Revised CAM-QTP-00 Functional with Improved Performance of Excited States Calculations

Yifan Jin and Rodney J. Bartlett

Quantum Theory Project and Department of Chemistry, University of Florida, Gainesville, FL, 32611-8435

Here we will present a new functionals derived from the CAM-QTP-00 published previously[1] with modified parameters. The CAM-QTP-00 functional is very successful in estimating the vertical ionization potentials and many other ground state properties but is just moderately good in excitation energy calculations. In the new functional the restriction for the core orbital is removed but the valence orbitals still have clear physical meaning as in CAM-QTP-00, that is, the negative of KS eigenvalues are close to the corresponding ionization potentials. Then the parameters that fulfill this requirement are applied to several molecules in a database with large number of states measured experimentally by TDDFT method so that the errors of the excitation energies could be minimized. We did a lot of benchmark calculations with our new functional and the results demonstrate that the accuracy of the excitation energy calculations especially the Rydberg transitions increased significantly. The mean absolute error of vertical excitation energies computed by the new functional is smaller than the vast majority of the other functionals. It could also reproduce many other properties quite well and has significant improvement over the CAM-QTP-00.

1. Verma, P.; Bartlett, R. J. *J. Chem. Phys.* **2014**, *140*, 18A534