

Strongly orthogonal geminals and group functions: size-extensive and variational reference states

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Two electron functions, called geminals, offer a valuable tool in many-electron theory for several reasons:

1. The N -electron wave function written in terms of geminals retains the formal simplicity of the Hartree-Fock wave function in many respects
2. Thinking in terms of geminals is close to the chemists' way of viewing the molecule, since geminals can usually be assigned to localized electron pairs.
3. Geminals can be considered as composite quasi-bosonic particles, built from two physical particles (electrons). In the second quantized formulation, this gives rise to a beautiful algebra
4. Upon inducing the strong orthogonality condition, the geminal wave function is extremely easy to deal with
5. The geminal wave function can be obtained by an exponential cluster operator acting on the Hartree-Fock determinant, thus it can be viewed as an approximate coupled-cluster wave function
6. Geminal-type wave functions can describe single-bond dissociation quite well, even if several distant single bonds dissociate at a time. Even for multiple-bond dissociation geminals do a much better job than many other standard methods like MPn or CCSD
7. The energy of an antisymmetrized product of strongly orthogonal geminals is a strict upper bound to the true energy (variational character)
8. A geminal-type wave function is multiplicatively separable upon dissociation to closed-shell fragments, facilitating size-extensivity.

The last two properties together are especially appealing, since most quantum chemical methods possess only one or the other, exclusively. However, there are some disadvantages of strongly orthogonal geminals which deserve a careful attention:

1. Strong orthogonality is a severe variational restriction
2. The perfect pairing approximation prevents inter-geminal correlation to be accounted for
3. For multiple bond dissociation, the spin state of the dissociated species is usually incorrect
4. Excited states are difficult to handle with geminals
5. Separating a molecule merely for two-electron fragments is unfortunate if one has inherently delocalized objects, such as a benzene ring
6. Geminals cannot describe strong correlation in systems showing truly collective phenomena.

As to the first three points, a way out is to consider geminal-type wave function as a highly correlated (multi) reference state, and look for their improvement by perturbational or cluster type methods. The second three points may require a different generalization: treatment of group functions composed by more than two electrons. The talk will review the properties of geminals and their possible improvements and generalizations.