

Selected CI and Jastrow-Free QMC Methods for Excited States

Anthony Scemama, Yann Garniron, Denis Jacquemin, Michel Caffarel &
Pierre-François (Titou) Loos

Laboratoire de Chimie et Physique Quantiques, UMR5626, Université Paul Sabatier, Toulouse, France

17th Dec 2018

- Selected CI and QMC



Anthony
Scemama



Yann
Garniron



Michel
Caffarel



Denis
Jacquemin

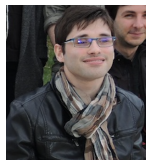
- Green function methods



Arjan
Berger



Pina
Romaniello

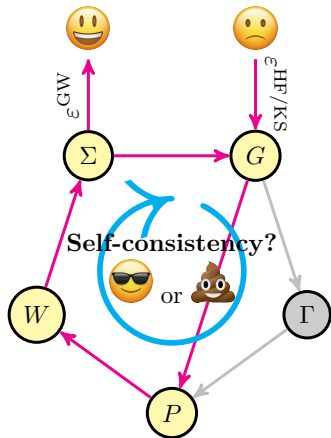


Mika
Vril

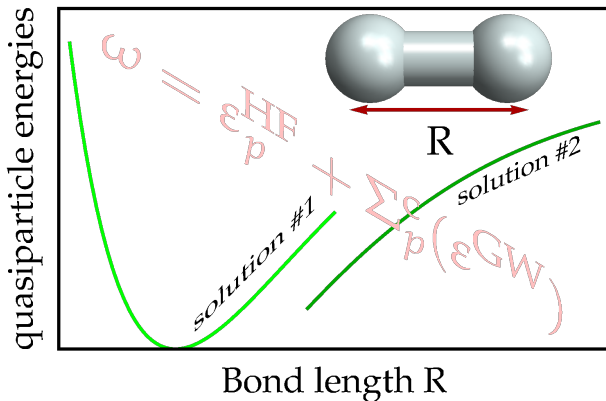
Section 2

Advertisement

Green functions and self-consistency: an unhappy marriage?



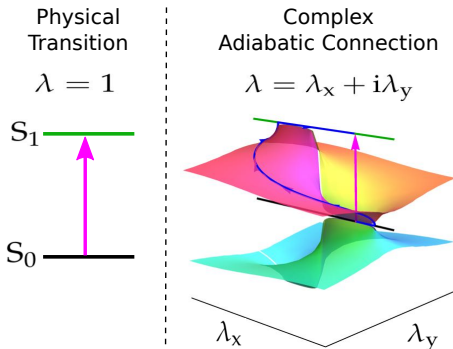
*"Green functions and self-consistency: insights from the spherium model",
Loos, Romaniello & Berger, JCTC 14 (2018) 3071*



"Unphysical discontinuities in GW methods",
 V ril, Romaniello, Berger & Loos, JCTC 14 (2018) 5220

How to morph ground state into excited state?

$$\hat{H} = -\frac{1}{2}\nabla^2 + \lambda \sum_{i<j} \frac{1}{r_{ij}}$$



“Complex Adiabatic Connection: a Hidden Non-Hermitian Path from Ground to Excited States”,

Burton, Thom & Loos, arXiv:1811.09164

Section 3

Selected CI: Theory

Flavours of selected CI (sCI)

“sCI methods provide near full CI (FCI) quality energies with only a small fraction of the determinants of the FCI space”

- CIPSI (Malrieu, Evangelisti, Angeli, Spiegelman, Caffarel, Scemama, etc)
- Heat-bath CI (Sharma & Umrigar)
- Adaptive sampling CI (Evangelista & Tubman)
- Incremental CI (Zimmerman)
- Iterative CI (Liu & Hoffmann)
- FCIQMC (Alavi & Booth)
- ...

CIPSI = CI using a Perturbative Selection made Iteratively

- Based on old idea by Bender and Davidson, and Whitten and Hackmeyer
Bender & Davidson, Phys. Rev. 183 (1969) 23
Whitten & Hackmeyer, JCP 51 (1969) 5584
- Further developments in Toulouse many years ago
Huron, Malrieu & Rancurel, JCP 58 (1973) 5745
- CIPSI \approx deterministic version of FCIQMC
Caffarel et al., Recent Progress in Quantum Monte Carlo (2016) Chap. 2, 15-46.
- CIPSI is a good candidate for massively parallel wave function calculations
Giner, Scemama & Caffarel, JCP 142 (2015) 044115
Caffarel et al., JCP 144 (2016) 151103
- Open-source code: [QUANTUM PACKAGE](https://github.com/scemama/quantum_package) (A. Scemama)
https://github.com/scemama/quantum_package

Quantum Package 2.0: an open-source determinant-driven suite of programs

Yann Garniron,^{1, a)} Kevin Gasperich,² Thomas Applencourt,² Anouar Benali,² Anthony Ferté,³ Barthélémy Pradines,³ Julien Paquier,³ Roland Assaraf,³ Peter Reinhardt,³ Julien Toulouse,³ Pierrette Barbaresco,⁴ Nicolas Renon,⁴ Mickaël Vériel,¹ Grégoire David,⁵ Jean-Paul Malrieu,¹ Pierre-François Loos,^{1, b)} Michel Caffarel,¹ Emmanuel Giner,³ and Anthony Scemama^{1, c)}

¹⁾Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, France

²⁾Computational Science Division, Argonne National Laboratory, Argonne, IL 60439, United States

³⁾Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, Sorbonne Université, CNRS, Paris, France

⁴⁾CALMIP, Université de Toulouse, CNRS, INPT, INSA, UPS, UMS 3667, France

⁵⁾Aix-Marseille Université, CNRS, ICR, Marseille, France

Quantum chemistry is a discipline which relies heavily on very expensive numerical computations. The scaling of correlated wave function methods lies, in their standard implementation, between $\mathcal{O}(N^5)$ and $\mathcal{O}(e^N)$, where N is proportional to the number of electrons of the system. Therefore, performing accurate calculations requires i) approximations that can lower the computational scaling, and ii) efficient implementations that take advantage of modern massively-parallel architectures. **QUANTUM PACKAGE** is an open-source programming environment for quantum chemistry specially designed for wave function methods. Its main goal is the development of determinant-driven selected configuration interaction (sCI) methods and multi-reference perturbation theory (MRPT). The determinant-driven framework allows the programmer to include any arbitrary set of determinants in the reference space, hence providing greater methodological freedoms. All the programs are developed with the IRPF90 code generator, which simplifies collaborative works and the development of new features. **QUANTUM PACKAGE** strives to allow easy implementation and experimentation of new methods, while making parallel computation as simple and efficient as possible on modern supercomputer architectures. Currently, the code has a parallel efficiency that enables routinely to realize runs on roughly 2000 CPU cores, with hundreds of millions of determinants in the reference space.



TOC graphical abstract

https://github.com/LCQP/quantum_package

Internal vs External

- **Green:** reference/variational/internal wave function (zeroth-order or model space)
- **Red:** perturbers or external wave function (first-order or perturbative space)

$$\begin{array}{l} \text{internal space } |I\rangle \\ \text{perturbers } |\alpha\rangle \end{array} \left\{ \begin{array}{|c|c|} \hline \mathbf{H}^{(0)} & \mathbf{h}^\dagger \\ \hline \mathbf{h} & \mathbf{H}^{(1)} \\ \hline \end{array} \right.$$

CIPSI algorithm

- 1 Define a (zeroth-order) *reference* wave function:

$$|\Psi^{(0)}\rangle = \sum_{I \in \mathcal{D}} c_I |I\rangle \quad E^{(0)} = \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle}$$

- 2 Generate *external determinants*:

$$\mathcal{A} = \left\{ (\forall I \in \mathcal{D}) (\forall \hat{T} \in \mathcal{T}_1 \cup \mathcal{T}_2) : |\alpha\rangle = \hat{T} |I\rangle \right\}$$

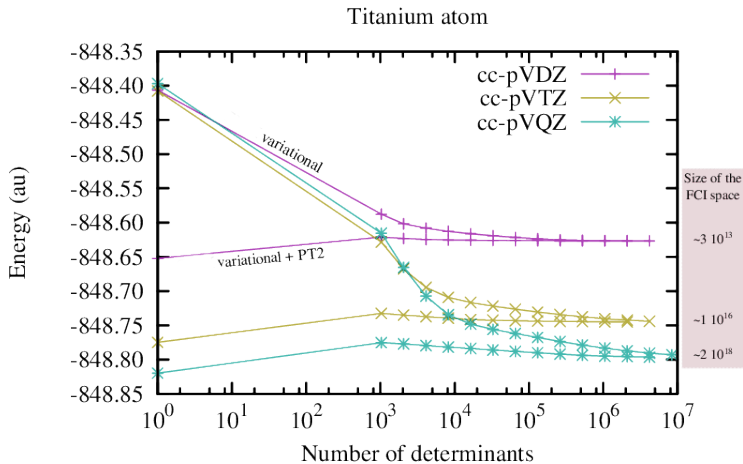
- 3 Second-order perturbative contribution of each $|\alpha\rangle$:

$$\delta E(\alpha) = \frac{|\langle \Psi^{(0)} | \hat{H} | \alpha \rangle|^2}{E^{(0)} - \langle \alpha | \hat{H} | \alpha \rangle}$$

- 4 Select $|\alpha\rangle$ with largest $\delta E(\alpha)$ and add them to \mathcal{D}
- 5 Diagonalize \hat{H} in $\mathcal{D} \Rightarrow$ update $|\Psi^{(0)}\rangle$ and $E^{(0)}$
- 6 Iterate

Huron, Malrieu & Rancurel, JCP 58 (1973) 5745

Giner, Scemama & Caffarel, JCP 142 (2015) 044115



Few remarks...

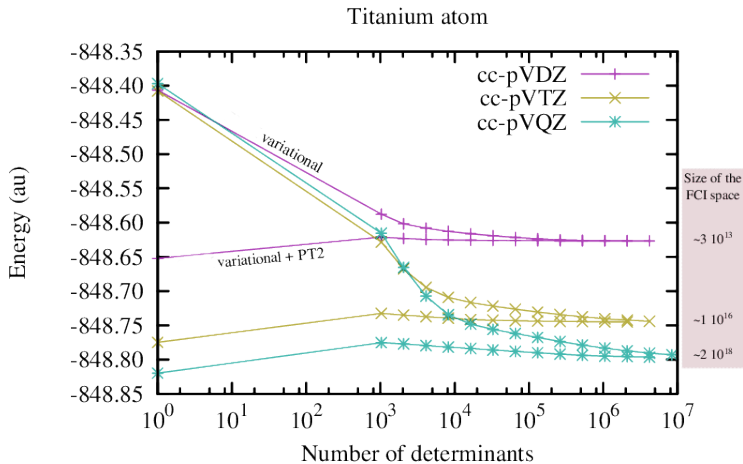
- When all $|I\rangle$ are selected, we obtain the FCI energy
- CIPSI is more an algorithm than a method
- Most of wave function methods can be performed à la CIPSI:
CIS, CID, CISD, CISDT, CAS, CASSD, MRCI, CC, MRCC, etc.

How do we know how far we are from the FCI limit?

- Second-order Epstein-Nesbet correction:

$$E^{(2)} = \sum_{\alpha} \delta E(\alpha)$$

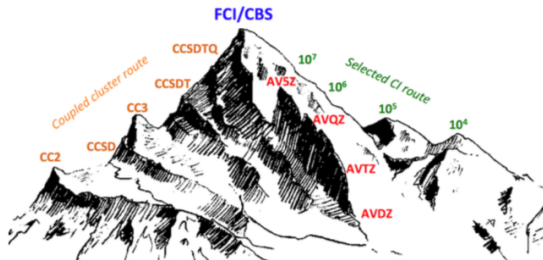
- $|\alpha\rangle$'s with largest $\delta E(\alpha)$ have been added to $\Psi^{(0)}$ previously
⇒ a *very large* number of *very small* contributions
- In practice, we use a semi-stochastic algorithm to compute $E^{(2)}$
⇒ *much faster!!*
Garniron, Scemama, Loos & Caffarel, JCP 147 (2017) 034101
- We *extrapolate* to $E^{(2)} = 0$ to reach the FCI limit (exFCI)



Section 4

Selected CI: Applications

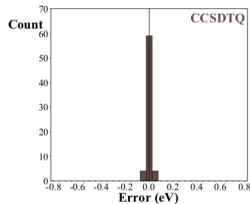
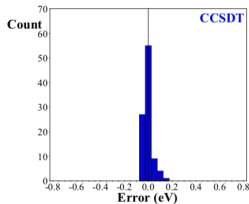
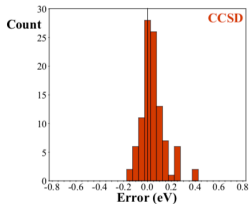
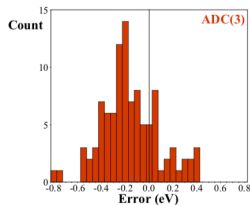
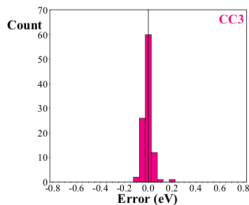
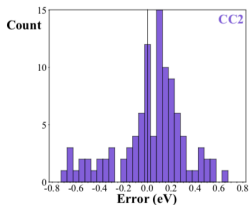
Highly-accurate reference energies for excited states



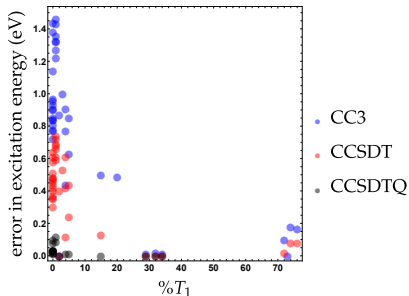
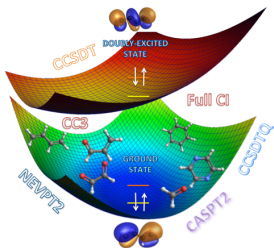
- 18 small molecules and 110 transition energies of various characters (valence, Rydberg, singlet, triplet, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, double excitations, etc)
- High-level CC calculations (up to CCSDTQP)
- sCI calculations (up to several millions of determinants)
- Large (diffuse) basis sets (AVXZ)

Loos, Scemama, Blondel, Garniron, Caffarel & Jacquemin JCTC 14 (2018) 4360

Benchmarking excited-state methods vs TBE/cc-pVTZ



Reference energies for double excitations



Loos, Boggio-Pasqua, Scemama, Caffarel & Jacquemin JCTC (submitted)
arXiv:1811.12861

Theoretical 0–0 Energies with Chemical Accuracy

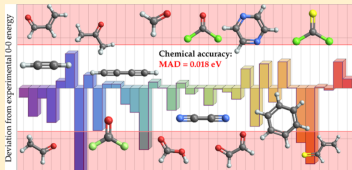
Pierre-François Loos,[†] Nicolas Galland,[‡] and Denis Jacquemin^{*,‡}

[†]Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, 31013 Toulouse Cedex 6, France

[‡]Laboratoire CEISAM - UMR CNR 6230, Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

Supporting Information

ABSTRACT: Ab initio calculation of electronic excitation energies with chemical accuracy (ca. 1 kcal·mol⁻¹ or 0.043 eV with respect to experiment) is a long-standing challenge in electronic structure theory. Indeed, the most advanced theories can, in practice, only be used to estimate vertical transition energies that cannot be measured experimentally, whereas the calculation of 0–0 energies requires excited-state structures and vibrations for both the ground and excited states, which drastically restrains the number of applicable methods. In this Letter, we present a composite computational protocol able to deliver chemically accurate theoretical 0–0 energies, with a mean absolute deviation of 0.018 eV for a set of 35 singlet valence states. Such accuracy, achievable for the valence states of small- and medium-sized molecules only, allows pinpointing questionable experimental assignments with very high confidence and constitutes a step toward quantitative prediction of excited-state properties.



Follow up: [Loos & Jacquemin JCTC \(submitted\) arXiv:1810.13035](#)

Section 5

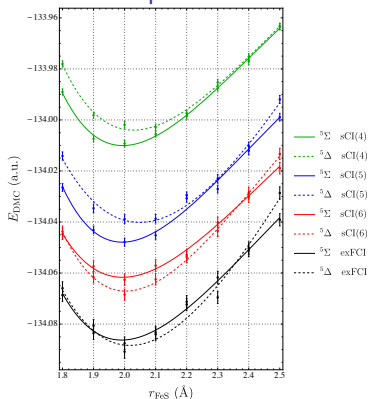
Quantum Monte Carlo

sCI-based trial wave function for QMC

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

- The **multideterminant part** is obtained via the (selected CI) CIPSI algorithm
Giner et al. CJC 91 (2013) 879; JCP 142 (2015) 044115
Caffarel et al. JCP 144 (2016) 151103
- We **may** or **may not** use a “minimal” (nodeless) **Jastrow** $J(\mathbf{R})$
⇒ Deterministic construction of the nodal surface
- Roughly speaking: DMC “completes” the basis...
- Open-source code: **QMC=CHEM** (A. Scemama)
<https://github.com/scemama/qmcchem>
- Interface for QMCPACK also available!

Dissociation profile



Method ^a	ϵ	N_{det}	$N_{\text{det}}^{\uparrow}$	$N_{\text{det}}^{\downarrow}$	acronym
sCI	10^{-4}	15 723	191	188	sCI(4)
	10^{-5}	269 393	986	1 191	sCI(5)
	10^{-6}	1 127 071	3 883	4 623	sCI(6)
	0	8 388 608	364 365	308 072	sCI(∞)
exFCI	—	$\sim 10^{27}$	$\sim 10^{16}$	$\sim 10^{11}$	FCI

^aBasis set: VTZ-ANO-BFD for Fe and VTZ-BFD for S

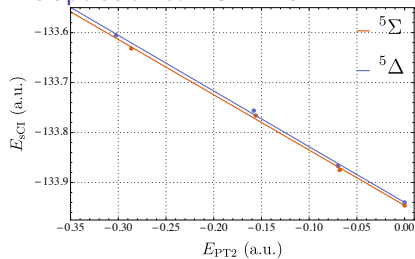
What	Who	D_0 (in eV)
Experiment	Matthew et al.	3.240 ± 0.003
CAS/Jastrow/opt	Hagagi-Mood/Luchow	3.159 ± 0.015
exFCI/DMC/extrap ^a	Scemama and co	3.271 ± 0.077

^aDMC: Stochastic reconfiguration (fixed number of walkers)

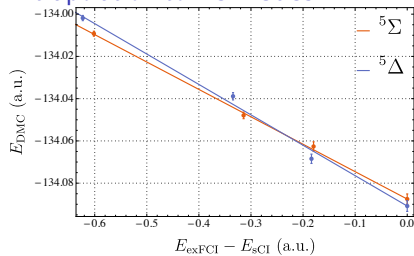
Hagagi-Mood & Luchow, JPCA 121 (2017) 6165

Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395

Extrapolation to FCI limit

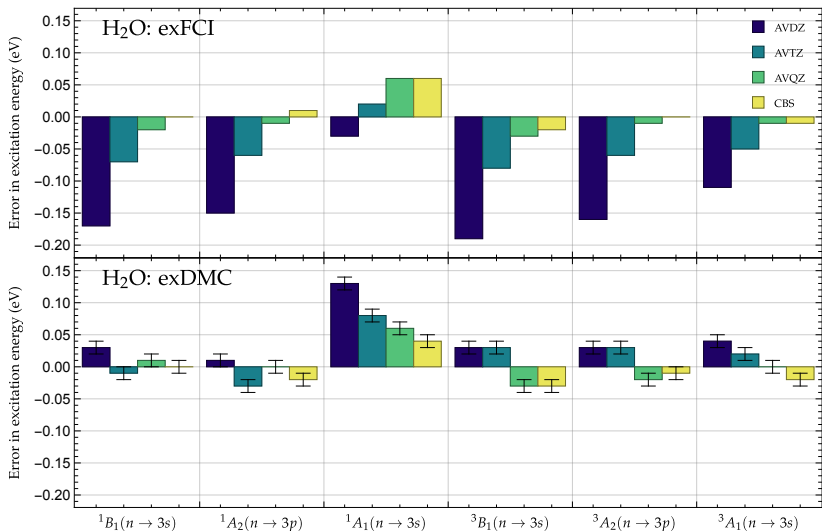


Extrapolation to FCI nodes



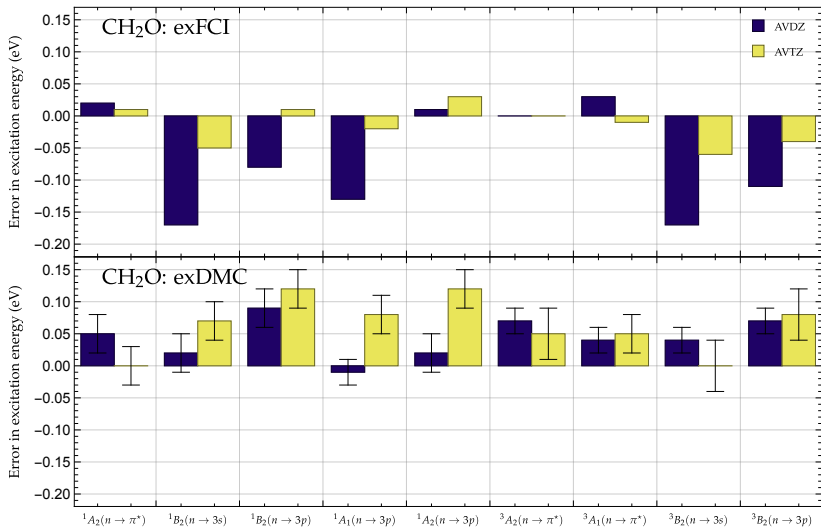
Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395

Fixed-node error in excited states: (all-electron) water



Scemama, Benali, Jacquemin, Caffarel & Loos, JCP 149 (2018) 034108

Fixed-node error in excited states: (all-electron) formaldehyde



Scemama, Benali, Jacquemin, Caffarel & Loos, JCP 149 (2018) 034108

Thank you!