Size-extensive wave functions for QMC: The J-LGVBn theory

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We show a new class of multideterminantal Jastrow-Slater wave functions constructed with localized orbitals and designed to describe complex potential energy surfaces of molecular systems for use in quantum Monte Carlo (QMC). Inspired by the generalized valence bond formalism, we elaborate a coupling scheme between electron pairs which progressively includes new classes of excitations in the determinantal component of the wave function. In this scheme, we exploit the local nature of the orbitals to construct wave functions which have increasing complexity but scale linearly. The resulting wave functions are compact, can correlate all valence electrons, and are size-extensive. We name these wave functions of the Jastrow linear generalized valence bond (J-LGVB) form [1]. The theory can be extended to include multiple coupling schemes characterized by different sets of localized orbitals, which enables the detailed study of large portions of the potential energy surface [2]. Moreover, for large molecular systems the method can be applied at a multi-level scheme to treat different regions of the molecule at different levels of the theory [3]. The performance has been assessed on a variety of homolytic fragmentations, on the calculation of barrier heights of five prototypical chemical reactions, and on a complex reaction path like that of the decomposition of α-hydroxy-dimethylnitrosamine.

1. F. Fracchia, C. Filippi and C. Amovilli, *J. Chem. Theor. Comput.* **8** (2012) 1943-1951.

2. F. Fracchia, C. Filippi and C. Amovilli, *J. Chem. Theor. Comput.* (2013) accepted for publication.

3. F. Fracchia, C. Filippi and C. Amovilli, (2013) submitted.