Hartree-Fock Stability

Applications to the Homogeneous Electron Gas

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Background Information

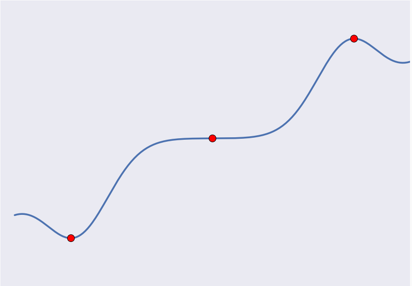
Levels of Hartree-Fock Theory

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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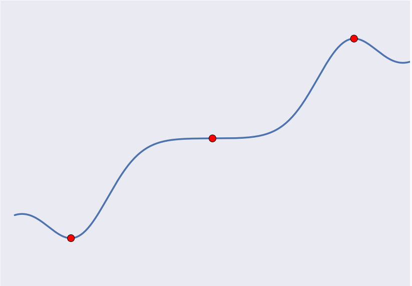
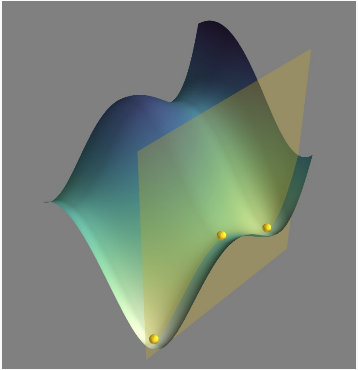
Within the Constrained Space



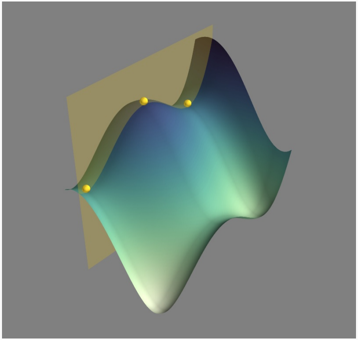
Restricted Minimization

- Restricted minima may correspond to minima in another dimension



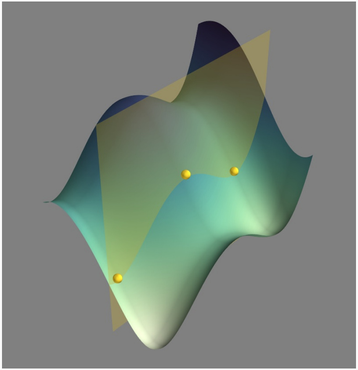
Restricted Minimization

- 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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- Solving the HF equations guarantees only that the energy is stationary. The first order variation is therefore 0.

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

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- 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

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

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

Hartree-Fock Stability Conditions

The eigenvalue equation can be factorized depending on symmetry.

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

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

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

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

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

Project Goal

- Can we use the HF-Stability analysis to determine where the HEG is unstable?

Overhauser, A. W. Phys. Rev. Lett. 1960, 4 (9), 462465.

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

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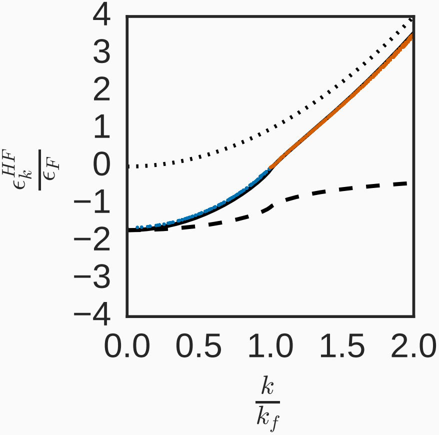
Results

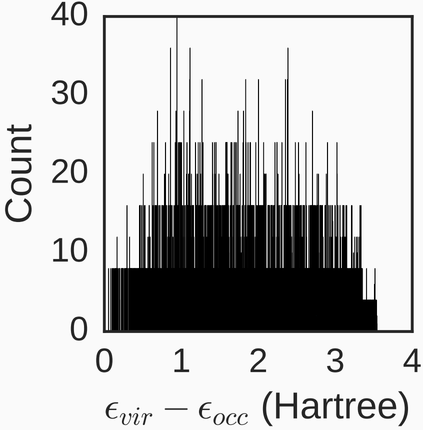
Orbital Energies

- Nk = 57 reproduces the orbital energies reasonably well
- Worst towards Γ, better for higher $|\vec{k}|$



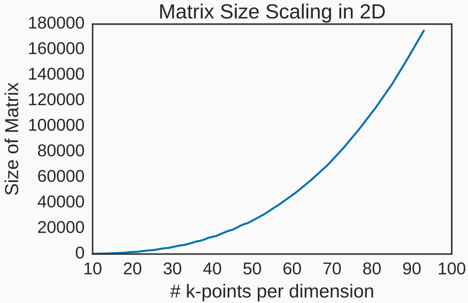
Matrix Diagonals

- Spectrum is Dense



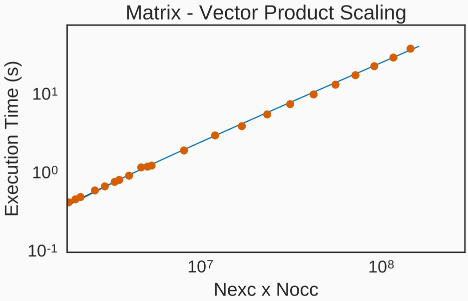
Matrix Size Scaling

- Scales as $2N_{exc}$
- N_{occ} and N_{vir} both scale with $N_{kpoints}^{D}$
- Use an iterative subspace method
- Jacobi-Davidson(-Liu)



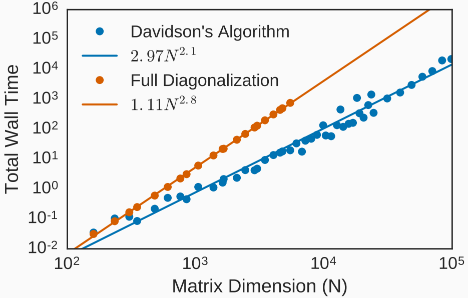
Matrix-Vector Scaling

- Scales as $N_{exc} \times N_{occ}$ due to momentum conservation



Davidson Scaling

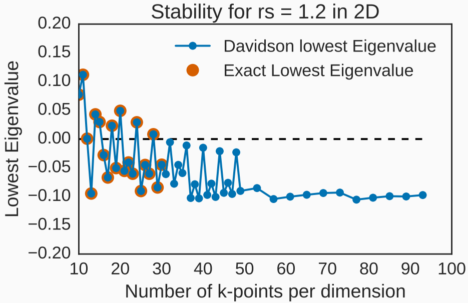
- Davidson is Asymptotically quadratic.
- Full diagonalization is almost cubic.
- Matrix multiplication is order[1] $log_2(7) \approx 2.807$



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



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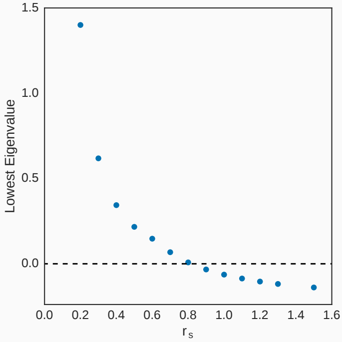
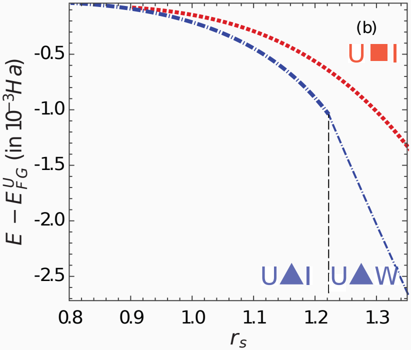
Dependence on r_s

Crossover from stable to unstable agrees with previous results.

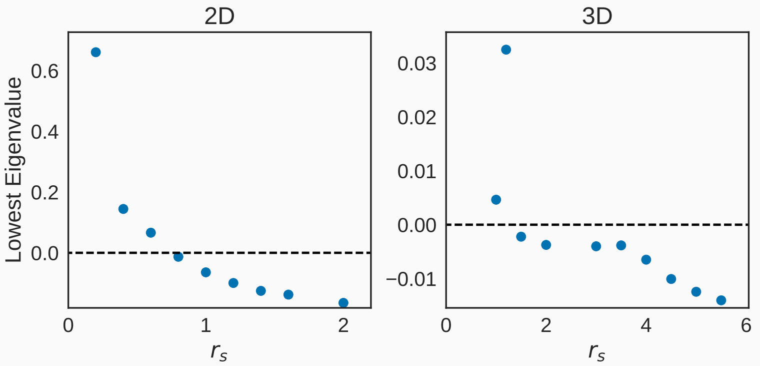




Bernu, B.; Delyon, F.; Holzmann, M.; Baguet, L. Phys. Rev. B 2011, 84 (11), 115115.

Dependence on r_s

3D data is currently inconclusive.



Questions?