Constrained-Pairing Mean-Field Theory

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Outline

• A novel model for strong correlations: Constrained-Pairing Mean-Field Theory

• Basic ideas about CPMFT and molecular dissociation examples

• Connection with UHF formalism

• Spin off: ROHF theory made simple
What is Static/Strong Correlation?

- It is all about **near-degeneracies**

- A single-determinant **RHF** wavefunction (with **correct symmetries**) becomes a **very poor descriptor** of the electronic structure

- **Static correlation examples:**
  - **Closed-shell H₂** at dissociation (**σ_g/σ_u** degeneracy)
    - Nonlocal, left-right correlation: the physics of **entanglement**
  - **Be atom**
    - Due to **2s²/2p²** near degeneracy
  - **Transition metals, lanthanides, and actinides**
    - Large **DOS** at Fermi energy => heavy fermions in solid state
How to deal with strong correlation?

- **Space- and spin-symmetry breaking** via an unrestricted formalism is the traditional way of dealing with nonlocal, left-right correlation in a computationally inexpensive manner.

- **Exchange hole localization** in DFT also incorporates static correlation but this introduces undesirable self-interaction error.

- **Breaking** space and spin symmetries have nasty consequences, e.g., on magnetic properties.

- **Correct** quantum numbers are hard to recover once symmetries are broken.
$H_2$: prototype of left-right static correlation
At dissociation, the symmetry-correct orbitals ($\sigma_g$ and $\sigma_u$) become degenerate.

$H_2$: prototype of left-right static correlation
$H_2$: prototype of left-right static correlation

Unrestricted scheme breaks symmetry to capture left-right correlation
Exchange-Correlation Hole Localization

- Concept of “hole”: depletion in density that diminishes electron-electron repulsion:

\[ E \text{ [x or c]} = - \int \int \rho(r) \rho_{\text{hole}}(r') / |r-r'| \]

- Holes are extensively used in DFT but can be rigorously calculated from wavefunctions

- \( H_2 \) near \( R_e \): both the exchange and correlation holes are localized with the reference electron

- \( H_2 \) at dissociation: exchange is completely delocalized over the two protons (exchange becomes nonlocal); correlation is nonlocal too and exactly cancels the exchange delocalization; \( XC \) hole is localized with the reference electron
2nd Flavor: Angular Static Correlation

• Related to near degeneracies in atoms

• Prototype case:
  4-electron series; 2s/2p near-degeneracy: Li−, Be, B+, C2+, N3+ ...

• When \( Z \to \infty \), atomic levels with same \( n \) but different \( L \) become degenerate ("angular" degeneracy)

• Correlation energy diverges as \(-0.01173 \ Z\)
Dynamic Correlation

• “Weak” as opposed to “strong” correlation

• Has strong basis set dependence because of electron-electron cusp (static correlation has weak basis set dependence)

• Ubiquitous in the 2e-series: He, Li+, Be²⁺...

• When \( Z \rightarrow \infty \), correlation energy goes to a constant (~44 mili \( E_H \)) independent of \( Z \)

• Treatable by perturbation or coupled-cluster theories
Strong Correlation Method Wish List

- Should preserve space and spin symmetries
- Should have low-computational cost (mean-field) instead of CASSCF or FCI combinatorial blowup
- Should cleanly separate static & dynamic correlation
- Should correctly dissociate any polyatomic molecule into ROHF atoms (or fragments)
- Should smoothly connect the dissociation limit (full entanglement) with the equilibrium region (where it should yield RHF in the absence of static correlation)
How do we accomplish this?

• The CPMFT energy functional (JCP 2009)

\[ E = 2 \sum h_{pq} P_{pq} + \sum [2(pq,rs)-(pr,qs)] P_{pq} P_{rs} - \sum (pr,qs) K_{pq} K_{rs} \]

where \( K^2 = P - P^2 \) \( P = P^\alpha = P^\beta \)

satisfies all requirements in the wish list if we let \( K \) be non-zero in an active space determined by the entangled electrons of the molecular ground-state dissociation limit.

• Without the active space constraint this model is not good (Staroverov & Scuseria 1HFB, 2002)

• \( K^2 \) is Yamaguchi’s “odd-electron distribution” (1978) identical to Staroverov & Davidson’s “density of effectively unpaired electrons” (2000)
CPMFT: The HFB connection

• The mean-field *model* Hamiltonian:

\[ H_0 = \sum_{pq} \left[ f_{pq} a_p^+ a_q - \Delta_{pq} a_p^+ a_q^+ - \Delta^*_{pq} a_p a_q \right] \]

breaks electron number conservation but introduces p-p and h-h correlations

• This theory is called Hartree-Fock-Bogoliubov (HFB) and requires attractive interactions for pairing (negative sign in \( \Delta > 0 \))

• A chemical potential is needed in HFB to control \( N_e \)

• The CPMFT energy functional is

\[ E_{CPMFT} = \langle 0 | H_0 | 0 \rangle \]

• CPMFT is solved by diagonalization of \( H_0 \) (twice the HF size)

\[ H_0 | 0 \rangle = E_{CPMFT} | 0 \rangle \]
CPMFT: The DMFT connection

- $H_o$ is no longer the mean field of the real (Coulomb) two-body Hamiltonian.

- $H_o$ corresponds to the mean field of a repulsive interaction $(2/r_{12})$ treated with HF plus an attractive pairing interaction $(-1/r_{12})$ treated with HFB.

- The resulting CPMFT energy expression is a “hybrid” of HF and HFB. It is a density matrix functional.

- The CPMFT energy expression defines a 2pdm: $\Gamma$

\[
E = \langle 0 | H_o | 0 \rangle = \text{Tr} \left[ H \Gamma \right]
\]

where $\Gamma_{pqr,s} = 2 P_{pq} P_{rs} - P_{pr} P_{qs} - K_{pr} K_{qs}$. 
**CPMFT: The key sign flip**

- **HFB:** \[ \Gamma_{pqrs} = 2 \, P_{pq} \, P_{rs} - P_{pr} \, P_{qs} + K_{pr} \, K_{qs} \]

- **CPMFT:** \[ \Gamma_{pqrs} = 2 \, P_{pq} \, P_{rs} - P_{pr} \, P_{qs} - K_{pr} \, K_{qs} \]

- Particle fluctuations: \( \sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 \)
  - **HFB:** \( \sigma_N^2 = \text{Tr} [P - P^2 + K^2] = 2 \, \text{Tr} [K^2] \)
  - **CPMFT:** \( \sigma_N^2 = \text{Tr} [P - P^2 - K^2] = 0 \)

- **CPMFT:** \( M_z = P_\alpha - P_\beta = 0 \)
  Spin density (magnetization) is zero everywhere for closed-shells

- Spin fluctuations: \( \sigma_S^2 = \langle S_z^2 \rangle - \langle S_z \rangle^2 \)
  - **HFB:** \( \sigma_S^2 = 0 \)
  - **CPMFT:** \( \sigma_S^2 = 3 \, \text{Tr} [K^2] \)
Is CPMFT rigorous?

• The CPMFT ansatz is unconventional but rigorously justified by:
  
  - Density Matrix Functional Theory
    • Gilbert Theorem \(\rightarrow\) license to model
  
  - Levy constrained-search and Legendre transform arguments prove the existence of a functional that takes the model to the exact answer

  - \(H_0\) is a well-defined model Hamiltonian [e.g. perturbation theory based on \((H-H_0)\) is a rigorous \(ab\ initio\) approach]

• The key ingredient of CPMFT is to limit pairings to an “active” space

• CPMFT details are in papers published in JCP 2009-10

$H_2$ cc-pV5Z

![Graph showing the energy curve for $H_2$ with different methods: RHF, UHF, 1HFB, CPMFT(2,2), and FCI. The energy (E in a.u.) is plotted against the interatomic distance ($R_{\text{H-H}}$ in Bohr). The graph illustrates the energy minima for different methods at various interatomic distances.]
$N_2$ 6-311++G**
$N_2 \ 6-311++G^{**}$

Dynamical correlation

Significant improvement!
Extension of CPMFT to hetero-nuclear dissociations:

CPMFT + $\Phi$

Note lack of CPMFT static correlation near Re
LiH

Note presence of CPMFT static correlation near Re
The skeptical in the audience ought to be thinking:

In many of the examples, **UHF** is not bad at all!

Why bother with **CPMFT**?
$CO_2$: a very challenging test!
The onset of strong correlation is connected to the appearance of the CPMFT solution

Two-level model system with two electrons:

Example 1. $H_2$ molecule in minimum basis:

The CPMFT solution along the dissociation path appears when:

$$\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} < \frac{1}{2} \left( J_{11} + J_{22} \right) - K_{12}$$

compared with the Coulson-Fischer point (RHF instability):

$$\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} < J_{12} - K_{12}$$

Example 2. Be atom min basis: same formula applies!
Addition of DFT dynamical correlation to CPMFT via alternative densities and tests on hydrogen networks

Constrained-Pairing Mean-Field Theory. III. Inclusion of Density Functional Exchange and Correlation Effects via Alternative Densities,
Dynamical Correlation

- **CPMFT** orbitals and **1pdm** are symmetry-adapted
  How do we add *dynamical correlation only*?

- **Answer**: Use **total** and **on-top** densities from **2pdm**
  ansatz as fundamental **DFT** variables → rewrite code?

- **Better Option**: create “alternative” alpha and beta
  densities derived from the **CPMFT 2pdm** ansatz

- Feed alternative densities into regular **DFT** correlation
  subroutines (eg, **TPSS**) to define **κTPSSc**

- **Related Work**: Becke, Savin, Stoll, **TCA 1995**
  Perdew, Savin, Burke, **PRA 1995**
Alternative Densities

We define alternative densities ($\chi$) from total ($\rho$) and on-top ($\Gamma$) densities:

\[
\chi_\alpha(r) = \frac{1}{2} \left( \rho(r) + \sqrt{\rho^2(r) - 2\Gamma(r)} \right)
\]

\[
\chi_\beta(r) = \frac{1}{2} \left( \rho(r) - \sqrt{\rho^2(r) - 2\Gamma(r)} \right)
\]

where \( \Gamma(r) = 2\rho_\alpha(r)\rho_\beta(r) - (\kappa^2_\alpha\beta(r) + \kappa^2_\beta\alpha(r)) \) and \( \chi_\alpha(r) + \chi_\beta(r) = \rho(r) \)

**Example:** $H_2$ molecule

(1) **At** $R_e$, \( \chi_\alpha(r) = \chi_\beta(r) = \rho_\alpha(r) = \rho_\beta(r) \) (RKS density)

(2) **At dissociation**, \( \chi_\alpha(r) = \rho(r) \) and \( \chi_\beta(r) = 0 \) (UKS-like density)

We change variables of $E_{xc}$:

\[
E_{xc}[\rho_\alpha, \rho_\beta, \cdots] \rightarrow E_{xc}[\chi_\alpha, \chi_\beta, \cdots]
\]

$H_2$ cc-pV5Z

![Graph of $E$ vs $R_{HH}$ for different methods, including RHF, UHF, 1HFB, CPMFT(2,2), CPMFT($\kappa$TPSSc), and FCI.](image)
Hydrogen networks exhibit a metal-insulator transition as $R_{H-H}$ increases.

When $R_{H-H}$ is

\[
\begin{align*}
\text{Short}: & \text{ metallic (for large } N_{\text{atom}}) \\
\text{Long}: & \text{ insulator} \\
\infty: & \text{ isolated } H \text{ atoms}
\end{align*}
\]

To see this transition on the correct non-magnetic (closed-shell) surface, CASSCF requires $10^{27}$ and $10^{123}$ configurations!!

CPMFT includes all required configurations to correctly model the metal-insulator transition and dissociation.
CPMFT does an excellent job
### Decay of off-diagonal density matrix terms $\gamma_{12}$

**TABLE I: Is a method capable of describing the metal-insulator transition?**

<table>
<thead>
<tr>
<th>Methods</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF</td>
<td>No</td>
</tr>
<tr>
<td>MP2</td>
<td>No</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>No convergence</td>
</tr>
<tr>
<td>DMRG</td>
<td>Yes, but only for 1D</td>
</tr>
<tr>
<td>CASSCF</td>
<td>Absolutely intractable</td>
</tr>
<tr>
<td>CPMFT</td>
<td>Yes in all cases</td>
</tr>
</tbody>
</table>

*Only CPMFT reveals the metal-insulator transition in 3D*
Connection to UHF formalism

T. Tsuchimochi, T. M. Henderson, G. E. Scuseria, and A. Savin
(J. Chem. Phys. to appear 28-SEP-10)
UHF, DMFT, and CPMFT

• In terms of charge and spin densities:
  \[ P = \frac{1}{2} (P_\alpha + P_\beta) \quad M = \frac{1}{2} (P_\alpha - P_\beta) \]
  and a closed-shell energy term:
  \[ E_{CS} = \sum_{ij} 2h_{ij} P_{ij} + \sum_{ijkl} [2(ij,kl)-(ik,jl)] P_{ij} P_{kl} \]

  The UHF energy expression is a DMFT:
  \[ E_{UHF} = E_{CS} [P] - \sum_{ijkl} (ik,jl) M_{ij} M_{kl} \]

• This has the same form as CPMFT
  \[ E_{CPMFT} = E_{CS} [P] - \sum_{ijkl} (ik,jl) K_{ij} K_{kl} \]

• Except that \( K = +\sqrt{P - P^2} \) is not \( M \)!
CPMFT and UHF

- Introduce alternative idempotent densities $A$ and $B$
  Define $P = \frac{1}{2}(A+B)$
  then $K^2 = P - P^2 = \frac{1}{4}(A-B)^2$
  So, $K = \frac{1}{2}|A-B|$ instead of $M = \frac{1}{2}(A-B)$

- This choice for $K$ maps CPMFT into a UHF-type framework where $P$ natural occupations occur in “corresponding pairs” $n_i + n_j = 1$
  This constraint was not present in the original CPMFT

- $F_A = \frac{\partial E}{\partial A}$, $F_B = \frac{\partial E}{\partial B}$ UHF-type solution

- Remarkably, unlike UHF, in this model: $M_z = 0$

- Implemented and tested: it works!
CPMFT Summary I

- Dissociates molecules fully accounting for left-right correlation
- Has mean-field (as opposed to combinatorial) computational cost
- The solution is obtained by diagonalization
- Yields correct symmetry natural orbitals and 1pdm everywhere
- Yields a definition for static correlation from the 2pdm ansatz
- Reduces to RHF in the absence of strong correlation
- Has the correct number of electrons on average \( \langle N \rangle = N_e \)
- Has the correct number of correlated electron pairs
- No fluctuations from the 2pdm: \( \sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = 0 \)
- No spurious spin density: \( M_z = 0 \)
CPMFT Summary II

- The number of parameters determining CPMFT is linear in the number of orbitals (same as UHF)

- The 1pdm is N-representable

- The 2pdm is not N-representable but contains physics connected with the concept of static/strong correlation

- CPMFT breaks the symmetry of the “alternative” densities A and B but preserves symmetries of the physical density P

- \( E = \langle 0 | H_0 | 0 \rangle = \text{Tr} \ [H \Gamma] \) wavefunction is gone...

- Results are different from UHF and PUHF
ROHF theory made simple

Problems with ROHF

• Roothaan's formalism defines the wavefunction and densities (both charge and spin) but orbitals and orbital energies are ambiguous and depend on choice of “coupling parameters”

• This is unsatisfactory for post-ROHF methods (correlation and excited states) as the results depend on these choices

• Long controversy in the literature for ~50 years
  No Koopman’s theorem in regular ROHF!

• Unphysical: why do we have the same orbitals and orbital energies for alpha and beta electrons if the potentials that they see are different? \( \Rightarrow \) the MOs should be different

• UHF is not the answer because of spin contamination

• Pople’s semicanonical orbitals are popular (“RO”) but need Roothaan’s formalism a priori [CPL 1991]
Attempts to fix ROHF

• Too many to discuss in detail...

• Not known how to do self-consistent PUHF

• Handy’s SUHF (spin-projected UHF) uses a single Lagrange multiplier $\Lambda$ to constrain: $[\hat{S}^2 -s(s+1)] = 0$
  • $\Lambda$ is infinity! $\Rightarrow$ not a practical scheme

• Our solution: CUHF
  • Using the UHF energy formula as a function of $P$ and $M$, constrain $M$ using (occ x vir) Lagrange multipliers
  • Solution for Lagrange multipliers is analytical

• It works! Crisp and quick convergence to ROHF energy and densities... Alpha orbitals and orbital energies are different from beta. CUHF carries no spin-contamination
### Errors (eV) on IPs ($-\varepsilon_{\text{HOMO}}$)

(24 open-shell systems)

<table>
<thead>
<tr>
<th></th>
<th>ROHF (MD)</th>
<th>ROHF (PGB)</th>
<th>CUHF</th>
<th>UHF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ME</strong></td>
<td>-7.38</td>
<td>0.57</td>
<td>0.54</td>
<td>0.68</td>
</tr>
<tr>
<td><strong>MAE</strong></td>
<td>7.38</td>
<td>0.64</td>
<td>0.61</td>
<td>0.71</td>
</tr>
</tbody>
</table>

**CUHF** gives good results and has no spin contamination

**CUHF** can predict both IPs & EAs
Valence and Rydberg excited states (eV) via quick & dirty TD-HF

<table>
<thead>
<tr>
<th></th>
<th>$\langle S^2 \rangle \cdot s(s+1)$</th>
<th>State</th>
<th>CUHF</th>
<th>UHF</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeF</td>
<td>0.001</td>
<td>$V_2^\Pi$</td>
<td>4.19</td>
<td>4.20</td>
<td>4.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_2^\Sigma^+$</td>
<td>6.33</td>
<td>6.34</td>
<td>6.16</td>
</tr>
<tr>
<td>$CH_3$</td>
<td>0.012</td>
<td>$R_2^2A'_1$</td>
<td>6.23</td>
<td>6.54</td>
<td>5.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_2^2A''_2$</td>
<td>7.34</td>
<td>7.73</td>
<td>7.44</td>
</tr>
<tr>
<td>CO$^+$</td>
<td>0.141</td>
<td>$V_2^\Pi$</td>
<td>4.84</td>
<td>6.93</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V_2^\Sigma^+$</td>
<td>9.81</td>
<td>11.10</td>
<td>5.82</td>
</tr>
<tr>
<td>CN</td>
<td>0.406</td>
<td>$V_2^\Pi$</td>
<td>0.95</td>
<td>4.13</td>
<td>1.32</td>
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<td></td>
<td></td>
<td>$V_2^\Sigma^+$</td>
<td>2.01</td>
<td>5.42</td>
<td>3.22</td>
</tr>
<tr>
<td>MAE</td>
<td></td>
<td></td>
<td>0.77</td>
<td>1.44</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Acknowledgements

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