

Quantum Chemistry – Final Project

1. Read thoroughly your course notes or the class notes (at least one time).
2. Download the following reference: *Phys. Rev. Lett.* **105**, 266802 (2010).
3. Read the paper carefully 4 times.
4. Read the paper one more time. During this iteration try to answer the following questions:
 - a. What is the main deficiency of Kohn-Sham (KS) Density Functional Theory (DFT) that the paper aims to address?
 - b. How is the fundamental gap defined, explain?
 - c. According to the paper, how is the KS gap defined? Assuming we had the exact exchange-correlation functional, would the fundamental gap match the KS gap?
 - d. What is the difference between the KS approach and the generalized KS (GKS) approach?
 - e. Explain the difference between a hybrid functional and a screened-hybrid functional.
 - f. Why do hybrid functionals work generally better in predicting bandgaps of solids than predicting HOMO-LUMO gaps of molecular systems?
 - g. Why do screened-hybrid functionals work generally better in predicting bandgaps of solids than predicting HOMO-LUMO gaps of molecular systems?
 - h. How is the optical gap defined? Why is it different from the fundamental gap?
 - i. What are range-separated hybrid functionals? How do they differ from full and screened hybrids?
 - j. What is the DFT version of Koopman's theorem? How does it differ from the case of HF theory?
 - k. Explain the logic behind Eq. (3). Why is Koopman's theorem violated in KS-DFT such that it has to be enforced in the GKS formalism?
 - l. Will the electron affinity of the N -electron system and the ionization potential of the $N+1$ electron system be the same? Why?
 - m. Why do the authors choose to calculate the ionization potential of the $N+1$ electron system where they really should have calculated the electron affinity of the N -electron system?
 - n. Explain the logic behind Eq. (4).

- o. For atomic HOMO-LUMO gap calculations describe how the screening factor (γ) varies for different atoms. Explain why.
 - p. Consider the calculation of the electronic properties of molecular chains. Based on quantum size effects considerations, how would you expect γ to change when the molecule is elongated?
 - q. The authors state that "for the molecular and nanocrystalline systems, the remaining difference between our results and the reference values may also reflect limitations of the reference. For molecules, vertical electron affinities are hard to come by owing to structural relaxation effects.". Suggest a way to overcome this problem.
 - r. The proposed method considerably improves the ability to calculate HOMO-LUMO gaps of atomic and molecular systems but not without a price – the optimal screening parameter is system dependent.
 - i. How many single-point DFT calculations are required by an empirically tuned screened-hybrid functional (MCY3 for example) to estimate the gap?
 - ii. What is the procedure to calculate the optimal γ in BNL*?
 - iii. What is the number of single-point calculations required for a given γ calculation?
 - iv. Estimate the number of single point calculations required for calculating the gap of a given molecule.
 - s. Is the method proposed in the letter fully *ab-initio* or does it rely on empirical fittings?
5. On the day of the exam we will meet and discuss the paper based on the abovementioned questions.
6. After this meeting, write your final project (not exceeding 5 pages!) based on your answers to the questions from above and using the following guidelines:
- a. What is the main problem addressed in the letter?
 - b. What was the state-of-the-art prior to the publication of the current work? Identify the main deficiency(ies) that are improved in the present study.
 - c. What is the solution proposed by the authors to these deficiencies?
 - d. Evaluate the performance of the proposed functional.
 - e. For the brave ones: can you think of possible extensions/improvements to the proposed method?