



# Hartree-Fock Stability and its Relation to Strong Correlation

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# Background Information

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# Correlation Energy

- The Molecular Electronic S.E. in the Born-Oppenheimer approximation

$$\left( \hat{T}_{elec} + \hat{V}_{elec-nuc} + \hat{V}_{exchange} + \hat{V}_{coulomb} \right) \Psi = E_{exact} \Psi$$

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$$E_{corr} = E_{exact} - E_{HF}$$

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- The correlation energy is recovered by post Hartree-Fock methods (CC, MBPT) which perform better the closer the HF solution is to the exact.

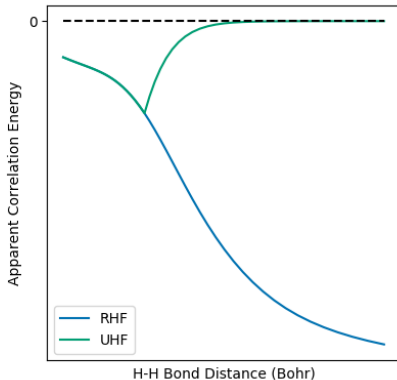
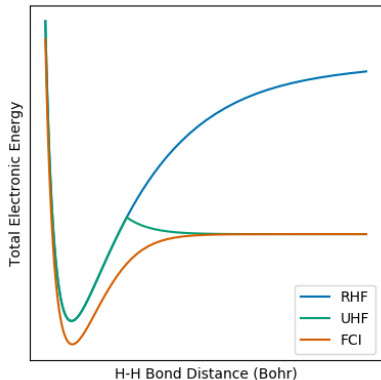
# Levels of Hartree-Fock Theory

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



# Case Study: $\text{H}_2$ Dissociation

Is this strong correlation or a bad reference?



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- Apply to systems (known molecules, periodic systems)

# Hartree-Fock Stability

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- This not the case if any **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 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<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.
- Characterized by  $r_s$ , inversely proportional to density
- 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,

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

- Where the 2D and 3D two electron integral is given by

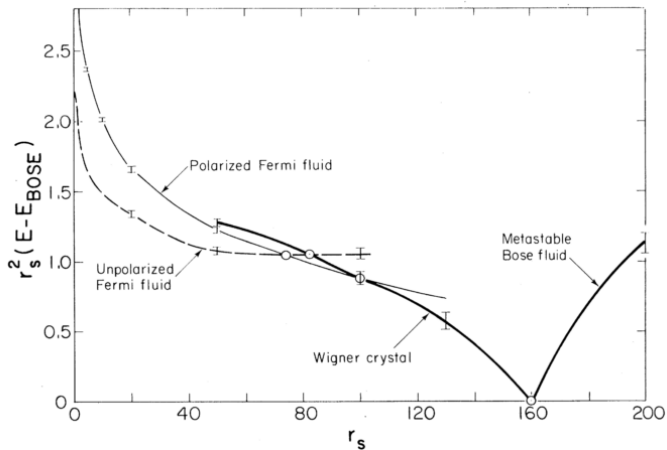
$$\langle \vec{k}, \vec{k}' | \vec{k}'', \vec{k}''' \rangle = \begin{cases} \frac{\pi}{V} \frac{2^{D-1}}{|\vec{k} - \vec{k}''|^{D-1}} & \vec{k}''' = \vec{k} + \vec{k}' - \vec{k}'' \\ 0 & \text{else} \end{cases}$$

- In 1D, if  $V(r_{12}) = V_0 \delta(r_{12})$ ,

$$\langle k, k' | k'', k''' \rangle = \begin{cases} V_0 ; & k''' = k + k' - k'' \\ 0 ; & \text{else} \end{cases} \quad (6)$$

# Exact Results

QMC Energies for various phases



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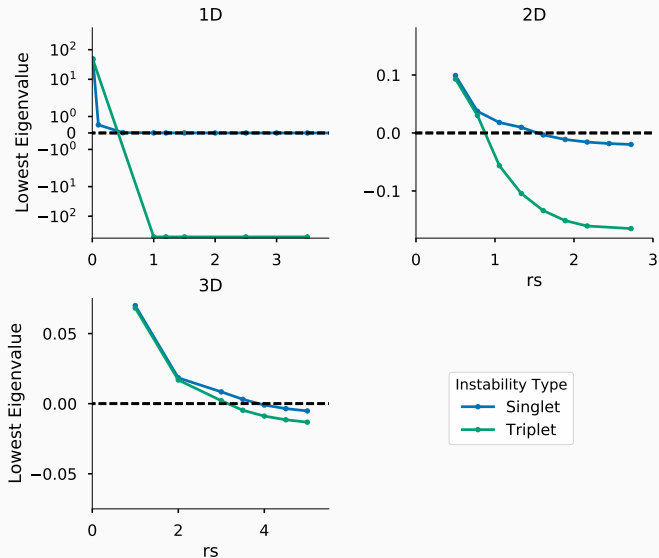
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- Can we show this numerically?
- (Future) Can we find a lower energy GHF solution to reduce “correlation energy”?

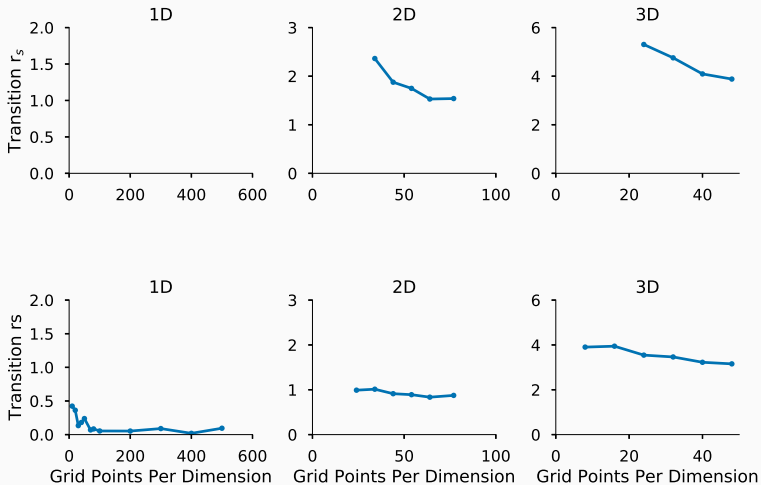
## Results

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# Stability Curves



# Convergence of Stability Curves



# Dependence on $r_s$

# Dimensions	Instability $r_s$	Literature
1	0.15	0 <sup>1</sup>
2	0.95	0.8 <sup>2</sup>
3	3.0	3.0 <sup>3</sup>

(1) Overhauser, A. W. Phys. Rev. 1962, 128 (3), 14371452.

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

(3) Baguet, L.; Delyon, F.; Bernu, B.; Holzmann, M. Phys. Rev. B 2014, 90 (16), 165131.

## **Future Directions**

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- Find the lowest energy GHF solution

(1) Ohno, K. Chem. Rec. 2016, 16 (5), 21982218.

(2) Supady, A.; Blum, V.; Baldauf, C. J. Chem. Inf. Model. 2015, 55 (11), 23382348.

# Brute Force GHF

- Find the lowest energy GHF solution
- Use algorithms inspired by similar problems (atomic configuration)

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- Find the lowest energy GHF solution
- Use algorithms inspired by similar problems (atomic configuration)
- Global Reaction Route Mapping (GRRM) / Anharmonic Downard Distortion (ADD)<sup>1</sup>

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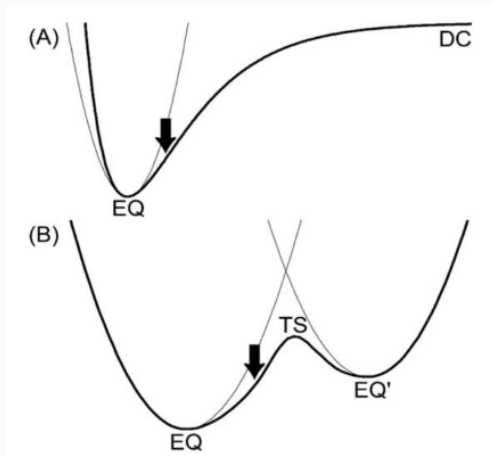
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- Genetic Algorithm<sup>2</sup>

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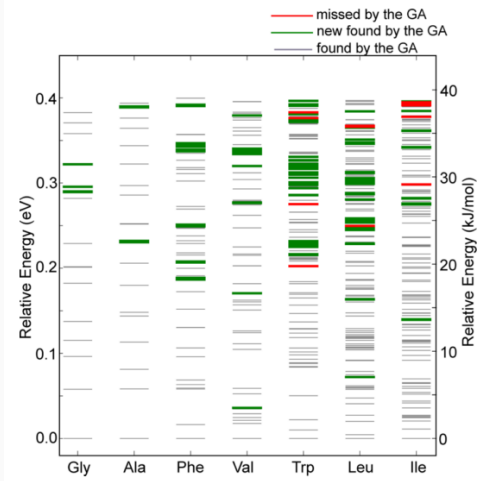
# Anharmonic Downward Distortion



Replace atomic coordinates with MO coefficients and vibrational information with MO eigenvalues/vectors

# Genetic Algorithm

Genetic Algorithm promising in finding many low energy solutions



# Proposal: Genetic Algorithm

- Use as the gene the density matrix / MO coefficients
- Less human input
- Less dependence on underlying PES structure
- How the HF solution gets found is irrelevant

# Concluding Remarks

- Paramagnetic HEG instabilities are successfully reproduced by the MO hessian approach
- HF Stability analysis can show when restrictions should be lifted
- It is feasible that even stable HF are not global minimum
- Other approaches should be used to find even lower energy HF solutions
- Inspiration from similar problems could help; GRRM or Genetic Algorithms



**Questions?**

# Iterative Subspace Eigenvalue Methods

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# Davidson's Algorithm

$\mathbf{Ax} = \lambda \mathbf{x}$	Eigenvalue Problem
$\mathbf{V} = [\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_M]$	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
$\mathbf{V} = [\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_M, \delta_1, \delta_2, \dots, \delta_I]$	Append to guess and restart
$\mathbf{V} = \textit{orthonormalized}(\mathbf{V})$	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:

1. Saad, Y. Numerical Methods for Large Eigenvalue Problems; SIAM, 2011.
2. Li, R.-C.; Zhang, L.-H. Convergence of Block Lanczos Method for Eigenvalue Clusters; 2013.

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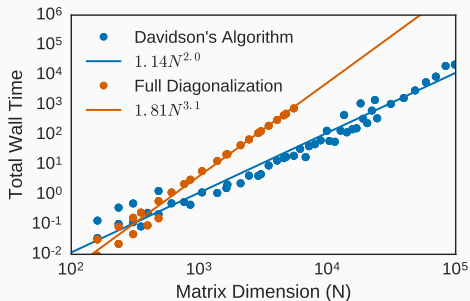
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- My recommendation for guess eigenvectors is

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

# 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>

# Orthogonalization

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

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

- The Gram-Schmidt procedure has numerical issues,

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

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

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

- May need multiple orthogonalization steps