Numerical Determination of the Hartree-Fock Stability of the Paramagnetic Electron Gas in 1, 2 and 3 Dimensions

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Abstract

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I. INTRODUCTION

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. increasing the accuracy of the resulting solution can be done by using a higher order of the theory. 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 [1]

$$E_{corr} = E_{exact} - E_{HF}. \tag{1}$$

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.

Previously it has been shown for finite systems with form-degenerate HOMO-LUMO, there always exists a symmetry-breaking instability[10]. Whether this theorem holds in the infinite case remains to be seen. To investigate HF instabilities in zero band gap solids, a natural starting point is the Homogeneous Electron Gas (HEG, often called Jellium or Uniform Electron Gas) model. The model consists of electrons in a box with periodic boundary conditions and the constraint that the entire system is charge-neutral via a uniform background positive charge. The resulting Coulomb interactions cancel exactly, and the only remaining terms are due to kinetic and exchange energies. Historically it was thought that the plane-wave paramagnetic solution to the HF equations for this model was the "correct" solution. However, in a landmark paper, Overhauser showed that certain symmetry broken solutions *always* have lower-energy than the paramagnetic solutions at all electron densities[11]. This hints at, but does not show, that the analogous triplet instability theorem persists in the infinite case.

Overhausers' paper sparked new interest in the HEG, and since then Energies of various phases thereof have been computed to great accuracy[12]. More recently, phase diagrams have been determined for the HEG in 2 and 3 dimensions[13–15]. 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. The motivation is two-fold. First, the numerical studies of this model can give computational evidence for or against the ubiquity of symmetry-breaking HF instabilities in metallic solids. Secondly, the instabilities can help in determining lower energy HF solutions of the HEG. This is because the study will reveal where the symmetry broken Hartree-Fock reference is needed. To date, an optimal form (i.e. minimal energy in the HF manifold) of the Hartree-Fock solution to the HEG remains unknown, even though exact energy (including correlation) is essentially known. Therefore determining a lower energy HF solution can yield insight into the effects of correlation of this fundamental physical model.

II. METHOD

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 lowers the energy, the solution is "unstable". A method for determining the stability of a Hartree-Fock solution was proposed by Thouless in 1960[3]. The condition was rederived into the expression familiar to quantum chemists by Cizek and Paldus in 1967[4]. 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[5]. Recently, the method has been used to aid the 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[6, 7]. The lower energy HF solutions in these studies were located by first finding the instabilities in the higher spin-symmetry solutions, then using this information to obtain "symmetry breaking" displacements that lower the energy.

To determine if there is indeed a symmetry-broken HF solution of lower energy, the usual method is to determine the stability of a found Hartree-Fock solution. Instabilities are indicated by a negative eigenvalue the Electronic Hessian,

$$\mathbf{H} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}, \tag{2}$$

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

$$A_{i\to a, j\to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib\rangle \,, \tag{3}$$

$$B_{i\to a, j\to b} = \langle ab||ij\rangle \,. \tag{4}$$

For a paramagnetic HF solution (RHF), the Orbital Hessian factorizes into the matrices known to chemists as the singlet and triplet instability matrices ($^{\mathbf{1}}\mathbf{H}$ and $^{\mathbf{3}}\mathbf{H}$, respectively)[5,

8].

$$^{1}A'_{i\to a,j\to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + 2\langle aj|ib\rangle - \langle aj|bi\rangle \tag{5a}$$

$$^{3}A'_{i\to a,j\to b} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} - \langle aj|bi\rangle \tag{5b}$$

$$^{1}B'_{i\to a,j\to b} = 2\langle ab|ij\rangle - \langle ab|ji\rangle \tag{5c}$$

$$^{3}B'_{i\to a,j\to b} = -\langle ab|ji\rangle \tag{5d}$$

The lowest eigenvalue of both of these matrices will reveal the stability of the RHF solution. If $^{1}\mathbf{H}$ has negative eigenvalues, the solution is unstable with respect to changes that preserve singlet character (singlet instability), while if $^{3}\mathbf{H}$ has negative eigenvalues, the solution is unstable towards displacements that would change the wavefunction towards a triplet state (triplet instability). The solution is stable if neither $^{1}\mathbf{H}$ nor $^{3}\mathbf{H}$ has a negative eigenvalue. An eigenvalue of 0 does not indicate instability, and this case is discussed in detail by Cui et al [9].

A. Method

Starting with the Jellium Hamiltonian in atomic units,

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2} + \frac{1}{2}\sum_{i<j}\frac{1}{|\vec{r}_i - \vec{r}_j|}, \tag{6}$$

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

$$\phi_{\vec{k}} = \frac{1}{\sqrt{L^D}} e^{i\vec{k}\vec{x}}, \tag{7}$$

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[13, 16]

$$\langle \vec{k}, \vec{k}'|\vec{k}'', \vec{k}'''\rangle \overset{\text{2D, 3D}}{=} \begin{cases} \frac{\pi}{L^D}\frac{2^{D-1}}{|\vec{k}-\vec{k}''|^{D-1}} & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' + n\vec{G} \textbf{ and } |\vec{k} - \vec{k}''| \neq 0 \\ 0 & \text{else,} \end{cases} \tag{8}$$

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

$$\epsilon_{\vec{k},\sigma} = \frac{\hbar^2\vec{k}^2}{2m} - \sum_{\vec{k}}^{|\vec{k}|<k_f} n_{\vec{k}\sigma}\langle \vec{k}, \vec{k}'|\vec{k}', \vec{k}\rangle, \tag{9}$$

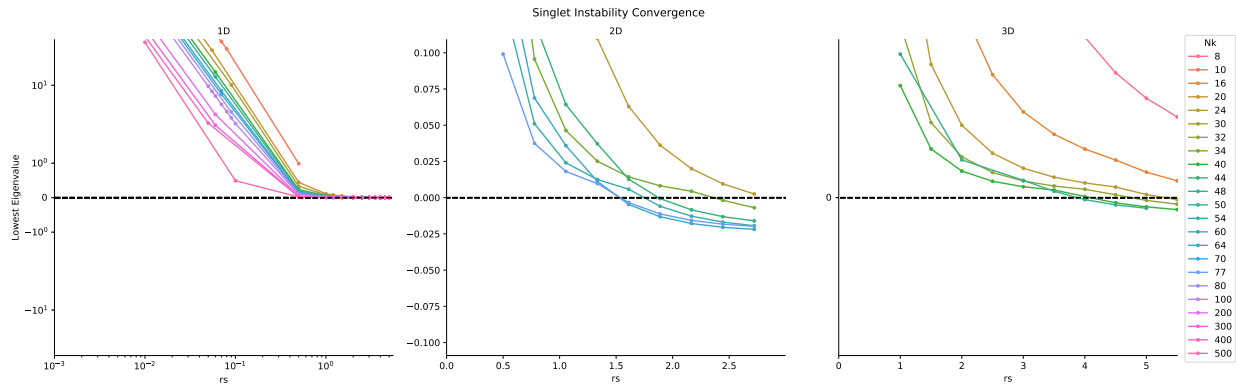

FIG. 1: The lowest eigenvalue of $^1\mathbf{H}$ as a function of r_s with increasing number of k-points in 1, 2 and 3 dimensions.

where $n_{\vec{k}\sigma}$ is the occupation number of the state with momentum $\vec{k}$ and spin σ [16]. In one dimension, the two electron integral diverges, and it is common to use a delta function interaction,

$$V(r_{12}) = V_0 \delta(r_{12}), \tag{10}$$

and the two electron integral in this case is simply

$$\langle \vec{k}, \vec{k}' | \vec{k}'', \vec{k}''' \rangle \overset{\text{1D}}{=} \begin{cases} V_0 & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' + n\vec{G} \\ 0 & \text{else.} \end{cases} \tag{11}$$

B. 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, the Wigner-Seitz radius, r_s). The 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, the Jacobi-Davidson algorithm was from the SLEPc library was used to calculated the lowest eigenvalues[17].

To determine the r_s at which the lowest eigenvalue of $\mathbf{H}$ changes sign, the lowest eigenvalues were linearly interpolated (this can easily be changed to one of [(linear, nearest, zero,

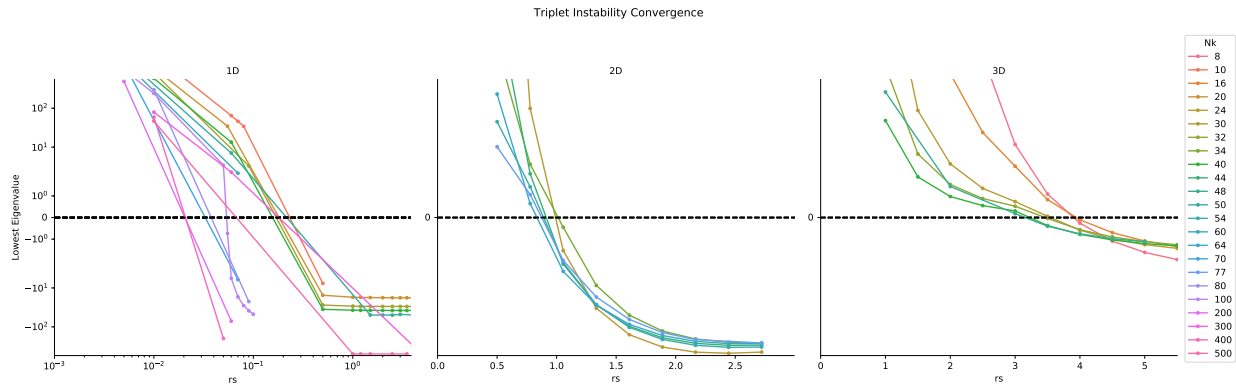

FIG. 2: The lowest eigenvalue of $^3\mathbf{H}$ as a function of r_s with increasing number of k-points in 1, 2 and 3 dimensions.

slinear, quadratic, cubic where zero, slinear, quadratic and cubic refer to a spline interpolation of zeroth, first, second or third order)] as a function of r_s and solving

$$\lambda_{min}(r_s) = 0. \tag{12}$$

The solution to eq. 12 is referred to as the transition r_s and this quantity was determined while increasing the number of k-points in the simulation to convergence (see Fig. 3).

D	Transition r_s
1	0.09
2	0.87
3	3.16

The transition r_s occurs at $r_s = 1$ in 2D and $r_s = 3$ in 3D (See Fig. **??** and Fig. 3). These results are consistent with those seen by other methods[14, 18]. On the other hand, the transition r_s for one dimension tends towards zero and stays quite close as the number of grid points increases. Indeed, numerical issues appear at very high density (low r_s) due to divergence of the two electron integrals in the asymptotic limit. With this in mind, it is clear at least that the instability in the 1D case persists even at very high densities (potentially all finite densities), which is to be expected from Overhauser's proof of instability at all values of r_s in 1D for the delta function potential [11].

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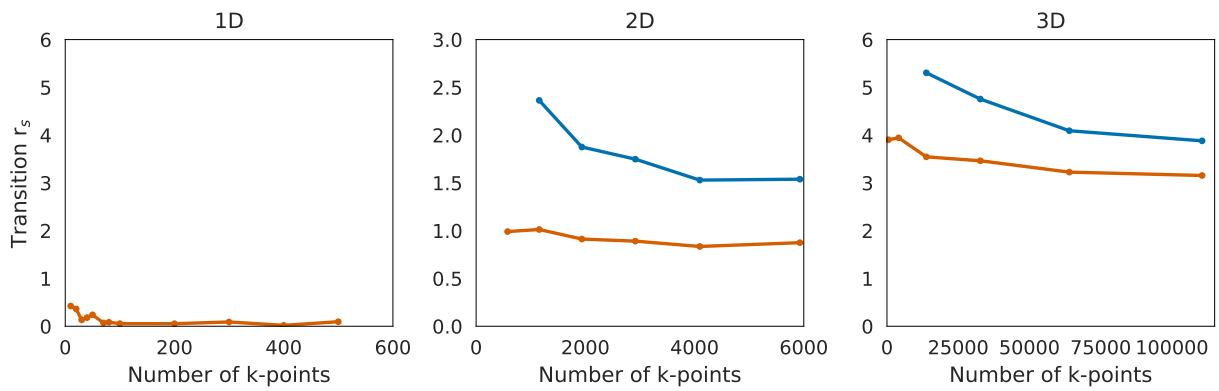

FIG. 3: The value of r_s at which the singlet (blue) and triplet (orange) instability occurs with increasing number of k-points in 1, 2 and 3 dimensions. In the 1D case (left), the singlet instability never appeared in the calculations performed.

III. REFERENCES

[1] I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics* (Cambridge University Press, 2009).

[2] J. A. Gomez, T. M. Henderson, and G. E. Scuseria, The Journal of Chemical Physics **144**, 244117 (2016).

[3] D. Thouless, Nuclear Physics **21**, 225 (1960).

[4] J. Cizek and J. Paldus, The Journal of Chemical Physics **47**, 3976 (1967).

[5] R. Seeger and J. A. Pople, The Journal of Chemical Physics **66**, 3045 (1977).

[6] P. Pulay and Z. Tótha, Preprint **164102**, 1 (2016).

[7] J. J. Goings, F. Ding, M. J. Frisch, and X. Li, The Journal of Chemical Physics **142**, 154109 (2015).

[8] T. H. Dunning, The Journal of Chemical Physics **47**, 1735 (1967).

[9] Y. Cui, I. W. Bulik, C. A. Jimenez-Hoyos, T. M. Henderson, and G. E. Scuseria, The Journal of Chemical Physics **139**, 154107 (2013), arXiv:arXiv:1310.0942v1.

[10] T. Yamada and S. Hirata, The Journal of Chemical Physics **143**, 114112 (2015).

[11] A. W. Overhauser, Physical Review **128**, 1437 (1962).

[12] D. M. Ceperley and B. J. Alder, Physical Review Letters **45**, 566 (1980).

[13] F. Delyon, M. Duneau, B. Bernu, and M. Holzmann, , 1 (2008), arXiv:0807.0770.

[14] B. Bernu, F. Delyon, M. Holzmann, and L. Baguet, Physical Review B **84**, 115115 (2011).

[15] L. Baguet, F. Delyon, B. Bernu, and M. Holzmann, Physical Review Letters **111**, 166402 (2013).

[16] G. Guiliani and G. Vignale, *Quantum Theory of the Electron Liquid* (Cambridge University Press, Cambridge, 2005).

[17] V. Hernandez, J. E. Roman, and V. Vidal, ACM Transactions on Mathematical Software **31**, 351 (2005).

[18] L. Baguet, F. Delyon, B. Bernu, and M. Holzmann, Physical Review B **90**, 165131 (2014), arXiv:arXiv:1404.7652v1.