Dispersion energy based on the multiconfigurational wavefunction for strongly correlated systems

Agnieszka Krzemińska, Michał Hapka, Katarzyna Pernal

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

The dispersion-driven interactions in strongly correlated systems pose a challenge due to the need to account for both dynamic correlation and the multireference character of the studied system. The CASSCF wavefunction provides a proper representation of static correlation and partial recovery of the intramonomer correlation effects. The remaining dynamic correlation that is missing manifests as dispersion. We showed how to rigorously extract the dispersion term in the interaction energy calculated with multiconfigurational (MC) wave functions in a way that avoids dispersion interaction double counting and consequently, we proposed a hybrid "CAS+dispersion" approach, in which the dispersion energy is calculated in the symmetry-adapted perturbation theory (SAPT) framework extended to MC wave functions, denoted SAPT(MC) [1]. Next to "CAS+dispersion" and SAPT(CAS), we explored the possibility of treating weakly-bound multireference systems using our hybrid lrAC0-srDFT approach [2], which combines description of the long-range correlation by the adiabatic connection approximation with short-range DFT. Here we apply all three methods to study representative ground- and excited-state complexes from the S66 benchmark dataset [3]. We show that SAPT(CAS) provides a valuable insight into changes of the interaction energy components upon electronic excitation [4]. All developed methods were implemented in the latest GammCor code release, updated at github.com/pernalk/GAMMCOR.

[1] M. Hapka, A. Krzemińska, K. Pernal; *J. Chem. Theory Comput.* 2020, 16, 10, 6280–6293.
[2] M. Hapka, E. Pastorczak, A. Krzemińska, K. Pernal; *J. Chem. Phys.* 2020, 152, 094102
[3] J. Řezáč, K. E. Riley, P. Hobza; *J. Chem. Theory Comput.* 2011, 7, 8, 2427–2438.
[4] M. R. Jangrouei, A. Krzemińska, M. Hapka, E. Pastorczak, K. Pernal, in preparation.