



Hartree-Fock Stability

Applications to the Homogeneous Electron Gas

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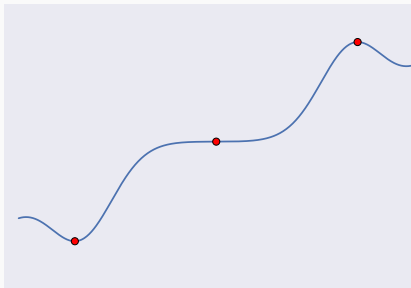
Background Information

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

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



Restricted Minimization

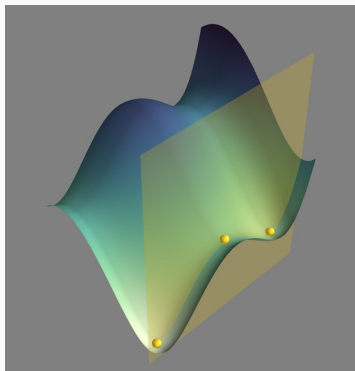
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Within the Constrained Space



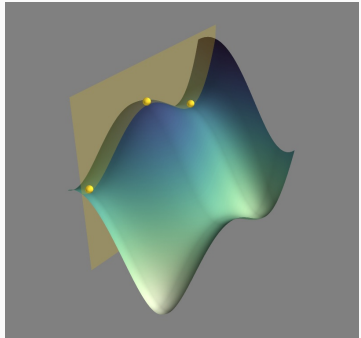
Restricted Minimization

- Restricted minima may correspond to minima in another dimension



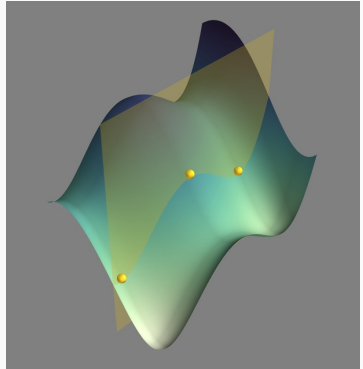
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- Restricted minima may correspond to minima in another dimension
- Restricted minima may correspond to maxima in another dimension



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



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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.
- Thouless¹ 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**

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

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- Where

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

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 & Pople¹

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,

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

- and the background and coulomb terms cancel exactly,

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

Brief Overview

- The discretized solutions are given by,

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

- Where the two electron integral is given by

$$\langle \vec{k}, \vec{k}' | \vec{k}'', \vec{k}''' \rangle \stackrel{2D, 3D}{=} \begin{cases} \frac{\pi}{V} \frac{2^{D-1}}{|\vec{k} - \vec{k}''|^{D-1}} & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' \\ 0 & \text{else} \end{cases}$$
$$\langle k, k' | k'', k''' \rangle \stackrel{1D}{=} \begin{cases} e^{|k-k''|^2 a^2} \text{Ei}(-|k-k''|^2 a^2) ; & k''' = k + k' - k'' \\ 0 ; & \text{else} \end{cases} \quad (6)$$

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- Can we show this numerically, and discriminate between RHF-UHF and RHF-GHF instability?

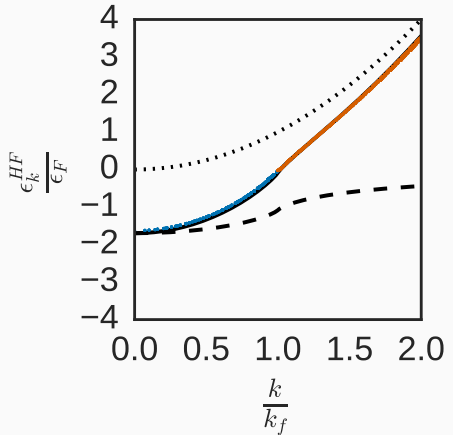
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- Can we show this numerically, and discriminate between RHF-UHF and RHF-GHF instability?
- (Future) Can we combine this with to improve the efficacy of correlation theories (CC, MBPT)?

Results

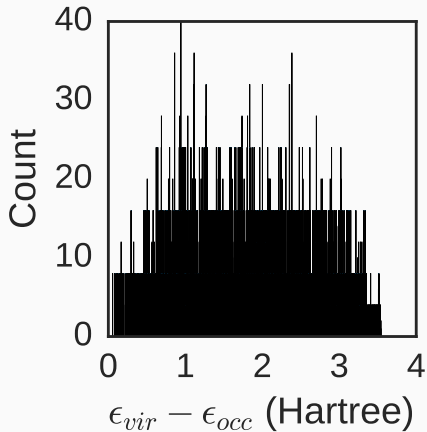
Orbital Energies

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



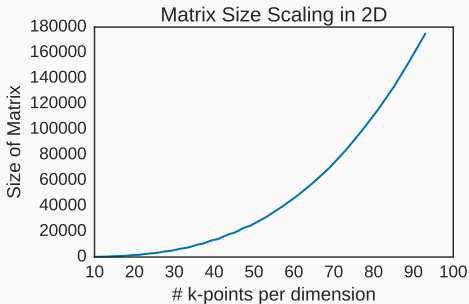
Matrix Diagonals

- Spectrum is Dense



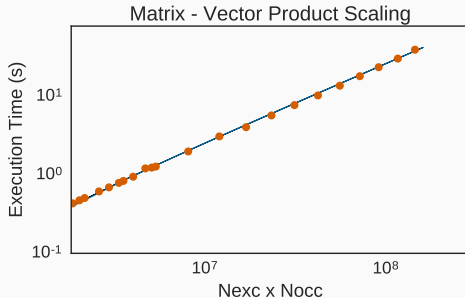
Matrix Size Scaling

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



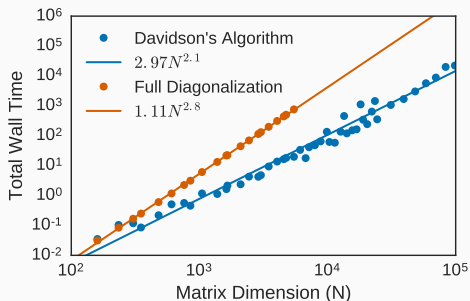
Matrix-Vector Scaling

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



Davidson Scaling

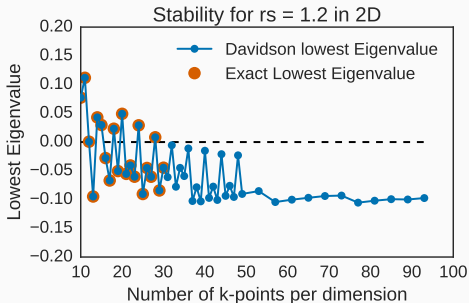
- Davidson is Asymptotically quadratic.
- Full diagonalization is almost cubic.
- Matrix multiplication is order¹ $\log_2(7) \approx 2.807$



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

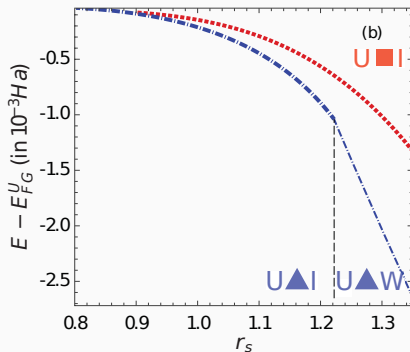
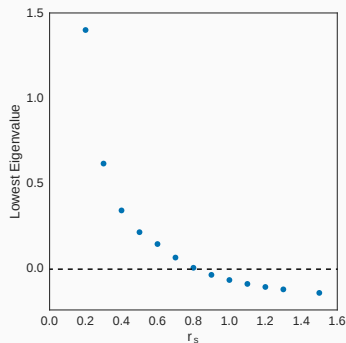
Efficacy of Davidson's Algorithm

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



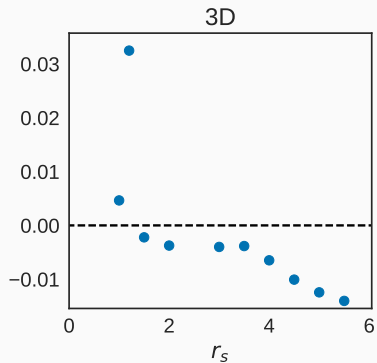
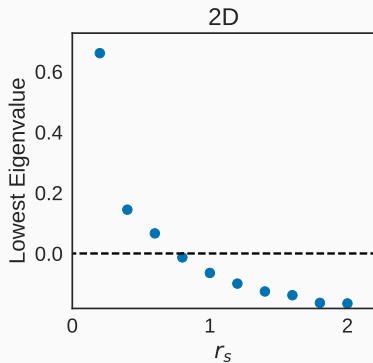
Dependence on r_s

Crossover from stable to unstable agrees with previous results.



Dependence on r_s

3D data is currently inconclusive.



Questions?