A Mean-Field Method for Electron Pairs: A New Twist on an Old Approach to Strong Electron Correlation

Paul W. Ayers[1]

1. Department of Chemistry & Chemical Biology; McMaster University, Canada

The correlation between different electrons' motions is mostly local (electrons that are far from each other tend to move independently) and it is dominated by the propensity of electrons to form pairs. This feature is not exploited in conventional quantum chemistry methods based on Slater determinants, which assume that electrons move quasi-independently. Nonetheless, approaches that use a Slater determinant as the starting point for further corrections (e.g., perturbation theory and coupled cluster) are very common, and often effective.

A Slater determinant wavefunction is an ineffective starting point for further approximations, however, when the distinction between occupied and unoccupied orbitals is unclear. In these sorts of strongly correlated systems, it is important to treat the correlation between pairs of electrons explicitly. One way to do this is to approximate the wavefunction as an antisymmetric product of two-electron wavefunctions, called geminals. Antisymmetric products of geminals (APG) are typically excellent at capturing strong "static" correlation, but they were believed to be computationally intractable unless the geminals were chosen to be strongly orthogonal (APSG). In APSG, however, there is no correlation between different subsets of orbitals; the APSG wavefunction is therefore intermediate between the orbital picture and the geminal picture, and cannot describe some strongly correlated systems (like BCS wavefunctions, where the antisymmetrized geminal power (AGP) wavefunction is appropriate). We have recently derived, and numerically tested, several new types of APGs. The geminals in these methods are allowed to be nonorthogonal, and therefore include APSG and AGP as special cases. However, the computational scaling of these methods, which can be viewed as mean-field models for electron pairs, is Hartree-Fock-like. Even though these methods are very affordable and are therefore suitable for applications to large systems, they come very close (typically within 10^{-5} Hartree) of factorial-cost wavefunction-based methods like seniority-zero configuration interaction (i.e., closed-shell MCSCF). The residual dynamical correlation can be recovered using perturbation theory.