The Algebraic Diagrammatic Construction Scheme for the Calculation of Electronic Excited States Employing Localized Orbitals

Michael Wormit, Jan Hendrik Starcke and Andreas Dreuw

Johann Wolfgang Goethe-University

Max von Laue-Str. 7, 60437, Frankfurt, Germany

The algebraic diagrammatic construction (ADC) scheme provides a way to derive methods for the calculation of electronic excited states based on perturbation theory. By employing the scheme for a given order in perturbation theory a hermitian, CI-like ADC matrix is obtained whose eigenvalues and eigenvectors yield the energies and transition moments of excited states, respectively. The second order variant ADC(2) performs similar to CIS(D) or CC2 producing reliable results for most optically allowed excited states. Yet, neither ADC(2) nor CC2 are sufficient to correctly describe highly correlated states, as they are e.g. present in the low-energy region of linear polyenes. An improved description of such states can be obtained by using an extended second order scheme ADC(2)-x which represents a compromise between the accuracy of higher order methods and the computational costs of ADC(2). It has been shown recently [1] that ADC(2)-x yields acceptable results for the energies of the lowest excited states in small linear polyenes.

To reduce the computational scaling of the ADC(2)-x method we have developed and implemented it in the Q-Chem package of programs employing localized occupied and virtual orbitals. By exploiting the locality of the orbitals a significant amount of doubles amplitudes can be neglected in the calculation which reduces the scaling of the method significantly without sacrificing accuracy. Several distinct models for neglecting doubles amplitudes based on orbital distances have been implemented and evaluated. The most promising model has been applied to a set of test molecules. Compared to non-local ADC calculations the results of the local version showed less than 0.15 eV deviation in the excitation energies of any of the calculated excited states.

Literature:

[1] J. H. Starcke, M. Wormit, J. Schirmer and A. Dreuw, *Chem. Phys.*, **329**, 39 (2006)