Electron excitation energies from reduced density matrices: extended random phase approximation and linear response theory approaches

Katarzyna Pernal[1]

[1] Institute of Physics, Technical University of Lodz, ul. Wólczańska 219, 90-924 Łódź, Poland

Reduced density matrices, RDM's, hold a promise of removing wavefunction from description of electronic systems and replacing a full N-electron Schrödinger equation by, in principle simpler, equations involving reduced density matrices only. Recently, methods that employ reduced density matrices in the description of time-dependent systems have emerged, which, accessing time-dependent 1-RDM or a frequency-dependent linear response function, allows one to obtain electronic excitation energies [1, 2]. Another possibility for obtaining excitation energies based solely on the ground state one- and two-electron reduced density matrices is offered by an approximation to the Rowe's equation of motion [3].

The approximation we have proposed involves expanding the excitation operator that enters the Rowe's equation up to all single excitations and some double excitations (the so-called diagonal doubles), assuming a correlated vacuum, and retaining only elements of 1- and 2-RDM's in the resulting equations [4]. The method, called Extended Random Phase Approximation 2 − ERPA2, has been applied together with the correlated RDM's resulting from the antisymmetrized product of strongly orthogonalized geminal (APSG) theory to a number of molecules. ERPA2 that employs the APSG 1- and 2-electron density matrices provides exact singlet excitation energies for two-electron systems and highly accurate excitations for four-electron species. This can be linked to the near-satisfaction of the killer condition by the excitation operator that underlies the method. For larger systems at equilibrium geometry ERPA is comparable in accuracy to RPA. The former method, however, is capable of reproducing double excitations (that RPA misses completely) but they are usually in large error. For molecules at stretched bond geometries ERPA outperforms RPA and predicts potential energy curves of the correct shape.

It can be shown that ERPA equations with the reduced density matrices obtained by employing the strongly orthogonal germinal theory are directly related to the linear response theory equations formulated within the APSG framework. This opens an avenue to proposing a range-separation scheme and employing short-range density functionals in ERPA equations, which, in turn, leads to a significant improvement in the accuracy of the predicted excitation energies.

[1] Pernal, K., Gritsenko, O., and Baerends, E. J. *Phys. Rev. A*, 75:012506, 2007.
[2] Giesbertz, K. J. H, Gritsenko, O. V., Baerends, E. J. *Phys. Rev. Lett.*, 105:013002, 2010.
[3] Rowe, D. J. *Rev. Mod. Phys*, 40:153, 1968.
[4] Chatterjee, K. and Pernal, K. *J. Chem. Phys.*, 137:204109, 2012.