Hartree-Fock Stability

Applications to the Homogeneous Electron Gas

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Table of contents

Background Information

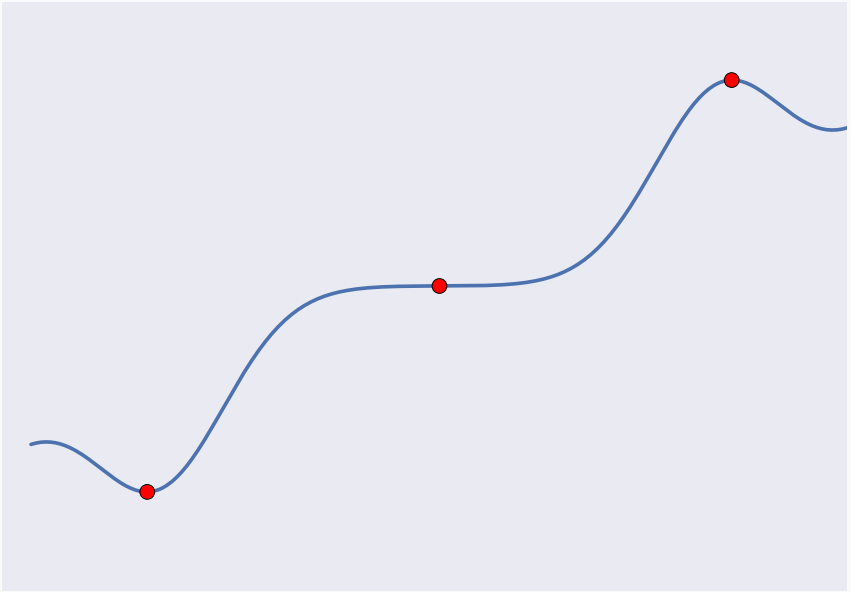
Levels of Hartree-Fock Theory

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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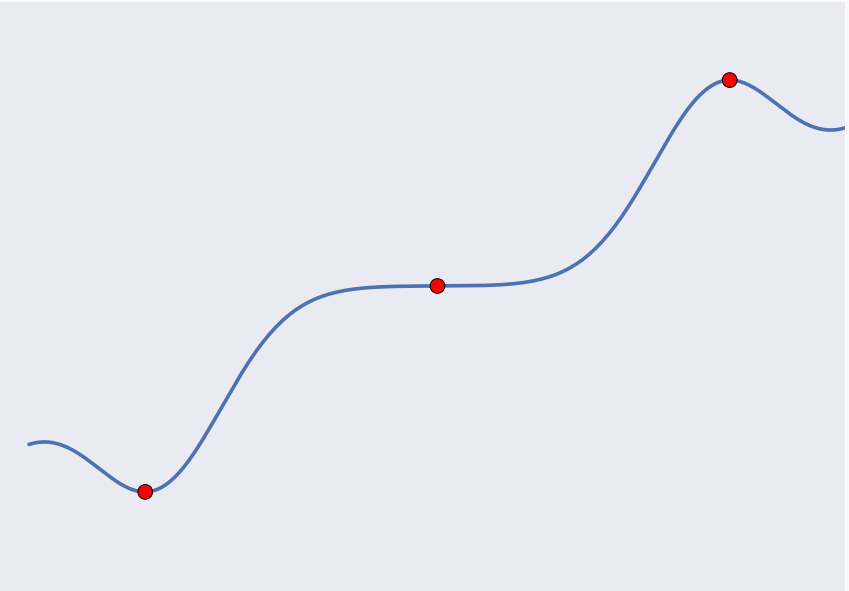
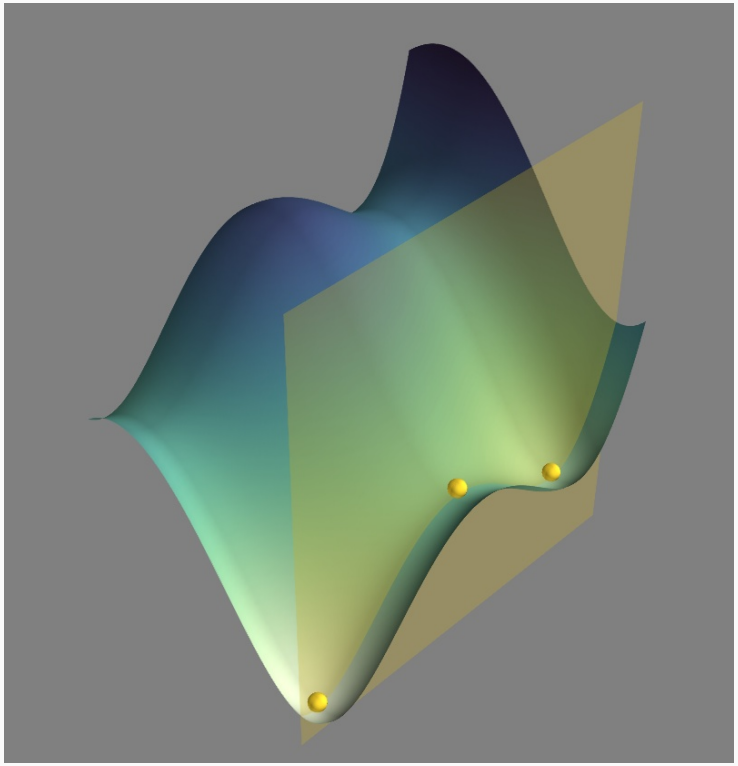
Within the Constrained Space



Restricted Minimization

- Restricted minima may correspond to minima in another dimension



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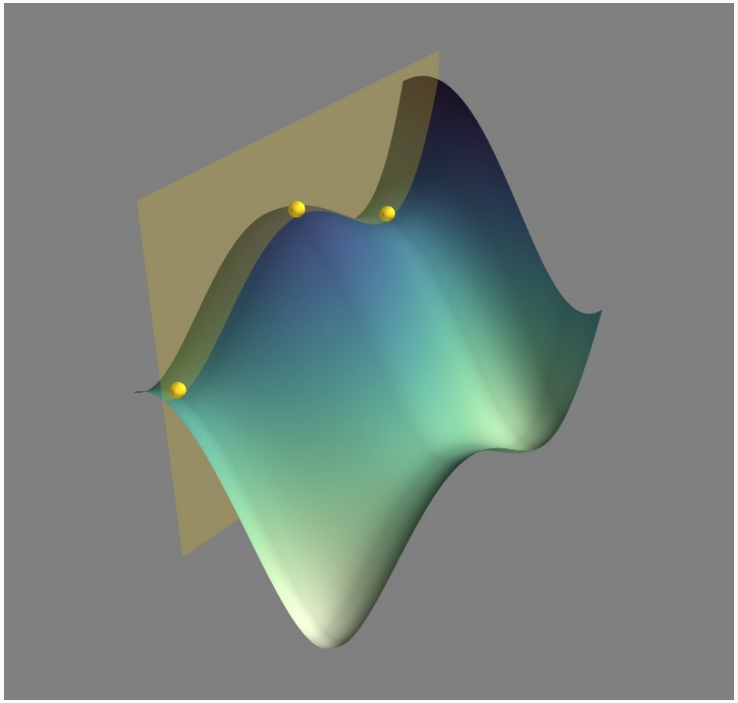

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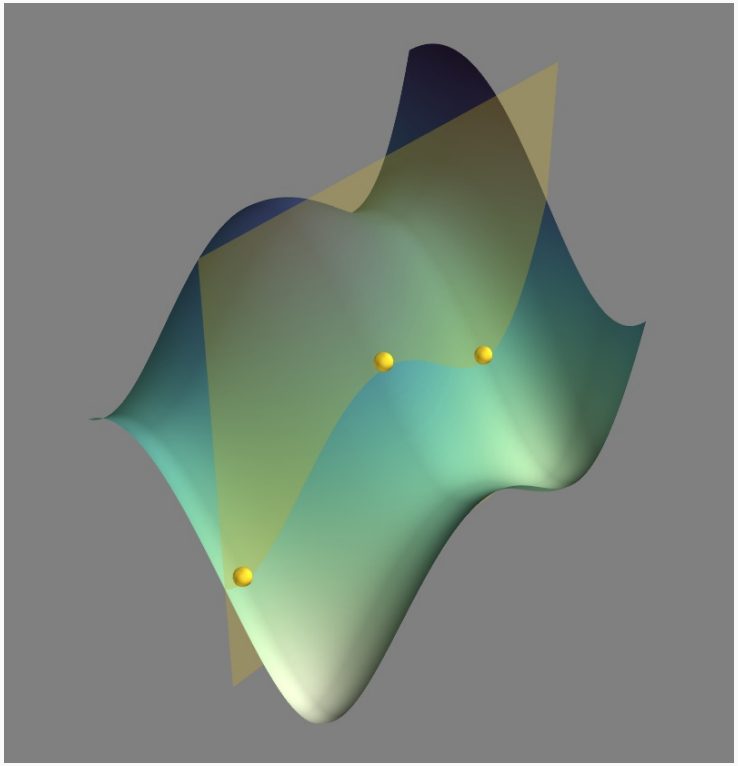
- Restricted minima may correspond to maxima in another dimension
- Restricted minima may be nonstationary



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- 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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Hartree-Fock Stability Conditions

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and to first order in ρ_{ai}, the elements of the density matrix are ,

$$\rho_{ai} = C_{ai}, \quad \rho_{ia} = C^*_{ai}. \tag{4}$$

Hartree-Fock Stability Conditions

The TDHF EoM becomes,

$$
\begin{aligned}
i\hbar \frac{dC_{ai}(t)}{dt} &= (\epsilon_a - \epsilon_i) \\
&+ \sum_{i}^{occ} \sum_{b}^{vir} \left[\langle aj||ib\rangle \, C_{bj}(t) + \langle ab||ij\rangle \, C_{bj}^{*}(t) \right]. \quad (5)
\end{aligned}
$$

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

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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

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

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- Where

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

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[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,

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

- and the background and coulomb terms cancel exactly,

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

Brief Overview

- The discretized solutions are given by,

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

- Where the two electron integral is given by

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

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

Notes on Iterative Subspace Eigenvalue Methods

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,

$$||\mathbf{Ax} - \lambda\mathbf{x}||, \tag{14}$$

  is below some threshold.
- The Lanczos and Arnoldi methods are the most commonly used[1], while the Davidson[2] 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.

Convergence Properties

- The convergence of these subspace algorithms depends on:

1. Saad, Y. Numerical Methods for Large Eigenvalue Problems; SIAM, 2011.
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- My recommendation for guess eigenvectors is

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

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Orthogonalization

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

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

- The Gram-Schmidt procedure has numerical issues,

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

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

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

- May need multiple orthogonalization steps

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- (Future) Can we combine this with to improve the efficacy of correlation theories (CC, MBPT)?

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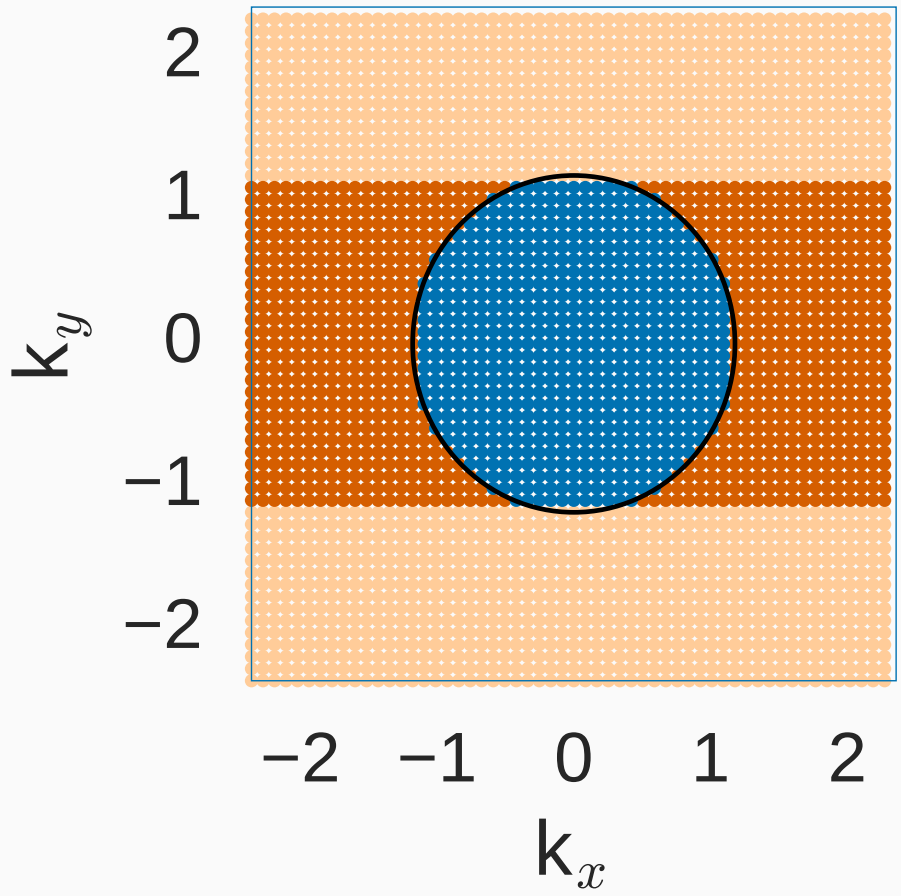
Results

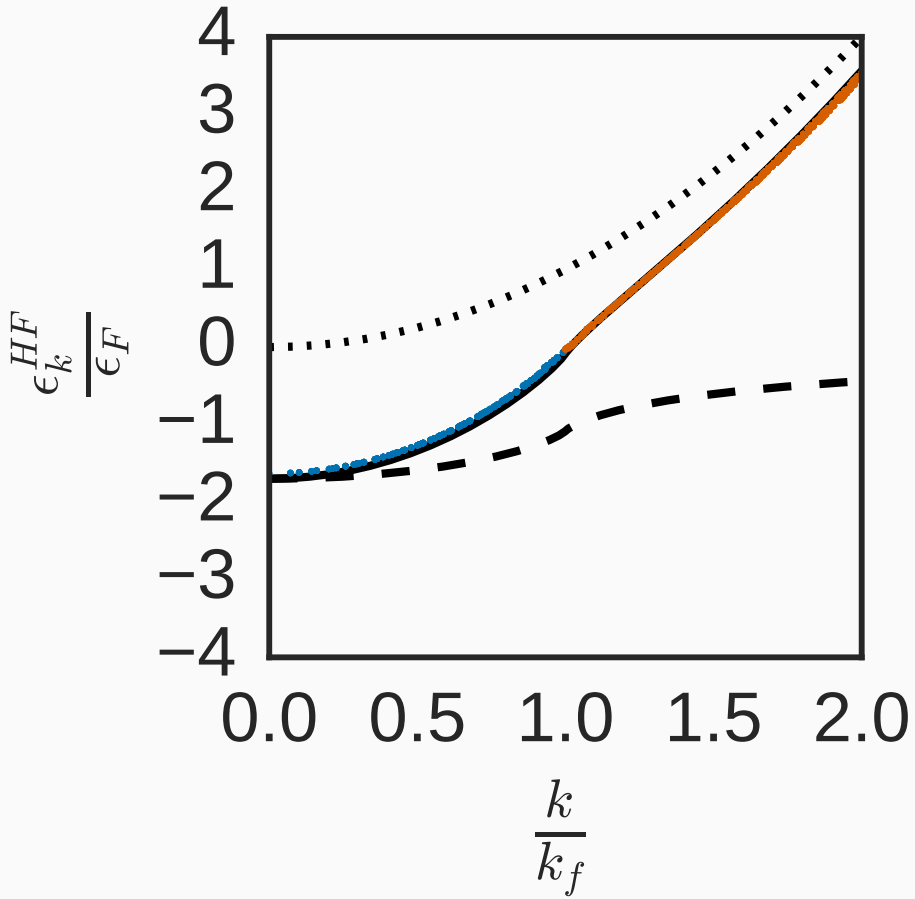
First Brillouin Zone

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



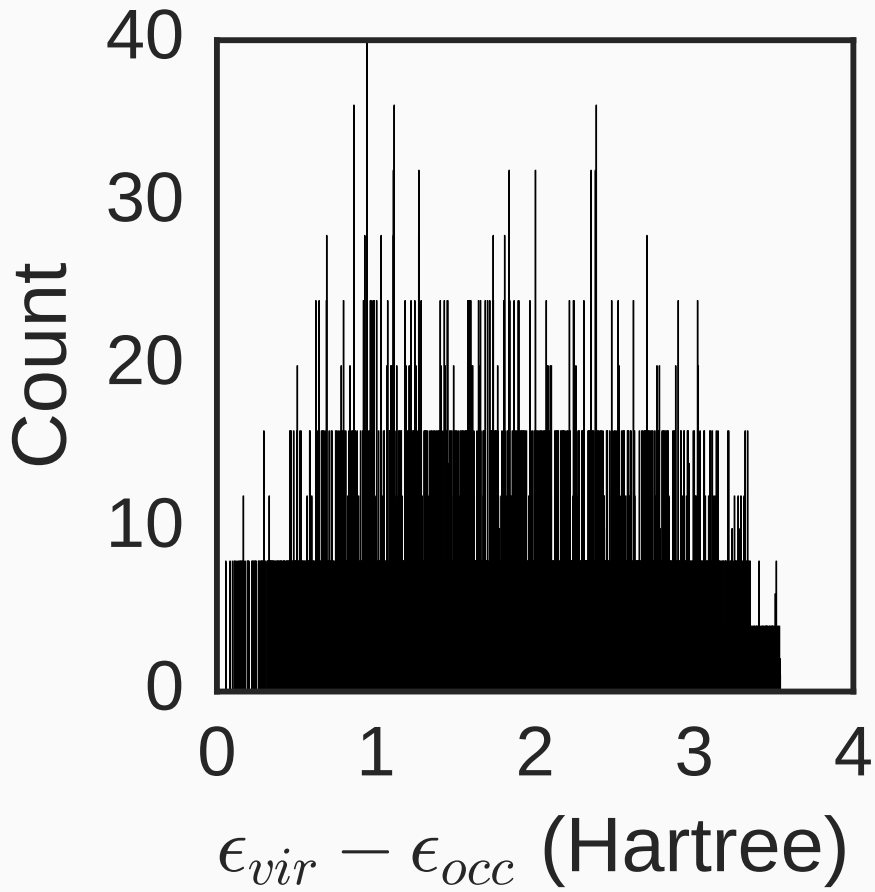
Orbital Energies

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



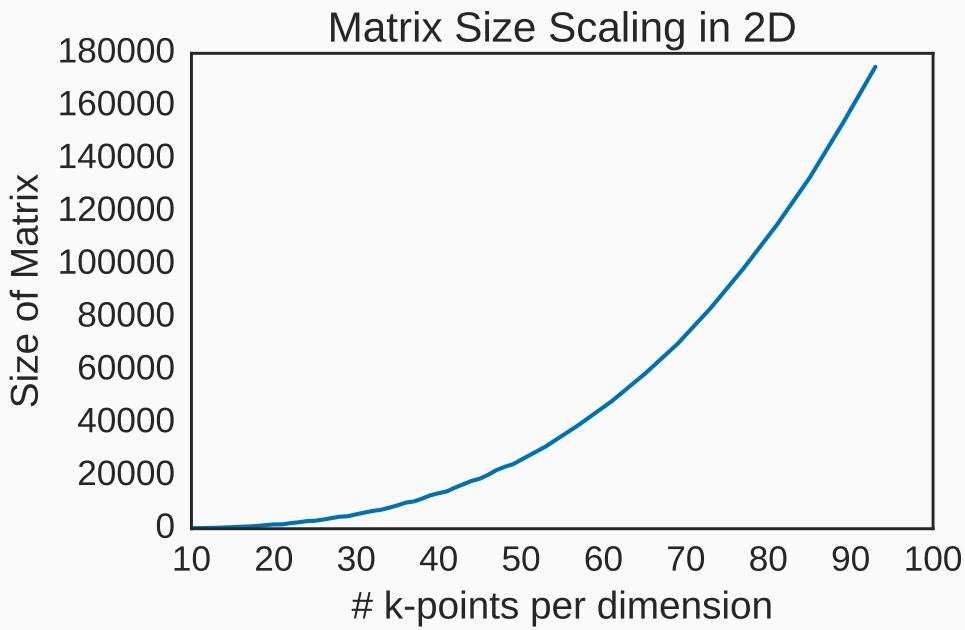
Matrix Diagonals

- Spectrum is Dense



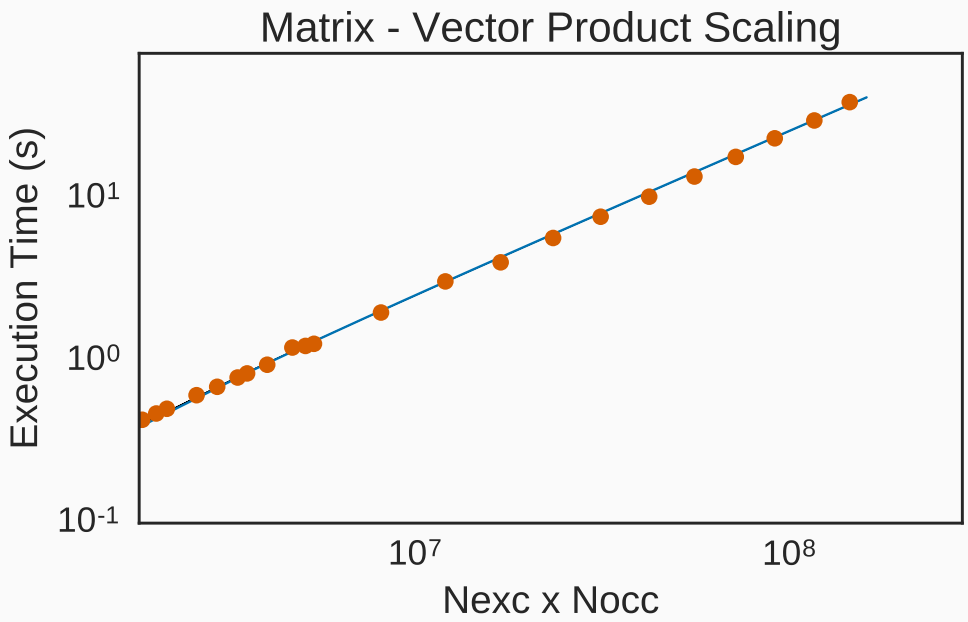
Matrix Size Scaling

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



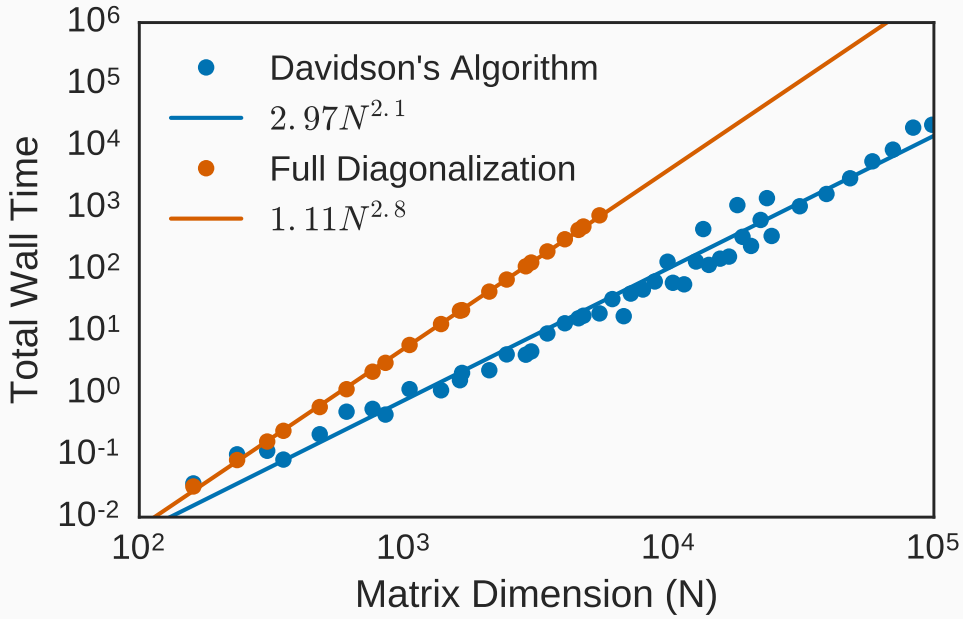
Matrix-Vector Scaling

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



Davidson Scaling

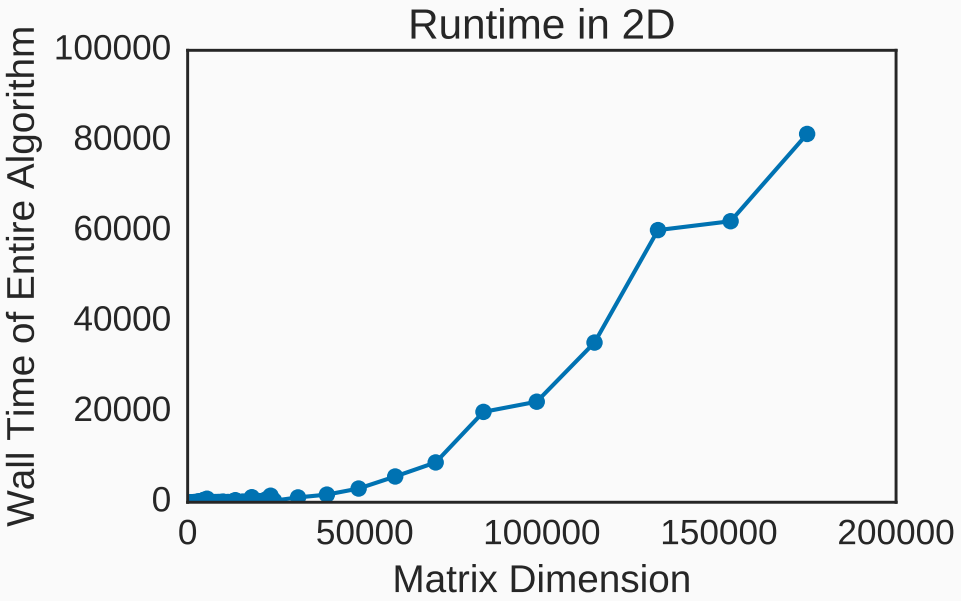
- Davidson is Asymptotically quadratic.
- Full diagonalization is almost cubic.
- Matrix multiplication is order[1] $log_2(7) \approx 2.807$



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

Algorithm Wall time

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



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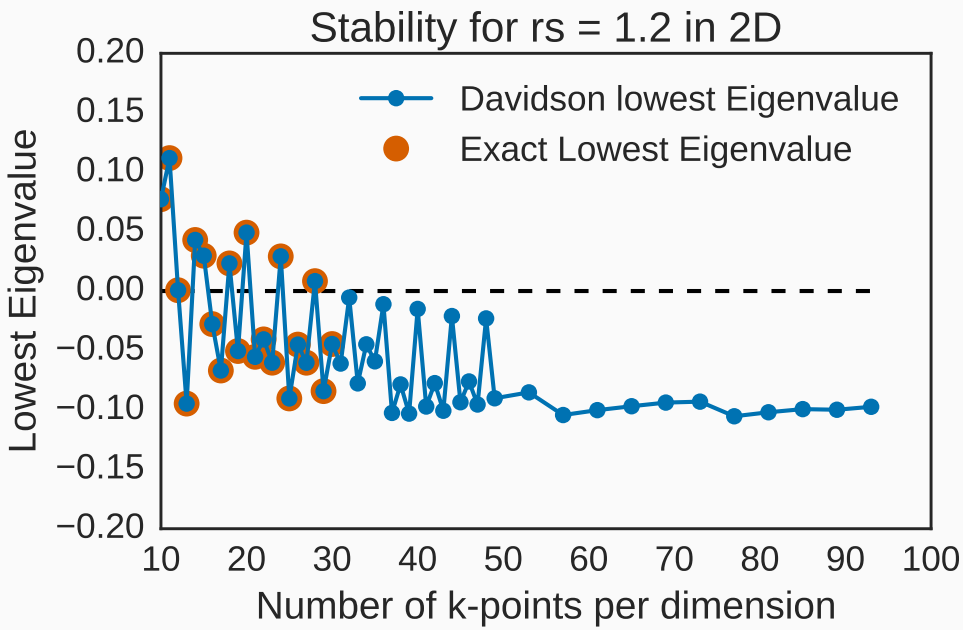
Efficacy of Davidson's Algorithm

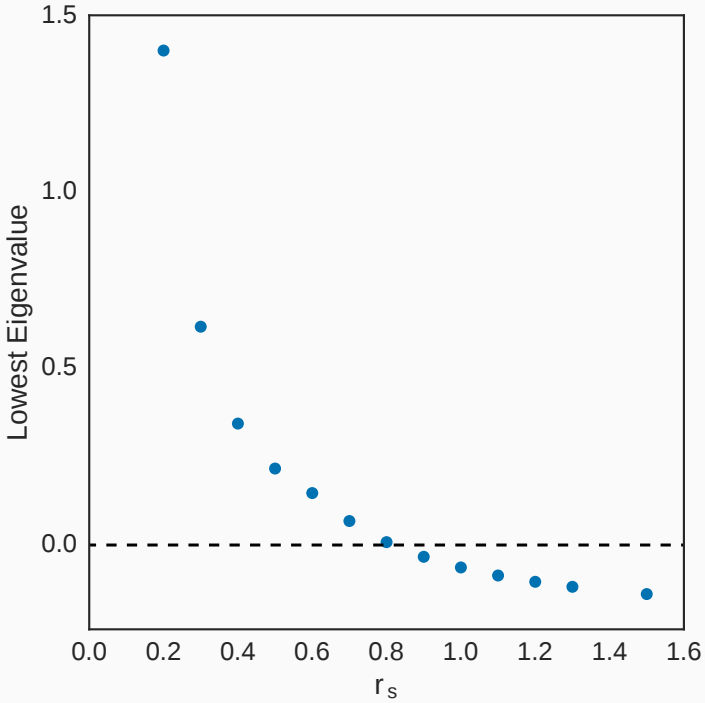
- Reproduces Exact result to machine precision in all test cases.
- Odd spikes are due to approximating circle by squares

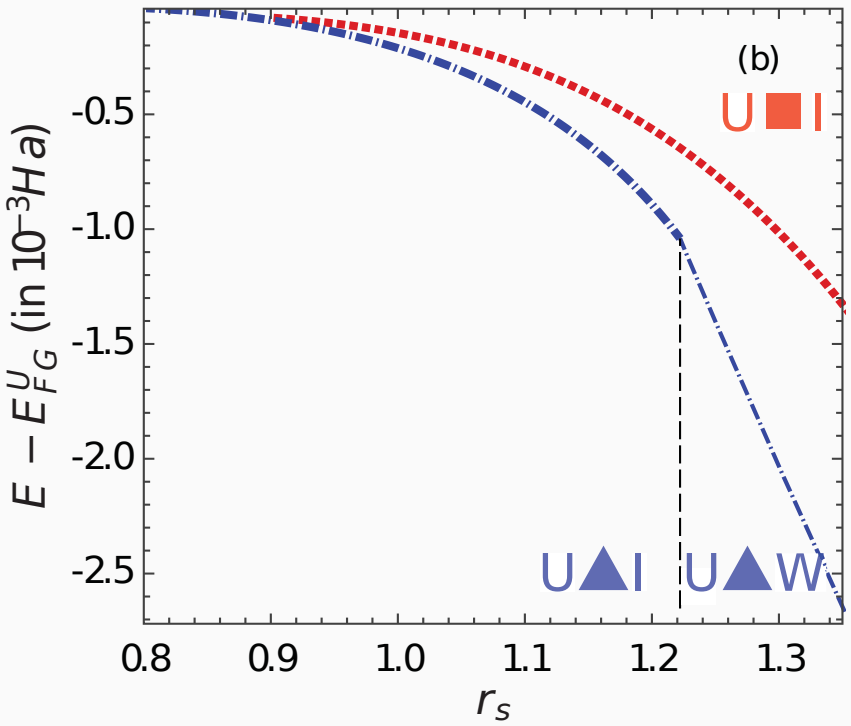


1) http://mathworld.wolfram.com/StrassenFormulas.html

Dependence on r_s

Crossover from stable to unstable agrees with previous results.





Concluding Remarks

Next Steps

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

Questions?