

Bogoliubov Coupled Cluster Theory for the Attractive Pairing Hamiltonian

Thomas M. Henderson

Department of Chemistry and Department of Physics and Astronomy
Rice University

April 1, 2015



Outline

1. Seniority and Strong Correlation

2. Theory

Pair Coupled Cluster Doubles

The Pairing Hamiltonian

BCS

Quasiparticle Pair Coupled Cluster Doubles

3. Results

4. Properties

5. Extended Coupled Cluster

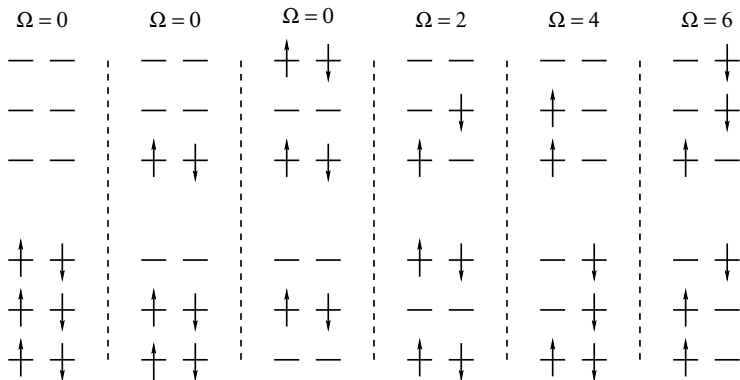
6. Conclusions

Seniority and Strong Correlation

- The seniority Ω is the number of singly occupied spatial orbitals.

Seniority and Strong Correlation

- The seniority Ω is the number of singly occupied spatial orbitals.

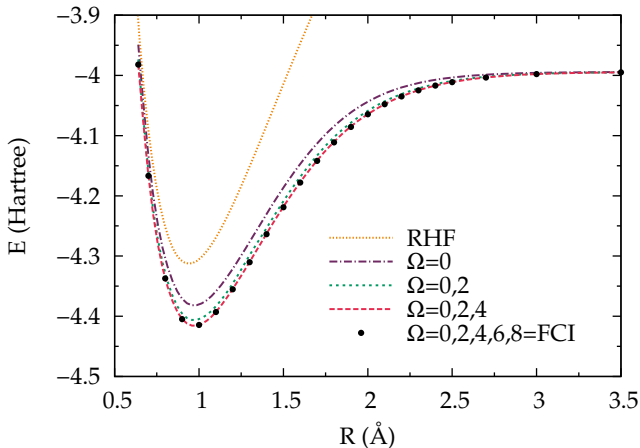


Seniority and Strong Correlation

- The seniority Ω is the number of singly occupied spatial orbitals.
- The $\Omega = 0$ CI often provides a reasonable description of strongly correlated systems.

Seniority and Strong Correlation

- The seniority Ω is the number of singly occupied spatial orbitals.
- The $\Omega = 0$ CI often provides a reasonable description of strongly correlated systems.

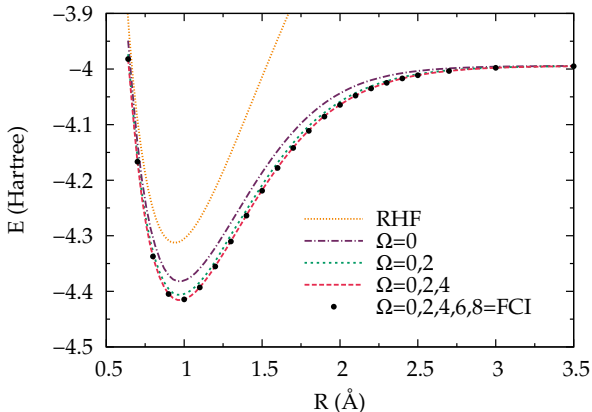


A Few Caveats...

- Results of $\Omega = 0$ CI are not invariant to occupied-occupied and virtual-virtual rotation.

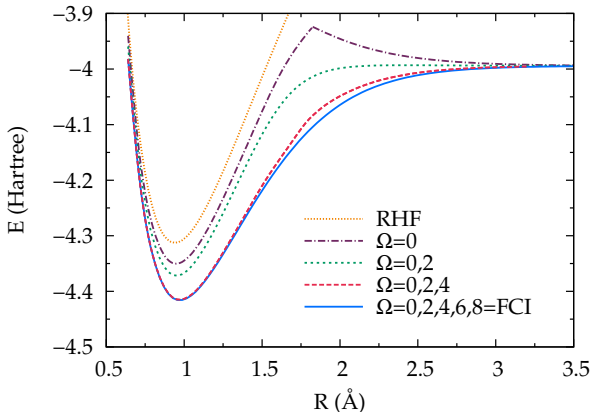
A Few Caveats...

- Results of $\Omega = 0$ CI are not invariant to occupied-occupied and virtual-virtual rotation.



A Few Caveats...

- Results of $\Omega = 0$ CI are not invariant to occupied-occupied and virtual-virtual rotation.

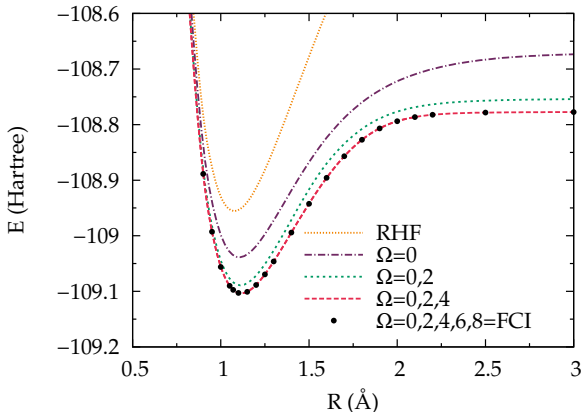


A Few Caveats...

- Results of $\Omega = 0$ CI are not invariant to occupied-occupied and virtual-virtual rotation.
- Sometimes $\Omega = 0$ is not enough to describe strong correlations.

A Few Caveats...

- Results of $\Omega = 0$ CI are not invariant to occupied-occupied and virtual-virtual rotation.
- Sometimes $\Omega = 0$ is not enough to describe strong correlations.



A Few Caveats...

- Results of $\Omega = 0$ CI are not invariant to occupied-occupied and virtual-virtual rotation.
- Sometimes $\Omega = 0$ is not enough to describe strong correlations.
- The cost of $\Omega = 0$ CI is too high for routine application.

Pair Coupled Cluster Doubles

- Pair CCD (*i.e.* $\Omega = 0$ CCD) with a suitable reference determinant and pairing scheme is surprisingly close to $\Omega = 0$ CI.
- The cost of p-CCD for a given set of orbitals and pairing scheme is $\mathcal{O}(N^3)$.
- Therefore,
 - If the reference determinant and pairing scheme can be readily obtained, and
 - If the p-CCD is close to $\Omega = 0$ CI, and
 - If the $\Omega = 0$ CI properly describes strong correlation,
 - Then p-CCD offers a cheap but accurate description of strong correlations (at least energetically).

The Pairing Hamiltonian

The pairing Hamiltonian is

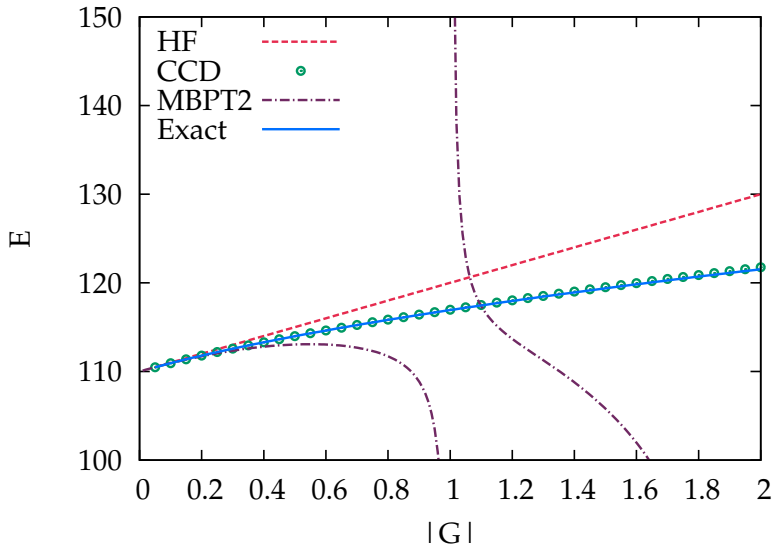
$$H = \sum \epsilon_p N_p - G \sum P_p^\dagger P_q$$

where

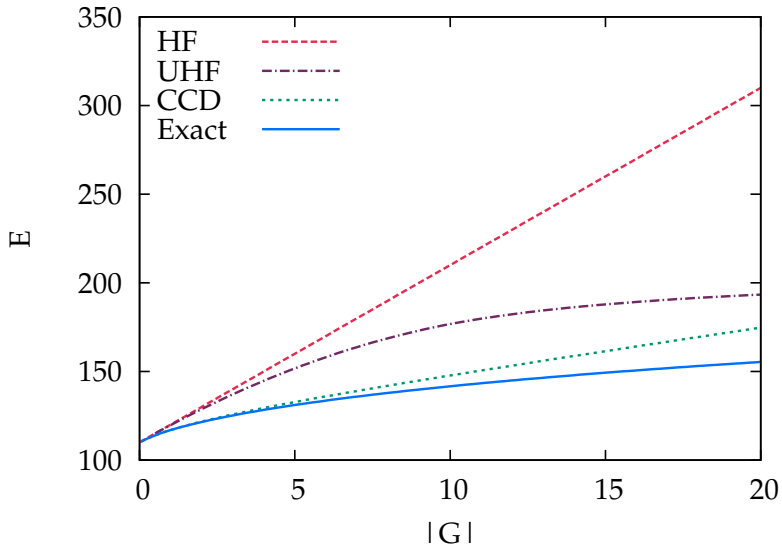
$$N_p = c_{p\uparrow}^\dagger c_{p\uparrow} + c_{p\downarrow}^\dagger c_{p\downarrow},$$
$$P_p^\dagger = c_{p\uparrow}^\dagger c_{p\downarrow}^\dagger.$$

- Originally designed to describe the Cooper problem of an electron pair interacting with a hole pair in the Fermi sea.
- The weakly attractive pairing Hamiltonian mimics the physics of the molecular Hamiltonian.
- The Hamiltonian has an intrinsic pairing scheme and seniority is a symmetry with a good quantum number.
- $\Omega = 0$ CI is thus exact...
- ...but not necessary, because the Hamiltonian is exactly solvable.

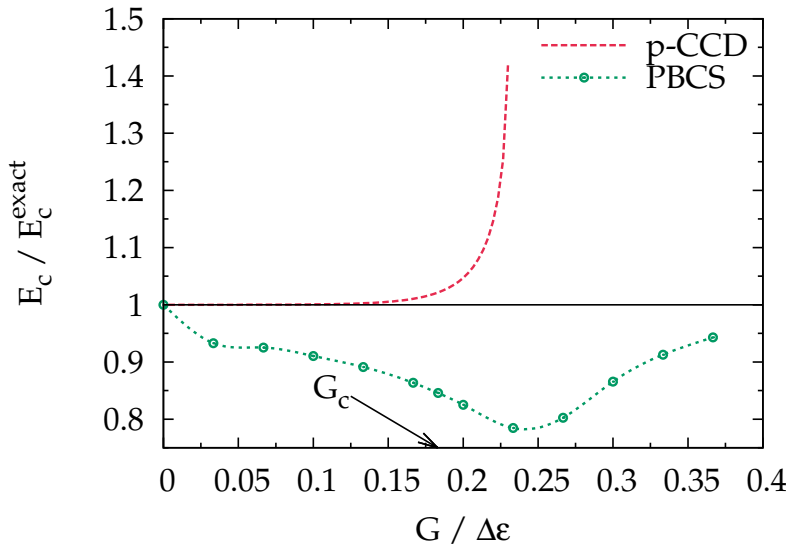
p-CCD for the Pairing Hamiltonian



p-CCD for the Pairing Hamiltonian



p-CCD for the Pairing Hamiltonian



A Few Words on BCS

- Define quasiparticle operators by the unitary transformation

$$c_{p\uparrow}^\dagger = u_p \alpha_{p\uparrow}^\dagger + v_p \alpha_{p\downarrow}$$

$$c_{p\downarrow}^\dagger = u_p \alpha_{p\downarrow}^\dagger - v_p \alpha_{p\uparrow}.$$

- Write a quasiparticle vacuum $|0\rangle = \prod \alpha_{p\uparrow} \alpha_{p\downarrow} |-\rangle$.
- Minimize the energy with respect to u_p and v_p .
- The quasiparticle vacuum may break number symmetry.
- Include a chemical potential to enforce that we have the right particle number on average.
- Hartree-Fock is a special limit ($v_{\text{occ}} = 1, u_{\text{virt}} = 1$).

For the pairing Hamiltonian, we have

$$0 = 2 \mathcal{F}_p u_p v_p - \Delta (u_p^2 - v_p^2)$$

$$\mathcal{F}_p = \epsilon_p - \lambda - G v_p^2$$

$$\Delta = G \sum u_p v_p$$

$$\langle N \rangle = 2 \sum v_p^2.$$

Number and Spin Symmetry Breaking

Let me define

$$E_{\text{cs}}[\mathbf{P}] = 2 \sum \langle i|h|j \rangle P_{ji} + \sum (2 \langle ij|v|kl \rangle - \langle ij|v|lk \rangle) P_{ki} P_{lj}.$$

UHF:

$$\begin{aligned} E &= E_{\text{cs}}[\mathbf{P}] - \sum \langle ij|v|kl \rangle M_{li} M_{kj}, \\ \mathbf{M}^2 &= \mathbf{P} - \mathbf{P}^2, \\ \mathbf{M} &= \mathbf{P} \mathbf{M} + \mathbf{M} \mathbf{P} \end{aligned}$$

RHFB:

$$\begin{aligned} E &= E_{\text{cs}}[\mathbf{P}] + \sum \langle ij|v|kl \rangle K_{ij} K_{kl}, \\ \mathbf{K}^2 &= \mathbf{P} - \mathbf{P}^2, \\ \mathbf{0} &= \mathbf{P} \mathbf{K} - \mathbf{K} \mathbf{P}. \end{aligned}$$

Number and Spin Symmetry Breaking

Notes:

- For real orbitals, the energy expressions are the same except for the sign on the static correlation piece.
- RHF_B reduces to RHF for repulsive interactions because the static correlation piece is non-negative and the minimum of the closed shell energy occurs at RHF.
- UHF reduces to RHF for attractive interactions because the static correlation piece is non-negative and the minimum of the closed shell energy occurs at RHF.
- That is, number symmetry breaking is to attractive interactions as spin symmetry breaking is to repulsive interactions.

Pair Coupled Cluster Doubles, Revisited

Let's start with the HF case:

- Write the wave function as $e^T|0\rangle$ where the cluster operator is

$$T = \sum_{ia} T_i^a P_a^\dagger P_i$$
$$P_p^\dagger = c_{p\uparrow}^\dagger c_{p\downarrow}^\dagger.$$

- Insert the CC wave function into the Schrödinger equation to get the working equations:

$$E = \langle 0 | e^{-T} H e^T | 0 \rangle$$
$$0 = \langle 0 | P_i^\dagger P_a e^{-T} H e^T | 0 \rangle.$$

Pair Quasiparticle CCD

The extension to the BCS case is straightforward:

- Write the wave function as $e^T|0\rangle$ where the cluster operator is

$$T = \frac{1}{2} \sum_{pq} T_{pq} \mathcal{P}_p^\dagger \mathcal{P}_q^\dagger$$

$$\mathcal{P}_p^\dagger = \alpha_{p\uparrow}^\dagger \alpha_{p\downarrow}^\dagger.$$

- Insert the CC wave function into the Schrödinger equation to get the working equations:

$$E = \langle 0 | e^{-T} H e^T | 0 \rangle,$$

$$0 = \langle 0 | \mathcal{P}_p \mathcal{P}_q e^{-T} H e^T | 0 \rangle.$$

NB: In the Hartree-Fock limit, we get

$$T = \sum_{ia} T_i^a P_a^\dagger P_i + \frac{1}{2} \sum_{ij} T_{ij} P_i P_j + \frac{1}{2} \sum_{ab} T_{ab} P_a^\dagger P_b^\dagger.$$

Brueckner Coupled Cluster

- Brueckner orbitals just adjust the reference determinant so that $T_1 = 0$.
- In the pairing Hamiltonian with a Hartree-Fock reference, $T_1 = 0$ by seniority symmetry.
- Once number symmetry is broken, this is not the case, so we add

$$0 = \langle 0 | \mathcal{P}_p e^{-T_2} H e^{T_2} | 0 \rangle.$$

and adjust u and v to satisfy this.

Brueckner Coupled Cluster

- Brueckner orbitals just adjust the reference determinant so that $T_1 = 0$.
- In the pairing Hamiltonian with a Hartree-Fock reference, $T_1 = 0$ by seniority symmetry.
- Once number symmetry is broken, this is not the case, so we add

$$0 = \langle 0 | \mathcal{P}_p e^{-T_2} H e^{T_2} | 0 \rangle.$$

and adjust u and v to satisfy this.

$$0 = 2 \mathcal{F}_p u_p v_p - \Delta (u_p^2 - v_p^2)$$

$$\mathcal{F}_p = \epsilon_p - \lambda - G v_p^2$$

$$\Delta = G \sum u_p v_p$$

$$\langle N \rangle = 2 \sum v_p^2.$$

Brueckner Coupled Cluster

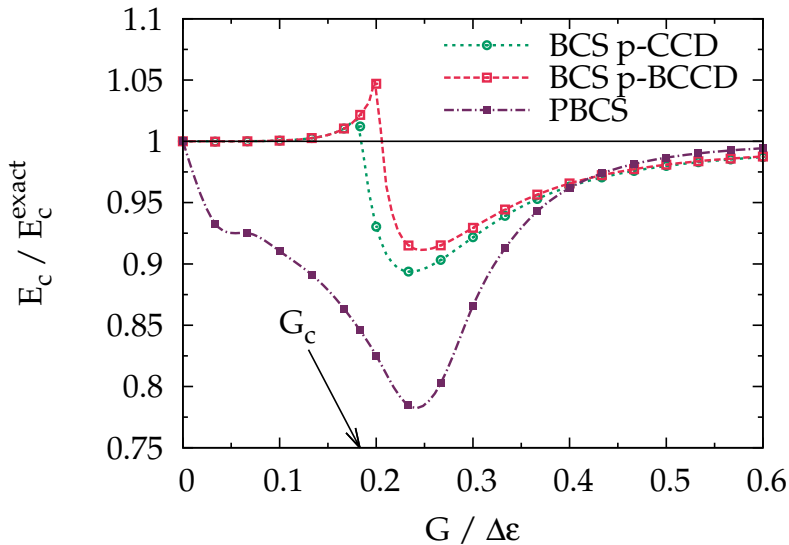
- Brueckner orbitals just adjust the reference determinant so that $T_1 = 0$.
- In the pairing Hamiltonian with a Hartree-Fock reference, $T_1 = 0$ by seniority symmetry.
- Once number symmetry is broken, this is not the case, so we add

$$0 = \langle 0 | \mathcal{P}_p e^{-T_2} H e^{T_2} | 0 \rangle.$$

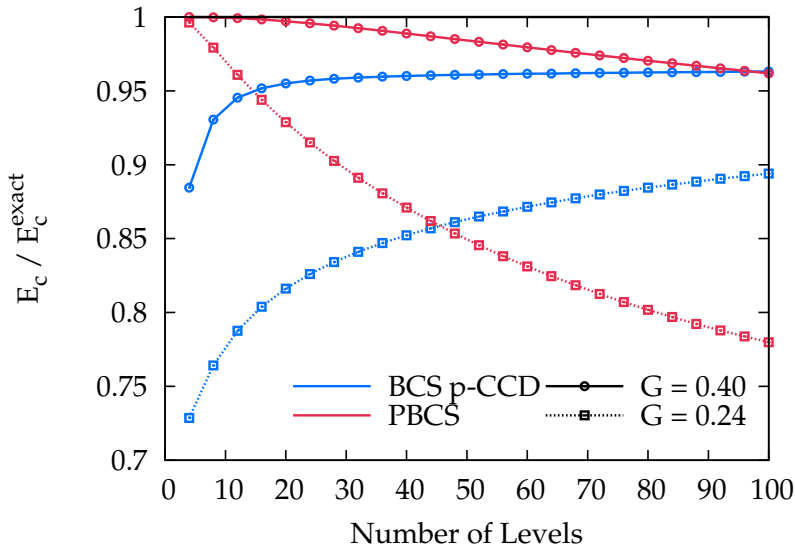
and adjust u and v to satisfy this.

$$\begin{aligned} 0 &= 2 \bar{\mathcal{F}}_p u_p v_p - \Delta \left(u_p^2 - v_p^2 \right) + c_p \\ \bar{\mathcal{F}}_p &= \epsilon_p - \lambda - G v_p^2 + G \sum_q \left(u_q^2 - v_q^2 \right) T_{pq} \\ c_p &= \sum_q T_{pq} \left[2 \mathcal{F}_q u_q v_q - \Delta \left(u_q^2 - v_q^2 \right) \right] \end{aligned}$$

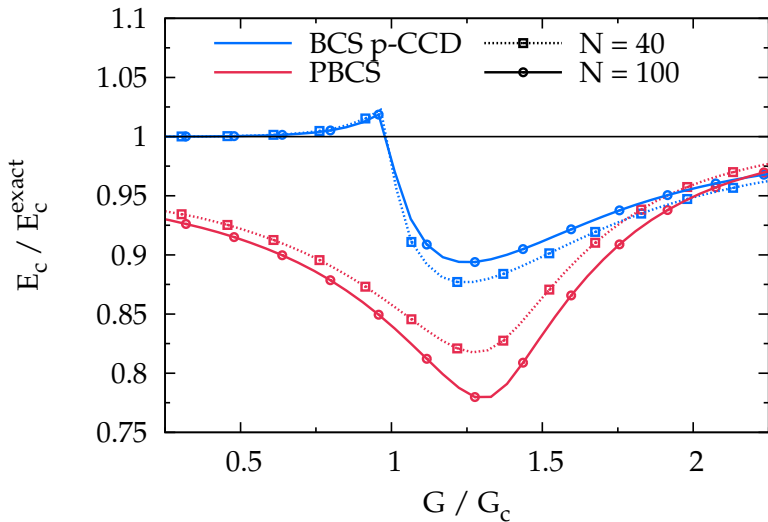
Attractive Pairing; $N = L = 100$



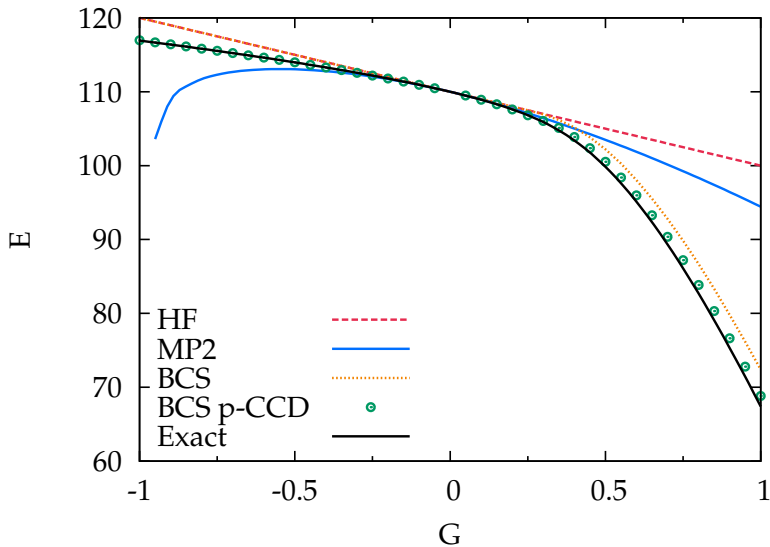
Dependence on Number of Levels



Dependence on Filling Fraction



Putting it Together



Calculation of Properties

- Properties can be evaluated as energy derivatives.
- As presented, we would need to know the derivatives of the amplitudes T_{pq} .
- As in standard CC, we can avoid this by introducing a Lagrangian.

Write a Lagrangian

$$\mathcal{L} = \langle 0 | (1 + Z) e^{-T} H e^T | 0 \rangle$$

in terms of the operator

$$Z = \frac{1}{2} \sum_{pq} Z_{pq} \mathcal{P}_p \mathcal{P}_q.$$

Calculation of Properties

- Note that for any Z_{pq} , we have $\mathcal{L} = E$ provided we satisfy the CC equations.
- In other words, we see that

$$\frac{\partial \mathcal{L}}{\partial Z_{pq}} = 0$$

is the amplitude equation.

- To select amplitudes Z_{pq} , we impose

$$\frac{\partial \mathcal{L}}{\partial T_{pq}} = 0.$$

- Then the Lagrangian is stationary with respect to T and Z , so we do not need their derivatives.

Calculation of Properties

Explicitly, we have

$$\frac{\partial \mathcal{L}}{\partial x} = \langle 0 | (1 + Z) e^{-T} \frac{\partial H}{\partial x} e^T | 0 \rangle + \sum_p \frac{\partial E_c}{\partial \theta_p} \frac{\partial \theta_p}{\partial x}$$

where I write the BCS amplitudes as

$$u_p = \cos(\theta_p),$$

$$v_p = \sin(\theta_p)$$

The second term is because while the BCS energy is stationary with respect to BCS amplitudes, the correlated energy is not!

We can get $\frac{\partial \theta_p}{\partial x}$ by differentiating the BCS amplitude equations:

Important: This term can be pretty large.

Calculation of Properties

- The BCS equations are

$$h_p^{2,0}[\theta(x)] + x V_p^{2,0}[\theta(x)] = 0$$

where V is the perturbation.

- The derivative with respect to x at $x = 0$ is just

$$\frac{\partial h_p^{2,0}}{\partial \theta_q} \frac{\partial \theta_q}{\partial x} + V_p^{2,0} = 0.$$

- Note that

$$\frac{\partial h_p^{2,0}}{\partial \theta_q} = \frac{\partial^2 E_{\text{BCS}}}{\partial \theta_p \partial \theta_q}$$

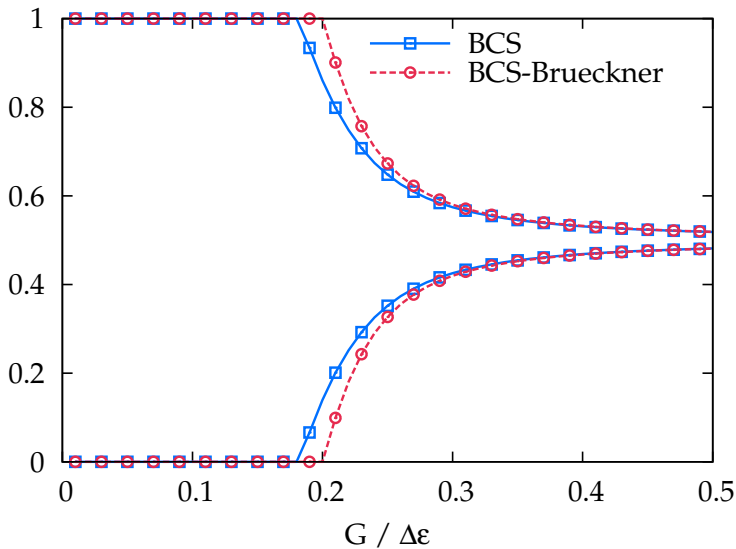
is the BCS quasiparticle Hessian \mathcal{M}_{pq} .

- Thus, we evaluate properties as

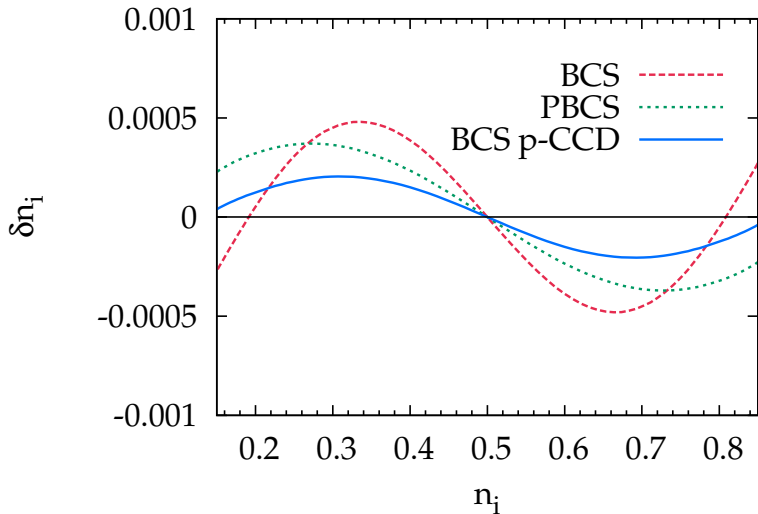
$$\frac{\partial \mathcal{L}}{\partial x} = \langle 0 | (1 + Z) e^{-T} V e^T | 0 \rangle - \mathbf{W}^\dagger \mathcal{M}^{-1} \mathbf{V}^{2,0}$$

where \mathbf{W} is the orbital gradient of the correlation energy.

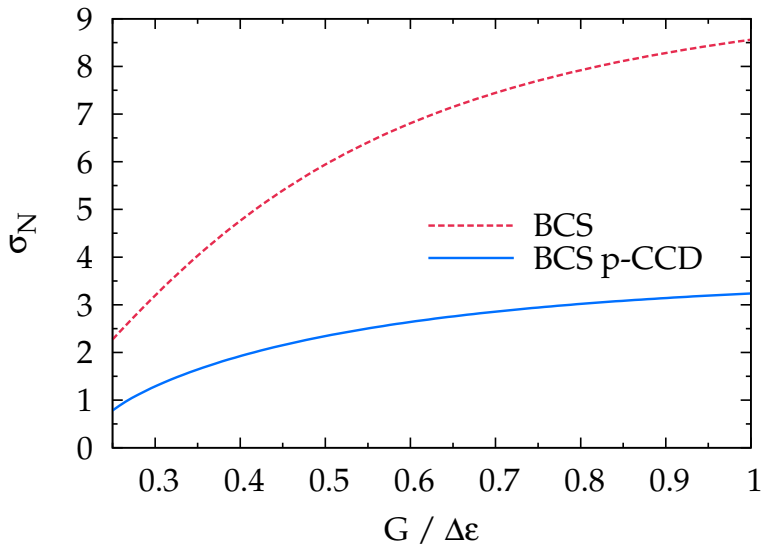
Occupation Numbers



Attractive Pairing; $N = L = 100$



Attractive Pairing; $N = L = 100$

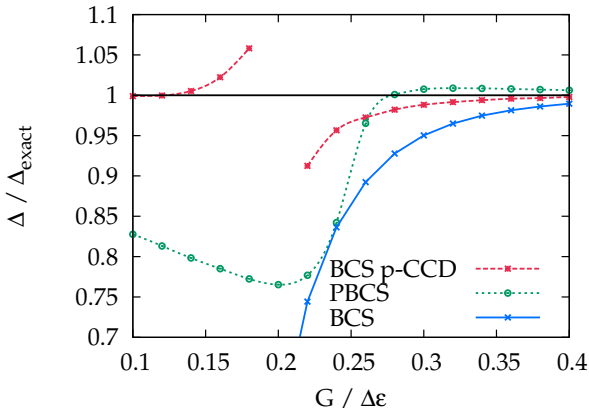


The Superconducting Gap

We can generalize the superconducting gap to

$$\Delta_0 = G \sum C_p$$

$$C_p^2 = \langle n_{p\uparrow} n_{p\downarrow} \rangle - \frac{1}{4} \langle n_{p\uparrow} + n_{p\downarrow} \rangle^2.$$



Beyond Traditional Coupled Cluster

- We've seen the CC Lagrangian

$$\mathcal{L} = \langle 0 | (1 + Z) e^{-T} H e^T | 0 \rangle.$$

- Next obvious step: more sophisticated left-hand state.
- Extended coupled cluster uses

$$\mathcal{L} = \langle 0 | e^Z e^{-T} H e^T | 0 \rangle.$$

- For typical problems, this is much more expensive than traditional coupled cluster.
- *Pair* extended coupled cluster not too expensive – $\mathcal{O}(N^3)$.

Quick Overview of Pair Extended Coupled Cluster

- Write a cluster operator

$$T = \sum_{ia} t_i^a P_a^\dagger P_i.$$

- Write a de-excitation operator

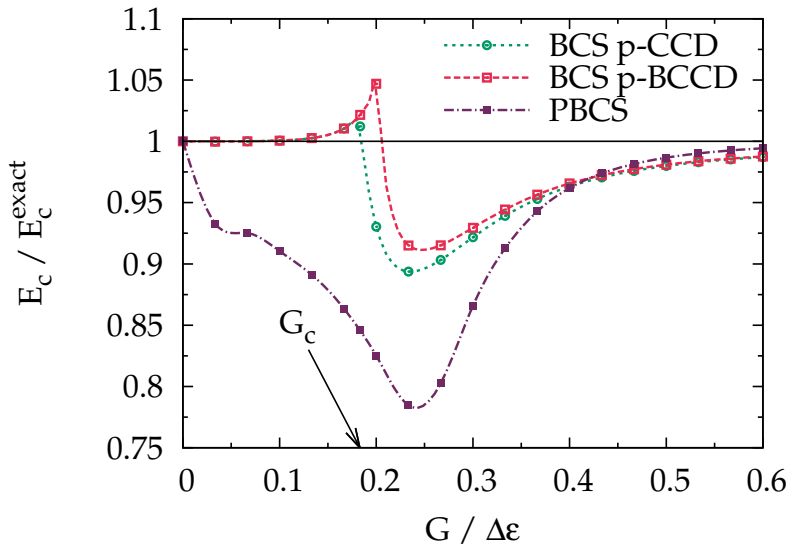
$$Z = \sum_{ia} z_a^i P_i^\dagger P_a.$$

- Write a Lagrangian

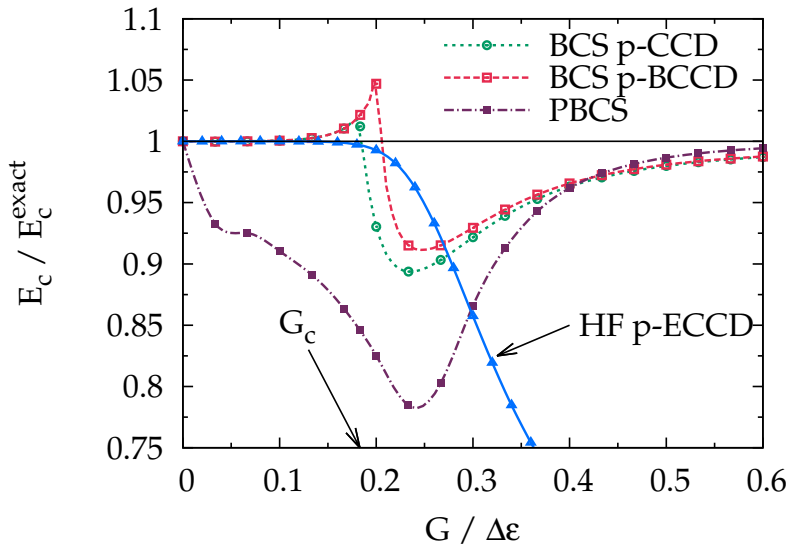
$$\mathcal{L} = \langle 0 | e^Z e^{-T} H e^T | 0 \rangle.$$

- Make the Lagrangian stationary with respect to t_i^a and z_a^i .

Attractive Pairing; $N = L = 100$



Attractive Pairing; $N = L = 100$



Bogoliubov Pair Extended Coupled Cluster

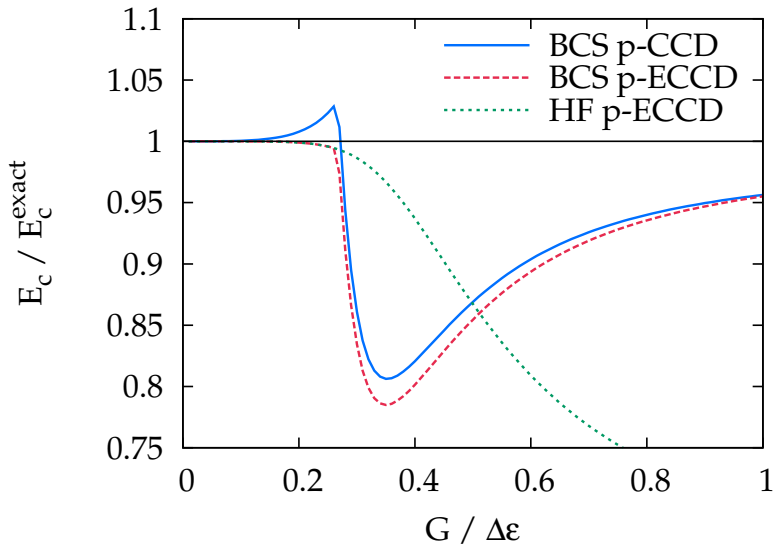
- Same basic idea, we

$$T = \frac{1}{2} \sum_{pq} T_{pq} \mathcal{P}_p^\dagger \mathcal{P}_q^\dagger,$$

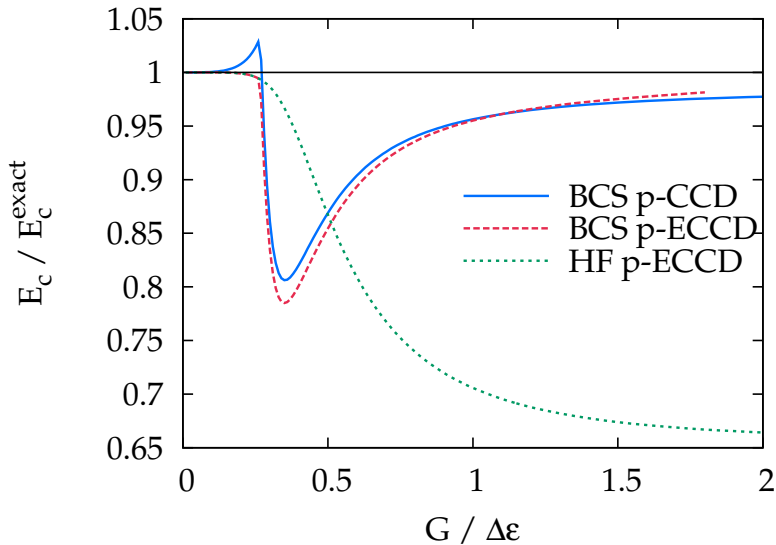
$$Z = \frac{1}{2} \sum_{pq} Z_{pq} \mathcal{P}_p \mathcal{P}_q.$$

- Computational scaling rises to $\mathcal{O}(N^4)$.
- Efficient $\mathcal{O}(N^4)$ code not finished....
- Inefficient $\mathcal{O}(N^6)$ code done.

Attractive Pairing; $N = L = 20$



Attractive Pairing; $N = L = 20$



Conclusions

- The p-CCD $\sim \Omega = 0$ CI holds even for fairly strongly repulsive pairing Hamiltonians.
- For strongly attractive pairing Hamiltonians, BCS-CCD works fairly well.
- The Brueckner mean-field of the BCS-CCD is trying to fix number symmetry breaking.
 - In doing so, the Brueckner is also making things worse near G_c .
 - For intermediate G , the Brueckner makes things better.
 - For large G , the Brueckner makes no real difference.
- For small systems, PBCS = AGP works very well, but it breaks down for larger N .
- In fact, for very large N , AGP = BCS.
- Pair quasiparticle CCD works across the whole range of G and N .
- Pair extended CCD seems to work pretty well for G not too large.
- Pair quasiparticle extended CCD does not seem to work...
- But with orbital optimization, pair quasiparticle extended CCD may be a very good method indeed.

Acknowledgments

Collaborators:

- Jorge Dukelsky (Instituto de Estructura de la Materia; Madrid)
- Gustavo Scuseria (Rice University)
- Thomas Duguet (Service de Physique Nucléaire; Centre de Saclay; Paris)
- Angelo Signoracci (Service de Physique Nucléaire; Centre de Saclay; Paris)

Calculations:

- Carlos Jiménez-Hoyos

Funding:

- Department of Energy
- Welch Foundation

Some Useful References

Pairing Hamiltonian Exact Solutions:

- R. W. Richardson, Phys. Lett. **3**, 277 (1963).
- R. W. Richardson, Phys. Rev. **141**, 949 (1966).

Pair Coupled Cluster:

- P. A. Limacher, P. W. Ayers, P. A. Johnson, S. de Baerdemacker, D. van Neck, and P. Bultinck, J. Chem. Theory Comput. **9**, 1394 (2013).
- TMH, G. E. Scuseria, J. Dukelsky, A. Signoracci, and T. Duguet, Phys. Rev. C **89**, 054305 (2014).
- TMH, I. W. Bulik, and G. E. Scuseria, arXiv:1503.04878.