Strong Correlations from Constrained Mean-Field Approaches

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One of the fundamental challenges in modern quantum chemistry is the efficient incorporation of strong correlations at low computational cost. Localizing the exchange hole and using symmetry broken orbitals in DFT are standard tricks towards achieving this goal. However, this is insufficient and unpleasant from the perspective that it goes hand-in-hand with the introduction of self-interaction error in an uncontrolled manner, one that has proven extremely difficult to overcome. Our work has recently focused on incorporating strong correlations into mean-field approaches via selective symmetry breaking followed by a restoration step. Constrained-pairing mean-field theory (CPMFT) [1] introduces pairings between electrons in an active space and yields a two-particle density matrix (2pdm) ansatz that exclusively describes strong correlations. The model breaks electron number conservation which is correct only on average but expectation values calculated from its effective 2pdm contain no particle number fluctuations. On the other hand, Constrained Unrestricted Hartree-Fock (CUHF) theory [2,3] limits spin symmetry breaking to an active space. Based on it, we have developed a novel approach for obtaining high-spin ROHF wave functions. If the active space is properly chosen, CUHF greatly benefits from a controlled broken-symmetry effect while avoiding the massive spin contamination of traditional UHF. Spin projection operators can be applied to restore symmetry and obtain multireference wave functions with moderate computational cost. Singlet-triplet energy splittings show that our scheme outperforms fully unrestricted methods. This constrained approach can be used in spin density functional theory with similar favorable effects.

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2. T. Tsuchimochi and G. E. Scuseria, *J. Chem. Phys*. **133**, 141102 (2010).
3. T. Tsuchimochi and G. E. Scuseria, *J. Chem. Phys*. **134**, 064101 (2011).