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A Dynamically Correlated, Strongly Orthogonal, Geminal Method Without Strong Orthogonality or the Double Counting Error[1]

BRETT CAGG, VITALY RASSOLOV, Univerity of South Carolina — The electron correlation problem poses a significant challenge to theorists. While Hartree-Fock theory has traditionally been recognized as the foundation of computational chemistry, it suffers from an insufficient description of correlated electron motion coupled with the assumption of a single configurational, ground state wavefunction. While the remedy to both of these deficiencies is known, and is realized in the full configuration interaction method, the computational expense incurred in resolving these issues makes the exact method impractical. Thus, the most successful computational methods attempt to correct these issues without incurring undue expense. A recently developed, variationally optimized, spin-unrestricted computational method based on strongly orthogonal geminals, called USSG, accounts for most multiconfigurational correlation effects in a computationally inexpensive and well-defined manner. Unfortunately, due to the form of the wavefunction, USSG still lacks a proper description of correlated electronic motion. While the multiconfigurational correlation is certainly the most computationally difficult form of correlation to incorporate, care must be taken to properly account for the missing correlation effects without double counting those already covered in USSG. Corrections developed to account for two separate portions of missing correlation in the USSG method are presented, and the effect of these corrections on dissociation energy prediction for 38 diatomic molecules are discussed.

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