Domain-based Pair Natural Orbitals for Excited States Using the Similarity Transformed Equation of Motion Formalism

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Although the concept of pair natural orbitals has been known for decades, it was only during the last ten years that they have been employed in the design of efficient computational algorithms for the calculation of accurate ground state energies.[1] The domain-based pair natural orbital (DLPNO) approach has been successfully used to accelerate coupled cluster (CC) methods for both closed and open shell ground states.[2] While it is now possible to obtain accurate ground state energies for molecules consisting of several hundred atoms, the application of PNOs for excited states has proved to be a harder problem. Although it is also possible to combine ground state DLPNO calculations with canonical excited state equation of motion (EOM) CC theory, the resulting methods still retain the prohibitive scaling of canonical CC theory.[3] On the other hand, the size of the excitation manifold can be reduced using a second similarity transformation so that the final diagonalization is carried out only in the space spanned by single exitations. The resulting similarity transformed EOM (STEOM) method[4] scales similarly to time dependent density functional theory (TDDFT), although it requires a ground state CC and ionized EOM calculations. Applying the DLPNO scheme to the latter, it is possible to carry out accurate wave function based calculations for excited states of $\sim$100 atom molecules using between 3,500 and 4,500 basis functions at near TDDFT cost but without neglecting the contributions of higher excitations. The ionization steps required by this method are already published,[5,6] and the details of the final DLPNO-STEOM method will be communicated in the near future. Since this method describes local and charge transfer excitations equally well, DLPNO-STEOM can be beneficially applied, among others, to compute the photochemical properties of larger molecular systems[7] or to obtain the optical bandgaps of semiconductors.[8]

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