

## ELECTRONIC STRUCTURE CALCULATIONS WITH GRAPHICALLY CONTRACTED FUNCTIONS

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### ABSTRACT

The computation of spectroscopic constants and property surfaces of molecules requires the accurate description of global potential energy surfaces. While traditional full configuration interaction (FCI) yields the exact solution of the molecular Schrödinger equation within a given basis set, the computational cost of solving the FCI equations scales exponentially with system size. In this work, we describe a method that is based on the Graphical Unitary Group Approach (1) and has the potential to overcome the limitations imposed by the exponential scaling of the FCI wave function. Within this formalism the wave function is expressed as a linear combination of graphically contracted functions (GCF), each of which is a multiconfigurational function that depends on a relatively small number of variational parameters (2-4). As will be discussed, this representation of the wave function has several favorable properties: (i) energies and density matrices may be computed very efficiently, (ii) because each GCF is an eigenfunction of the total spin operator, the wave function does not suffer from spin contamination, (iii) there is no size-consistency error due to excitation level limitations, and (iv) the solution does not depend on a reference wave function. It will be shown that the method yields accurate potential energy surfaces with a relatively small number of GCFs, and that coupling of orbital rotations with the optimization of the variational parameters may further improve the accuracy of computed energies.

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### REFERENCES

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