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, we performed the time-dependent (TD) density functional theory (DFT) calculations on the tetraphenylehtene – bis(thiophen-2-methyl)amine (TPE-BTA), which shows a turn-on bright green fluorescence along with high sensitivity toward Hg^{2+}, to discover the structures of TPE-BTA complex with Hg^{2+}. However, we found that only x2c-TZVPPall, all electron (AE) basis set, for the Hg^{2+} ion successfully reproduces the absorption and vibrationally resolved fluorescence spectra close to the experimental spectra, but all the tested effective core potential (ECP) basis sets, such as Lanl2DZ, CRENBL, def2-TZVP, and aug-cc-pVTZ-PP, failed to find the excited state geometries producing the fluorescence spectra. In addition, the ECP basis sets provided too small HOMO-LUMO gaps during optimization process of the first excited state.

2. Specific usage status of the system and calculation method

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

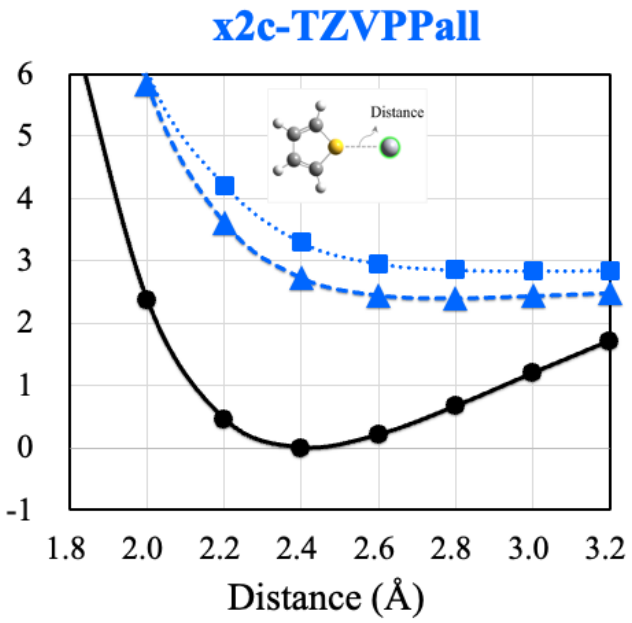

Fig. 1. The change of relative potential energy surface according to the distance between thiophene (sulfur) and Hg^{2+} calculated using x2c-TZVPPall.

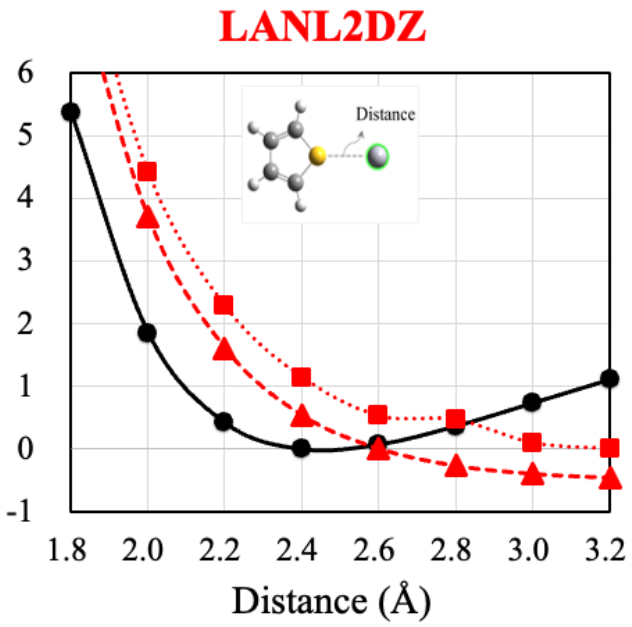

Fig. 2. The change of relative potential energy surface according to the distance between thiophene (sulfur) and Hg^{2+} calculated using x2c-TZVPPall.

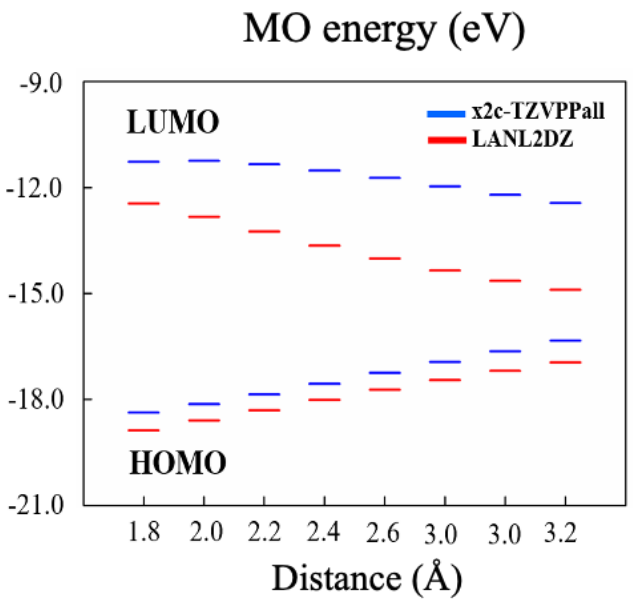

Fig. 3. The change of the molecular orbital (MO) energies according to the distance between thiophene (sulfur) and Hg^{2+} calculated using x2c-TZVPPall.

3. Result

We show why ECP basis set totally failed to calculate the optimized structure containing Hg^{2+} ion. The ECP basis sets provide the rapidly decreased HOMO-LUMO gaps with the distance between ligand and Hg^{2+} increased whereas x2c-TZVPPall shows gradually decreasing HOMO-LUMO gaps. Furthermore, the ECP basis sets calculate too weak binding energies in the excited states between the ligand and Hg2+. We carefully suggest that at least the system containing Hg2+ ion should be calculated using all electron basis set to escape from erroneous behavior in the excited states coming from ECP basis sets.

4. Conclusion

All the tested ECP basis sets, such as Lanl2DZ, CRENBL, def2-TZVP, and aug-cc-pVTZ-PP, provide too small band gaps of the complex with Hg^{2+} in the S_1 state optimization process, which eventually disable to obtain the optimized structure of the complex and its fluorescence spectra.

On the other hand, x2c-TZVPPall which is all electron basis set provides large band gaps of the S_1 state in the optimization process compared to ECP basis sets. ECP basis sets provide lower energy of the S_1 state than the S_0 state according to increase of the distance between sulfur of thiophene and Hg^{2+}, which is the main reason of failed excited state geometry optimization calculations using ECP basis sets.

5. Schedule and prospect for the future

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

Fiscal Year 2023 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. “Quinoline-derived electron-donating/withdrawing fluorophores for hydrazine detection and applications in environment and bioimaging” Kanagaraj Rajalakshmi, Selvaraj Muthusamy,* Ho-Jin Lee, Palanisamy Kannan,* Dongwei Zhu, Rathna Silviya Lodi, Meng Xie, Jimin Xie, Jong-Won Song,* Yuanguo Xu,* Spectrochim. Acta A Mol. Biomol. Spectrosc. 304, 123282 (2024) [DOI:10.1016/j.saa.2023.123282].

2. “Dual-channel fluorescent probe for discriminative detection of H2S and N2H4: Exploring sensing mechanism and real-time applications” Kanagaraj Rajalakshmi, Selvaraj Muthusamy,* Ho-Jin Lee, Palanisamy Kannan,* Dongwei Zhu, Jong-Won Song, Yun-Sik Nam, Dong Nyoung Heo, Il Keun Kwon, Zhibin Luo, Yuanguo Xu,* J. Hazard. Mater. 465, 133036 (2024) [DOI: 10.1016/j.jhazmat.2023.133036].

[Conference Proceedings]

[Oral presentation]

[Poster presentation]

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