Reparameterized nonlocal correlation density functional adapted for dispersionless CAS wave functional (CAS-reVV10).

Mohammad Reza Jangrouei[1] and Katarzyna Pernal[1]

Institute of Physics, Lodz University of Technology, ul. Wolczanska 217/221, 93-005 Lodz, Poland

Abstract

This work proposes a reparameterization of the VV10 nonlocal correlation density functional [1], which corrects the CASSCF energy for the dispersion contribution and is applicable to excited states. The success of VV10 in tuning it with other functionals motivates our attempt to combine it with CASSCF to describe molecular interactions. For this purpose, VV10 should be reparameterized to only take into account the missing part of the long-range correlation in the supermolecular CAS which is the dispersion energy [2]. We tuned the VV10 parameters using counterpoise-corrected correlation interaction energies calculated for the training set, which includes dimers of argon, water, and ethanol. As a benchmark for functional training, SAPT(DFT) dispersion, and exchange dispersion energies are employed.

The reparameterized VV10 functional adapted with CAS (CAS-reVV10) has been tested on two test sets. On the first set, consisting of 8 molecular dimers in their ground state and 60 data points, the resulted mean absolute percentage error and mean error amount to 14% and -0.13 kcal·mol^{-1}, respectively. The second set consisted of 8 molecular dimers in ground- and excited-state and 64 data points. The achieved mean absolute percentage error and mean unsigned error are 9.03% and 0.42 kcal·mol^{-1} for the ground-state and 10.77% and 0.49 kcal·mol^{-1} for the excited-state dimers.

Due to its reasonable accuracy, low computational cost, and applicability with localized exciton, the CAS-reVV10 can be a valuable method for large systems [3].

References

1. Vydrov, O.A., Van Voorhis, T.: Nonlocal van der waals density functional: The simpler the better 133(24), 244103 (2010), https://doi.org/10.1063/1.3521275
2. Hapka, M., Krzemińska, A., Pernal, K.: How much dispersion energy is included in the multiconfigurational interaction energy? Journal of Chemical Theory and Computation 16(10), 6280–6293 (2020), https://doi.org/10.1021/acs.jctc.0c00681, pMID: 32877179
3. Jangrouei, M.R., Krzemińska, A., Hapka, M., Pastorczak, E., Pernal, K.: Dispersion interactions in exciton-localized states. theory and applications to $\pi - \pi^*$ and $n - \pi^*$ excited states. Journal of Chemical Theory and Computation 0(0), null (0), https://doi.org/10.1021/acs.jctc.2c00221