Hartree-Fock Stability Analysis of the Paramagnetic Homogeneous Electron Gas in 1, 2 and 3 Dimensions.

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I. ABSTRACT

II. INTRODUCTION

III. METHODS

We consider the paramagnetic state of the Homogeneous Electron Gas (HEG) in a D-dimensional box of length L. All states below the fermi wave vector, k_f are doubly occupied, and all above are virtual. According to Guiliani and Vignale[1], k_f is given by equation 1 for 1, 2 and 3 dimensions.

$$k_f = \begin{cases} (3\pi^2 n)^{\frac{1}{3}} = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s a_0} & 3D \\ (2\pi n)^{\frac{1}{2}} = \frac{\sqrt{2}}{r_s a_0} & 2D \\ \frac{\pi}{2} n = \frac{\pi}{4 r_s a_0} & 1D \end{cases} \tag{1}$$

The Hartree-Fock Hamiltonian is defined in the usual way for the HEG in that the positive background charge exactly cancels the electron-electron coulomb interaction. One solution of the Hartree-Fock equation is a set of plane waves,

$$\phi_k(\vec{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{D^N}}, \tag{2}$$

defined with periodic boundary conditions[2]. Do determine the stability of these RHF solutions, we use the method introduced by Thouless [3], and further chatagerized by Seeger and Pople [4]. The solutions of the Hartree-Fock equations are unstable when the Molecular Orbital Hessian,

$$\mathbf{H} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}, \tag{3}$$

has any strictly negative eigenvalues. An unstable HF solution is one that is a stationary solution to the HF equations, but has a negative second-order variation in the energy with respect to electronic oscillations. Thus, a solution being unstable is a sufficient condition for another solution of lower energy existing.

The square matrices $\mathbf{A}$ and $\mathbf{B}$ are defined in terms of the excitations of the system, and thus have the size of the number of possible excitations. Their elements are

$$\begin{aligned} A_{\mathbf{k}_i \to \mathbf{k}_a, \mathbf{k}_j \to \mathbf{k}_b} &= (\epsilon_{\mathbf{k}_a} - \epsilon_{\mathbf{k}_i})\delta_{\mathbf{k}_i \mathbf{k}_j}\delta_{\mathbf{k}_a \mathbf{k}_b} + \langle \mathbf{k}_a \mathbf{k}_j || \mathbf{k}_i \mathbf{k}_b \rangle \\ B_{\mathbf{k}_i \to \mathbf{k}_a, \mathbf{k}_j \to \mathbf{k}_b} &= \langle \mathbf{k}_a \mathbf{k}_b || \mathbf{k}_i \mathbf{k}_j \rangle , \end{aligned} \tag{4}$$

where $\epsilon_{\mathbf{k}_i}$ is the i'th eigenvalue of the one-electron Fock operator. The convention for the two electron integrals is,

$$\langle \mathbf{k}_p \mathbf{k}_q | \mathbf{k}_r \mathbf{k}_s \rangle = \int\int \phi^*_{\mathbf{k}_p}(\mathbf{x}_1)\phi^*_{\mathbf{k}_q}(\mathbf{x}_2)\frac{1}{r_{12}}\phi_{\mathbf{k}_r}(\mathbf{x}_1)\phi_{\mathbf{k}_s}(\mathbf{x}_2)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2, \tag{5}$$

$$\langle \mathbf{k}_p \mathbf{k}_q || \mathbf{k}_r \mathbf{k}_s \rangle = \langle \mathbf{k}_p \mathbf{k}_q | \mathbf{k}_r \mathbf{k}_s \rangle - \langle \mathbf{k}_p \mathbf{k}_q | \mathbf{k}_s \mathbf{k}_r \rangle \tag{6}$$

and the integration is over both Cartesian and spin coordinates. The analytic form of the two electron integral for the case of the HEG is given by

$$\langle \mathbf{k}_p \mathbf{k}_q || \mathbf{k}_r \mathbf{k}_s \rangle \overset{\text{2D, 3D}}{=} \begin{cases} \frac{\pi}{\Omega} \frac{2^{D-1}}{|\mathbf{k}_p - \mathbf{k}_r|^{D-1}} & \mathbf{k}_s + \mathbf{k}_r = \mathbf{k}_p + \mathbf{k}_q \text{ and } |\mathbf{k}_p - \mathbf{k}_r| \neq 0 \\ 0 & \text{else} \end{cases} \tag{7a}$$

$$\langle \mathbf{k}_p \mathbf{k}_q || \mathbf{k}_r \mathbf{k}_s \rangle \overset{\text{1D}}{=} \begin{cases} e^{|\mathbf{k}_p - \mathbf{k}_r|^2 a^2} \text{Ei}(-|\mathbf{k}_p - \mathbf{k}_r|^2 a^2) & \mathbf{k}_s + \mathbf{k}_r = \mathbf{k}_p + \mathbf{k}_q \text{ and } |\mathbf{k}_p - \mathbf{k}_r| \neq 0 \\ 0 & \text{else} \end{cases}, \tag{7b}$$

where Ω is the direct lattice volume. [5] [1]. Ei(x) denotes the exponential integral function and the parameter a in 1D is the radius of a cylinder that approximates a 1D system (For more details we refer the reader to reference [1]). The eigenenergies of the one particle Fock operator can be determined by evaluating

$$\epsilon_{\mathbf{k}_p} = \frac{\hbar^2 |\mathbf{k}_p|^2}{2m} - \sum_{\mathbf{k}_i}^{occ} n_{\mathbf{k}_i} \langle \mathbf{k}_p, \mathbf{k}_i | \mathbf{k}_i, \mathbf{k}_p \rangle \tag{8}$$

Where $n_{\mathbf{k}_i}$ is the occupation number of the state $\mathbf{k}_i$ and spin [1].

A program was implemented to calculate the stability of the HEG with a simple cubic lattice in 1, 2 and 3 dimensions. As we are only interested in the presence of any number of negative eigenvalues, it suffices to calculate the lowest eigenvalue and determine its sign. Due to the sparse and diagonally dominant nature of $\mathbf{H}$, this is a natural candidate for the Jacobi-Davidson Algorithm [6]. The algorithm was implented using the SLEPc package, an extension of the PETSc suite [7][8].

IV. DISCUSSION

V. CONCLUSION

VI. ACKNOWLEDGEMENTS

VII. REFERENCES

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