Hartree-Fock Stability and its Relation to Strong Correlation

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November 7, 2017

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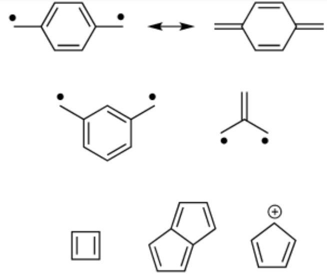
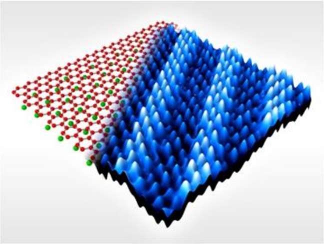
Background Information

We Have Trouble Calculating...

Polyradicals with degenerate triplet HOMO



Broken Symmetry Periodic Systems



(Diradicals): Manabu Abe Chemical Reviews 2013 113 (9), 7011-7088
(Periodic): K.C. Rahnejat et al, Nature Comm. 2, 2011, 558

The Electronic Structure Approach

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

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

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- in Hartree-Fock theory is replaced by

$$\left(\hat{T}_{elec} + \hat{V}_{elec-nuc} + \hat{V}_{\text{mean-field}}\right)\Psi = E_{HF}\Psi$$

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- the difference between the two energies is the correlation energy

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

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Post-Hartree-Fock

- 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?

(Diradicals): Manabu Abe Chemical Reviews 2013 113 (9), 7011-7088
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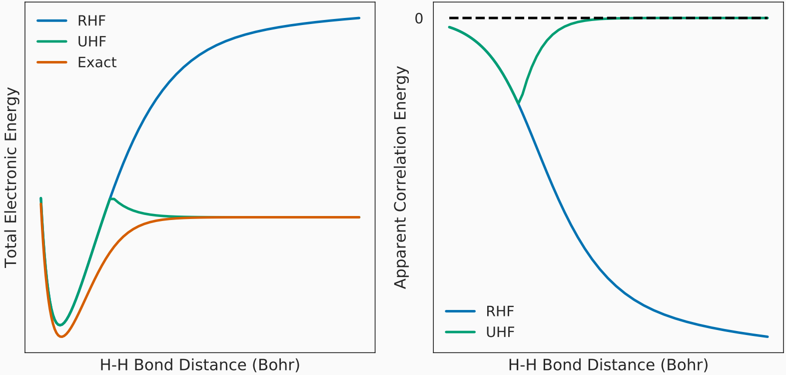
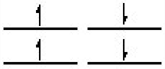
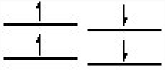
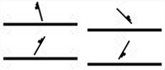
Case Study: H_2 Dissociation

Is this a lot of correlation or a bad reference?

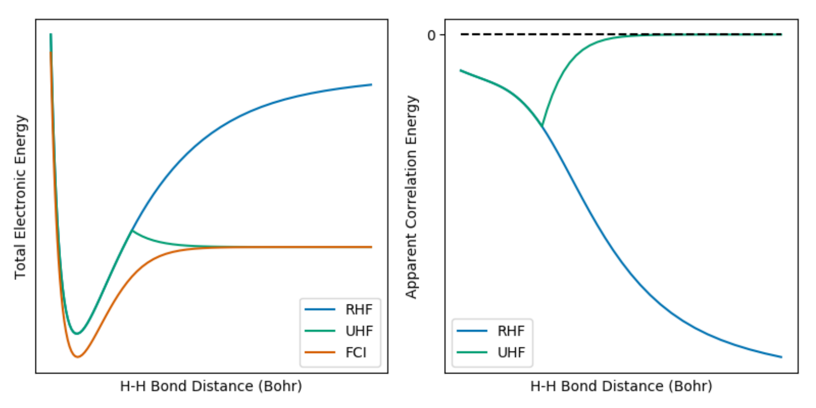


Hartree-Fock Theory is Almost Always Restricted

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

Seeger, R.; Pople, J. A. J. Chem. Phys. 1977, 66 (7), 3045.

Case Study: H_2 Dissociation



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

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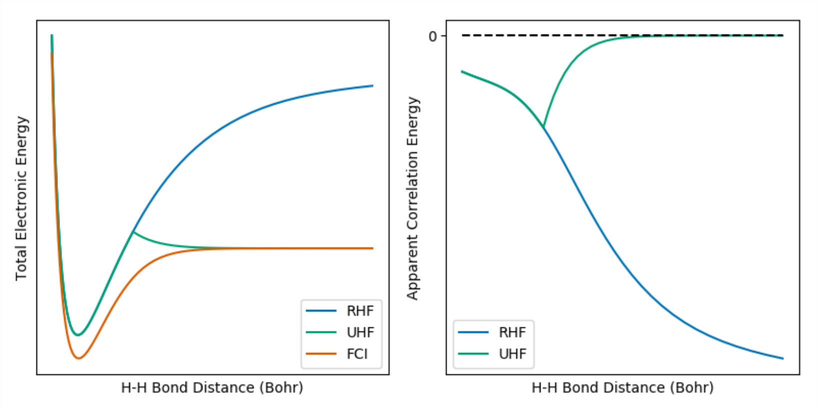

- Is this situation unique to H_2 or is it common ?
- Can we identify when a better HF solution is necessary?

Hartree-Fock Stability

Hartree-Fock Stability Conditions

- Solving the HF equations guarantees only that the energy is stationary.

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- The solution is unstable if any Orbital Hessian (aka stability matrix, electronic + Hessian) eigenvalues are negative, indicating that it's not a minimum

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

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- Where

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

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- To determine instabilities, find the lowest eigenvalue

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Hartree-Fock Stability Conditions

The Matrix Equation Factorizes

Singlet and Triplet Instabilities (RHF - RHF) and (RHF - UHF)

1) Seeger, R.; Pople, J. A. J. Chem. Phys. 1977, 66 (7), 3045.

Homogeneous Electron Gas

why

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Brief Overview of HEG

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- The total charge is constrained to be neutral,

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

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- and the background and coulomb terms cancel exactly,

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

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- The discretized solutions are given by,

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

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

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

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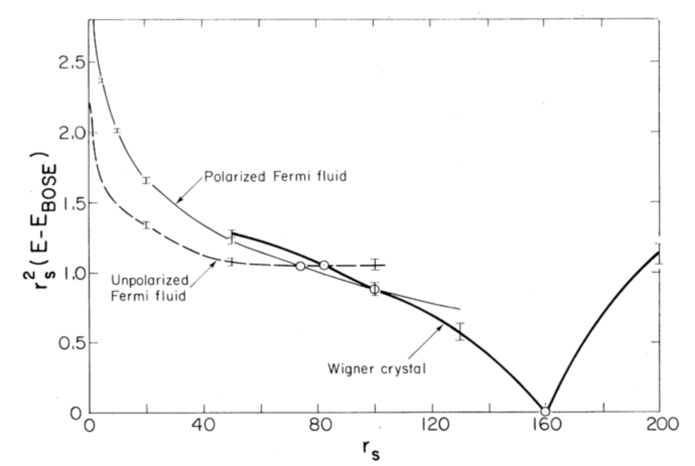
Energies of Some Phases are Known Exactly

QMC Energies for various phases



Applying HF-Stability to HEG

- Will this predict the known tendency of crystallization at low density?

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

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- Overhauser's theorem states that the GHF solution persists at all densities for the HEG[1].

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Applying HF-Stability to HEG

- Will this predict the known tendency of crystallization at low density?
- Overhauser's theorem states that the GHF solution persists at all densities for the HEG[1].
    - Can we show this numerically?

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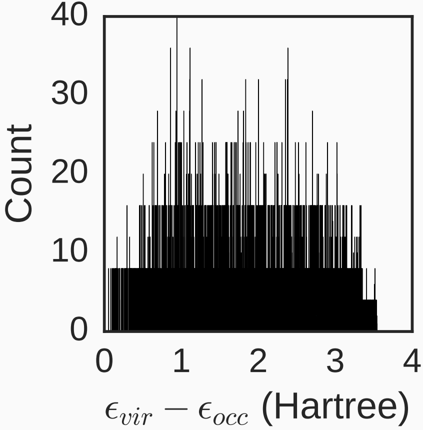
Implementation

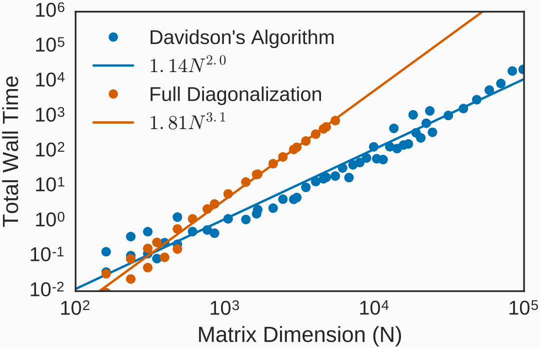
Technical Challenges

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



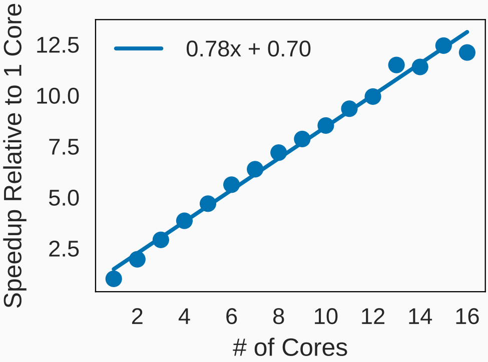
Implementation Solutions 1: Davidson's Algorithm

- 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

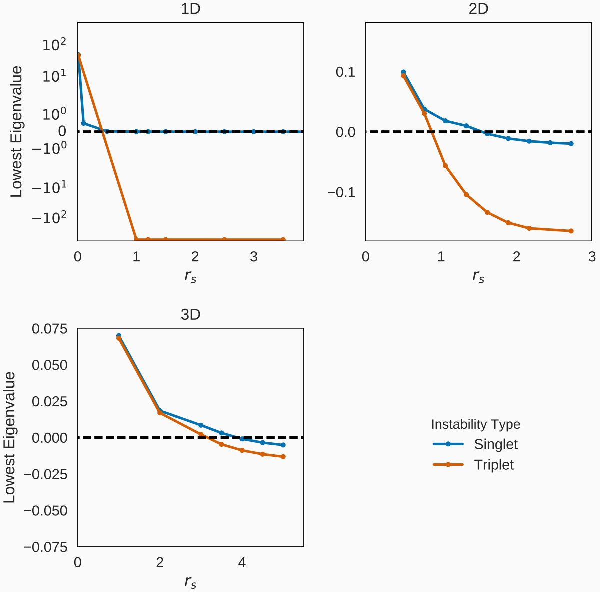
- Enables utilization of Blue Waters
- Depending on # of cores, 400-1000 fold speedup compared to serial
- This enabled me to compute 3D results



Results

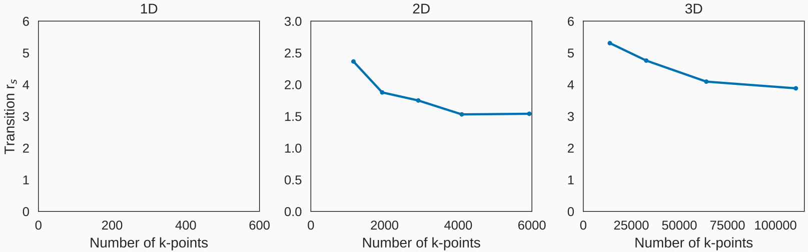
Stability Curves Show Clear Transition

add each to own slide



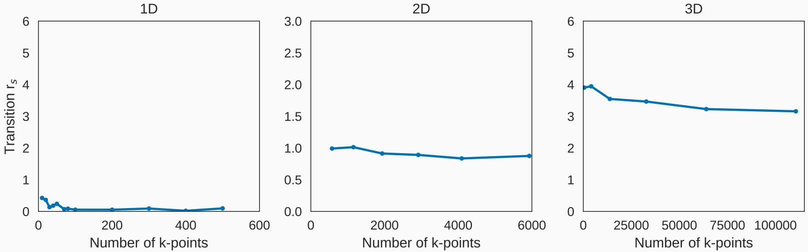
Stability Onset Converges With k-points

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

Brute Force GHF

- 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

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Brute Force GHF

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- Genetic Algorithm[2]

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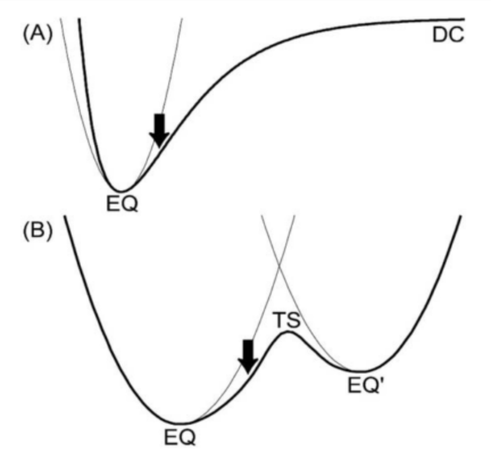
Anharmonic Downard Distortion



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

Figure reproduced from: Ohno, K. Chem. Rec. 2016, 16 (5), 21982218.

Genetic Algorithm

Genetic Algorithm promising in finding many low energy solutions

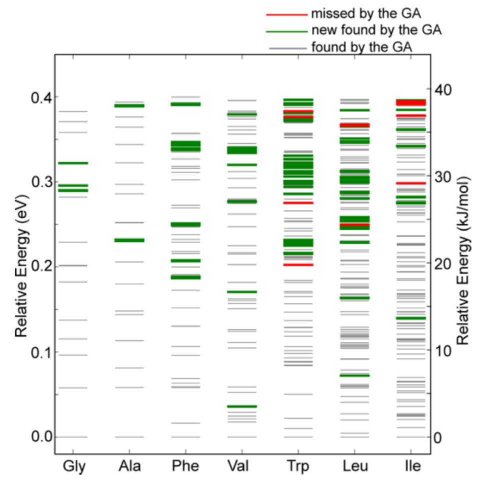


Figure reproduced from: Supady, A.; Blum, V.; Baldauf, C. J. Chem. Inf. Model. 2015, 55 (11), 23382348.

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 Faucheaux
    - 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,

$$i\hbar\frac{\partial\rho}{\partial t} = [T + U, \rho]\,, \tag{7}$$

Thouless, D. J. The Quantum Mechanics of Many-Body Systems, 2nd ed.; Dover: 1972. (p. 114)

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Where U is the self-consistent potential,

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

$$\rho_{ai} = C_{ai}, \quad \rho_{ia} = C^*_{ai}. \tag{10}$$

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Hartree-Fock Stability Derivation

The TDHF EoM becomes,

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

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The solutions are complex exponentials,

$$
C_{ai}\left(t\right) = \alpha X_{ai} e^{-i\omega t} + \alpha^{*} Y_{ai}^{*} e^{i\omega^{*} t}, \quad (12)
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$$C_{ai}(t) = \alpha X_{ai} e^{-i\omega t} + \alpha^* Y^*_{ai} e^{i\omega^* t}, \tag{12}$$

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

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

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

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

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

Thouless, D. J. The Quantum Mechanics of Many-Body Systems, 2nd ed.; Dover: 1972. (p. 114)

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

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

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

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

Correlation Energy Increases at Small Gap

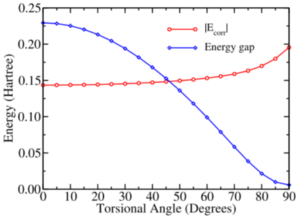

FIG. 6: Correlation energy and energy gap for the twisted ethylene C_2H_4 as a function of the torsion angle around the C=C double bond.

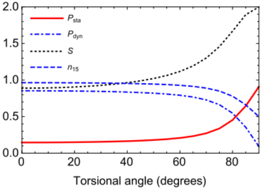

FIG. 7: Correlation curves for ethylene. P_{sta} and P_{dyn} as well as the occupancy of the highest occupied natural spin-orbital and the von Neumann entropy S are plotted as functions of the torsion angle around the C=C double bond.

Figure reproduced from: Benavides-Riveros, C. L.; Lathiotakis, N. N.; Marques, M. A. L. 2017, 111.

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.

Phillips, P. Advanced Solid State Physics, 2nd ed.; Cambridge University Press: Cambridge, 2012.

Iterative Subspace Eigenvalue Methods

Davidson's Algorithm

$\mathbf{Ax} = \lambda \mathbf{x}$	Eigenvalue Problem
$\mathbf{V} = [\mathbf{v_1}, \mathbf{v_2}, ..., \mathbf{v_M}]$	Guess vectors
$\tilde{\mathbf{A}} = \mathbf{V}^\dagger \mathbf{AV}$	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
$\mathbf{V} = [\mathbf{v_1}, \mathbf{v_2}, ..., \mathbf{v_M}, \delta_1, \delta_2, ..., \delta_l]$	Append to guess and restart
$\mathbf{V} = \mathit{orthonormalized}(\mathbf{V})$	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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- They can have convergence issues if:
  - The block size is too small compared to degeneracy
  - The approximate eigenvectors become non-orthogonal
- My recommendation for guess eigenvectors is

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

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.

Orthogonalization

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

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

- The Gram-Schmidt procedure has numerical issues,

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

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

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

- May need multiple orthogonalization steps

Hern, V.; Tom, A.; Vidal, V. SLEPc Technical Reports, 2007.