

Excited-state methods based on state-averaged long-range CASSCF short-range DFT

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In the present work we propose two distinct state-averaging (SA)-based methodologies for the calculation of excited states, in conjunction with the long-range complete active space self-consistent field (CASSCF) short-range density functional theory (DFT) approach (CAS-srDFT).¹ The state-specific density ansatz, termed SA-CAS-srDFT, initially determines the variational parameters of an approximate srDFT functional that operates with state-averaged densities. Subsequent to convergence, the CAS-srDFT energies of each state are computed from the state-specific one- and two-body densities. The second approach is termed configuration interaction (CI)-srDFT, for which a first-order correction is added to the approximate SA density CAS-srDFT functionals. Unlike the state-specific density approach SA-CAS-srDFT, diagonalisation of the first-order corrected effective Hamiltonian CI matrix yields orthonormal CI solutions for every state. In both approaches, the total one-body and on-top pair density (OTPD) was employed for the final energy evaluation. It was observed that the CI-srDFT approach gives physically correct potential curves for ethylene, in contrast to SA-CAS-srDFT. Moreover, the CI-srDFT approach demonstrates a reduced dependence of excitation energies on the number of states in the average when compared to the SA-CAS-srDFT method. The accuracy of the various CAS-srDFT methods was investigated for 139 singlet excitation energies of 28 typical organic chromophores. The two excited-state approaches in conjunction with multiconfiguration pair-density functional theory (MC-PDFT) were also employed in the benchmark study for comparing the accuracy with CAS-srDFT. It was found that CI-srDFT methods are more accurate than their SA counterparts, giving a mean absolute error of just 0.17 eV when using the sr-ctPBE functional. The accuracy of the new SA-based CAS-srDFT methods was observed to be impressive for organic molecules; however, this was not found to be transferable when investigating excited states of transition-metal complexes. In fact, none of the CASSCF-DFT excited-state methods introduced in this study, and also MC-PDFT, were found to provide a consistent improvement of CASSCF excitation energies.

1. B. Helmich-Paris, E. R. Kjellgren, H. J. Aa. Jensen, *Phys. Chem. Chem. Phys.* 2025, 27, 15331.