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

Health / First Aid / Smith & Nephew

Biostep collagen matrix dressing 4" x 4" (1/ea)

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More delivery & pickup options

Qty: 1

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Collagen Matrix dressing

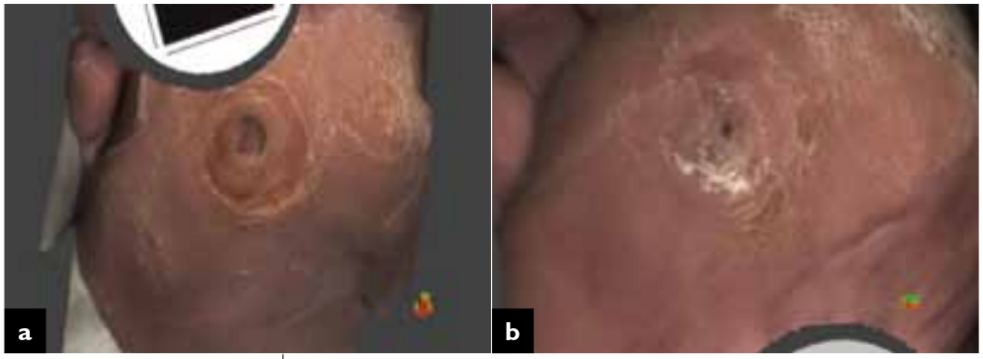

Fig 2. Patient 5, showing the DFU of 2 months' duration at study start (a) and after 3 weeks' treatment with the collagen matrix wound dressing (b)

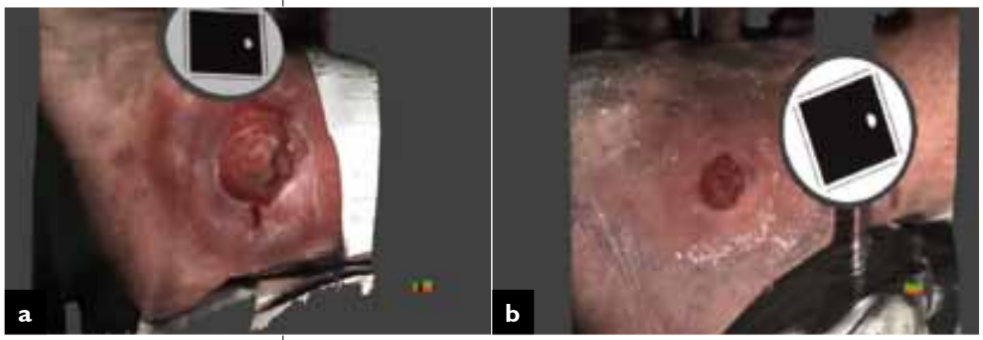

Fig 3. Patient 6 presented with a wound containing about 30% slough at the start of treatment (a); this devitalised tissue may account for the modest decrease in wound area (b)

[1]

[1] Haycocks, S. et al, "Collagen matrix wound dressings and the treatment of DFUs", *Journal of wound care*, 22 7, 369-70, 372-5, (2013).

Hamiltonian Matrix dressing

- We try to solve : $\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle$
- Wave function in FCI space : $\left|\Psi\right\rangle = \sum_i^{N_{\text{FCI}}} c_i \left|i\right\rangle$
- Project on $\left\langle i\right|$: $\left\langle i\right|\hat{H}\left|\Psi\right\rangle = E\left\langle i|\Psi\right\rangle$
- Rewrite : $\sum_j^{N_{\text{FCI}}} H_{ij}c_j - Ec_i = 0$

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- Rewrite : $\sum_j^{N_{\text{FCI}}} H_{ij} c_j - E c_i = 0$

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_{det} $|i\rangle$'s on which we project : internal space
- All other determinants (astronomical number) $|\alpha\rangle$: external space

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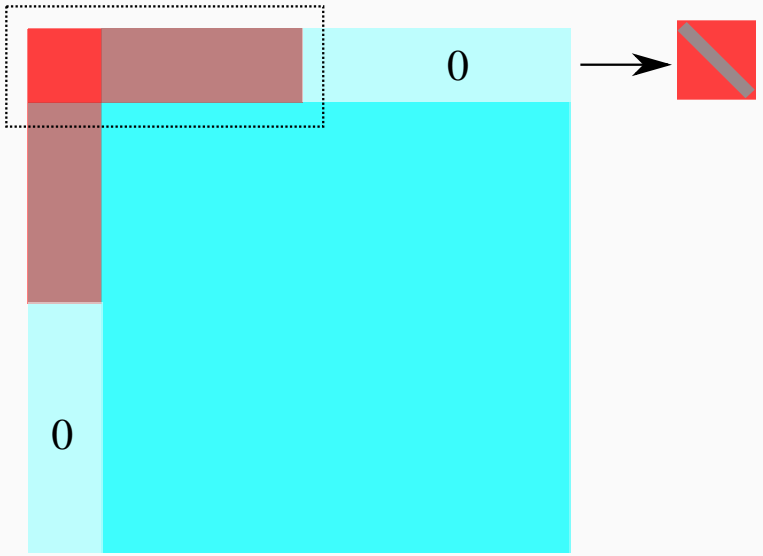
Dressed CI Hamiltonian



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_α's are the FCI coefficients, diagonalizing $\tilde{H}$ gives

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

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Two questions

1. How do I choose the set of $|i\rangle$'s ?
2. How do I guess the coefficients c_α ?

CIPSI dressed by perturbation

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[2] Y. Garniron *et al*, J. Chem. Phys. 149, 064103 (2018).

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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

[2] Y. Garniron *et al*, J. Chem. Phys. 149, 064103 (2018).

CIPSI

- 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

[3] B. Huron, J. P. Malrieu, and P. Rancurel, J. Chem. Phys. 58, 5745 (1973).

Randomized PT2

Idea[4]

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

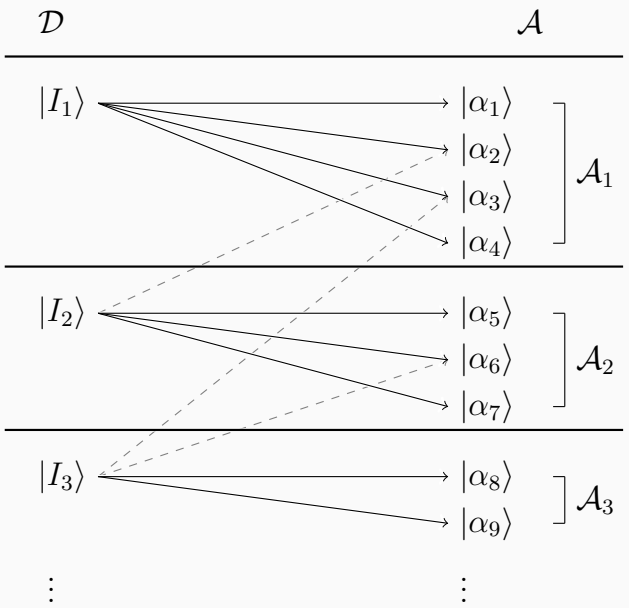
Properties

- Converges to the exact result in finite time
- Scales as $\sim 1/t^3$
- Massively parallel
- Enables a randomized CIPSI implementation[5]

[4] Y. Garniron *et al*, J. Chem. Phys. 147, 034101 (2017).
[5] Y. Garniron *et al*, J. Chem. Theory Comput. 156, 3591 (2019).

Randomized PT2

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



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

$$= \sum_{i}^{N_{\text{det}}} p_i \frac{\epsilon_i}{p_i} = \left\langle \frac{\epsilon_i}{p_i} \right\rangle_{p_i}$$

Stochastic dressing

Stochastically dressed matrix elements:

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

$$= H_{ii} + \frac{1}{c_i} \sum_{j}^{N_{\text{det}}} \sum_{\alpha \in \mathcal{A}_j} H_{i\alpha} c_\alpha$$

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

$$= H_{ii} + \frac{1}{c_i} \left\langle \frac{\delta_{ij}}{p_j} \right\rangle_{p_j}$$

Results

Charge delocalization in $CuCl_2$

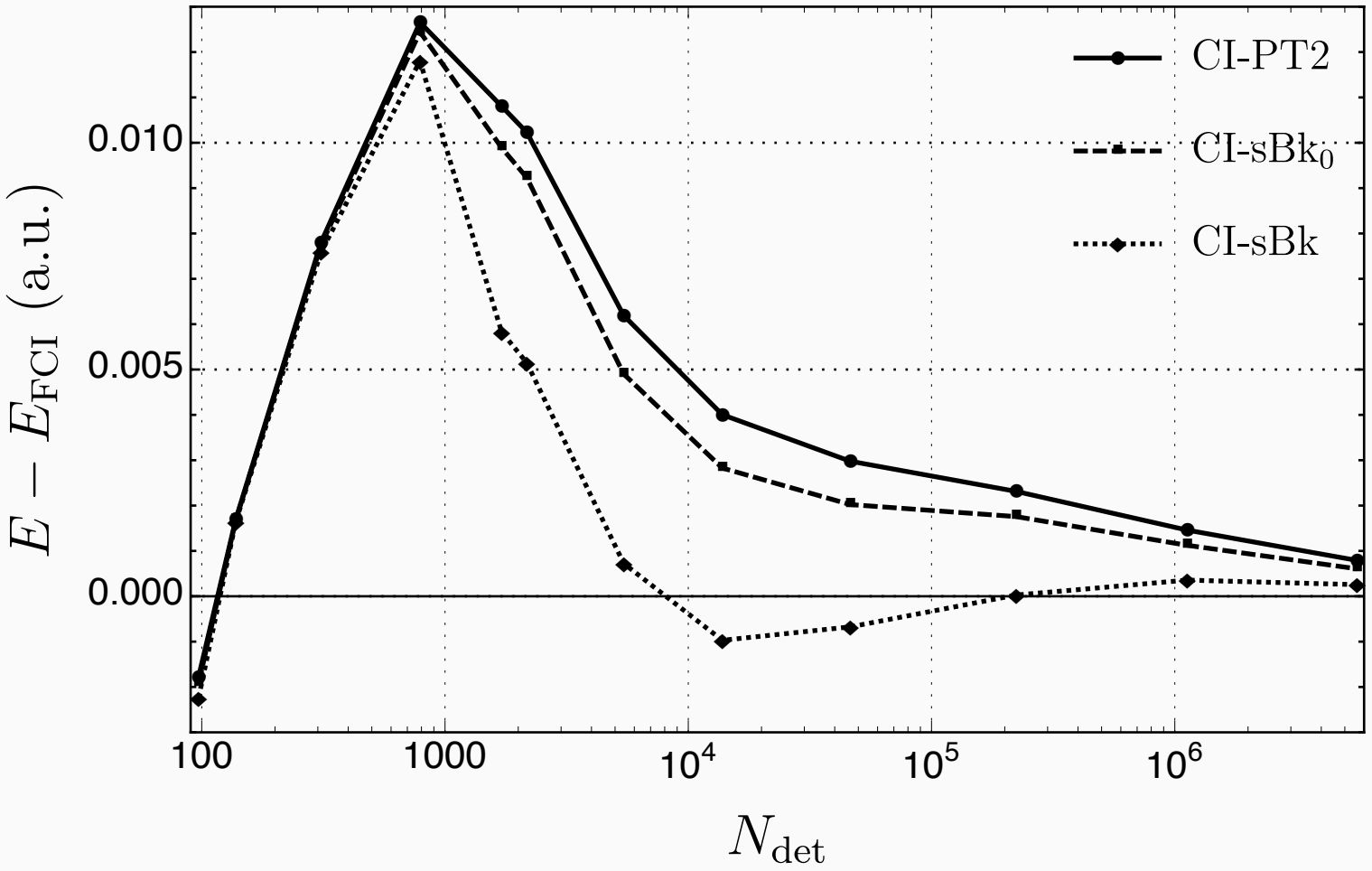
Two dominant configurations in FCI

1. ^{-}Cl — Cu^{2+} — Cl^{-}
2. ^{-}Cl — Cu^{+} — $Cl \longleftrightarrow Cl$ — Cu^{+} — Cl^{-}

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

[6] Caffarel et al, J. Chem. Theory Comput. 10, 12, 5286 (2014).

Results


CI-PT2
CI-sBk$_0$
CI-sBk
0.010
0.005
0.000
100
1000
10^4
10^5
10^6
$E - E_{\mathrm{FCI}}$ (a.u.)
N_{det}

Multi-reference coupled cluster

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1. How do I choose the set of $|i\rangle$'s ?

2. How do I guess the coefficients c_α ?

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Multi-reference coupled cluster

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   Coupled Cluster Ansätz, and iterative dressing.

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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[7]

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

[7] E. Giner *et al*, J. Chem. Phys. 144, 064101 (2016).

Amplitudes

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

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

Least-squares fitting of the CAS-SD wave function[8]:

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

[8] Y. Garniron *et al*, J. Chem. Phys. 146, 154107 (2017).

Results

Non-parallelism errors (NPE) and maximum errors with respect to the Full-CI potential energy surface ($\mathrm{m}E_\mathrm{h}$)

	CAS-SD		μ-MR-CCSD	
	NPE	Max Error	NPE	Max Error
C_2H_6	5.1	35.5	3.5	8.3
F_2	3.8	19.8	1.5	3.8
C_2H_4 twist	1.5	27.7	0.5	6.5
BeH_2	2.9	4.1	1.7	2.1
H_2O	1.9	4.8	0.5	1.3
C_2H_4 stretch	2.7	20.0	1.8	6.0
N_2	1.7	9.0	0.3	2.3
F_2 $^3\Sigma_u^+(m_s = 1)$	2.6	18.6	1.2	3.3
F_2 $^3\Sigma_u^+(m_s = 0)$	2.6	18.6	1.1	3.3
FH	2.6	14.6	1.8	4.0

Explicitly correlated Full CI

$F12$ scheme

Ansatz

$$|\Psi\rangle = \left(1 + \hat{Q}\, f_{12} \hat{S}_{xy}\right) |\Psi_{\mathrm{FCI}}\rangle$$

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

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

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

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

Implementation

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

$$\begin{aligned}\langle i|\hat{H}|F\rangle &= \langle i|\hat{H}\hat{Q}\, f_{12}\hat{S}_{xy}|\Psi_{\mathrm{FCI}}\rangle \\ &= \sum_{\alpha\in\mathrm{CABS}} \langle I|\hat{H}\,|\alpha\rangle\langle\alpha|\, f_{12}\hat{S}_{xy}|\Psi_{\mathrm{FCI}}\rangle \\ &= \sum_{\alpha\in\mathrm{CABS}} \langle i|\,\hat{H}\,|\alpha\rangle\,\langle\alpha|\, f_{12}\hat{S}_{xy}\,|\Psi_{\mathrm{FCI}}\rangle\end{aligned}$$

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

Preliminary results

Helium atom

Method	Basis	Total energy (au)
FCI	cc-pVDZ	-2.887 595
	cc-pVTZ	-2.900 232
	cc-pVQZ	-2.902 411
	∞	-2.903 724
CCSD-F12b	cc-pVDZ-F12	-2.902 251
	cc-pVTZ-F12	-2.903 380
	cc-pVQZ-F12	-2.903 581
FCI-F12	cc-pVDZ-F12	-2.903 041
	cc-pVTZ-F12	-2.903 000
	cc-pVQZ-F12	-2.903 047

Preliminary results

Lithium atom

Method	Basis	Total energy (au)
FCI	cc-pVDZ	-7.466 025
	cc-pVTZ	-7.474 251
	cc-pVQZ	-7.476 373
	∞	-7.478 060
CCSD-F12b	cc-pVDZ-F12	-7.476 884
	cc-pVTZ-F12	-7.477 461
	cc-pVQZ-F12	-7.477 718
FCI-F12	cc-pVDZ-F12	-7.479 199

How to dress for success?

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