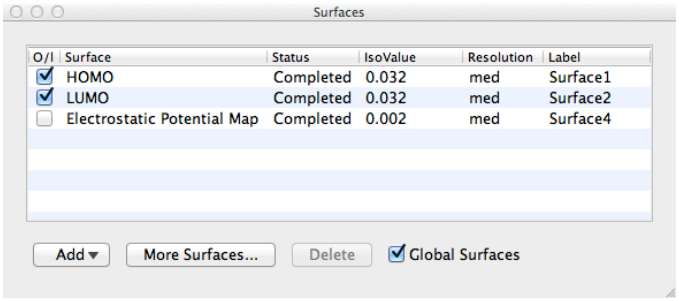
4.3 Surfaces: HOMO, LUMO, and electrostatic potential map

Now lets display the Orbital Energy: Display->Orbital Energy. The values will be displayed for HOMO/LUMO. (see Figure below) Note: the values are given in eV.

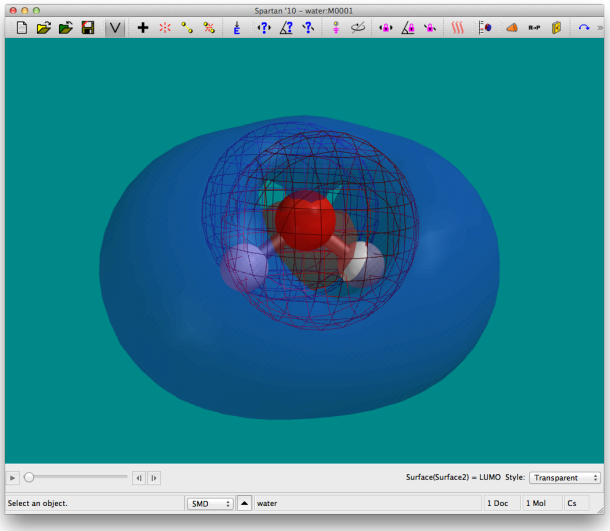


To display surfaces, open the menu window, Display->Surfaces. Note: If the check box is missing open Surface menu, calculation needs to be performed: Setup->Surface and submit surface calculation.

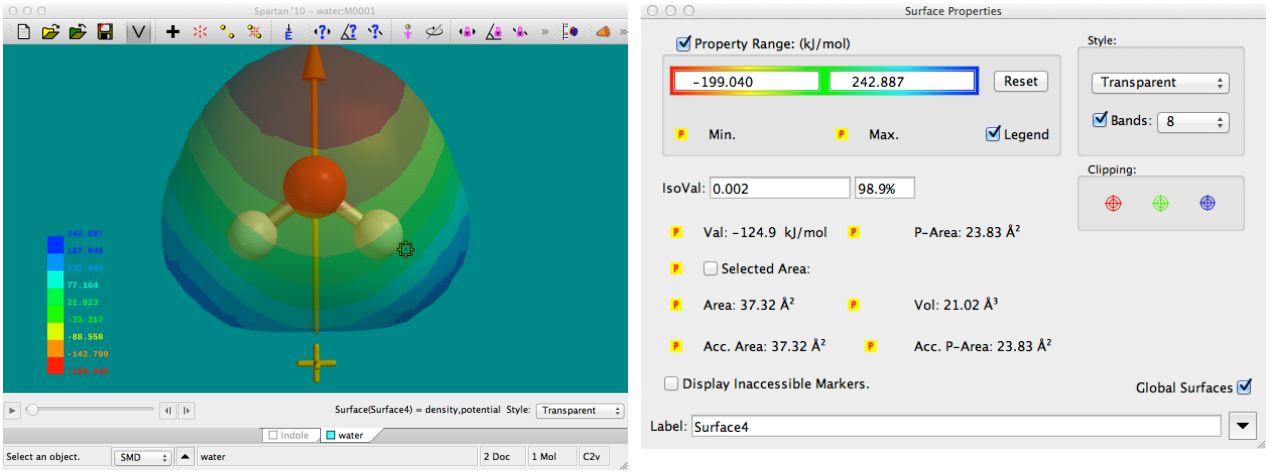
From the Add drop down menu select HOMO and LUMO. Now check the boxes next to the names (see Figure below).



Both surfaces will be displayed. Click anywhere on HOMO and the Surface Style button will appear. Select representation, so that the water molecule will be visible. Repeat for LUMO. (see Figure below).

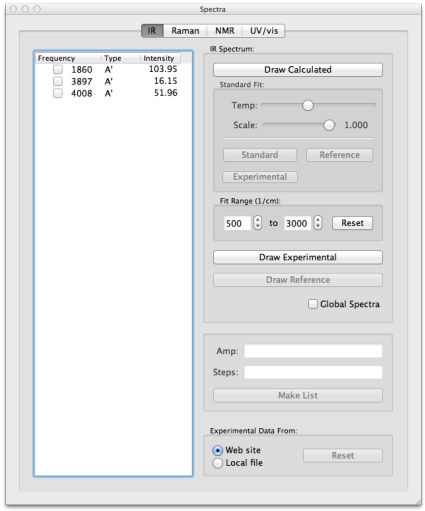


Now lets draw the **Electrostatic Potential map,** in the Display-> Surface menu uncheck HOMO/LUMO boxes and check Electrostatic Potential map box. Click anywhere in the displayed surface and open Display->Properties menu. The Surface Properties window will be shown. Observe the range of values (see Figure below). Check the Legend box (Properties). Change surface Style to transparent. The main Spartan window now should have water molecule, visible through Electrostatic Potential map surface and the legend (see Figure below). Hint: make sure you are in the View mode (V).



Display the dipole vector again. (Recall: Molecular Properties Menu). Reflect on the charge density distribution. Now hide all the surfaces and the legend.

4.4 Normal modes: frequencies and visualization



To display the IR spectra select the IR tab in Display->Spectra (see Figure left). Note the frequencies. To visualize the modes check one by one the three boxes on the left of the frequencies. Observe the motions. Why there are 3 normal modes in a water molecule? Record the frequencies.

Systematic errors of Hartree-Fock methods: frequencies are about 10-15% larger then measured. Click on the Draw Experimental button and the experimental spectra from the Spartan database will be drawn. Note that there is a shift in the frequencies. In practice the calculated spectra are scaled. Click on the Draw Calculated button. In the Spectra window in the IR Spectra click on the Experimental button. The calculated spectra will be scaled, the graph will be shifted, and once you click in the field where frequencies are reported the values will be updated. Review the scaled frequencies and the scaling factor.

4.5 Raman and NMR spectra

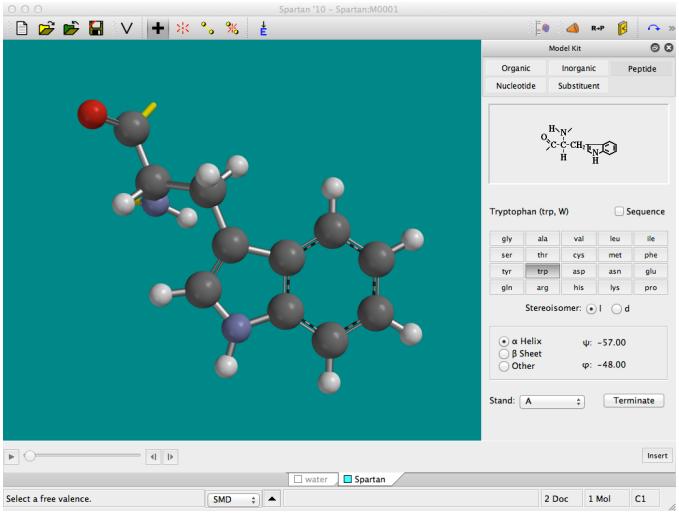
Display the spectra: Display->Spectra. Reflect on the results. Save your work into the same name, water.spardir.

5. Single point energy (SPE), normal mode, UV/vis and electrostatic potential map calculations for indole (analogue of tryptophan)

5.1 Prepare a molecule of indole an analogue of Trp. Open a new document in Spartan. Click the Add Fragment button ("+"). On the Model Kit panel click the Peptide button and

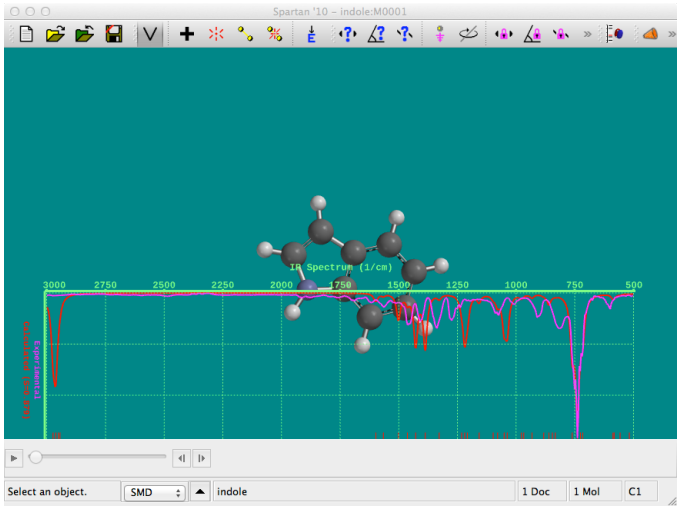
select Trp (see Figure below). Once the Trp button is pressed click anywhere in the green field and Trp with backbone segment will be shown. Now convert the molecule to indole removing backbone atoms (Use: **>.<** button next to the **+** button.). Save your work as indole.spardir.

5.2 Setup (as for water) and perform the following calculations: single point energy, IR, UV/viz, Orbital and Energies, Thermodynamics, and Vibrational Modes. Note: these calculations will take longer than for water molecule, about 10 min. Open Monitor: Options->Monitor to follow the progress of the calculation. When calculation is complete save your work to indole.spardir once the calculation is complete.



5.3 Indole thermodynamics. Review the values of energy, ZPE and of the dipole moment as well as how many basis functions were used for the calculation (hint: see the output file).

5.4 IR spectrum. Display the calculated and experimental IR spectra. Scale the calculated spectra to match the 750 cm^{-1} peaks (by using the slide or pressing the Experimental button). Report the scaling constant you used for the match. Visualize few vibrational modes. Note the selected frequency will be shown as a circle on the graph. What kind of vibration leads to the 750 cm^{-1} ?



5.6 UV/vis spectra. Display calculated and experimental UV/vis spectra. Was the UV/vis calculation accurate? Review frequencies for the UV/vis.

6. Proton affinity of water calculation (complete only if time allows)

6.1 Introduction

Proton affinity of the reaction A- + H+ -> AH is defined to be:

$$P(A) = -\Delta H = -\Delta E + RT$$

The energy of a non-linear molecule is

$$E(T) = E_{rot}(T) + E_{transl}(T) + ZPE + E'_{vib}(T) + E_{elec}$$

where ZPE – the zero point energy of the normal modes; both E_{rot} and E_{transl} equal (3/2)RT; E'_{vib} can be neglected in comparison to ZPE. We will calculate the energy change from the reactants A^- and H^+ to the product AH. The rotational energy of remains constant (proton has no rotational energy) and the translational energy of the proton contributes –(3/2)RT. Excluding the vibrational contributions, we have

$$P(A) = -\Delta E - \Delta ZPE + (5/2)RT$$

Thus we need to calculate two contributions: the change in electronic energy (zero contribution for proton):

$$\Delta E_{elec} = E_{elec}(H_3O^+) - E_{elec}(H_2O)$$

and the difference in ZPE.

Plan of the calculation: 1) optimize structures of the two molecules and calculate the energies; 2) calculate ZPE from normal modes. This discussion is based on [3].

6.2 Optimize geometry and calculate energies for H_20 and H_3O^+

Build molecule of water, save it as water631.spardir and prepare Geometry Optimization calculation with HF/6-31G*. Also mark IR (why do we need IR?) and Orbitals and Energies (see Fig.) Submit the calculation. It will be completed in few minutes.

Record the values of energy, E(H_2O)=-76.0107465 a.u., and zero point energy ZPE(H_20)=60.32 kJ/mol.

Recall: 1 Hartree =627.509 kcal/mol and 1kcal/mol =4.184 kJ/mol, kT=0.5922 kcal/mol, for T=298K.

Build molecule of hydronium, H_3O^+, save as h30.spardir and repeat above calculation. Hint: use the sp3 nitrogen and then convert it to oxygen. Note: select Cation for the Charge. Submit the calculation. It will be completed in few minutes.

Record the values of energy, E(H_3O^+)=-76.2865521 a.u., and zero point energy, ZPE(H_3O^+)=90.45 kJ/mol.

Now proton affinity of water:

P(A)= -ΔE-ΔZPE+(5/2)RT=-[E(H_3O^+)-E(H_20)]-[ZPE(H_3O^+)-ZPE(H_20)]+(5/2)RT= 173.07-7.2+(5/2)*0.5922=167.35 kcal/mol.

Compare to the experimental value of 166.59 kcal/mol. We achieved a respectable accuracy for a not expensive calculation.

7. Proton affinity of methanol calculation (complete only if time allowsReport)

Build molecules of methanol, CH_3OH and CH_3O^+. Follow the steps above with the same level of theory. How accuracy of this calculation compares to accuracy of the proton affinity calculation for water?

8. Summary

This tutorial covered basics of building molecules, preparing and performing single point energy and geometry optimization calculations, displaying calculated characteristics of the molecules. Calculation of proton affinity was introduced.

9. Contact

If you found errors/typos or have suggestions or comments on material in this tutorial please contact me.

10. Bibliography

1. Spartan'10 Tutorial and User' Guide, Wavefunction, Inc., 2012
http://downloads.wavefun.com/Spartan10Manual.pdf

2. C. Cramer, Essentials of Computational Chemistry: Theories and Models, Wiley, 2nd edition, 2004

3. M. Dittrich, Introduction to QM simulations, Tutorial, 2003, http://www.ks.uiuc.edu/Training/SumSchool/materials/tutorials/05-qm-tutorial/qm_tutorial.pdf