Nakatsuji Theorem, Nooijen Conjecture, and Constrained Coupled-Cluster Theory

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Abstract

The Fock space Hamiltonian H for an n-electron system in a finite one-electron basis of dimension m is characterized by $d = O(m^4)$ matrix elements. The eigenstates of this Hamiltonian, i.e. the full-CI states Ψ depend, however, on the usually much larger set of $N = O(m^n)$ parameters. Starting from a theorem by Nakatsuji, according to which it is sufficient for a full-CI wave function to satisfy a d-dimensional set of 'contracted Schrödinger equations', Nooijen has proposed a d-dimensional parametrization of a full-CI state in terms of the so-called CCGSD (coupled-cluster with generalized single and double substitutions) ansatz. This ansatz, which has found a controversial echo, cannot be exact, if one requires that the parameters in this ansatz are finite. A key feature is that the d-dimensional basis of Fock space operators does not span a Lie algebra. An analysis of the GCCSD ansatz, including its reformulation to intermediate normalization, and its perturbative analysis, opens the possibility to consider a simplified 'constrained' coupled-cluster ansatz, especially to express cluster operators of rank 3 and higher in terms of d parameters only.

W. Kutzelnigg and D. Mukherjee, *Minimal parametrization of an n-electron state* Phys. Rev. A 71, 022502 (2005), and papers quoted there.