Dressing the CI matrix with explicit correlation

(early stage)

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WATOC17 (Munich, Germany)

29th Aug 2017

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 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-Dìaz,[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-Dìaz,[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

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)

Garniron, Scemama, Loos & Caffarel, JCP 147 (2017) 034101

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

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

⇒ **Explicitly-correlated FCI (selected if possible), i.e. FCI-F12 method**
Booth et al. JCP 137 (2012) 164112; Kersten et al. JCP 145 (2016) 054117

Ansatz

Wave function ansatz

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

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

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

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

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

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

Dressing term

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

$\Rightarrow$ 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

THE JOURNAL OF CHEMICAL PHYSICS **147**, 024103 (2017)

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

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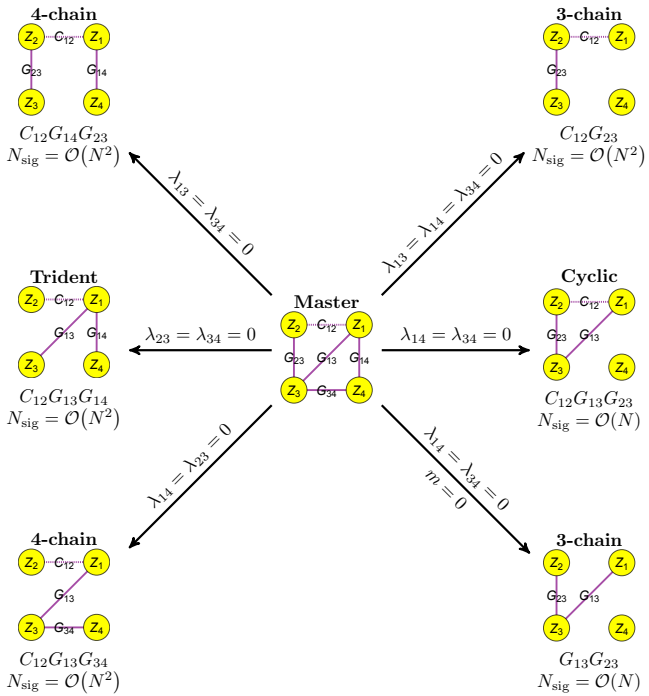
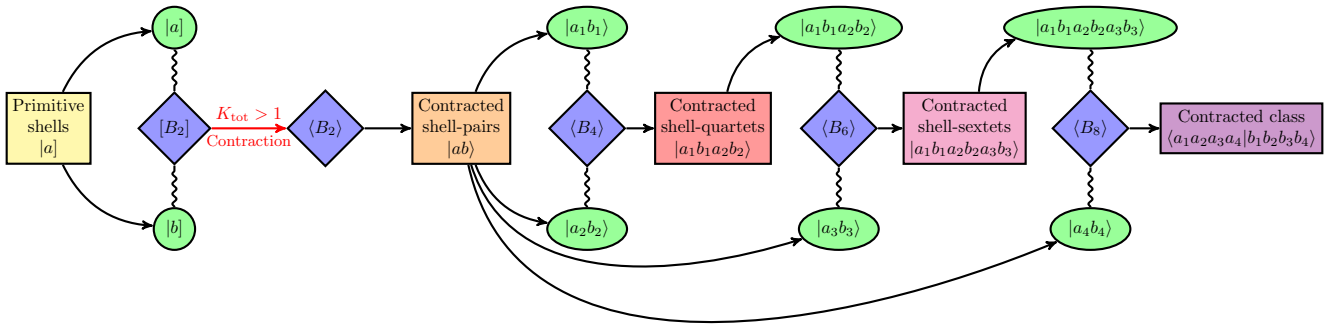
(Received 26 April 2017; accepted 22 June 2017; published online 11 July 2017)

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

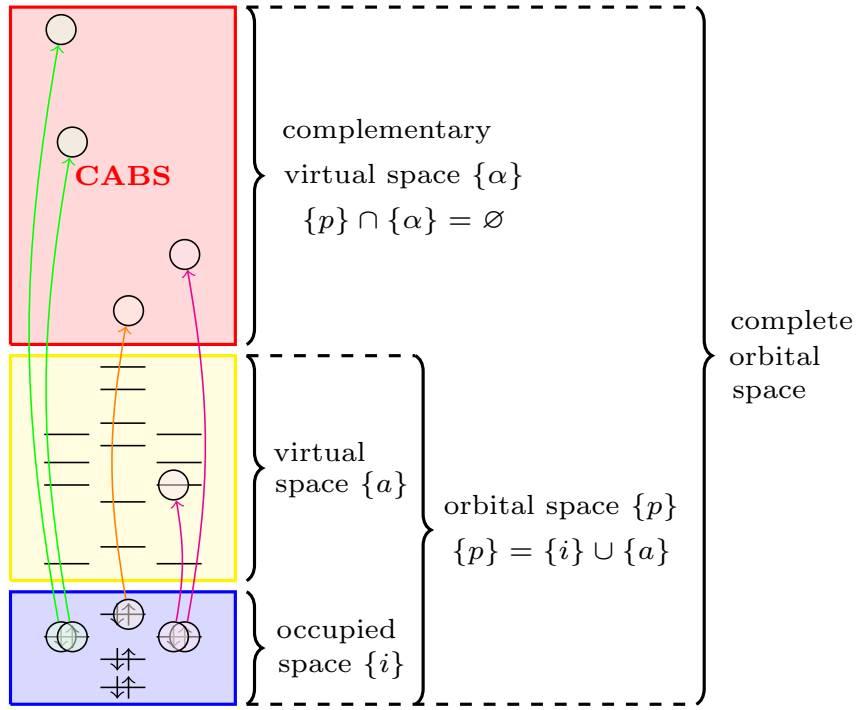
Resolution of the identity (RI) approximation

RI approximation

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

Dressing term

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



Valeev, CPL 395 (2004) 190

Algorithm

Self-consistent dressing of the FCI matrix

procedure DRESSED FCI-F12

Perform a (selected) FCI calculation to get $|D\rangle = \sum_I c_I |I\rangle$
Compute extra integrals, e.g. $\langle I|\hat{H}f|J\rangle$

while $|\Delta E| > \tau$ **do**
Determine t_I's to satisfy e-e cusp conditions
Form the dressed Hamiltonian $\mathring{H}$
Diagonalize $\mathring{H}$ to get a new set of c_I's and energy E
end while

Return useful quantities for QMC, i.e. c_I's and t_I's

end procedure

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

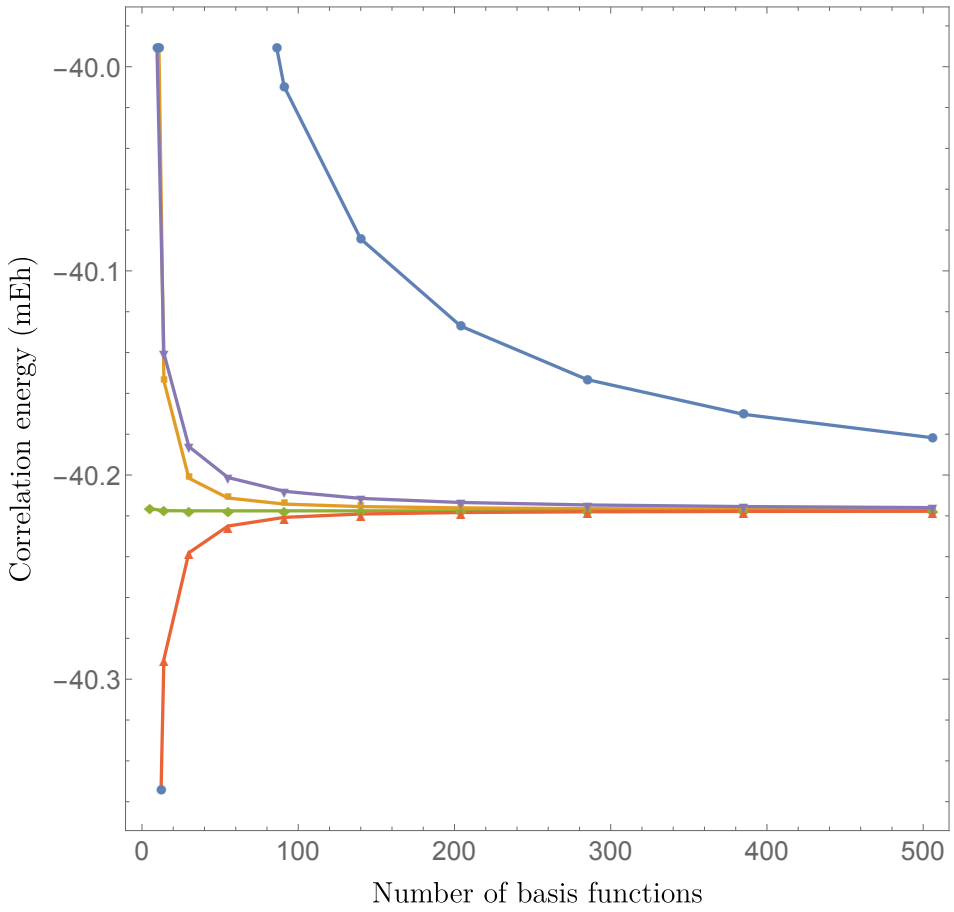
Illustrative calculations on a two-electron system

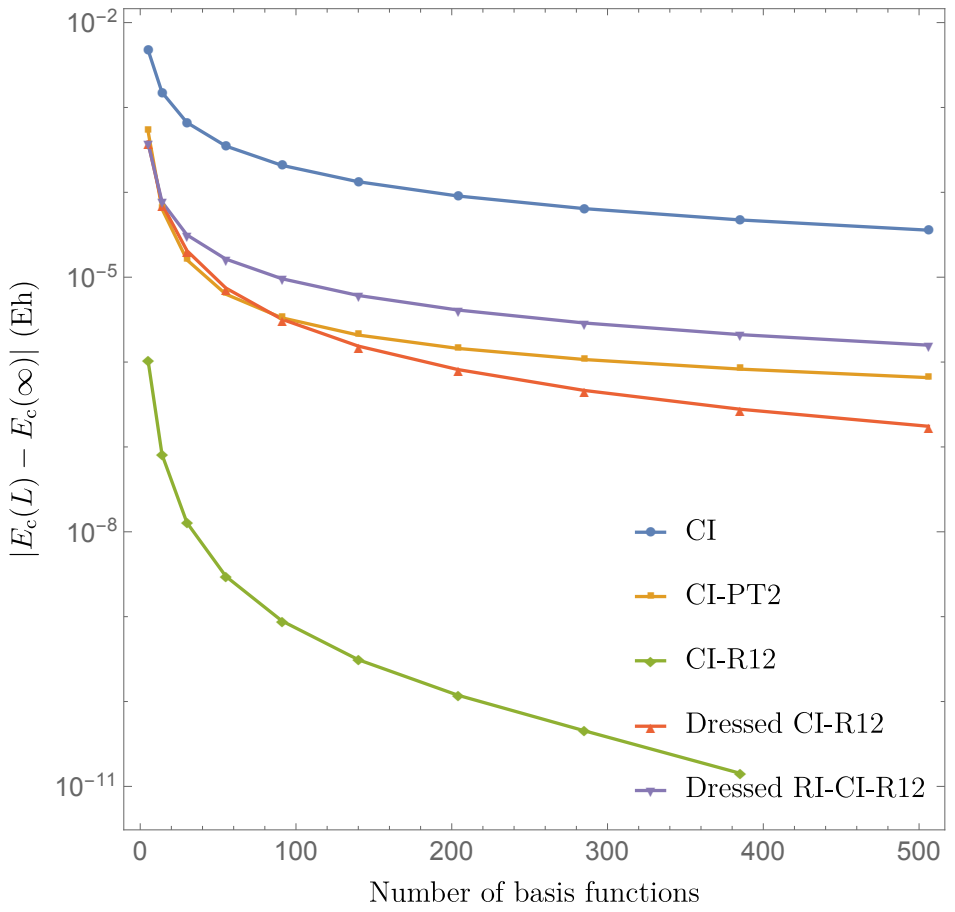
Paradigm: *"Two electrons on a glome"*

- 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: $R = 1$, $L_{\mathrm{RI}} = 3L$ 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.

Acknowledgements, Collaborators and Funding

- David Tew & Seiichiro Ten-no for discussions
- Collaborators: Anthony Scemama & Michel Caffarel

- Job & Money: ANU, ARC and CNRS

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