Perspective
Volume 16:8, 2022

Journal of Generalized Lie Theory and Applications

ISSN: 1736-4337 Open Access

Universal Interpretation of Self-Consistent Arena Elucidation Space Using Basin Hopping

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Introduction

For the continued development and application of computational approaches that use selfconsistent field solutions as reference wavefunctions, reliable global elucidation of (subsets of) selfconsistent field solutions is required. We present the development and implementation of a stochastic approach for performing global elucidation of self-consistent field solutions by leveraging the relationship between global optimization and global elucidation problems. We discuss the algorithm's design, which involves combining basin-hopping search algorithms with a Lie algebraic approach to linearize self-consistent field solution space while preserving desired spin-symmetry properties of the wavefunction. Due to its use as a model system for global self-consistent field solution exploration algorithms, the algorithm's performance is demonstrated on a minimal basis C2v H4 [1].

Nonlinear self-consistent field (SCF) methods, such as HartreeFock (HF) and density functional theory (DFT), are among the most powerful tools for calculating electronic structure. The factorial complexity of determining the wavefunction is reduced to quartic scaling by treating electronelectron interactions in the mean-field limit, while subsequent developments have enabled linear scaling to be realised under advantageous conditions. Although HF and DFT provide a valid description of the electronic structure of the ground state around most molecules' equilibrium geometries, the single-reference construction is prone to variational collapse and is unable to account for strong correlation caused by near degeneracies in electron configurations. As a result, SCF approaches have not been widely used in studies of electronic excited states.

Instead, a number of methods have been developed that are based on the explicit construction of the multireference wavefunction as well as response-based methods. However, if the problem of variational collapse can be solved, mean-field descriptions of excited states can frequently provide a reasonable description of electronic structure or serve as a foundation for subsequent post-HF treatments. The goal of this work is to create a method for identifying the subset of low-energy SCF solutions that typically best represent or correlate most strongly with the chemically most relevant ground and lowlying excited electronic states, as well as to create a method for targeting SCF solution subspaces that can be used in a "divide and conquer" exploration of the global SCF solution space [2].

To realise simulation methods based on a meanfield description of electronic excited states, variational collapse in the SCF optimization that results from lowest energy orbital occupation in the Aufbau scheme must be avoided. As a result, there has been a surge in interest in the development of optimization techniques that overcome SCF's bias toward the lowest energy solution of a given symmetry irreducible representation. The maximum overlap method (MOM) developed by Gill and colleagues determines the set of occupied orbitals at each iteration of the SCF procedure as those with the greatest overlap with the previous iteration's set of occupied orbitals [3].

Because of the nonlinearity of the SCF equations, there is no analytical method for determining the number or existence of SCF solutions, though limits for the number of solutions can be obtained. Nonetheless, there are several approaches to attempting to elucidate the set of SCF solutions. Thom and HeadGordon's metadynamics-inspired approach employs a modified Fock matrix with a biassing function to steer the SCF optimizer away from previously identified solutions and explore SCF solution space deterministically. The homotopic relationship between an initial set of arbitrary polynomials and the construction of the HF equations was exploited by Kowalski and Jankowski via parameterization of the density matrix [4].

Discussion

To demonstrate the utility of basin hopping in exploring the SCF solution space, we present three applications of the proposed algorithm in this section. First, we investigate H4 to see how the parameters (magnitude of perturbation vector, maximum number of iterations, and temperature) affect the types of solutions found, the number of solutions found, and the efficiency with which those solutions are found.

We describe the first application of stochastic approaches to global elucidation of SCF solutions in this paper. The SCF solution space is described using a Lie algebraic approach combined with an exponential map, which linearizes the vector space and thus provides a path for search algorithm implementation. 34 Because local minimizations can identify solution sets in the simulation, a basin-hopping algorithm is used. We will first summarise the Lie algebraic framework and the basin hopping algorithm before delving into technical aspects of the basin hopping algorithm's implementation as applied to the electronic structure problem. Following that, we will investigate the effect of parameter selection on algorithm performance and demonstrate the approach's utility on chemical systems [5].

Conclusion

The number of SCF solutions identified is reduced by an order of magnitude when the core orbitals are excluded (note the logarithmic scale on the y axis). However, comparing the number of solutions less than 10 eV higher in energy from the lowest energy SCF solution revealed that removing core orbital rotations from the perturbation vector significantly improved the basin hopping simulation's ability to find lower energy solutions, which are generally more relevant to chemical problems. In fact, the average relative energy of SCF solutions with and without core orbitals differed by over 1700 eV, indicating that most of the SCF solutions identified will involve core orbital excitations if valence occupied orbitals are not selected.

Acknowledgement

None.

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Received: 01 August, 2022, Manuscript No: glta-22-83719; **Editor Assigned:** 03 August, 2022, PreQC No: P-83719; **Reviewed:** 15 August, 2022, QC No: Q-83719; **Revised:** 20 August, 2022, Manuscript No: R-83719; **Published:** 27 August, 2022, DOI: 10.37421/1736-4337.2022.16.361

Conflict of Interest

There are no conflicts of interest by author.

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How to cite this article: Alice, Jessica. "Universal Interpretation of Self-Consistent Arena Elucidation Space Using Basin Hopping." J Generalized Lie Theory App 16 (2022): 361.