

Correlation Methods Using Non-Orthogonal Orbitals

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ABSTRACT: Whenever a molecule contains atoms that have singly occupied orbitals with small overlap, the standard single configuration approaches become ineffective. Such orbitals occur for example during the formation and breaking of chemical bonds and at equilibrium distances for molecules containing transition metals. For such systems, the use of wave functions with non-orthogonal orbitals have great advantages: the simplest forms of these have an accuracy comparable to that of standard CASSCF wave functions using much smaller sets of parameters.

New algorithms have recently been introduced for the optimization of CI-coefficients and orbitals for wave functions with non-orthogonal orbitals. The computational complexity of these new methods is much smaller than that of previously developed methods for non-orthogonal orbitals and standard CASSCF calculations. The efficiency of the method is demonstrated by calculations on molecules with two or three transition metal atoms, thereby mimicking CASSCF calculations with upto 18 electrons in 18 orbitals. A discussion of the extension of the methods to include dynamic correlation is finally discussed.