Usage Report for Fiscal Year 2022

Project Title:

Development of new long-range corrected density functional theory and its applications

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1. Background and purpose of the project, relationship of the project with other projects

Recently, many studies on intramolecular charge-transfer (CT) excitations with various molecules have been performed through theoretical methods like long-range corrected (LC) density functional theory (DFT), but there has been no report on the intramolecular CT excitation process between donor and acceptor through the simplest chain, the polyethylene oligomer bridge. In this project, we investigate whether a polyalkane chain connecting donor and acceptor has an effect on intramolecular CT excitation energy, and if so, how much it affects CT excitation energy. To find this out, we will first perform accurate EOM-CCSD calculations of intramolecular CT excitations of polyalkane end-capped with $–NH_2$ and $–NO_2$ on both sides [$H_2N–(CH_2–CH_2)_n–NO_2$] as electron donor-acceptors with increasing chain number, n.

2. Specific usage status of the system and calculation method

In this project, we used 25.8% of bwmpc (759,504.9 hour) for this project and other researches which will be submitted to publications.

3. Result

To see the effect of polyalkyl single bond C–C chain, $–(CH_2–CH_2)_n–$, on CT excitation energies between $–NH_2$ and $–NO_2$, we also calculated the intermolecular CT excitation energies between NH_3 and HNO_2 with identical distances between $H_2N–(CH_2–CH_2)_n–NO_2$. In addition, we also compared the CT excitation energies between $–NH_2$ and $–NO_2$ in $H_2N–(CH=CH)_n–NO_2$ (n=1~10) [alkene-bridge]. Since it is proven that LC-BOP simultaneously provides the closest results to the EOM-CCSD of all the LC functionals in all the excitation energies with various kinds of mediums, such as $–(CH_2–CH_2)_n–$, –(CH=CH)n–, and vacuum (through space), we utilized only the CT excitation energies of LC-BOP. Note that the CT excitation through space is specially called intermolecular CT excitation. We additionally propose another intermolecular CT excitation model made by eliminating the polyene chain, $–(CH=CH)_n–$, from $H_2N–(CH=CH)n–NO_2$ (n=1~10) structures to consider the effect of structural differences more rigorously. We call it "alkene-vacuum" here, and we call the former made by eliminating the polyalkane chain, $H_2N–(CH_2–CH_2)_n–NO_2$ "alkane-vacuum" (Figure 2). Only the CT excitation energies in $H_2N–(CH=CH)_n–NO_2$ are characteristic of intramolecular CT excitation energies, in that CT excitation energies decrease as R increases while the other three increase. As a result, the CT excitation energies taking place in $H_2N–(CH_2–CH_2)_n–NO_2$ [alkane-bridge] are found to be substantially similar to $H_3N……HNO_2$ (alkane-vacuum) ones (Figure 1). Therefore, we can recognize that the CT excitations through the polyalkane chain are a kind of intermolecular CT excitation. In other words, CT excitations through the polyalkane chain are substantially the same as those through space. The differences (about 1 eV) between alkane-vacuum and alkene-vacuum are due to structural and orientation differences.

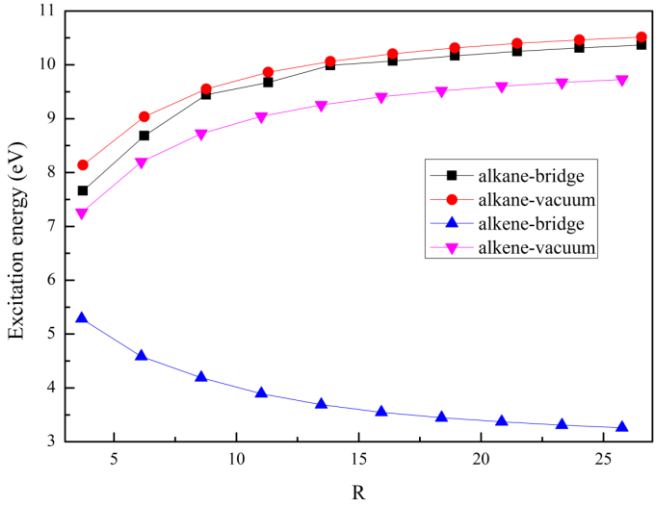

Figure 1: Dependence of CT excitation energies (eV) of LC-BOP over R (Å) between -NH_2 and -NO_2 of polyalkane and polyene (n=1~10) between NH_3 and HNO_2 of alkane-bridge and alkene-bridge.

4. Conclusion

In this study, we compared TD-DFT results of charge transfer (CT) excitations between polyalkane [–$(CH_2–CH_2)_n$–: n=1~10] bridged –NH_2 and –NO_2 with EOM-CCSD (n=1~5) results and found that LC-BOP with μ=0.47 can calculate the closest CT excitation energies to the CCSD results. Then, LC-BOP results let us found that the CT excitation energies between polyalkane bridged –NH_2 and –NO_2 are almost the same as those between NH_3 and HNO_2 through space, which shows that the polyalkane chain has no effect on the CT excitation energies and acts like a vacuum. In other words, the CT excitation energies of donor and acceptor through the polyalkane chain increases with the distance between donor and acceptor, R, while the polyene chain, –$(CH_2=CH_2)_n$–, plays a role in decreasing the CT excitation energies as R increases.

5. Schedule and prospect for the future

6. If no job was executed, specify the reason.

Fiscal Year 2022 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. “Is charge-transfer excitation through a polyalkane single-bond chain an intra-molecular charge-transfer?: EOM-CCSD and LC-BOP study” Jong-Won Song* and Kimihiko Hirao, Chem. Phys. Lett. 796, 139563 (2022) [DOI:10.1088/1361-648X/ac54e3].

2. “Vertical ionization potential benchmarks from Koopmans prediction of Kohn–Sham theory with long-range corrected (LC) functional” Kimihiko Hirao, Han-Seok Bae, Jong-Won Song, and Bun Chan, J. Phys.: Condens. Mattter (Special Issue: Enrico Clementi) 34, 194001 (2022) [DOI:10.1088/1361-648X/ac54e3].

[Conference Proceedings]

[Oral presentation]

[Poster presentation]

[Others (Book, Press release, etc.)]