

Linear scaled coupled cluster properties using local correlation methods

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*This work is supported by the Air Force Office of Scientific
Research under contract number FA-9550-04-1-01*

We have developed a localized coupled cluster (CC) method to compute the properties of large systems using equation of motion (EOM) and effective Hamiltonian approaches based on the natural linear scaled CC method. The method relies on the transferability of the CC response matrix in terms of transferable multi-centered natural localized molecular orbitals which allow a decomposition of the electronic structure into effective functional group contributions. Localization of the virtuals into orthogonal orbitals is possible because the orbitals derive from the 1-matrix. Despite the fact that the left hand eigenstate of the response matrix is parameterized by a linear non-extensive de-excitation operator, we find that this operator is transferable in analogy with the ground state excitation operator. Dynamic polarizabilities provide the excited state spectrum in agreement with EOM methods. Dispersion coefficients are determined using an integration over polarizabilities at imaginary frequencies. Applications to tryptophan and polyglycine as a function of sodium D-line frequencies are presented. We are able to reproduce over 99% of the correlated dynamic polarizability which is obtained with conventional methods for cc-pVDZ tetra-glycine. Not surprisingly, we find that for non-chromophoric systems this percentage decreases as we approach a singularity, due to the delocalized nature of the excited state wavefunctions.