"Applications of 'Iterative' Natural Orbitals"

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Natural orbitals, championed by Per-Olov Löwdin [1], are of particular interest in quantum chemistry as they offer routes to reducing the cost of correlated calculations via truncation of the virtual space. Several schemes that approximate these natural orbitals have been investigated in the literature, such as the frozen natural orbitals—pioneered by Barr and Davidson [2]—that are employed by Bartlett [3] and Krylov [4], and the pair natural orbitals discussed by W. Meyer [5] and used in the CBS thermochemistry [6]. However, the natural orbitals proposed by Löwdin are obtained by diagonalization of the full one-particle density matrix, and necessarily mix the occupied and virtual space. Their construction must then be an iterative procedure, which is discussed here in the context of both RHF and ROHF reference wavefunctions.

We compare the behavior of these iterative natural orbitals (INOs) to that of canonical orbitals in the calculation of equilibrium geometries and harmonic frequencies for a handful of small molecules, and investigate possible virtual space truncation schemes (similar to those proposed by Sarangi *et al.* [4]) as applied to the HCN isomerization potential energy surface.

References

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