Computational Chemistry and Materials Modeling
Homework 3, due date is set in Canvas LMS
Topic: computational chemistry of molecules with DFT

Notes: *In multiple choice problems explain your answer. Add references if needed. Your solution must be uploaded as a single file "YourName.pdf" or "YourName.zip".*

1. (Lab) Take a molecule consisting at least of 10 atoms and having a singlet ground state. Using ab initio DFT in vacuo and in dichloromethane:

- Optimize ground state geometry. Plot frontier orbitals and determine their energies. Calculate the HOMO-LUMO gap.

- Calculate 10-20 singlet excited states and plot the UV-Vis absorption spectrum. Explain the oscillator strength and nature of the lowest excited states in terms of MOs.

- If technically feasible, optimize geometry of S_1 state (lowest excited singlet) and calculate the fluorescence energy and Stokes shift. Estimate the radiative lifetime of S_1 state.

- Optimize geometry of T_1 state (lowest energy triplet). Calculate the phosphorescence energy using both ΔSCF and TDDFT approaches. Explain the nature of the T_1 state in terms of MOs.

- Optimize geometry of cation/anion. Calculate IP/EA for both vertical and "slow" electron detachment/attachment.

- Explain geometry changes of the relaxed S_1, T_1, cation/anion relative to the ground state. Calculate the corresponding vibrational relaxation energies and solvation energies.

- Compare HOMO-LUMO gap, singlet and triplet excitation energies in vacuo and in the solvent.

- Compare vertical and relaxed IP/EA in vacuo and in the solvent.

- Calculate IR and Raman spectra.

The solution should be prepared in the form of a written report supplemented by the required technical files: xyz-geometries, mgf/out-orbitals, program run log-files, figures not inserted into the report etc. Be prepared to give a 5 min presentation of everything that you consider nontrivial in your work.

Comments to all the exercises: 1) "method" means determination of both electronic structure level and basis set, e.g. CCSD(T)/6-31G*, B3LYP/aug-cc-pVQZ, MP2/LANL2DZ; 2) Briefly explain your answers.

2. Which method(s) you would likely use to study dispersive interactions in a naphthalene dimer?

3. To mimic experimental data in solution, when you would like to add solvent effects (e.g. PCM model) to your calculations of (A) Neutral singlet ground state, (B) Neutral singlet excited state, (C) Neutral triplet state, (D) Anion/cation ground state?

4. The calculations of vibrational normal modes of some molecule gave the following frequencies (cm^{-1}, negative means imaginary): -50.6, -15.1, -3.2, 4.5, 106.7. How do you interpret these results?

5. Which nuclei of paracetamol molecule produce no strong NMR signal for their most abundant isotope?