Domain-based Local Pair Natural Orbitals for Ionized States

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The application of the successful domain-based pair natural orbital (DLPNO) scheme of Neese[1] to excited states has proved to be a difficult task. It has become clear from the work of Hättig that ground state pair natural orbitals (PNO) are ill suited to the description of some excited states (charge transfer states in particular).[2] To overcome this issue, Hättig proposed the usage of state specific PNOs, while the recent work of Valeev[3] makes use of state averaged PNOs. In our earlier work,[4] we combined ground state PNOs with other ways of reducing the excitation manifold within the equation of motion (EOM) coupled cluster (CC) method. However, beyond excitation energies (EE), the EOM method is also suitable for the computation of ionization potentials (IP) and electron attachments (EA). In this regard, frozen natural orbitals (FNO) were applied successfully to the IP problem by Krylov,[5] who also pointed out the difficulties of applying FNOs to computing EAs. More recently, Schütz reported an efficient local implementation of the EOM-IP method at the second order CC (CC2) level.[6] In a similar spirit, we have implemented a near linear scaling DLPNO-IP method that uses ground state PNOs.[7] It is also possible to implement an efficient DLPNO-EA method by keeping some of the terms in the equations in the canonical basis and thereby sacrificing linear scaling.[8] My contribution will be devoted to the description of the DLPNO-IP and DLPNO-EA methods and to their possible applications and limitations.

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