Dressing the CI matrix with explicit correlation

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Accurate energies with quantum Monte Carlo (QMC)

Trial wave function for QMC

$$\Psi_T(\boldsymbol{R}) = e^{J(\boldsymbol{R})} \sum_I c_I D_I^\uparrow(\boldsymbol{R}^\uparrow) \, D_I^\downarrow(\boldsymbol{R}^\downarrow)$$

- The multideterminant part is obtained via the (selected FCI) CIPSI algorithm
  Giner et al. JCP 142 (2015) 044115
- We **may** use a "minimal" (nodeless) Jastrow $J(\boldsymbol{R})$

The water molecule [Caffarel et al. JCP 144 (2016) 151103]

TABLE II. All-electron DMC energies (in a.u.) obtained with CIPSI nodes for each basis set. Second column: Increase of CPU time due to the use of the large multideterminant expansion.

Basis set[Ndets]	$T_{CPU}(Ndets)/T_{CPU}(1det)$	E_0^{DMC}
cc-pCVDZ[172 256]	~101	−76.415 71(20)
cc-pCVTZ[640 426]	~185	−76.431 82(19)
cc-pCVQZ[666 927]	~128	−76.436 22(14)
cc-pCV5Z[1 423 377]	~235	−76.437 44(18)

TABLE III. Comparison of nonrelativistic ground-state total energies of water obtained with the most accurate theoretical methods. Energies in a.u.

Clark et al.,[20] DMC (upper bound)	−76.436 8(4)
This work, DMC (upper bound)	−76.437 44(18)
Almora-Diaz,[27] CISDTQQnSx (upper bound)	−76.434 3
Helgaker et al.,[29] R12-CCSD(T)	−76.439(2)
Muller and Kutzelnigg,[30] R12-CCSD(T)	−76.437 3
Almora-Diaz,[27] FCI + CBS	−76.438 6(9)
Halkier et al.,[31] CCSD(T) + CBS	−76.438 6
Bytautas and Ruedenberg,[32] FCI + CBS	−76.439 0(4)
This work, DMC + CBS	−76.438 94(12)
Experimentally derived estimate[25]	−76.438 9

Chromium dimer

Hybrid stochastic-deterministic calculation of the second-order perturbative contribution of multireference perturbation theory

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Table: Variational ground-state energy $E^{(0)}$ and second-order contribution $E^{(2)}$ of the Cr_2 molecule with bond length 1.68 Å computed with various basis sets. For all basis sets, the reference is composed of 2×10^7 determinants selected in the valence FCI space (28 electrons).

Reference	Basis	Active space	$E^{(0)}$	$E^{(2)}$	$E^{(0)} + E^{(2)}$
CIPSI	cc-pVDZ	(28e,76o)	$-2087.227\,883\,3$	$-0.068\,334(1)$	$-2087.296\,217(1)$
	cc-pVTZ	(28e,126o)	$-2087.449\,781\,7$	$-0.124\,676(1)$	$-2087.574\,423(1)$
	cc-pVQZ	(28e,176o)	$-2087.513\,373\,3$	$-0.155\,957(1)$	$-2087.669\,330(1)$

$\Rightarrow$ **We need to get to the CBS limit faster!**

QMC without Jastrow: dissociation of FeS

FeS, FN-DMC / CIPSI(8M dets) / VTZ-ANO-BFD

Legend:
$^5\Delta$ 500 dets CASSCF
$^5\Sigma$ 500 dets CASSCF
$^5\Delta$ 18 000 dets FCI
$^5\Sigma$ 18 000 dets FCI
$^5\Delta$ 235 000 dets FCI
$^5\Sigma$ 235 000 dets FCI
$^5\Sigma$ 1 000 000 dets FCI
$^5\Delta$ 1 000 000 dets FCI
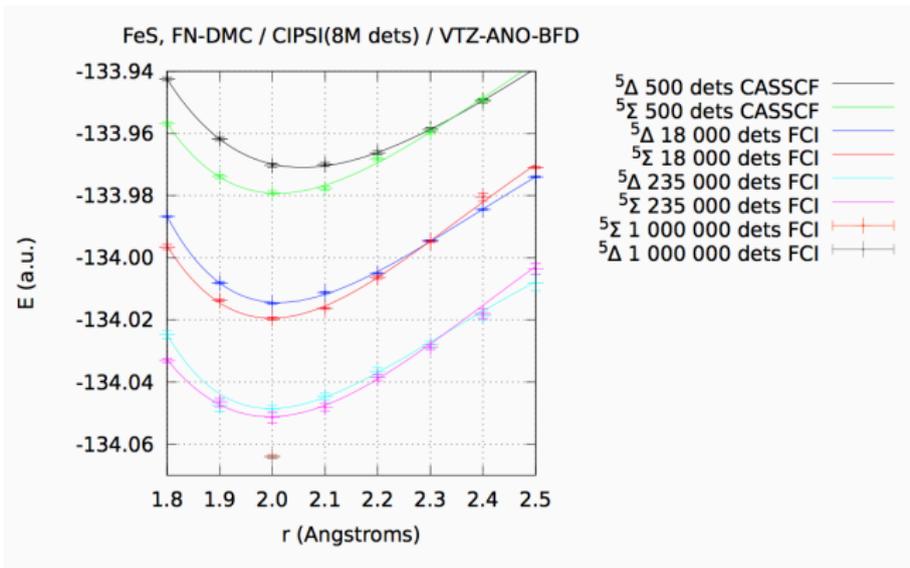
What	Who	D_0 (in eV)
Exp.	Matthew et al.	3.240 ± 0.003
CAS/Jastrow/opt	Hagagi-Mood/Luchow	3.159 ± 0.015
FCI/DMC/extrap	Scemama and co	3.170 ± 0.015

Hagagi-Mood & Luchow, JPCA 121 (2017) 6165

Issues

What we don't want...

- ☹ redundant work between Jastrow and multideterminant part
- ☹ chemical intuition and/or user input
- ☹☹ stochastic optimization

What we want...

- ☺ a systematic, black-box procedure
- ☺ compact FCI expansions
- ☺ the exact (non-relativistic) energy, i.e. minimizing the fixed-node error
- ☺☺ a massively parallel implementation

$\Rightarrow$ **Explicitly-correlated FCI (selected if possible), i.e. FCI-F12 method**

Ansatz

Wave function ansatz

$$|\Psi\rangle = \underbrace{|D\rangle}_{\text{conventional FCI}} + \underbrace{|F\rangle}_{\text{explicitly correlated}}$$

$$|D\rangle = \sum_I c_I |I\rangle \qquad\qquad |F\rangle = \sum_I t_I \hat{Q} f |I\rangle$$

projector: $\hat{Q} = \hat{1} - \sum_I |I\rangle\langle I|$ $\qquad$ correlation factor: $f = \sum_{i<j} f_{ij}$

Correlation factor: Slater geminal fitted with Gaussian geminals

$$f_{12} = \frac{1 - \exp(-\lambda r_{12})}{\lambda} = r_{12} + \mathcal{O}\left(r_{12}^2\right) \qquad \underbrace{\exp(-\lambda r_{12})}_{\text{Slater geminal}} \approx \sum_{\nu=1}^{N_{GG}} a_\nu \underbrace{\exp\left(-\lambda_\nu r_{12}^2\right)}_{\text{Gaussian geminal}}$$

Ten-no, CPL 398 (2004) 56; Tew & Klopper, JCP 123 (2005) 074101

Effective Hamiltonian theory

Dressing the FCI matrix

$$\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle \quad \xrightarrow{\langle I|\times} \quad c_I\left[H_{II} + c_I^{-1}\langle I|\hat{H}|F\rangle - E\right] + \sum_{J\neq I} c_J H_{IJ} = 0.$$

$$\mathring{H}_{IJ} = \begin{cases} H_{II} + c_I^{-1}\langle I|\hat{H}|F\rangle, & \text{if } I = J, \\ H_{IJ}, & \text{otherwise.} \end{cases}$$

Dressing term

$$\langle I|\hat{H}|F\rangle = \sum_J t_J \underbrace{\left[\langle I|\hat{H}f|J\rangle - \sum_K H_{IK} f_{KJ}\right]}_{\text{incomplete basis set correction}},$$

$\Rightarrow$ The amplitudes t_I's are obtained to satisfy the e-e cusp conditions (SP ansatz)
   Ten-no, JCP 121 (2004) 117

Three- and four-electron integrals over Gaussian geminals

Three- and four-electron integrals involving Gaussian geminals: Fundamental integrals, upper bounds, and recurrence relations

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We report the three main ingredients to calculate three- and four-electron integrals over Gaussian basis functions involving Gaussian geminal operators: fundamental integrals, upper bounds, and recurrence relations. In particular, we consider the three- and four-electron integrals that may arise in explicitly correlated F12 methods. A straightforward method to obtain the fundamental integrals is given. We derive vertical, transfer, and horizontal recurrence relations to build up angular momentum over the centers. Strong, simple, and scaling-consistent upper bounds are also reported. This latest ingredient allows us to compute only the $\mathcal{O}(N^2)$ significant three- and four-electron integrals, avoiding the computation of the very large number of negligible integrals. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4991733]
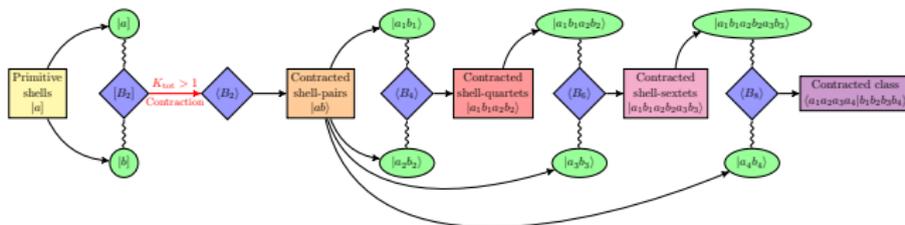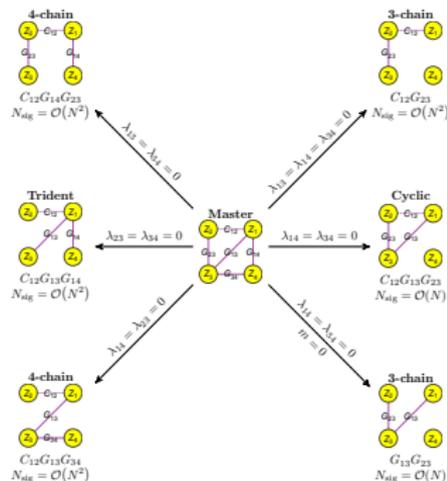
Barca, Loos & Gill, in preparation

Resolution of the identity (RI) approximation

RI approximation

$$\hat{1} = \sum_{A \in \mathcal{A}}^{\infty} |A\rangle\langle A|$$

Dressing term

$$\langle I|\hat{H}|F\rangle = \sum_{J} t_J \left[\sum_{A \in \mathcal{A}} H_{IA} f_{AJ} - \sum_{K \in \mathcal{D}} H_{IK} f_{KJ} \right]$$

$$= \sum_{J} t_J \sum_{X \in \mathcal{C}} H_{IX} f_{XJ},$$

CABS

complementary
virtual space $\{\alpha\}$
$\{p\} \cap \{\alpha\} = \varnothing$

complete
orbital
space

virtual
space $\{a\}$

orbital space $\{p\}$
$\{p\} = \{i\} \cup \{a\}$

occupied
space $\{i\}$
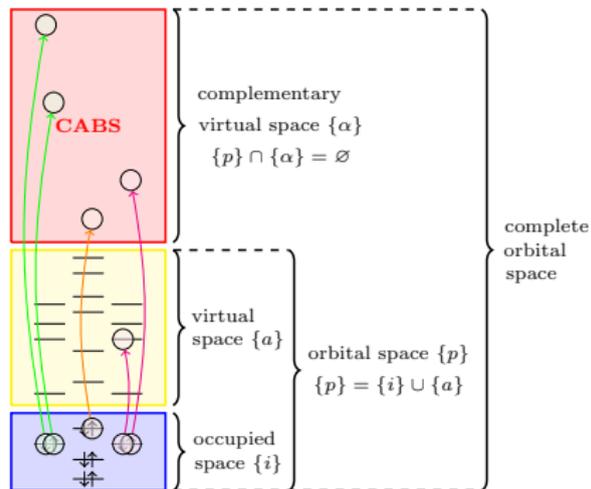
Valeev, CPL 395 (2004) 190

Algorithm

Self-consistent dressing of the FCI matrix

1: **procedure** DRESSED FCI-F12
2:
3:     Perform a (selected) FCI calculation to get $|D\rangle = \sum_I c_I |I\rangle$
4:     Compute extra integrals, e.g. $\langle I|\hat{H}f|J\rangle$
5:
6:     **while** $|\Delta E| > \tau$ **do**
7:         Determine t_I's to satisfy e-e cusp conditions
8:         Form the dressed Hamiltonian $\overset{\circ}{H}$
9:         Diagonalize $\overset{\circ}{H}$ to get a new set of c_I's and energy E
10:     **end while**
11:
12:     Return useful quantities for QMC, i.e. c_I's and t_I's
13:
14: **end procedure**

$\Rightarrow$ It can be "embedded" in the Davidson diagonalization

Illustrative calculations on a two-electron system

Paradigm: *"Two electrons on a 3-sphere"*

- Singlet pair of electrons on a surface of a 3-sphere of radius $R \Rightarrow$ uniform density!
  Loos & Gill PRL 103 (2009) 123008; JCP 135 (2011) 214111

- Everything can be done analytically $\Rightarrow$ great to test approximation(s)!
  Loos & Gill PRA 79 (2009) 062517

- For $R = 1$, $E_c \approx -40.2$ mE$_h$ $\Rightarrow$ similar to He!
  Loos & Gill PRL 105 (2010) 113001; CPL 500 (2010) 1

Illustrative calculations on a two-electron system

Convergence of the correlation energy: $R = 1$, $L_{RI} = 3L$ and $f_{12} = r_{12}$
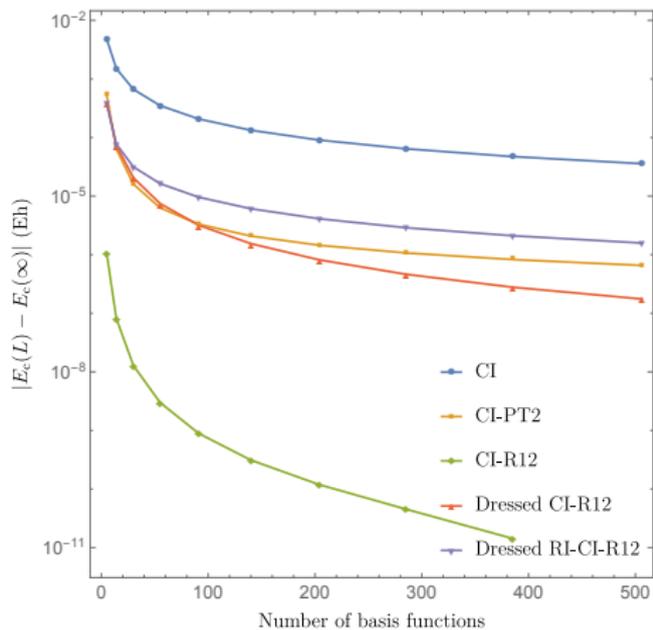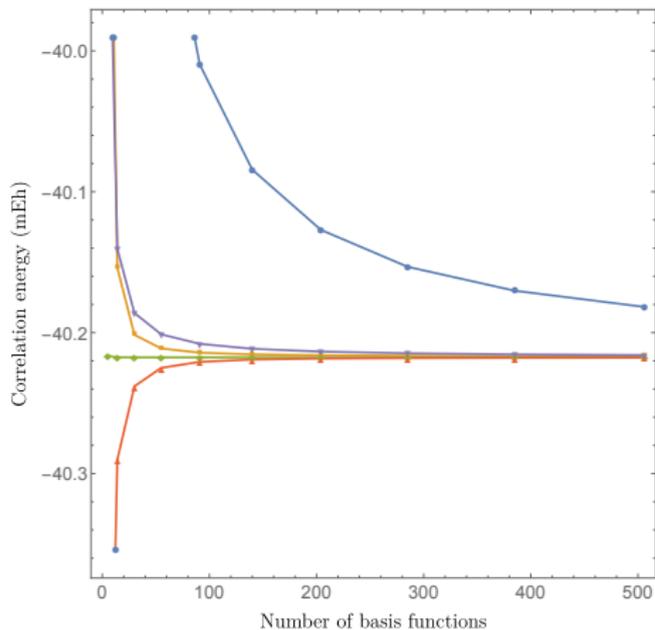
Concluding remarks

Things to explore further...

- Design a selected version of the algorithm

- Three-electron integrals or RI tricks?

- More generally, how do we get the nodes right?

Future directions...

- Efficient and massively parallel implementation in QUANTUM PACKAGE
  https://github.com/LCPQ/quantum_package

- We are currently working on a similar methodology to enforce the electron-nucleus cusp in QMC calculations
  Loos, Scemama & Caffarel, in preparation.