



# Hartree-Fock Stability

## Applications to the Homogeneous Electron Gas

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# Background Information

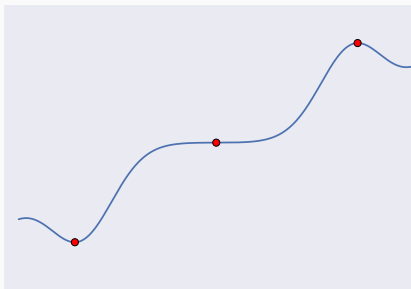
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# Levels of Hartree-Fock Theory

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

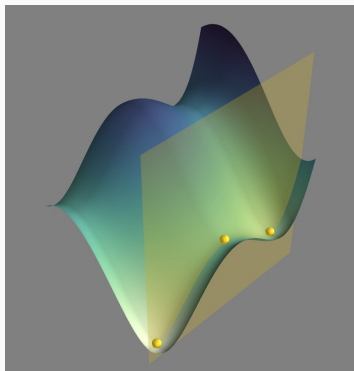
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## Within the Constrained Space



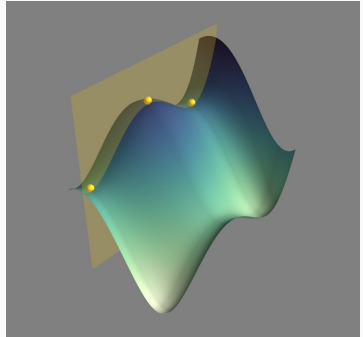
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- Restricted minima may correspond to minima in another dimension



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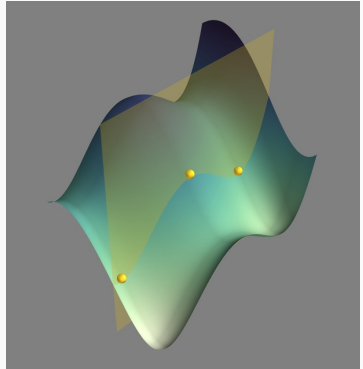
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# Restricted Minimization

- 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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- 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<sup>1</sup> showed a physically motivated derivation using Time-Dependent Hartree-Fock theory (TDHF).

# Hartree-Fock Stability Conditions

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and to first order in  $\rho_{ai}$ , the elements of the density matrix are ,

$$\rho_{ai} = C_{ai}, \quad \rho_{ia} = C_{ai}^*. \quad (4)$$

# Hartree-Fock Stability Conditions

The TDHF EoM becomes,

$$i\hbar \frac{dC_{ai}(t)}{dt} = (\epsilon_a - \epsilon_i) + \sum_i^{occ} \sum_b^{vir} [\langle aj || ib \rangle C_{bj}(t) + \langle ab || ij \rangle C_{bj}^*(t)] . \quad (5)$$

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whose amplitudes,  $X_{ai}$  and  $Y_{ai}$  satisfy,

$$\begin{aligned} (\epsilon_a - \epsilon_i) X_{ai} + \sum_i^{occ} \sum_b^{vir} [\langle aj||ib \rangle X_{bj} + \langle ab||ij \rangle Y_{bj}] &= \hbar\omega X_{ai} \\ (\epsilon_a - \epsilon_i) Y_{ai} + \sum_i^{occ} \sum_b^{vir} [\langle aj||ib \rangle X_{bj} + \langle ab||ij \rangle Y_{bj}] &= -\hbar\omega Y_{ai}. \end{aligned} \quad (7)$$

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These are the equations of the Random Phase Approximation (RPA)

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

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \quad (8)$$

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- Where

$$\begin{aligned} A_{ia,jb} &= \langle i^a | H - E_0 | j^b \rangle = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle aj || ib \rangle \\ B_{ia,jb} &= \langle ij^a | H - E_0 | 0 \rangle = \langle ab || ij \rangle. \end{aligned} \quad (9)$$

# 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<sup>1</sup>

# Homogeneous Electron Gas

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# 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,

$$V_{bg}(\mathbf{r}) = \sum_i \frac{-Ze^2}{|\mathbf{r} - \mathbf{R}_i|} \rightarrow -e^2 \int \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad (10)$$

- and the background and coulomb terms cancel exactly,

$$V_{ee} = e^2 \int \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \quad (11)$$

# Brief Overview

- The discretized solutions are given by,

$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m} - \sum_{\vec{k}'}^{|\vec{k}'| < k_f} \langle \vec{k}, \vec{k}' | \vec{k}', \vec{k} \rangle \quad (12)$$

- Where the two electron integral is given by

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

$$\langle k, k' | k'', k''' \rangle \stackrel{1D}{=} \begin{cases} e^{|k-k''|^2 a^2} \text{Ei}(-|k-k''|^2 a^2) ; & k''' = k + k' - k'' \\ 0 ; & \text{else} \end{cases} \quad (13)$$

# Notes on Iterative Subspace Eigenvalue Methods

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# Subspace Methods in 1 Slide

- Sometimes the eigenvalue problem is too large to solve completely, and only a few eigenpairs are needed
- Subspace methods allow for finding some eigenpairs without full diagonalization.
- They need only a matrix-vector product (maybe diagonal elements too).
- A small subspace is constructed, then expanded slowly until the eigenpair residual norm,

$$||\mathbf{Ax} - \lambda\mathbf{x}||, \quad (14)$$

is below some threshold.

- The **Lanczos** and **Arnoldi** methods are the most commonly used<sup>1</sup>, while the **Davidson**<sup>2</sup> method is likely more useful in a majority of chemical applications.

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

2. Davidson, E. R. J. Comput. Phys. 1975, 17 (1), 8794.



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- My recommendation for guess eigenvectors is

$$v_j^{(i)} = \text{normalize} \left( \frac{1}{|A_{ii} - A_{jj}| + 1} \right). \quad (15)$$

# Orthogonalization

- The condition number,  $\kappa$ , is bound from below by

$$\kappa \geq \frac{\text{Max}(A_{ii})}{\text{Min}(A_{jj})} \quad (16)$$

- The Gram-Schmidt procedure has numerical issues,

$$\|\mathbf{I} - \mathbf{Q}^T \mathbf{Q}\| \leq \frac{\alpha \kappa^2}{1 - \beta \kappa^2}. \quad (17)$$

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

$$\|\mathbf{I} - \mathbf{Q}^T \mathbf{Q}\| \leq \frac{\gamma \kappa}{1 - \eta \kappa} \quad (18)$$

- May need multiple orthogonalization steps

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



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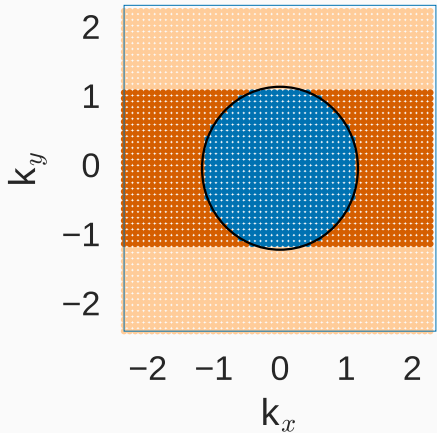
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- It is known that the RHF-GHF instability persists at all densities for the HEG<sup>1</sup>.
- Can we show this numerically, and discriminate between RHF-UHF and RHF-GHF instability?
- (Future) Can we combine this with to improve the efficacy of correlation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

## Results

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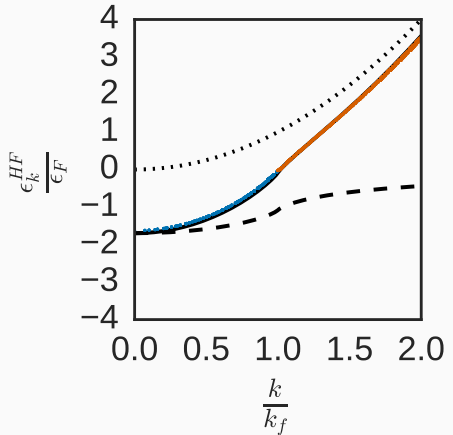
# First Brillouin Zone

- Excite Only in the X direction
- -X virtuals matter due to  $\vec{k}' = \vec{k} + \vec{G}$



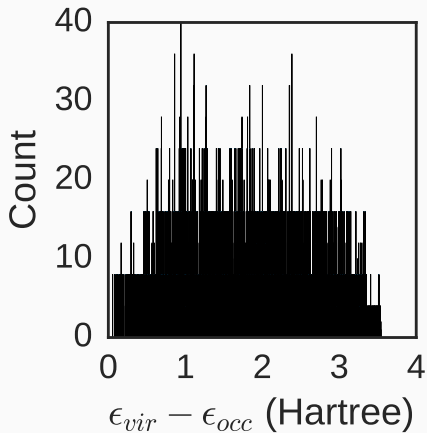
# Orbital Energies

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



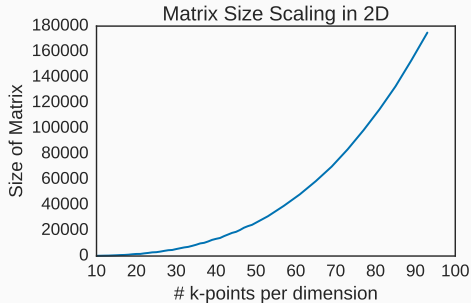
# Matrix Diagonals

- Spectrum is Dense



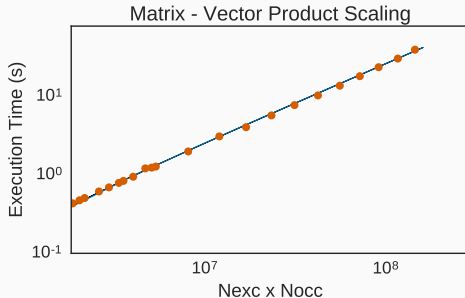
# Matrix Size Scaling

- Scales as  $2N_{exc}$
- $N_{occ}$  and  $N_{vir}$  both scale with  $N_{kpoints}^D$



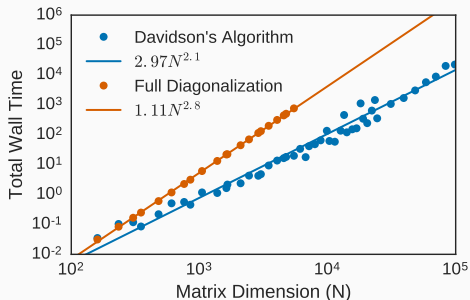
# Matrix-Vector Scaling

- 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<sup>1</sup>  $\log_2(7) \approx 2.807$

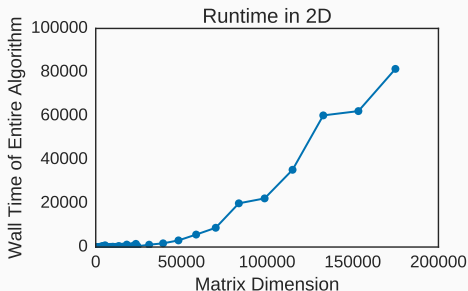


1) <http://mathworld.wolfram.com/StrassenFormulas.html>



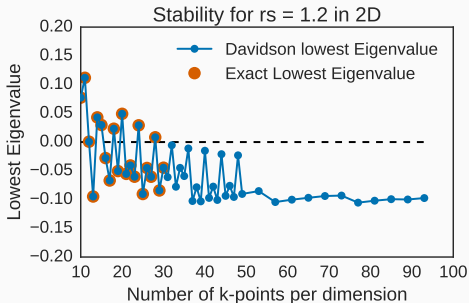
# Algorithm Wall time

- Roughly quadratic wrt matrix dimension.
- Outliers correspond to high condition number



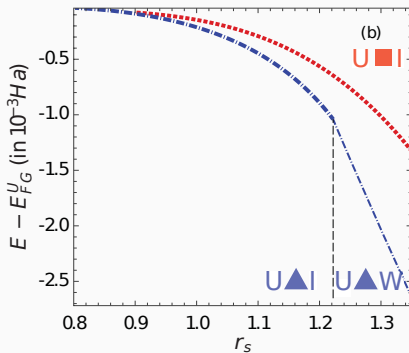
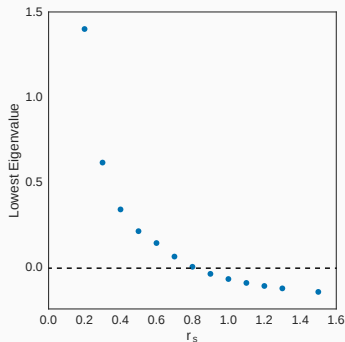
# Efficacy of Davidson's Algorithm

- 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.



## Concluding Remarks

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## Next Steps

Objective	Human Time	Computer Time
Other instabilities in 2D	30 mins	Week
All 3D	$\frac{1}{2}$ Day	>Weeks? Parallel?

**Questions?**