



Hartree-Fock Stability and its Relation to Strong Correlation

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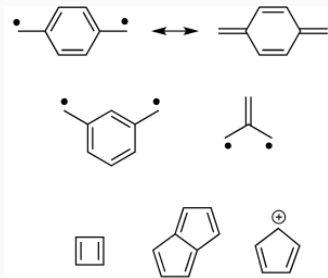
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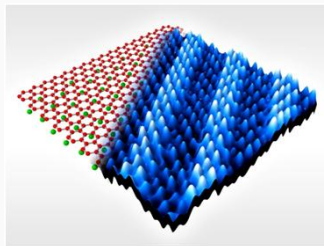
Background Information

We Have Trouble Calculating...

Polyradicals with degenerate triplet
HOMO



Broken Symmetry Periodic Systems



The Electronic Structure Approach

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

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

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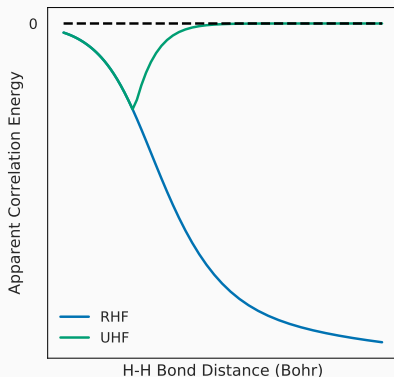
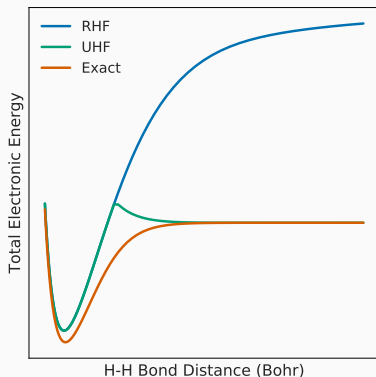
- the difference between the two energies is the correlation energy

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

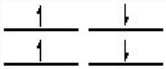
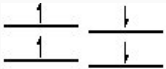
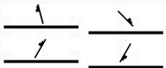
- The correlation energy is recovered by post Hartree-Fock methods (CC, MBPT) which perform better the closer the HF solution is to the exact.
- These methods may fail if the HF solution is far from the exact
- Can we remedy this by finding a better HF solution?
- To what extent are systems with large correlation energies insufficiently described by HF?

Case Study: H_2 Dissociation

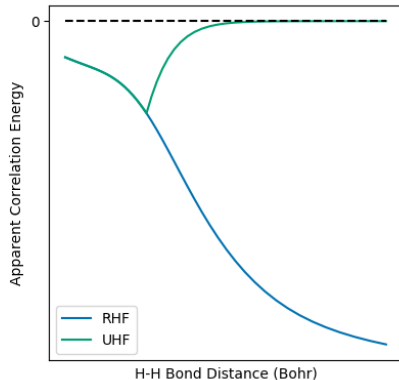
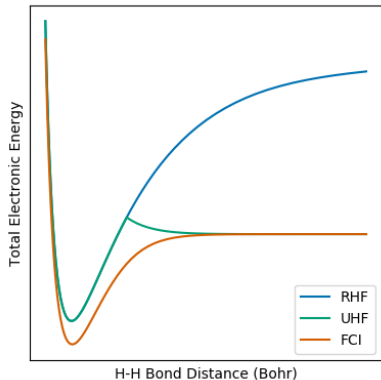
Is this a lot of correlation or a bad reference?



Hartree-Fock Theory is Almost Always Restricted

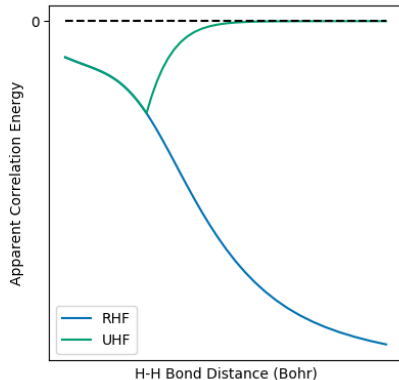
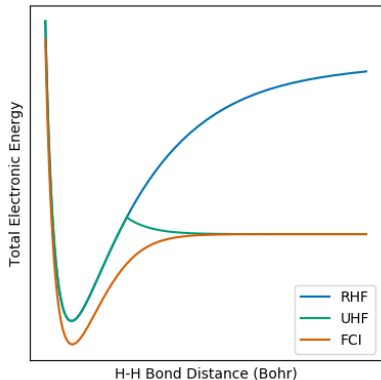
Method	Spinorbital	DoF	Eigenfunction of
Restricted		$N/2$	\hat{S}^2, \hat{S}_z
Unrestricted		N	\hat{S}_z
General		$2N$	Neither

Case Study: H_2 Dissociation



- Is this situation unique to H_2 or is it common ?

Case Study: H_2 Dissociation



- Is this situation unique to H_2 or is it common ?
- Can we identify when a better HF solution is necessary?

Hartree-Fock Stability

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

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- Where

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

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- To determine instabilities, find the lowest eigenvalue

Hartree-Fock Stability Conditions

- The Matrix Equation Factorizes after spin integration

$$\begin{bmatrix} {}^1\mathbf{H} & \mathbf{0} \\ \mathbf{0} & {}^3\mathbf{H} \end{bmatrix} \begin{bmatrix} {}^1\mathbf{x} \\ {}^3\mathbf{x} \end{bmatrix} = \omega \begin{bmatrix} {}^1\mathbf{x} \\ {}^3\mathbf{x} \end{bmatrix}$$

- ${}^1\mathbf{H}$ = Singlet Instability Matrix (RHF \rightarrow RHF)
- ${}^3\mathbf{H}$ = Triplet Instability Matrix (RHF \rightarrow UHF)
- If the lowest eigenvalue of either is negative, solution is unstable

Homogeneous Electron Gas

Why HEG?

- In finite systems with degenerate HOMO-LUMO, an RHF solution is always triplet unstable¹
- Does this hold for infinite systems?
- Overhauser's theorem suggests that this always holds in 1D² HEG
- Can we show this and investigate 2D and 3D?

(1) Yamada, T.; Hirata, S. J. Chem. Phys. 2015, 143 (11), 114112.

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

Brief Overview of HEG

- Homogeneous Electron Gas (HEG) model, also known as Uniform Electron Gas or Jellium Model.

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- The total charge is constrained to be neutral,

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

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- 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 of HEG

- The discretized solutions are given by,

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

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

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

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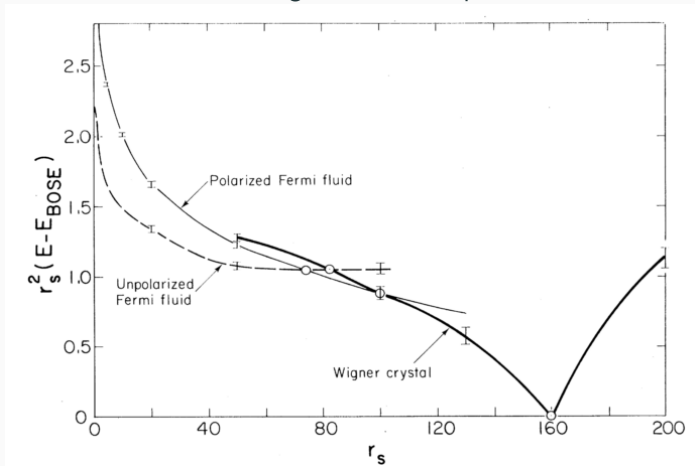
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- In 1D, if $V(r_{12}) = V_0 \delta(r_{12})$,

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

Energies of Some Phases are Known Exactly

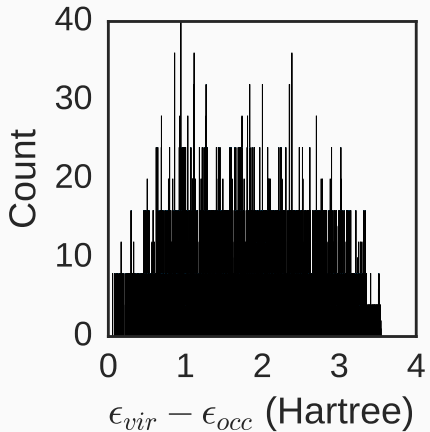
QMC Energies for various phases



Implementation

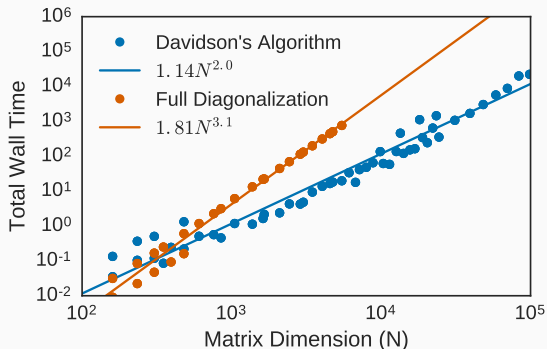
Technical Challenges

- **H** Too big to construct or diagonalize
- Spectrum is dense, leading to numerical issues



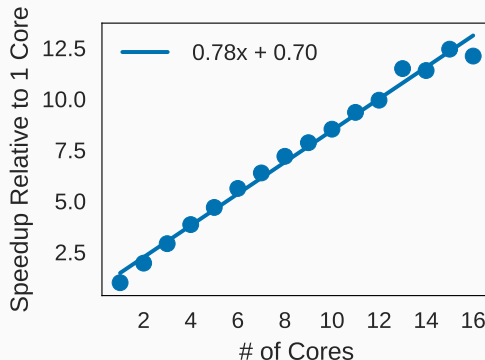
Implementation Solutions 1: Davidson's Algorithm

- Only need the lowest eigenvalue
- Davidson requires no explicit matrix storage
- Careful choice of initial guess circumvents numerical issues
- Still slow for large N



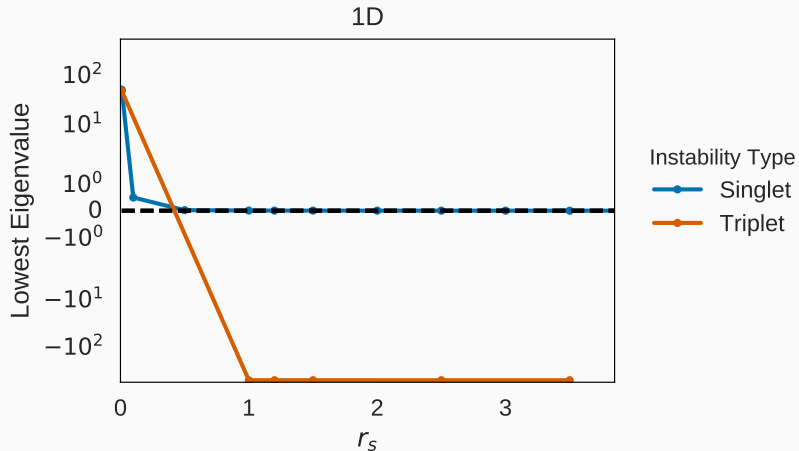
Implementation Solutions 2: Parallelization

- Enables utilization of Blue Waters
- Depending on # of cores, 400-1000 fold speedup compared to serial
- This enabled me to compute 3D results

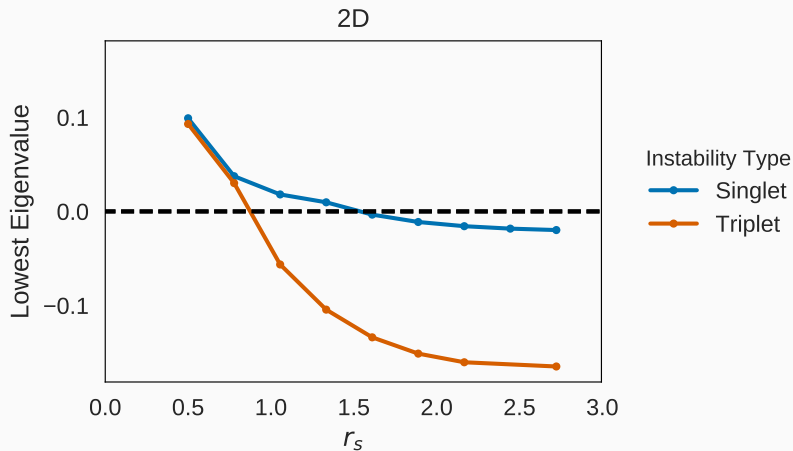


Results

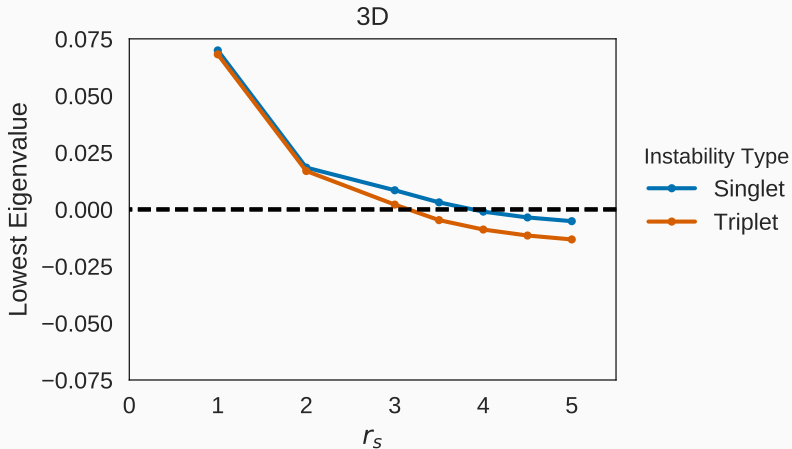
Stability Curves Show Clear Transition



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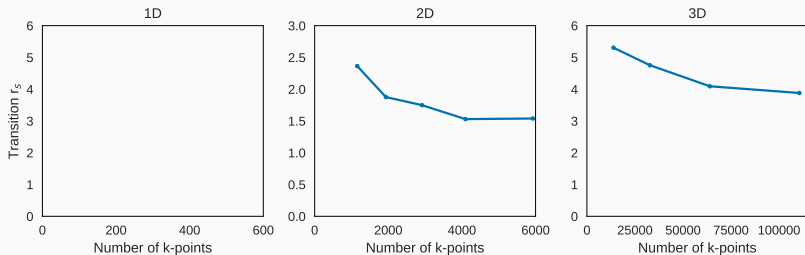


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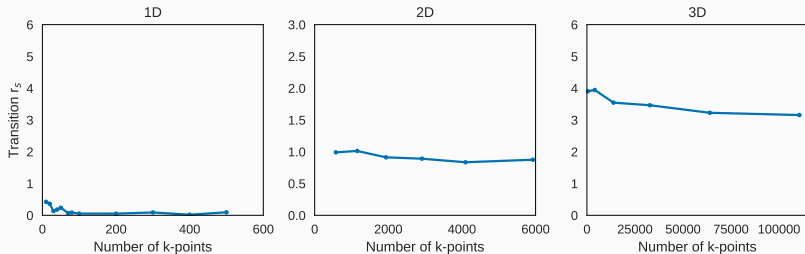
Stability Onset Converges With k-points

Singlet Instabilities



Stability Onset Converges With k-points

Triplet Instabilities



Transitions are Consistent with Others

# Dimensions	Instability r_s	Phase Boundary r_s
1	0.(1)	0 ¹
2	0.8(7)	0.8 ²
3	3.(2)	3.0 ³

(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.

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...

Future Directions

- 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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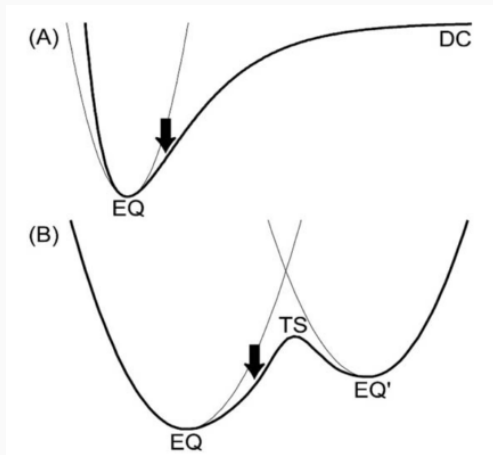
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- Genetic Algorithm²

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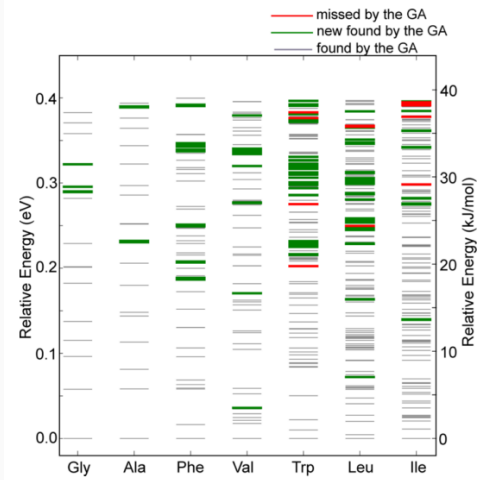
Anharmonic Downward Distortion



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

Acknowledgements

- Advisor: So Hirata
- Group Members:
 - Misha Salim
 - Jacob Fauchaux
 - Alex Doran
 - Cole Johnson
 - Punit Jha
 - Alexander Kunitsa
 - Jun Zhang
- Libraries:
 - PETSc
 - SLEPc
- And the Blue Waters / NCSA Support Staff

Questions?

Hartree-Fock Stability Derivation

The TDHF solution is given by the Liouville Von-Neumann Equation of Motion,

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Under the restrictions,

$$\rho^2 = \rho \quad \text{and} \quad \rho^\dagger = \rho, \quad (9)$$

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

$$\rho_{ai} = C_{ai}, \quad \rho_{ia} = C_{ai}^*. \quad (10)$$

Hartree-Fock Stability Derivation

The TDHF EoM becomes,

$$i\hbar \frac{dC_{ai}(t)}{dt} = (\epsilon_a - \epsilon_i) + \sum_i^{occ} \sum_b^{vir} [\langle aj || ib \rangle C_{bj}(t) + \langle ab || ij \rangle C_{bj}^*(t)] . \quad (11)$$

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

$$\begin{aligned} (\epsilon_a - \epsilon_i) X_{ai} + \sum_i^{occ} \sum_b^{vir} [\langle aj||ib \rangle X_{bj} + \langle ab||ij \rangle Y_{bj}] &= \hbar\omega X_{ai} \\ (\epsilon_a - \epsilon_i) Y_{ai} + \sum_i^{occ} \sum_b^{vir} [\langle aj||ib \rangle X_{bj} + \langle ab||ij \rangle Y_{bj}] &= -\hbar\omega Y_{ai}. \end{aligned} \quad (13)$$

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

Matrix Factorizations

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{d} \\ \mathbf{d}^* \end{bmatrix} = 2E_2 \begin{bmatrix} \mathbf{d} \\ \mathbf{d}^* \end{bmatrix}$$

We can now apply the similarity transform defined by the Unitary matrix

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{bmatrix} \mathbf{I} & -\mathbf{I} \\ \mathbf{I} & \mathbf{I} \end{bmatrix}$$

after which the transformed eigenvalue problem has the form

$$\begin{aligned} \frac{1}{2} \begin{bmatrix} \mathbf{A} + \mathbf{B} + \mathbf{A}^* + \mathbf{B}^* & -\mathbf{A} + \mathbf{A}^* + \mathbf{B} - \mathbf{B}^* \\ -\mathbf{A} + \mathbf{A}^* - \mathbf{B} + \mathbf{B}^* & \mathbf{A}^* + \mathbf{A} - \mathbf{B} - \mathbf{B}^* \end{bmatrix} \begin{bmatrix} \mathbf{d} + \mathbf{d}^* \\ \mathbf{d} - \mathbf{d}^* \end{bmatrix} &= 2E_2 \begin{bmatrix} \mathbf{d} + \mathbf{d}^* \\ -\mathbf{d} + \mathbf{d}^* \end{bmatrix} \\ &= 2E_2 \begin{bmatrix} \text{Re}(\mathbf{d}) \\ \text{Im}(\mathbf{d}) \end{bmatrix} \end{aligned}$$

If \mathbf{A} and \mathbf{B} are both real, $\mathbf{A} = \mathbf{A}^*$ and $\mathbf{B} = \mathbf{B}^*$ and the above simplifies to

$$\begin{bmatrix} \mathbf{A} + \mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A} - \mathbf{B} \end{bmatrix} \begin{bmatrix} \text{Re}(\mathbf{d}) \\ \text{Im}(\mathbf{d}) \end{bmatrix} = 2E_2 \begin{bmatrix} \text{Re}(\mathbf{d}) \\ \text{Im}(\mathbf{d}) \end{bmatrix}$$

Correlation Energy Increases at Small Gap

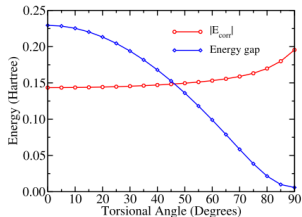


FIG. 6: Correlation energy and energy gap for the twisted ethylene C_2H_4 as a function of the torsion angle around the $\text{C}=\text{C}$ double bond.

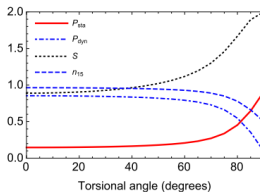


FIG. 7: Correlation curves for ethylene. P_{sta} and P_{dyn} as well as the occupancy of the highest occupied natural spin-orbital and the von Neumann entropy S are plotted as functions of the torsion angle around the $\text{C}=\text{C}$ double bond.

Physicist's Strong Correlation

However, because all repulsive short-range interactions renormalize towards the Fermi surface, their presence does not destroy the underlying free-particle picture of a Fermi Liquid. That is, the interactions can be integrated out, leaving behind renormalized electron or quasi-particle states. Hence, in a Fermi liquid there is a simple principle that can be invoked to lay plain that free electrons are the propagating degrees of freedom. Without the assumption of a Fermi surface, no principle exists that allows us to smooth away the interactions. We refer to such problems as being strongly correlated, namely those in which no obvious principle, ... exists that governs the renormalization of the electron-electron interactions.

Iterative Subspace Eigenvalue Methods

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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 - The approximate eigenvectors become non-orthogonal
- My recommendation for guess eigenvectors is

$$v_j^{(i)} = \textit{normalize} \left(\frac{1}{|A_{ii} - A_{jj}| + 1} \right). \quad (14)$$

Orthogonalization

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

$$\kappa \geq \frac{\text{Max}(A_{ii})}{\text{Min}(A_{jj})} \quad (15)$$

- The Gram-Schmidt procedure has numerical issues,

$$\|\mathbf{I} - \mathbf{Q}^T \mathbf{Q}\| \leq \frac{\alpha \kappa^2}{1 - \beta \kappa^2}. \quad (16)$$

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

$$\|\mathbf{I} - \mathbf{Q}^T \mathbf{Q}\| \leq \frac{\gamma \kappa}{1 - \eta \kappa} \quad (17)$$

- May need multiple orthogonalization steps