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**Constrained Active Space Unrestricted Mean-Field Approaches for Controlling Spin-Contamination** TAKASHI TSUCHIMOCHI, GUSTAVO E. SCUSERIA, Department of Chemistry, Rice University — We have recently shown that unrestricted Hartree-Fock (UHF) variationally reduces to high-spin restricted open-shell Hartree-Fock when constraints are imposed on the eigenvalues of the spin density matrix [T. Tsuchimochi and G. E. Scuseria, *J. Chem. Phys.* **133**, 141102 (2010)]. We here generalize these ideas and propose to control spin-contamination in UHF by releasing the constraints in an active space while imposing them elsewhere. If the active space is properly chosen, our constrained UHF (CUHF) method greatly benefits from a controlled broken-symmetry effect while avoiding the massive spin contamination arising in the traditional UHF. We apply Löwdin's projection operator to CUHF and obtain multireference wave functions with moderate computational cost. We report results on singlet-triplet energy gaps to show that our constrained scheme outperforms fully unrestricted methods. This constrained approach can be readily used in Kohn-Sham (KS) density functional theory with similar favorable effects, provided that spin-contamination is given by the KS orbitals as in UHF.

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