Hartree-Fock Stability of the Electron Gas

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Table of contents

Background Information

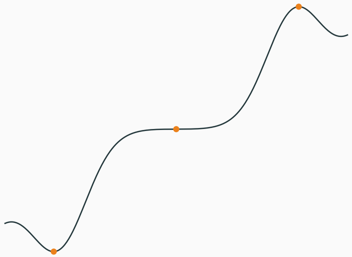
Levels of Hartree-Fock Theory

Method	Spinorbital	DoF	Eigenfunction of
Restricted	$\chi_j^{\alpha}(\vec{r},\sigma) = \sum_{i=1}^{N} c_{ij}\phi_i(\vec{r})\,\alpha(\sigma)$ $\chi_j^{\beta}(\vec{r},\sigma) = \sum_{i=1}^{N} c_{ij}\phi_i(\vec{r})\,\beta(\sigma)$	N/2	$\hat{S}^2$, $\hat{S}_z$
Unrestricted	$\chi_j^{\alpha}(\vec{r},\sigma) = \sum_{i=1}^{N} c_{ij}^{\alpha}\phi_i(\vec{r})\alpha(\sigma)$ $\chi_j^{\beta}(\vec{r},\sigma) = \sum_{i=1}^{N} c_{ij}^{\beta}\phi_i(\vec{r})\beta(\sigma)$	N	$\hat{S}_z$
General	$\chi_j(\vec{r},\sigma) = \sum_{i=1}^{N}[c_{ij}^{\alpha}\phi_i(\vec{r})\,\alpha(\sigma)$ $+c_{ij}^{\beta}\phi_i(\vec{r})\beta(\sigma)]$	2N	Neither

Seeger, R.; Pople, J. A. J. Chem. Phys. 1977, 66 (7), 3045.

Restricted Minimization

- Hartee-Fock SCF guarantees only stationary energy w.r.t. change in orbitals
- The solution may be a maximum, minimum or saddle point



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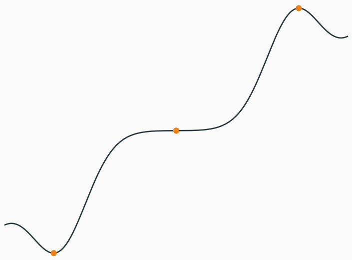
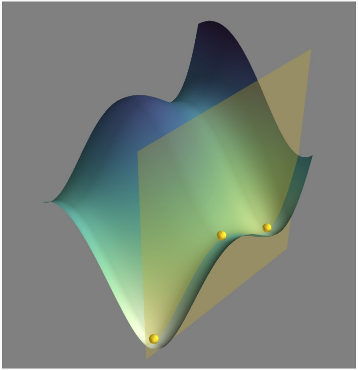
Within the Constrained Space



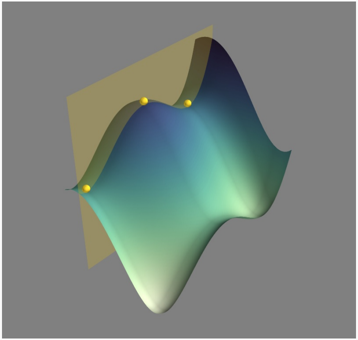
Restricted Minimization

- Restricted minima may correspond to minima in another dimension



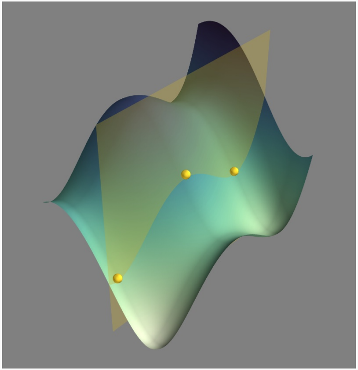
Restricted Minimization

- Restricted minima may correspond to minima in another dimension
- Restricted minima may correspond to maxima in another dimension



Restricted Minimization

- Restricted minima may correspond to minima in another dimension
- Restricted minima may correspond to maxima in another dimension
- Restricted minima may be nonstationary



Hartree-Fock Stability

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Thouless, D. J. The Quantum Mechanics of Many-Body Systems, 2nd ed.; Dover: 1972. (p. 114)

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- We need to know if this is indeed a minimum.
- We can determine this if we inspect the second order variation in the energy.
- Thouless[1] showed a physically motivated derivation using Time-Dependent Hartree-Fock theory (TDHF).

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- The RPA frequencies are imaginary when the Orbital Hessian (aka stability matrix, electronic Hessian) eigenvalues are negative

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \tag{1}$$

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- Where

$$\begin{aligned} A_{ia,jb} &= \langle {}_i^a | H - E_0 | {}_j^b \rangle = (\epsilon_a - \epsilon_i)\, \delta_{ij}\delta_{ab} + \langle aj || ib \rangle \\ B_{ia,jb} &= \langle {}_{ij}^{ab} | H - E_0 | 0 \rangle = \langle ab || ij \rangle \,. \end{aligned} \tag{2}$$

Seeger, R.; Pople, J. A. J. Chem. Phys. 1977, 66 (7), 3045.

Hartree-Fock Stability Conditions

The Matrix Equation Factorizes

Solution Type	Space Type					
	Real RHF	Complex RHF	Real UHF	Complex UHF	Real GHF	Complex GHF
Real RHF	$^1\mathbf{A}' + {}^1\mathbf{B}'$	$^1\mathbf{A}' - {}^1\mathbf{B}'$	$^3\mathbf{A}' + {}^3\mathbf{B}'$	$^3\mathbf{A}' - {}^3\mathbf{B}'$	$^3\mathbf{A}' + {}^3\mathbf{B}'$	$^3\mathbf{A}' - {}^3\mathbf{B}'$
Complex RHF	-	$^1\mathbf{H}'$	-	$^3\mathbf{H}'$	-	$^3\mathbf{H}'$
Real UHF	-	-	$\mathbf{A}' + \mathbf{B}'$	$\mathbf{A}' - \mathbf{B}'$	$\mathbf{A}'' + \mathbf{B}''$	$\mathbf{A}'' - \mathbf{B}''$
Complex UHF	-	-	-	$\mathbf{H}'$	-	$\mathbf{H}'$
Real GHF	-	-	-	-	$\mathbf{A} - \mathbf{B}$	$\mathbf{A} - \mathbf{B}$
Complex GHF	-	-	-	-	-	$\mathbf{H}$

Table reproduced from Seeger & Pople[1]

1) Seeger, R.; Pople, J. A. J. Chem. Phys. 1977, 66 (7), 3045.

Homogeneous Electron Gas

Brief Overview

- Homogeneous Electron Gas (HEG) model, also known as Uniform Electron Gas or Jellium Model.
- Electrons in a box with "smeared" nuclei $\rightarrow$ uniform positive background charge
- The total charge is constrained to be neutral,

$$V_{bg}(\mathbf{r}) = \sum_i \frac{-Ze^2}{|\mathbf{r} - \mathbf{R_i}|} \rightarrow -e^2 \int \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \tag{3}$$

- and the background and coulomb terms cancel exactly,

$$V_{ee} = e^2 \int \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \tag{4}$$

Phillips, P. Advanced Solid State Physics, 2nd ed.; Cambridge University Press: Cambridge, 2012.

Brief Overview

- The discretized solutions are given by,

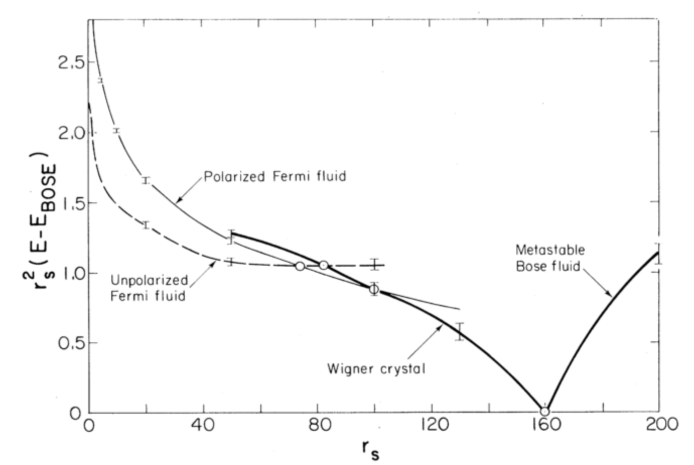
$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m} - \sum_{\vec{k}'}^{|\vec{k}'|<k_f} \langle \vec{k}, \vec{k}' | \vec{k}', \vec{k} \rangle \tag{5}$$

- Where the two electron integral is given by

$$\langle \vec{k}, \vec{k}' | \vec{k}'', \vec{k}''' \rangle \overset{\text{2D, 3D}}{=} \begin{cases} \frac{\pi}{V} \frac{2^{D-1}}{|\vec{k}-\vec{k}''|^{D-1}} & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' \\ 0 & \text{else} \end{cases}$$

$$\langle k, k' | k'', k''' \rangle \overset{\text{1D}}{=} \begin{cases} \frac{\pi}{V} e^{|k-k''|^2 a^2} \mathrm{Ei}(-|k-k''|^2 a^2) \; ; & k''' = k + k' - k'' \\ 0 \; ; & \text{else} \end{cases} \tag{6}$$

QMC Energies for various phases



Ceperley, D. M.; Alder, B. J. Phys. Rev. Lett. 1980, 45 (7), 566569.

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- It is known that the GHF solution persists at all densities for the HEG[1].

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- It is known that the GHF solution persists at all densities for the HEG[1].
- Can we show this numerically?
- (Future) Can we combine this with to improve the efficacy of correlation theories (CC, MBPT)?

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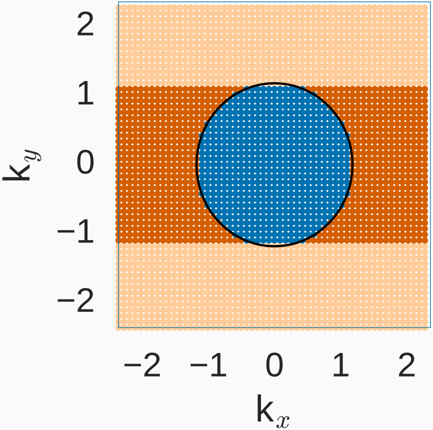
Results

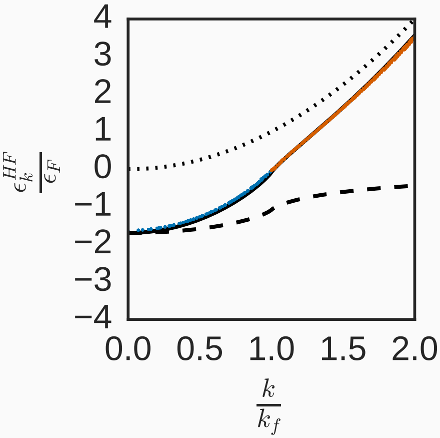
First Brillouin Zone

- Excite Ony in one direction
- Consider only First BZ due to $\vec{k}' = \vec{k} + \vec{G}$

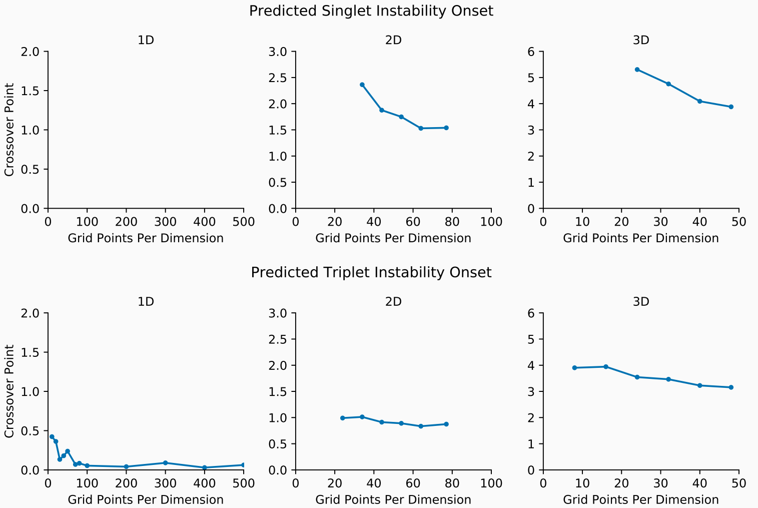


Orbital Energies

- 57 grid points per dimension reproduces the orbital energies reasonably well
- Worst towards Γ, better for higher $|\vec{k}|$

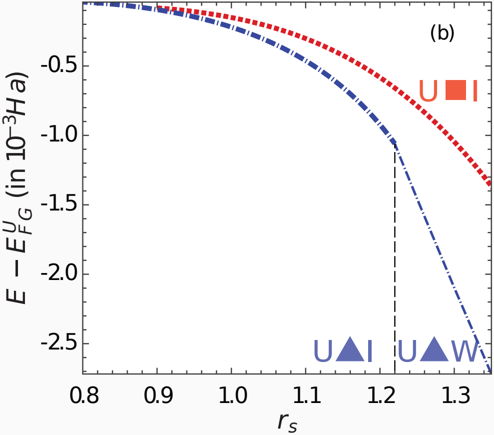


Convergence of Stability Curves



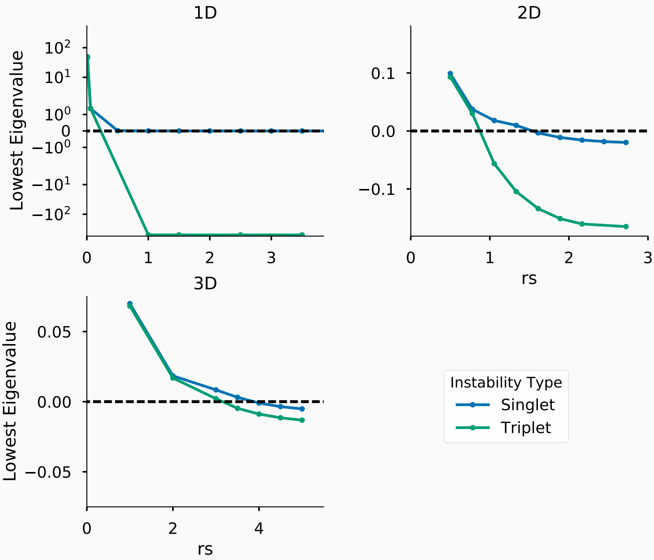
Dependence on r_s

Previously reported transition in 2d: $rs \approx 0.8$



Bernu, B.; Delyon, F.; Holzmann, M.; Baguet, L. Phys. Rev. B 2011, 84 (11), 115115.

Final Stability Curves



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Concluding Remarks

Conclusions

- Numerical studies likely support Overhauser's theorem in 1D
- Stability corresponds with direct phase calculations in 2D
- In 3D, predicts transition at higher density than is currently known via other methods.

Next Steps

- Directly calculate more exotic spin phases of HEG within HF theory
- Use those as starting points for CC, MBPT theories
- Apply a similar approach to finite molecular systems

Questions?

Iterative Subspace Eigenvalue Methods

Davidson's Algorithm

$\mathbf{A}\mathbf{x} = \lambda\mathbf{x}$	Eigenvalue Problem
$\mathbf{V} = [\mathbf{v_1}, \mathbf{v_2}, ..., \mathbf{v_M}]$	Guess vectors
$\tilde{\mathbf{A}} = \mathbf{V}^{\dagger}\mathbf{A}\mathbf{V}$	Transform into subspace
$\tilde{\mathbf{A}}\tilde{\mathbf{x}} = \tilde{\lambda}\tilde{\mathbf{x}}$	Solve the subspace problem
$\mathbf{x_i} \approx \mathbf{x}_i^R = \mathbf{V}\tilde{\mathbf{x}}_i$	Approximate eigenvectors
$\lambda_i \approx \lambda_i^R = \tilde{\lambda}_i$	Approximate eigenvalues
$\mathbf{r}_i = (\mathbf{A} - \lambda_i \mathbf{I})\, \mathbf{x}_i^R$	Calculate the residue
$\delta_i = c_i \mathbf{r}_i$	Correction vectors
$c_i = \frac{1}{\lambda_i \mathbf{I} - \mathbf{D}}$	Diagonal Precondition
$\mathbf{V} = [\mathbf{v_1}, \mathbf{v_2}, ..., \mathbf{v_M}, \delta_1, \delta_2, ..., \delta_l]$	Append to guess and restart
$\mathbf{V} = \mathit{orthonormalized}(\mathbf{V})$	Ensure orthonormal projection

1. Saad, Y. Numerical Methods for Large Eigenvalue Problems; SIAM, 2011.
2. Davidson, E. R. J. Comput. Phys. 1975, 17 (1), 8794.

Convergence Properties

- The convergence of these subspace algorithms depends on:

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  - The approximate eigenvectors become non-orthogonal
- My recommendation for guess eigenvectors is

$$v_j^{(i)} = normalize\left(\frac{1}{|A_{ii} - A_{jj}| + 1}\right). \tag{7}$$

1. Saad, Y. Numerical Methods for Large Eigenvalue Problems; SIAM, 2011.
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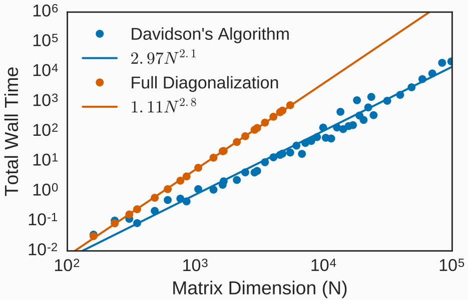
Davidson Scaling

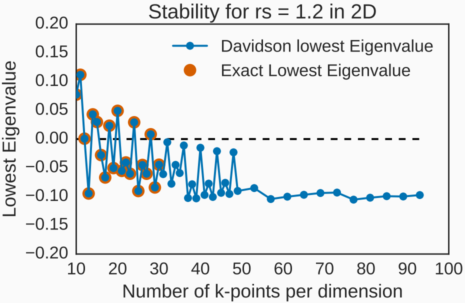
- Davidson is Asymptotically quadratic.
- Full diagonalization is almost cubic.
- Matrix multiplication is order[1] $log_2(7) \approx 2.807$



1) http://mathworld.wolfram.com/StrassenFormulas.html

Efficacy of Davidson's Algorithm

- Reproduces Exact result to machine precision in all test cases.
- Odd spikes are due to approximating circle by squares



Orthogonalization

- The condition number, κ, is bound from below by

$$\kappa \geq \frac{Max(A_{ii})}{Min(A_{jj})} \tag{8}$$

- The Gram-Schmidt procedure has numerical issues,

$$||\mathbf{I} - \mathbf{Q}^{\mathbf{T}}\mathbf{Q}|| \leq \frac{\alpha\kappa^2}{1 - \beta\kappa^2}. \tag{9}$$

- Modified Gram-Schmidt is better, but not perfect,

$$||\mathbf{I} - \mathbf{Q}^{\mathbf{T}}\mathbf{Q}|| \leq \frac{\gamma\kappa}{1 - \eta\kappa} \tag{10}$$

- May need multiple orthogonalization steps

Hern, V.; Tom, A.; Vidal, V. SLEPc Technical Reports, 2007.