Hartree-Fock Stability Theory and its Relation to Correlation Theories

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I. BACKGROUND INFORMATION AND ACCOMPLISHMENTS

A. Hartree-Fock Stability

Hartree-Fock (HF) Theory has been the foundation for *ab initio* electronic structure theory throughout its history. An often overlooked aspect of the theory is that there are many solutions to the HF equations for a given system, but being a solution to the Hartree-Fock equation ensures only that the solution is stationary with respect to the determined orbitals. If the solution is indeed a minimum, it is called "stable", while if there is any displacement in the electronic structure which reduces the energy, the solution is "unstable". A method for determining the stability of a Hartree-Fock solution was proposed by Thouless in 1960[1]. The condition was rederived into the expression familiar to quantum chemists by Cizek and Paldus in 1967[2]. Furthermore, the stability equations factorize depending on the symmetry of the Hartree-Fock eigenfunctions. To this end, Seeger and Pople outlined a hierarchical approach to systematically evaluate the stability of HF states in the restricted, unrestricted and generalized Hartree-Fock procedures[3]. Recently, the method has been used to aid the in search for the lowest energy Unrestricted Hartree-Fock (UHF) solutions in molecules, as well as the General Hartree-Fock (GHF) solutions in geometrically frustrated hydrogen rings which cannot conform even to the UHF scheme [4][5].

The usual method of determining stability of a Hartree-Fock solution is to look for a negative eigenvalue the Electronic Hessian,

$$\mathbf{H} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}, \tag{1}$$

where the matrices $\mathbf{A}$ and $\mathbf{B}$ have dimension $N_{occupied} \times N_{virtual}$ with elements given by

$$A_{i\to a, j\to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib\rangle\,, \tag{2}$$

$$B_{i\to a, j\to b} = \langle ab||ij\rangle\,. \tag{3}$$

If $\mathbf{H}$ has a negative eigenvalue, this indicates an instability. For a paramagnetic HF solution, the equations factorize into the matrices known to chemists as the singlet and triplet instability matrices [6][3],

$$^{1}A'_{i\to a,j\to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + 2\langle aj|ib\rangle - \langle aj|bi\rangle \tag{4a}$$

$$^{3}A'_{i\to a,j\to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - \langle aj|bi\rangle \tag{4b}$$

$$^{1}B'_{i\to a,j\to b} = 2\langle ab|ij\rangle - \langle ab|ji\rangle \tag{4c}$$

$$^{3}B'_{i\to a,j\to b} = -\langle ab|ji\rangle \tag{4d}$$

where the $1,3$ denote singlet and triplet instabilities, respectively. The lowest eigenvalue of both of these matrices will reveal the stability of the RHF solution. If they are both positive, the solution is stable with respect to symmetry breaking, while negative eigenvalues in either indicate instability with respect to either triplet or singlet perturbations (or both). An eigenvalue of 0 does not indicate instability, and this case is discussed in detail by Cui et al [7].

B. Hartee-Fock Stability of the Homogeneous Electron Gas

The Homogeneous Electron Gas (HEG) model of metallic systems is a convenient starting point for this study. The Energies of various phases thereof have been computed to great accuracy [8], while plane wave solutions to the Hartree-Fock equations can be demonstrated analytically [9]. Furthermore, within the Hartree-Fock approximation, it has been known for half a century that broken symmetry solutions are always lower in energy compared to their paramagnetic counterparts [10]. More recently, phase diagrams have been determined for the HEG in 2 and 3 dimensions[11][12][13]. In all cases the phase diagrams are made by computing the energies of the polarized and unpolarized states, and comparing them. This approach necessitates that the form of the solutions is known ahead of time.

The present work focuses on directly calculating the Hartree-Fock stability of the paramagnetic homogeneous electron gas as a function of electron density. In this way it is possible to map out where the symmetry broken Hartree-Fock reference is needed.

C. Method

Starting with the Jellium Hamiltonian in atomic units,

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2} + \frac{1}{2}\sum_{i<j}\frac{1}{|\vec{r}_i - \vec{r}_j|}, \tag{5}$$

one solution to the Hartree-Fock equations in D dimensions are plane waves of the form

$$\phi_{\vec{k}} = \frac{1}{\sqrt{L^D}} e^{i\vec{k}\vec{x}}, \tag{6}$$

where L is the length of one side of the direct lattice with cubic symmetry. Using this as the basis for the rest of the analysis, the two electron repulsion integrals are analytic and well-behaved in two and three dimensions [11][14]

$$\langle \vec{k}, \vec{k}' | \vec{k}'', \vec{k}''' \rangle \overset{\text{2D, 3D}}{=} \begin{cases} \frac{\pi}{\Omega} \frac{2^{D-1}}{|\vec{k}-\vec{k}''|^{D-1}} & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' + n\vec{G} \textbf{ and } |\vec{k} - \vec{k}''| \neq 0 \\ 0 & \text{else} \end{cases} \tag{7}$$

where Ω is the direct lattice volume and $n\vec{G}$ is any integer times a reciprocal lattice vector of the system. The orbital energies are

$$\epsilon_{\vec{k},\sigma} = \frac{\hbar^2 \vec{k}^2}{2m} - \sum_{\vec{k}}^{|\vec{k}|<k_f} n_{\vec{k}\sigma} \langle \vec{k}, \vec{k}' | \vec{k}', \vec{k} \rangle \,, \tag{8}$$

where $n_{\vec{k}\sigma}$ is the occupation number of the state with momentum $\vec{k}$ and spin σ [14].

D. Results

Using the equations for energies and two electron integrals, the stability analysis was performed on the paramagnetic HEG model as a function of electron density (or equivalently, r_s). The naive approach of explicitly constructing and diagonalizing the orbital hessian is intractable both in terms of memory and calculation time requirements. Since the instability condition is that the any eigenvalue is negative, it suffices to calculate the sign of only the lowest eigenvalue. This is a task well suited for an iterative subspace solver. To this end a parallel version of the Jacobi-Davidson algorithm was implemented by representing the matrix as a matrix-vector product (made possible by the SLEPc library[15]). This allowed for two necessary optimizations. First, the algorithmic change from full diagonalization to a subspace algorithm reduces the memory requirements from $O(N^2)$ to $O(N)$ and the computational scaling from $O(N^3)$ to $O(N^2)$. Secondly, the parallelization of the algorithm allows the program to be run on the Blue Waters supercomputer with about 80% strong parallel scaling efficiency.

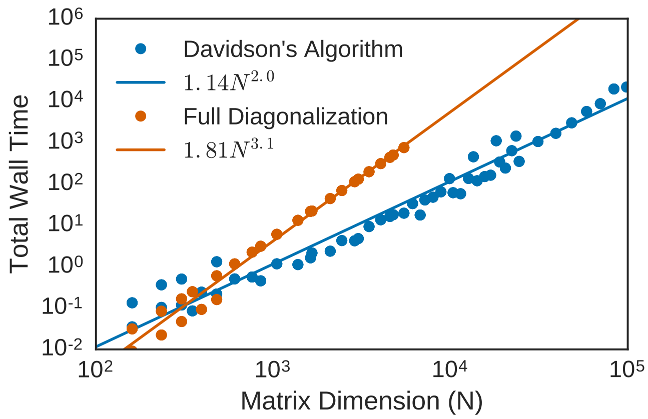

FIG. 1: The asymptotic scaling of both algorithms behaves as expected.

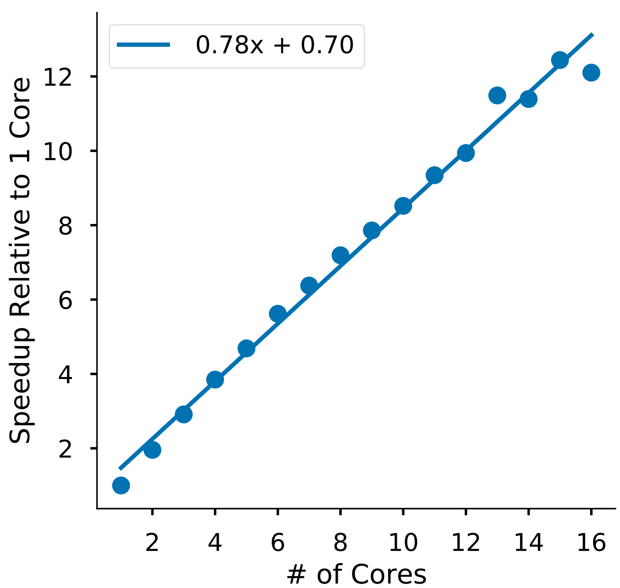

FIG. 2: The speedup of the entire calculation as the number of computer cores is sufficiently linear.

These optimizations allow the calculation to be performed with enough grid points to

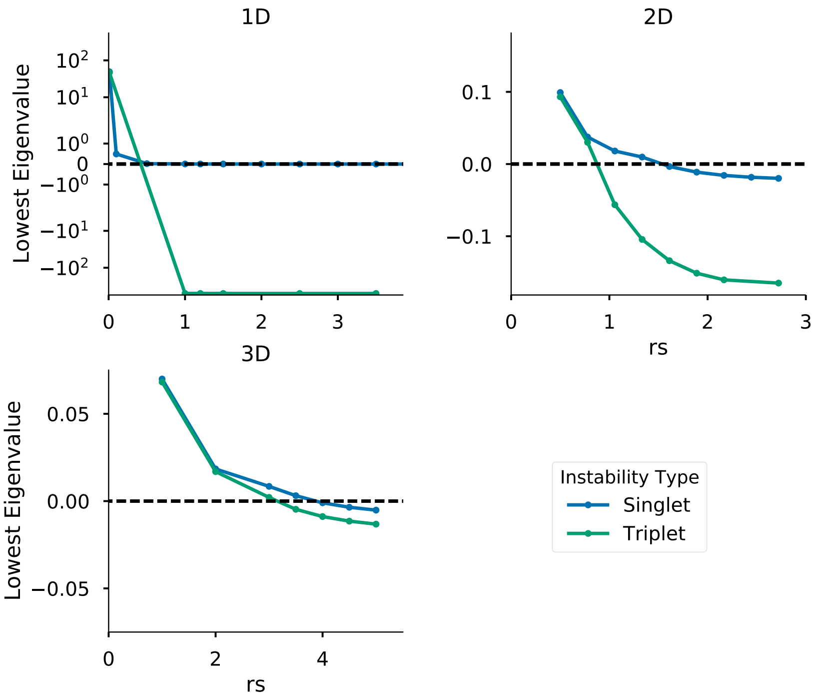

FIG. 3: The Lowest eigenvalues of the triplet and singlet instability matrices in 1, 2 and 3 dimensions.

In each case, there is a clear density at which the triplet instability appears, and persists beyond. Tracking this quantity as a function of number of grid points in the calculation reveals that this "transition r_s" occurs at $r_s = 1$ in 2D and $r_s = 3$ in 3D. These results are consistent with those seen by other methods. [16][12]

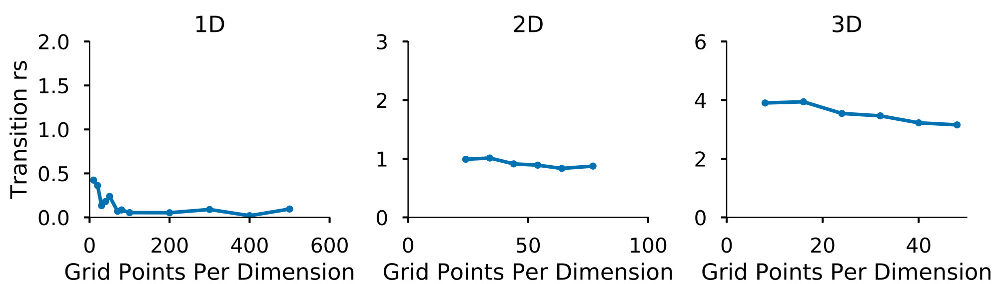

FIG. 4: The Lowest eigenvalues of the triplet and singlet instability matrices in 1, 2 and 3 dimensions.

II. GOALS AND RELEVANCE OF PROPOSED RESEARCH

The goal of electronic structure theory is to solve the electronic Schrödinger equation for a molecule or solid state system. The prevailing approach in *ab initio* quantum chemistry is to first compute a self-consistent single-determinant Hartree-Fock (HF) solution which will serve as a reference for many-body perturbative (MP) or coupled-cluster (CC) approaches. Implicit in these methods is the assumption that the reference wave function will be sufficiently close to the exact solution of the Schrödinger equation to converge to the correct answer in a computationally feasible manner. Both the MP and CC approaches have the attractive quality that they are systematically improvable, i.e. more computational power can be used on a problem to increase the accuracy of the resulting solution. These so-called post-Hartree-Fock methods are able to recover more of the total electronic energy by accounting for the *correlation energy* in the system. Traditionally, the correlation energy is defined by the difference between the exact energy and the Hartree-Fock energy [17]

$$E_{corr} = E_{exact} - E_{HF} \tag{9}$$

In many cases the correlation energy is relatively small and the Hartree-Fock reference captures a significant portion of the exact total energy. In such cases, the prevailing approach is usually successful and has only implementation issues for larger systems. On the other hand there are systems which are not well treated by this approach, which are often called "strongly correlated". Examples of such systems are those with degenerate or near-degenerate HOMO-LUMO gaps, metallic solids or molecules close to breaking bonds. Oftentimes for such systems the traditional Hartree-Fock solutions are not even qualitatively correct, implying inadequacies in either the single-reference or mean-field approach.

It is often neglected, however, that the usual way for computing a Hartree-Fock solution in practice is to use a restricted form of the single determinantal wavefunction. In the Restricted Hartree-Fock (RHF), the wave function is restricted to be an eigenfunction of the $\hat{S}^2$ and $\hat{S}_z$ operators, while in the Unrestricted variant (UHF), the wave function need only be an eigenfunction of the $\hat{S}_z$. There is yet another lesser-known variation of the theory, known as General Hartree-Fock (GHF), which assumes no spin-symmetries in the wave function. This allows for greater variational flexibility at the cost of "broken symmetry". Together these three levels of Hartree-Fock theory form a heirarchy of increasing parameter space within which to minimize the total energy. Thus the term "Hartree-Fock Energy" is inherently ambigious; this fact calling into question commonly held ideas about correlation and Hartree-Fock theory. Take for example the dissociation curve of H_2 in the RHF and UHF approximations, compared with the exact solution obtained by full configuration-interaction in the complete basis set limit.

H2 curve pic

The correlation energy for the RHF reference case is dramatically larger than that for the UHF reference. In other words, *the correlation energy is, by definition, inherently coupled to the Hartree-Fock reference.* The given example is well understood, but it brings to mind a more general idea that there may be more cases where apparently large correlation energies are due to simply using and inadequate level of Hartree-Fock theory. Scuseria and coworkers have leveraged this idea to create new coupled cluster theories while preserving the symmetry of the reference [18]. While the exact wave function of will have the same symmetry as the exact Hamiltonian, it is important to remember that the Hartree-Fock Hamiltonian is not exact, and we may have something to gain by taking the variational principal at face value; lower energy is always better. For certain observables this is not the case, but for energies alone we are free to maintain this mindset. Therefore the overarching theme of the proposed work is that *many examples of strong correlation may be illusory, and in order to find out we have to find lower energy Hartree-Fock solutions, even at the cost of broken symmetry.*

III. REFERENCES

[1] D. Thouless, Nuclear Physics **21**, 225 (1960), ISSN 00295582, URL `http://linkinghub.elsevier.com/retrieve/pii/0029558260900481`.

[2] J. Cizek and J. Paldus, The Journal of Chemical Physics **47**, 3976 (1967), ISSN 00219606, URL `http://scitation.aip.org/content/aip/journal/jcp/47/10/10.1063/1.1701562`.

[3] R. Seeger and J. A. Pople, The Journal of Chemical Physics **66**, 3045 (1977), ISSN 00219606, URL `http://scitation.aip.org/content/aip/journal/jcp/66/7/10.1063/1.434318`.

[4] P. Pulay and Z. Tótha, Preprint **164102**, 1 (2016), ISSN 0021-9606, URL `http://dx.doi.org/10.1063/1.4964903`.

[5] J. J. Goings, F. Ding, M. J. Frisch, and X. Li, The Journal of Chemical Physics **142**, 154109 (2015), ISSN 0021-9606, URL `http://dx.doi.org/10.1063/1.4918561http://scitation.aip.org/content/aip/journal/jcp/142/15/10.1063/1.4918561`.

[6] T. H. Dunning, The Journal of Chemical Physics **47**, 1735 (1967), ISSN 00219606, URL `http://scitation.aip.org/content/aip/journal/jcp/47/5/10.1063/1.1712158`.

[7] Y. Cui, I. W. Bulik, C. A. Jimenez-Hoyos, T. M. Henderson, and G. E. Scuseria, The Journal of Chemical Physics **139**, 154107 (2013), ISSN 00219606, arXiv:1310.0942v1, URL `http://scitation.aip.org/content/aip/journal/jcp/139/15/`

10.1063/1.4824905.

[8] D. M. Ceperley and B. J. Alder, Physical Review Letters **45**, 566 (1980), ISSN 0031-9007, URL http://link.aps.org/doi/10.1103/PhysRevLett.45.566.

[9] P. Phillips, *Advanced Solid State Physics* (Cambridge University Press, Cambridge, 2012), 2nd ed., ISBN 978-0-521-19490-7.

[10] A. W. Overhauser, Physical Review **128**, 1437 (1962), ISSN 0031-899X, URL http://link.aps.org/doi/10.1103/PhysRev.128.1437.

[11] F. Delyon, M. Duneau, B. Bernu, and M. Holzmann, pp. 1–12 (2008), 0807.0770, URL http://arxiv.org/abs/0807.0770.

[12] B. Bernu, F. Delyon, M. Holzmann, and L. Baguet, Physical Review B **84**, 115115 (2011), ISSN 1098-0121, URL http://link.aps.org/doi/10.1103/PhysRevB.84.115115.

[13] L. Baguet, F. Delyon, B. Bernu, and M. Holzmann, Physical Review Letters **111**, 166402 (2013), ISSN 0031-9007, URL http://link.aps.org/doi/10.1103/PhysRevLett.111.166402.

[14] G. Guiliani and G. Vignale, *Quantum Theory of the Electron Liquid* (Cambridge University Press, Cambridge, 2005), ISBN 978-0-521-82112-6.

[15] V. Hernandez, J. E. Roman, and V. Vidal, ACM Transactions on Mathematical Software **31**, 351 (2005), ISSN 00983500, URL http://portal.acm.org/citation.cfm?doid=1089014.1089019.

[16] L. Baguet, F. Delyon, B. Bernu, and M. Holzmann, Physical Review B **90**, 165131 (2014), ISSN 1098-0121, arXiv:1404.7652v1, URL http://link.aps.org/doi/10.1103/PhysRevB.90.165131.

[17] I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics* (Cambridge University Press, 2009), ISBN 978-0-521-81832-2.

[18] J. A. Gomez, T. M. Henderson, and G. E. Scuseria, The Journal of Chemical Physics **144**, 244117 (2016), ISSN 0021-9606, URL http://scitation.aip.org/content/aip/journal/jcp/144/24/10.1063/1.4954891.