SOLITONIC NATURAL ORBITALS

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Natural orbitals (NOs) and their occupancies constitute a convenient and conceptually appealing representation of the one-electron reduced density matrix from which all one-electron properties (including the majority of indices of interest to chemists) follow. However, their importance notwithstanding, some of the properties of the NOs are not fully understood. In particular, the existence of unoccupied NOs (UNOs) has been the subject of several studies with contradictory conclusions.

This talk focuses on our recent investigation of the elusive UNOs that employs a combination of rigorous analysis and extensive highly accurate numerical calculations aiming at elucidation of the sign patterns exhibited by the natural amplitudes pertaining to the NOs of two-electron systems in singlet ground states. First, the universal presence of exactly one positive-valued natural amplitude ("the normal sign pattern") in systems with electron-electron interactions sufficiently weak in comparison to those with the external potential is rigorously proven. This result assures the vanishing of the occupation numbers of the NOs at certain values of the nuclear charge in the helium isoelectronic series or/and at certain internuclear distances in the H_2 molecule. Second, the evolution of the natural amplitudes of the harmonium atom in its ground state with the confinement strength ω is thoroughly studied. The presence of the normal sign pattern for all $\omega \geq ½$ is demonstrated. Even more importantly, the existence of unusual weakly occupied NOs corresponding to positive-valued natural amplitudes at weak confinements is revealed. These solitonic NOs, whose shapes remain almost invariant as their radial positions drift toward infinity upon the critical values of ω being approached from below, exhibit strong radial localization. Their asymptotic properties are extracted from the numerical data and their relevance to electronic structure calculations on fully Coulombic systems is discussed.