Project Title:

Computation of frontier orbital energies for atoms and molecules using LC-DFT

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Description of the project

1. Background and purpose of the project, relationship of the project with other projects: It has been shown that the LC fucntionals give HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies close to the minus vertical ionisation potential (IPs) and electron affinity (EAs) while both IPs and EAs are significantly underestimated by other functionals. However, the tested systems included a small set of atoms and molecules. Therefore, it would be significant to test the applicability of LC functionals (such as LC-BOP and LCgau-BOP) for a larger set of molecules.

2. Specific usage status of the system and calculation method: All the computations were performed using Gaussian 09 software. We performed CCSD(T) as well as DFT calculations. We used mostly 4 to 8 cores for our calculations.

3. Result: The frontier orbital energies and HOMO-LUMO gaps were compared with the vertical ionization potentials (IPs), electron affinities, and fundamental gaps respectively, using CCSD(T)/6-311++G(3df,3pd) for 113 molecules. We found that the LC functionals (LC-BOP and LCgau-BOP) satisfy Koopmans' theorem and reproduce HOMO-LUMO energy gaps better than BOP, B3LYP, and M06-2x functionals. The results are based on the calculation of 113 molecules used in the IP131 database. Our calculations also suggest that the LC functionals perform better than the recently proposed ωM05-D functional with the same IP131 database. The correlation and relaxation energies were calculated and compared with BOP, B3LYP, M06-2x and HF. It was observed that the LC functionals include relaxation and correlation effects which in turn are reflected in reproducing correct orbital energies. Thus, the orbital energy and orbitals in LC-DFT now has a strict physical meaning provided one uses a long-range corrected density functional. In addition, we also scanned the parameter μ which is used in controlling the inter-electronic range of separation and found that the present μ value of 0.47 $bohr^{-1}$ is close to the value of 0.46 $bohr^{-1}$ optimized against the IP131 database.

4. Conclusion: LC fucntionals satisfy Koopmans' theorem and calculation of fundamental gaps, ionization potential and electron affinity can be reproduced with a single SCF calculation. However, further work needs to be done to test the value of range-separated parameter for larger sized molecules.

5. Schedule and prospect for the future: We would like to test the LC functionals for even larger systems and see the applicability of such functional in reproducing IP, EA and fundamental gap.

6. If no job was executed, specify the reason. Not applicable

Fiscal Year 2012 List of Publications Resulting from the Use of RICC
[Publication]

"Long-range Corrected Density Functionals Satisfy Koopmans' Theorem: Calculation of Correlation and Relaxation Energies" **R. Kar**, J.-W. Song, K. Hirao *J. Comp. Chem.* (2013) doi: 10.1002/jcc.23222