Some applications of dressing to configuration interaction matrices

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LCPQ: Lab. Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse
Matrix dressing
Collagen Matrix dressing

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Collagen Matrix dressing

Fig 2. Patient 5, showing the DFU of 2 months' duration at study start (a) and after 3 weeks' treatment with the collagen matrix wound dressing (b)

Fig 3. Patient 6 presented with a wound containing about 30% slough at the start of treatment (a); this devitalised tissue may account for the modest decrease in wound area (b)

Hamiltonian Matrix dressing

- We try to solve: \( \hat{H} |\Psi\rangle = E |\Psi\rangle \)
- Wave function in FCI space: \( |\Psi\rangle = \sum_{i}^{N_{\text{FCI}}} c_i |i\rangle \)
- Project on \( \langle i | : \langle i | \hat{H} |\Psi\rangle = E \langle i |\Psi\rangle \)
- Rewrite: \( \sum_{j}^{N_{\text{FCI}}} H_{ij} c_j - E c_i = 0 \)
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CI equation projected on \( \langle i| \)

\[
(H_{ii} - E) c_i + \sum_{j \neq i}^{N_{\text{FCI}}} H_{ij} c_j = 0
\]
Dressed CI Hamiltonian

- There are too many determinants, so we don’t solve exactly the problem
- We choose $N_{\text{det}} |i\rangle$’s on which we project: internal space
- All other determinants (astronomical number) $|\alpha\rangle$: external space
Dressed CI Hamiltonian

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CI equation projected on $\langle i |$

$$(H_{ii} - E) c_i + \sum_{j \neq i}^{N_{\text{det}}} H_{ij} c_j + \sum_{\alpha} H_{i\alpha} c_\alpha = 0$$
Dressed CI Hamiltonian

Diagonal dressing

\[
\left( H_{ii} + \frac{1}{c_i} \sum_{\alpha} H_{i\alpha} c_{\alpha} - E \right) c_i + \sum_{j \neq i}^{N_{\text{det}}} H_{ij} c_j = 0
\]
Dressed CI Hamiltonian

Diagonal dressing

\[
\left( \tilde{H}_{ii} - E \right) c_i + \sum_{j \neq i}^{N_{\text{det}}} \tilde{H}_{ij} c_j = 0
\]

If the \(c_\alpha\)'s are the FCI coefficients, diagonalizing \(\tilde{H}\) gives

- the FCI energy
- the projection of the FCI eigenstate on the \(|i\rangle\)'s
Dressed CI Hamiltonian

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If the \(c_\alpha\)'s are the FCI coefficients, diagonalizing \(\tilde{H}\) gives

- the FCI energy
- the projection of the FCI eigenstate on the \(|i\rangle\)'s

Two questions

1. How do I choose the set of \(|i\rangle\)'s ?
2. How do I guess the coefficients \(c_\alpha\) ?
CIPSI dressed by perturbation
CIPSI dressed by perturbation

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   Obtained by perturbation theory

\[ c_\alpha = \frac{\langle \alpha | \hat{H} | \psi \rangle}{E - H_{\alpha\alpha}}, \]

and iterative dressing.

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Bonus question

- How do I make it fast?

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Bonus question

- How do I make it fast?
  Acceleration using a stochastic algorithm

---

• Very old idea$^3$

• Start with an internal space

• For each determinant $|\alpha\rangle$, get a perturbative estimate of its contribution to the correlation energy:

$$e_\alpha = \frac{\langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle}{E - H_{\alpha\alpha}}$$

• If $|e_\alpha|$ is large enough, $|\alpha\rangle$ enters in the internal space ($|\alpha\rangle$)

• Diagonalize $\hat{H}$ in the new internal space

• Iterate

---

Randomized PT2

Idea\textsuperscript{4}

- Avoid the exploration of all $|\alpha\rangle$'s
- Converge within a given statistical error

Properties

- Converges to the exact result in finite time
- Scales as $\sim 1/t^3$
- Massively parallel
- Enables a randomized CIPS\textsuperscript{5}I implementation

Randomized PT2

Pack the $|\alpha\rangle$’s in groups associated with $|i\rangle$’s

\[ \mathcal{D} \quad \mathcal{A} \]

\[ |I_1\rangle \quad |\alpha_1\rangle \]
\[ |\alpha_2\rangle \]
\[ |\alpha_3\rangle \]
\[ |\alpha_4\rangle \]
\[ A_1 \]

\[ |I_2\rangle \quad |\alpha_5\rangle \]
\[ |\alpha_6\rangle \]
\[ |\alpha_7\rangle \]
\[ A_2 \]

\[ |I_3\rangle \quad |\alpha_8\rangle \]
\[ |\alpha_9\rangle \]
\[ A_3 \]

\[ \vdots \quad \vdots \]

\[ E_{\text{PT2}} = \sum_{i} \sum_{\alpha \in \mathcal{A}_i} \frac{\langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle}{E - H_{\alpha\alpha}} = \sum_{i} \epsilon_i \]

\[ = \sum_{i} p_i \frac{\epsilon_i}{p_i} = \left\langle \frac{\epsilon_i}{p_i} \right\rangle_{p_i} \]
Stochastic dressing

Stochastically dressed matrix elements:

\[ \tilde{H}_{ii} = H_{ii} + \frac{1}{c_i} \sum_{\alpha} H_{i\alpha} c_{\alpha} \]

\[ = H_{ii} + \frac{1}{c_i} \sum_{j}^{N_{\text{det}}} \sum_{\alpha \in A_j} H_{i\alpha} c_{\alpha} \]

\[ = H_{ii} + \frac{1}{c_i} \sum_{j}^{N_{\text{det}}} \delta_{ij} = H_{ii} + \frac{1}{c_i} \sum_{j}^{N_{\text{det}}} p_j \frac{\delta_{ij}}{p_j} \]

\[ = H_{ii} + \frac{1}{c_i} \left\langle \frac{\delta_{ij}}{p_j} \right\rangle p_j \]
Results

Charge delocalization in CuCl$_2$

Two dominant configurations in FCI

1. $^-\text{Cl} \rightarrow \text{Cu}^{2+} \rightarrow \text{Cl}^-$
2. $^-\text{Cl} \rightarrow \text{Cu}^+ \rightarrow \text{Cl} \leftrightarrow \text{Cl} \rightarrow \text{Cu}^+ \rightarrow \text{Cl}^-$

The two configurations differ by a single excitation $\rightarrow$ Very slow convergence of the wave function with CIPSI.$^6$

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Results

\[ E - E_{\text{FCI}} \text{ (a.u.)} \]

\[ N_{\text{det}} \]

- CI-PT2
- CI-sBk
- CI-sBk\_0
Multi-reference coupled cluster
Multi-reference coupled cluster

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   CAS + Singles and Doubles

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   Coupled Cluster Ans"atz, and iterative dressing.

Multi-reference coupled cluster

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Protocol\(^7\)

- Guess the amplitudes of the single and double excitations from the CAS-SD wave function

---

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Protocol\textsuperscript{7}

- Guess the amplitudes of the single and double excitations from the CAS-SD wave function
- Use these amplitudes to build $\Psi_{\text{MRCC}}$
- $c_\alpha = \langle \alpha | \Psi_{\text{MRCC}} \rangle$
- Diagonalize $\tilde{H}$ and iterate.

Amplitudes

$$\Psi_{\text{CAS-SD}} = \Psi_{\text{CAS}} + \sum_{i \in \text{SD}} c_i |i\rangle$$

$$\tilde{\Psi}_{\text{CAS-SD}} = \left(1 + \sum_{ia} t_i^a \hat{T}_i^a + \sum_{ijab} \left(t_i^a \hat{T}_i^a \right) \left(t_j^b \hat{T}_j^b \right) + t_{ij}^{ab} \hat{T}_{ij}^{ab} \right) \Psi_{\text{CAS}}$$

Least-squares fitting of the CAS-SD wave function\(^8\):

$$\arg \min_{t_i^a, t_{ij}^{ab}} \left| \Psi_{\text{CAS-SD}} - \tilde{\Psi}_{\text{CAS-SD}} \right|$$

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## Results

Non-parallelism errors (NPE) and maximum errors with respect to the Full-CI potential energy surface ($mE_h$)

<table>
<thead>
<tr>
<th></th>
<th>CAS-SD</th>
<th></th>
<th>$\mu$-MR-CCSD</th>
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<td>NPE</td>
<td>Max Error</td>
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<td>$N_2$</td>
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<td>$F_2 , ^3\Sigma_u^+ (m_s = 1)$</td>
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<td>3.3</td>
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<td>$FH$</td>
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<td>14.6</td>
<td>1.8</td>
<td>4.0</td>
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</table>
Explicitly correlated Full CI
F12 scheme

**Ansatz**

\[
|\psi\rangle = \left(1 + \hat{Q} f_{12} \hat{S}_{xy}\right) |\psi_{FCI}\rangle
\]

- Conventional part (Full-CI): \( |\psi_{FCI}\rangle = \sum_i c_i |i\rangle \)
- Explicitly correlated part: \( |F\rangle = \hat{Q} f_{12} \hat{S}_{xy} |\psi_{FCI}\rangle \)
- \( f_{12}(r_{12}) = -\frac{1}{\lambda} e^{-\lambda r_{12}} \).
- \( \hat{S}_{xy} \) ensures that the cusp conditions are satisfied
- \( \hat{Q} = \hat{1} - \sum_i |i\rangle\langle i| \) ensuring that \( \langle \psi_{FCI}|F\rangle = 0 \)

\[
|\psi\rangle = |\psi_{FCI}\rangle + |F\rangle
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   $|\alpha\rangle = |F\rangle$, $c_\alpha = 1$

$$|\Psi\rangle = |\Psi_{\text{FCI}}\rangle + |F\rangle$$

$$\tilde{H}_{ii} = H_{ii} + \frac{1}{c_i} \langle i | \hat{H} | F \rangle$$
Implementation

- $\langle i | \hat{H} | F \rangle$ requires three-electron integrals.
- We have used an auxiliary basis for practical reasons

\[
\langle i | \hat{H} | F \rangle = \langle i | \hat{H} \hat{Q} f_{12} \hat{S}_{xy} | \Psi_{\text{FCI}} \rangle = \sum_{\alpha \in \text{CABS}} \langle i | \hat{H} | \alpha \rangle \langle \alpha | f_{12} \hat{S}_{xy} | \Psi_{\text{FCI}} \rangle
\]

- $|\alpha\rangle$'s : Determinants excited in the complementary auxiliary basis set
- $c_{\alpha} = \langle \alpha | f_{12} \hat{S}_{xy} | \Psi_{\text{FCI}} \rangle$
## Preliminary results

### Helium atom

<table>
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<th>Method</th>
<th>Basis</th>
<th>Total energy (au)</th>
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<tbody>
<tr>
<td>FCI</td>
<td>cc-pVDZ</td>
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<td>FCI</td>
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