

Post-modern valence bond theory

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Wave function-based quantum chemistry has two traditional lines of development one based on molecular orbitals (MOs), and the other on valence bond (VB) theory. Both offer advantages and disadvantages for the challenging problem of describing strong correlations, such as the breaking of chemical bonds, or the low-spin (antiferromagnetic) coupling of electrons on different centers. Within spin-coupled VB (SCVB) theory, the target wave function consists of a set of non-orthogonal orbitals, one for each valence electron, that are spin-coupled together into a state of the desired overall spin-multiplicity. Exact solution of the VB problem is exponentially difficult with molecular size, and therefore approximations are imperative.

The Coupled Cluster Valence Bond (CCVB) method¹ is a recently proposed way of addressing the computational bottleneck of SCVB calculations. CCVB can exactly separate (in a specific sense) any system of $2n$ active valence electrons into atomic products without spin-contamination, as long as unrestricted Hartree-Fock can also reach the correct (spin contaminated) asymptote. This is accomplished with only n^2 spin-coupling coefficients, which is less than the number of molecular orbital coefficients! For computational tractability, the orbitals are defined to obey strong orthogonality between pairs, but are non-orthogonal within a pair, similar to the simpler perfect pairing method, which can be viewed as the reference wave function for CCVB. I shall describe the formalism and selected applications of the CCVB method, in comparison to SCVB, and complete active space calculations. CCVB appears to be a very effective method of treating problems with strong spin correlations between electrons, although some limitations emerge in problems where resonance effects are important.

[1] D.W. Small and M. Head-Gordon, J. Chem. Phys. **130**, 084103 (2009).