Usage Report for Fiscal Year 2020

Project Title:

Rigorous higher-order DFT

Name:

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

Density functional theory (DFT) is ubiquitous for modern computational chemistry studies. With computational resource support from RIKEN, we have in the past few years developed advanced range-separated DFT methods. We have demonstrated the superior applicability of these methods to thermochemical properties of ground-state molecules.

Because of the physically sound foundation in the formulation of these methods, in principle, they would also be applicable to excited state species. Importantly, the use of our methods should enable an approach for obtaining excited-state properties with ground-state calculations. The concept behind this approach is considerably simpler than the conventional TD-DFT scheme for excited states, and consequently it would be more cost-effective than TD-DFT by a significant margin.

To test our hypothesis and to thereby establish an increased utility of our methods, we have examined a wider range of excited state energies with our methods and the associated new approach. The insights that we gain from these investigations will be used to further refine our DFT methods and our approach to excited-state computations.

2. Specific usage status of the system and calculation method

This project employs the Gaussian program on Hokusai, as well as a wide range of standard quantum chemistry software packages such as Molpro, Q-Chem and Orca. These tools enable us to access a diverse range of quantum chemistry methodologies, from highly accurate coupled-cluster methods at the one end, with which accurate reference data can be obtained, to a vast collection of over 200 DFT methods at the other end, with which a baseline for comparison with our methods can be established.

Limited amount of highly accurate reference data is also available from literature for atoms and small molecular systems from water and carbon monoxide to benzene and pyridine. Because the computation of excited-state energies can be challenging for even the highest-level methods that are currently available, in our investigations, we focus mainly on such systems for robust comparison with reference data of the highest quality.

In addition to energy, other properties of excited states are also important for practical applications and thus have been examined extensively by experiment. A key property is the probability of transition from ground state, which manifest as the intensity in a UV spectrum. Importantly, it is of direct relevance to the harvesting of light energy and hence application in renewable technology. We have also carried out investigations into this aspect.

3. Result

The success of our DFT method is based on its proper treatment of the so-called exchange interaction. While our formulation by design attempts to adhere to this principle as closely as possible, the DFT method itself is not an exact method and therefore its accuracy is not guaranteed. We hypothesize that systematic tuning of the method for different classes of systems can provide useful guidelines for its usage. We indeed find minor adjustments to the "μ" parameter to be useful in maximizing accuracy. In

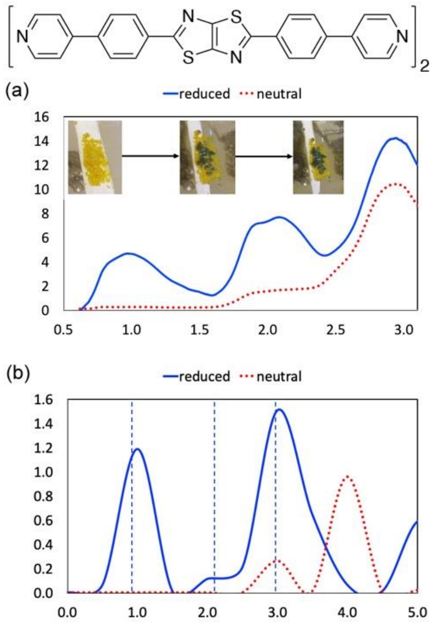
method		scheme 1		scheme 2		scheme 3		ΔSCF		TD-DFT	
μ		1st group	2nd group	1st group	2nd group	1st group	2nd group	1st group	2nd group	1st group	2nd group
0.47	MAD	0.72	0.76	0.50	0.33	0.13	0.09	0.49	0.47	0.39	0.42
	(MD)	(0.72)	(0.76)	(−0.50)	(−0.33)	(0.12)	(−0.08)	(−0.49)	(−0.47)	(0.39)	(0.42)
0.40	MAD	0.49	0.54	0.43	0.37	0.14	0.13	0.41	0.44	0.18	0.24
	(MD)	(0.49)	(0.54)	(−0.43)	(−0.37)	(−0.14)	(−0.13)	(−0.41)	(−0.44)	(0.18)	(0.24)
0.35	MAD	0.25	0.37	0.39	0.38	0.18	0.20	0.39	0.44	0.06	0.12
	(MD)	(0.25)	(0.37)	(−0.39)	(−0.38)	(−0.18)	−0.20	(−0.39)	(−0.44)	(−0.04)	(0.12)
0.30	MAD	0.04	0.12	0.36	0.41	0.26	0.29	0.36	0.44	0.30	0.06
	(MD)	(−0.04)	(0.09)	(−0.36)	(−0.41)	(−0.26)	(−0.29)	(−0.36)	(−0.44)	(−0.30)	(−0.06)
0.25	MAD	0.44	0.28	0.34	0.43	0.37	0.40	0.33	0.44	0.65	0.42
	(MD)	(−0.44)	(−0.28)	(−0.34)	(−0.43)	(−0.37)	(−0.40)	(−0.33)	(−0.44)	(−0.65)	(−0.39)

general, the error in our approach (~0.1–0.2 eV) is similar to those for high-level "EOM-CCSD" method (~0.15 eV) but our results are obtained at a much lower computational cost.

We have further tested our approach for larger aromatic systems. These species are models for nanocarbon materials, and they are therefore relevant to application in advanced electronics. For these systems, we find a more substantial dependence of the accuracy on the μ parameter (see Table above). The dependency is quite systematic, and we have accordingly formulated guidelines for the estimation of the optimal value of μ as a function of the size of the system. In general, our best approach (scheme 1) with an optimal μ of 0.3 leads to results that are comparable in accuracy to the more costly TD-DFT method.

In our investigation into the use of our approach for the simulation of UV spectrum, we also find a dependence on the μ parameter for the excitation energies. However, the excitation intensity is rather insensitive to the value of μ. As a result, good qualitative spectrum can be obtained regardless. Importantly, the optimal μ falls in a narrow range for similar systems, thus facilitating comparison and tuning of molecular structure for advancing practical applications in, for example, electrochromic device.

Our next figure demonstrates such an application to the key organic component of a metal–organic framework with electrochromic properties. We can see how our simulated spectra in (b) accurately reproduce the change in UV absorption upon electrochemical reduction when compared with the experimental spectra in (a).



4. Conclusion

We have examined the application of our advanced range-separated DFT methods in conjunction with a simple ground-state-type approach for the computation of excited state properties. Our results show that this low-cost scheme yields accurate excitation energies and intensities. The accuracy shows a minor dependence on a single μ parameter in our DFT method. Importantly, variation in optimal μ is systematic and predictable, with the optimal value being comparable for similar systems, and minor change in μ does not alter the qualitative picture by any means. These characteristics validate the robustness of our approach for general usage in an efficient manner.

5. Schedule and prospect for the future

Our future investigations will involve application of our scheme for the discovery of advanced materials. We will also explore its use for additional excited-state properties such as transition kinetics.

Usage Report for Fiscal Year 2020

Fiscal Year 2020 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. Re-Examining the Electronic Structure of Fluorescent Tetra-Silver Clusters in Zeolites. Chan, B. *Phys. Chem. Chem. Phys.* **2021**, *23*, 1984.
2. Core-Level Excitation Energies of Nucleic Acid Bases Expressed as Orbital Energies of the Kohn–Sham Density Functional Theory with Long-Range Corrected Functionals. Hirao, K. Nakajima, T.; Chan, B. Song, J.-W.; Bae, H.-S. *J. Phys. Chem. A* **2020**, *124*, 10482.
3. Charge-Transfer Excitation Energies Expressed as Orbital Energies of Kohn–Sham Density Functional Theory with Long-Range Corrected Functionals. Hirao, K.; Chan, B.; Song, J.-W.; Bae, H.-S. *J. Phys. Chem. A* **2020**, *124*, 8079.
4. Rapid Prediction of Ultraviolet–Visible Spectra from Conventional (Non-Time-Dependent) Density Functional Theory Calculations. Chan, B.; Hirao, K. *J. Phys. Chem. Lett.* **2020**, *11*, 7882.
5. Excitation Energies Expressed as Orbital Energies of Kohn‑Sham Density Functional Theory with Long-Range Corrected Functionals. Hirao, K.; Chan, B.; Song, J. ‑ W.; Bhattarai, K.; Tewary, S. *J. Comput. Chem.* **2020**, *41*, 1368.