Habilitation à diriger les recherches:

A Curvy View on Electronic Correlation

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Research

- **2005-2008: PhD** at UHP (Nancy) with Xavier Assfeld
  - *Development and application of QM/MM methods*
- **2008-2013: Postdoc** at ANU (Australia) with Peter Gill
  - Exact solutions of the Schrödinger equation
  - Uniform electron gases (UEGs)
  - Correlation effects in two-electron systems
- **2013-2016: Senior lecturer** and **Group leader** at ANU
  - Quantum Monte Carlo (QMC) & Fermionic nodes
  - Density-functional approximations (DFAs)
  - Explicitly-correlated F12 methods
- **2017-Armageddon: CNRS researcher** at the LCPQ

Teaching

- **2004: Teaching assistant** in Computational Chemistry (UHP)
- **2005-2008: Teaching assistant** in Chemistry/Mathematics (UHP)
- **2016-2017: Senior Lecturer** (ANU)
  - Courses in Computational Chemistry and Molecular Modelling
  - Mentoring and supervising from 1st- to 3rd-year students ("PhB" program)
- **2017-2018: Teaching assistant** (ISAE-SUPAERO)
  - Numerical analysis labs
- **2014 & 2016:** Quantum and Computational Chemistry Student Conference (NZ)
  - QMC in 2014 & DFT in 2016
  - Co-organiser (with Deborah Crittenden) in 2016
- **2018:** TCCM winter school LTTC (France)
  - Theory and implementation of DFT methods

Short CV

- 59 publications & 27 oral communications (17 invited lectures)
- Grants (Australian Research Council)
  1. Early-career researcher award (2013-2017)
  2. Discovery project grant (2014-2017)
- Co-supervision (with Peter Gill) of two PhD students (ANU)
  1. Caleb Ball: One-dimensional Chemistry
  2. Giuseppe Barca: Many-electron integrals
- Supervision of 2 postdocs (ANU)
  1. Davids Agboola: Low-density electron gases
  2. Marat Sibaev: QMC on curved manifolds
- Supervision of 2 Master students and many undergraduate students (ANU)
  1. Anneke Knol: QMC for low-density electron gases
  2. Fergus Rogers: Symmetry-broken solutions
- Currently supervising two Master students (UPS)
  1. Mickael Very: Stochastic quantum Chemistry
  2. Lea Brooks (with Arjan Berger and Stefano Evangelisti): Wigner crystals

Current Research

- Dressing strategies (with Anthony Scemama and Michel Caffarel)
  - Dressing of the CI matrix with explicit correlation
  - Dressing the e-n cusp into MOs
- Selected CI for "challenging" Chemistry (with AS and MC)
  - FeS dimer (with Yann Garniron)
  - Cyanine dyes (with Thibaud Etienne)
  - Benchmarking excited state methods (with Denis Jacquemin)
- Green function-based methods (with Arjan Berger)
  - Approximations in GW and BSE for model systems
  - Implementation of G0W0, evGW, qsGW, BSE, GF2, GF3, pp-RPA, etc
- Many-electron integrals (with AS)
  - General integral package (molecules, materials, ECP, etc)
  - Three- and four-electron integrals for explicitly-correlated methods
- Making quantum Chemistry great again! (with AS and MC)
  - Stochastic MRPT, MP2, RPA, GF2, GW, CC, . . . with zero variance

Overview

Section 2

Introduction

Electronic correlation

Why bother with electron correlation?

$$\boxed{E_c = E_{exact} - E_{HF}}$$

- ☺ HF theory ignores correlation and gives 99% of the energy
- ☺ It is often accurate for the prediction of molecular structures
- ☺ It is computationally cheap and can be applied to large systems
- ☹ Unfortunately, the final 1% can have important chemical effects
- ☹ This is particularly true when bonds are broken and/or formed
- ☹ Thus, realistic chemistry requires a good treatment of correlation

Electronic correlation

Some random thoughts on electron correlation

- The concept was introduced at the dawn of quantum chemistry
  Wigner Phys Rev 46 (1934) 1002
- Its definition was agreed somewhat later
  Löwdin Adv Chem Phys 2 (1959) 207
- ☹ One Nobel Laureate used to refer to it as "the stupidity energy"
  Feynmann (1972)
- ☺ There have been recent heroic calculations on the helium atom
  Nakashima & Nakatsuji J Chem Phys 127 (2007) 224104
- ☹ "We conclude that theoretical understanding here lags well behind the power of available computing machinery"
  Schwartz Int J Mod Phys E 15 (2006) 877

Pursuit of E_{He}

History of accurate (non-relativistic) calculation on the He atom

"For thousands of years mathematicians have enjoyed competing with one other to compute ever more digits of the number π. Among modern physicists, a close analogy is computation of the ground state energy of the helium atom, begun 75 years ago by E. A. Hylleraas."

Schwartz Int J Mod Phys E 15 (2006) 877

Year	Authors	Energy (a.u.)
1929	Hylleraas	-2.902 43
1957	Kinoshita	-2.903 722 5
1966	Frankowski & Pekeris	-2.903 724 377 032 6
1994	Thakkar & Koga	-2.903 724 377 034 114 4
1998	Goldman	-2.903 724 377 034 119 594
1999	Drake	-2.903 724 377 034 119 596
2002	Sims & Hagstrom	-2.903 724 377 034 119 598 299
2002	Drake et al.	-2.903 724 377 034 119 598 305
2002	Korobov	-2.903 724 377 034 119 598 311 158 7
2006	Schwartz	-2.903 724 377 034 119 598 311 159 245 194 404 440 049 5
2007	Nakashima & Nakatsuji	-2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 37

Nakashima & Nakatsuji J Chem Phys 127 (2007) 224104

Section 3

The "spherium" model

Why bother with electron(s) on a sphere?

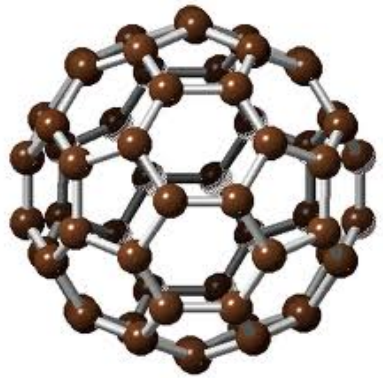
Arguments for high-impact journals

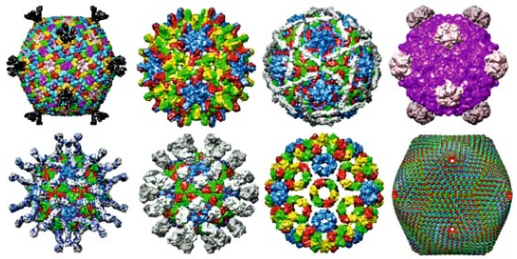
It can be experimentally realized:

- Multielectron bubbles in liquid helium
- Arrangements of protein subunits on spherical viruses
- Colloid particles in colloidosomes
- Fullerene-like molecules: C_{60}, C_{240}, C_{540}, ...

Our arguments...

- It yielded a number of unexpected discoveries
- This is actually related to "real" quantum Chemistry





The spherium atom: electron(s) on a sphere of radius R

One electron on a sphere

$$\hat{H} = -\frac{1}{2}\nabla^2$$

Solution:
$Y_{\ell m}(\theta, \phi) \Rightarrow$ Boring!!!

Two electrons on a sphere

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{1}{r_{12}}$$

Solution:
??? $\Rightarrow$ Exciting!!!

Loos & Gill Phys Rev A 79 (2009) 062517

Let's play a game...

First, we solved the Schrödinger equation numerically, e.g.

$$R = 1, \quad E_{\rm Sp} = 0.852\ 781\ 065\ 056\ 462\ 665\ 400\ 437\ 966\ 038\ 710\ 264\ \ldots$$
$$R = 100, \quad E_{\rm Sp} = 0.005\ 487\ 412\ 426\ 784\ 081\ 726\ 642\ 485\ 484\ 213\ 968\ \ldots$$

Observation:

— With a small expansion $\psi = \sum_k c_k r_{12}^k$, one can get many digits! —

Is it trying to tell us something?

Loos & Gill Phys Rev A 79 (2009) 062517

Hamiltonian of the ground state

$$\hat{H} = \left(\frac{r_{12}^2}{4R^2} - 1 \right) \frac{d^2}{dr_{12}^2} + \left(\frac{3r_{12}}{4R^2} - \frac{1}{r_{12}} \right) \frac{d}{dr_{12}} + \frac{1}{r_{12}}$$

Frobenius method

We seek polynomial solutions: $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{\ell=0}^{\infty} c_\ell r_{12}^\ell$

Analytical solutions

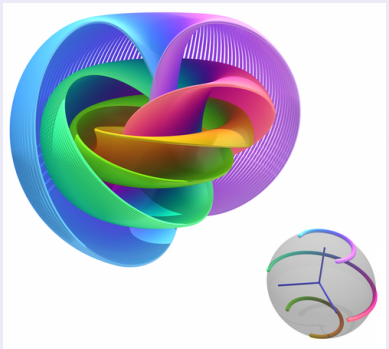
$$\begin{array}{lll} R = \sqrt{3}/2 & E = 1 & \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 + r_{12} \\ R = \sqrt{7} & E = 2/7 & \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 + r_{12} + \frac{5}{28} r_{12}^2 \\ \vdots & \vdots & \vdots \end{array}$$

Loos & Gill Phys Rev Lett 103 (2009) 123008

The glomium atom: electron(s) on a glome

What is a "glome"?

A glome is a 3-sphere, i.e. the surface of a 4-dimensional ball



$$\hat{H} = \left(\frac{r_{12}^2}{4R^2} - 1\right)\frac{d^2}{dr_{12}^2} + \left(\frac{5r_{12}}{4R^2} - \frac{2}{r_{12}}\right)\frac{d}{dr_{12}} + \frac{1}{r_{12}}$$

Analytical solutions

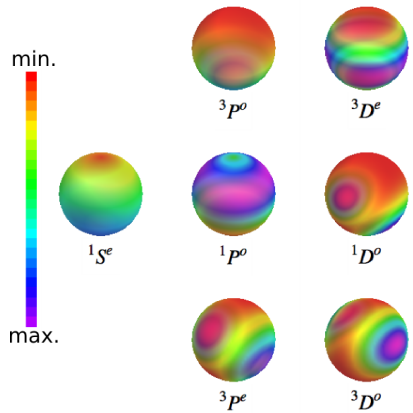
$$\begin{array}{lll} R = \sqrt{10}/2 & E = 1/2 & \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 + \frac{1}{2} r_{12} \\ R = \sqrt{66}/2 & E = 2/11 & \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 + \frac{1}{2} r_{12} + \frac{7}{132} r_{12}^2 \\ \vdots & \vdots & \vdots \end{array}$$

Generalization to a D-dimensional space

Simplest exact solutions for a D-sphere

D	$4R^2$	E	$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$
1	6	$2/3$	$r_{12}(1 + r_{12}/2)$
2	3	1	$1 + r_{12}$
3	10	$1/2$	$1 + r_{12}/2$
4	21	$1/3$	$1 + r_{12}/3$
$\vdots$	$\vdots$	$\vdots$	$\vdots$
D	$(2D-1)(D-1)$	$1/(D-1)$	$1 + r_{12}/(D-1)$
$\vdots$	$\vdots$	$\vdots$	$\vdots$

— Kato's cusp conditions are identical to real systems —



Loos & Gill Phys Rev Lett 103 (2009) 123008; Mol Phys 108 (2010) 2527

Section 4

Uniform electron gases

The uniform electron gas in Flatland

The infinite uniform electron gas (IUEG)

- ☺ One of the most popular models in condensed matter physics
- ☺ Characterized by one parameter: Seitz radius $r_s \propto \rho^{-1/D}$
- ☹ Clearly suitable for metals. Less clearly suitable for molecules

The "jellium" recipe

1. Put n electrons into a D-dimensional cube of volume V
2. Add a background of positive "jelly" to achieve neutrality
3. Increase both n and V so that $\rho = n/V$ remains constant
4. In the limit as $n \to \infty$ and $V \to \infty$, one obtains an infinite UEG

Parr & Yang, *DFT for atoms and molecules* (1989)
Loos & Gill, WIREs Comput Mol Sci 6 (2016) 410

The uniform electron gas in Sphereland

Finite UEGs (FUEGs)

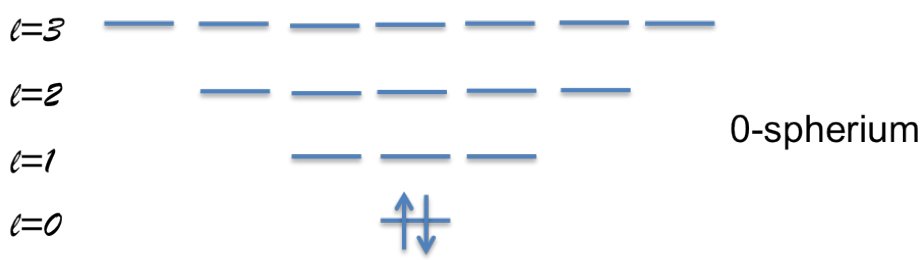
- One can also construct UEGs using a finite number of electrons
- The recipe:
  1. Put n electrons onto a D-dimensional sphere
  2. Add a background positive charge to achieve neutrality
  3. That's all

☺ For $n \to \infty$, we get the infinite UEG!!

Loos & Gill, JCP 135 (2011) 214111
Gill & Loos, TCA 131 (2012) 1069

Uniform electron gases in Sphereland

We fill each (hyper)spherical harmonic $Y_{\ell m(n)}$ up to $\ell = L$ with one spin-up and one spin-down electron



L-Spherium

$$\sum_{m=-\ell}^{\ell} |Y_{\ell m}(\theta,\phi)|^2 = \frac{2\ell+1}{4\pi}$$

$$\rho = \frac{2(L+1)^2}{4\pi R^2} = \frac{1}{\pi r_s^2}$$

L-Glomium

$$\sum_{m=0}^{\ell} \sum_{n=-m}^{m} |Y_{\ell mn}(\chi,\theta,\phi)|^2 = \frac{(\ell+1)^2}{2\pi^2}$$

$$\rho = \frac{2(L+1)(L+2)(2L+3)/3}{4\pi^2 R^3} = \frac{3}{4\pi r_s^3}$$

Loos & Gill, JCP 135 (2011) 214111

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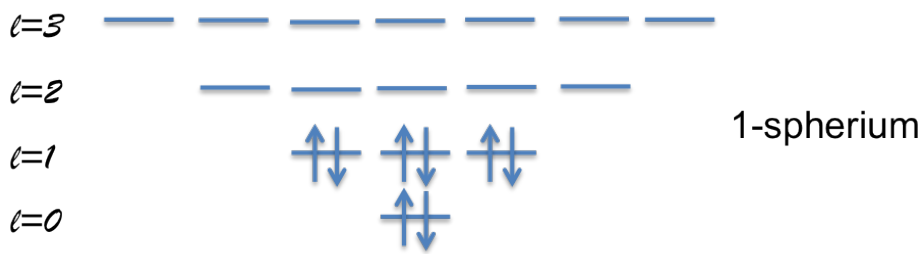

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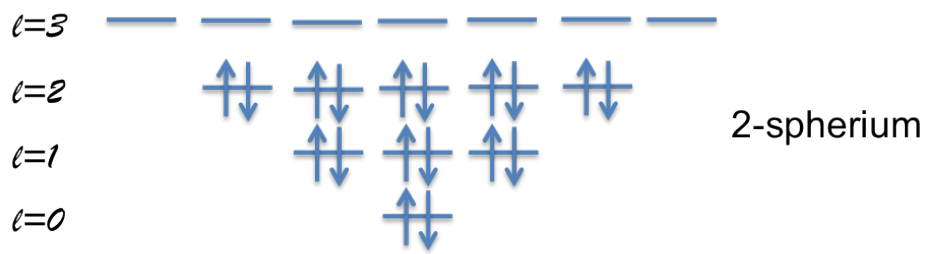

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$$\rho = \frac{2(L+1)^2}{4\pi R^2} = \frac{1}{\pi r_s^2}$$

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$$\sum_{m=0}^{\ell} \sum_{n=-m}^{m} |Y_{\ell mn}(\chi,\theta,\phi)|^2 = \frac{(\ell+1)^2}{2\pi^2}$$

$$\rho = \frac{2(L+1)(L+2)(2L+3)/3}{4\pi^2 R^3} = \frac{3}{4\pi r_s^3}$$

Loos & Gill, JCP 135 (2011) 214111

Non-uniqueness of the uniform electron gas

Are jellium-based functionals accurate for finite UEGs?

		Exact			Jellium-based Kohn-Sham DFT						Error
	$2R$	E_T	E_{ee}	E	T_S	E_V	E_J	$-E_X$	$-E_c^{jell}$	E_{KS}	$E_{KS} - E$
0-sph.	$\sqrt{3}$	0.0520	0.4480	1/2	0	0	1.1547	0.4901	0.1028	0.562	0.062
	$\sqrt{28}$	0.0186	0.1243	1/7	0	0	0.3780	0.1604	0.0593	0.158	0.015
0-glo.	$\sqrt{10}$	0.0142	0.2358	1/4	0	0	0.5368	0.2178	0.0437	0.275	0.025
	$\sqrt{66}$	0.0078	0.0831	1/11	0	0	0.2090	0.0848	0.0270	0.097	0.006

Why? We are missing some two-electron information

Loos & Gill, PRL 103 (2009) 123008
Gill & Loos, TCA 131 (2012) 1069

Curvature of the Fermi hole

The curvature of the Fermi hole* is ($0 \leq \alpha < \infty$):

$$\boxed{\alpha = \frac{\tau - \tau_W}{\tau_{IUEG}} = \frac{\tau}{\tau_{IUEG}} - \frac{x^2}{4 C_F}} \qquad C_F = \frac{3}{5}(6\pi^2)^{2/3}$$

$\tau = \sum_i^{occ} |\nabla \psi_i|^2$ is the kinetic energy density

$\tau_W = \frac{|\nabla \rho|^2}{4\,\rho}$ is the von Weizsäcker kinetic energy density

$\tau_{IUEG} = C_F\,\rho^{5/3}$ is the kinetic energy density of the IUEG

Becke & Edgecombe, JCP 92 (1990) 5397
Loos, Ball & Gill, JCP 140 (2014) 18A524
Loos, JCP 146 (2017) 114108

*Remember ELF!? ELF $= (1+\alpha^2)^{-1}$

High-density ($r_s \to 0$) limit: L-spherium vs 2D jellium

$$\boxed{e_{\text{jellium}}^{\text{2D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + \lambda_1 r_s \ln r_s + O(r_s)}$$

$\varepsilon_{-2} =$

$\varepsilon_{-1} =$

$\varepsilon_{0,\text{J}} =$

$\varepsilon_{0,\text{K}} =$

$\lambda_1 =$

Loos & Gill, PRB 83 (2011) 233102; ibid 84 (2011) 033103

High-density ($r_s \to 0$) limit: L-spherium vs 2D jellium

$$\boxed{e_{\text{jellium}}^{\text{2D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + \lambda_1 r_s \ln r_s + O(r_s)}$$

$$\varepsilon_{-2} = + \frac{L(L+2)}{2(L+1)^2}$$

$$\varepsilon_{-1} = - \frac{1}{\sqrt{2}} F \left[\begin{matrix} -L, & L+2, & \frac{1}{2}, & -\frac{1}{2} \\ -L-\frac{1}{2}, & L+\frac{3}{2}, & 2 & \end{matrix} \right]$$

$$\varepsilon_{0,\text{J}} = - \frac{2}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle^2}{\kappa_a + \kappa_b - \kappa_i - \kappa_j}$$

$$\varepsilon_{0,\text{K}} = \frac{1}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle\langle ba|ij\rangle}{\kappa_a + \kappa_b - \kappa_i - \kappa_j}$$

$$\lambda_1 = \text{(resummation)}$$

Loos & Gill, PRB 83 (2011) 233102; ibid 84 (2011) 033103

High-density ($r_s \to 0$) limit: L-spherium vs 2D jellium

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$$\varepsilon_{-2} = + \frac{L(L+2)}{2(L+1)^2} \qquad \xrightarrow[L\to\infty]{} + \frac{1}{2}$$

$$\varepsilon_{-1} = - \frac{1}{\sqrt{2}} F \left[\begin{matrix} -L, & L+2, & \frac{1}{2}, & -\frac{1}{2} \\ -L-\frac{1}{2}, & L+\frac{3}{2}, & 2 & \end{matrix} \right] \qquad \xrightarrow[L\to\infty]{} - \frac{4\sqrt{2}}{3\pi}$$

$$\varepsilon_{0,\text{J}} = - \frac{2}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle^2}{\kappa_a + \kappa_b - \kappa_i - \kappa_j} \qquad \xrightarrow[L\to\infty]{} \ln 2 - 1$$

$$\varepsilon_{0,\text{K}} = \frac{1}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle\langle ba|ij\rangle}{\kappa_a + \kappa_b - \kappa_i - \kappa_j} \qquad \xrightarrow[L\to\infty]{} G - \frac{8}{\pi^2}\beta(4)$$

$$\lambda_1 = (\text{resummation}) \qquad \xrightarrow[L\to\infty]{} - \sqrt{2}\left(\frac{10}{3\pi} - 1\right)$$

Loos & Gill, PRB 83 (2011) 233102; ibid 84 (2011) 033103

High-density ($r_s \to 0$) limit: L-spherium vs 2D jellium

$$\boxed{e_{\text{jellium}}^{\text{2D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + \lambda_1 r_s \ln r_s + O(r_s)}$$

$$\varepsilon_{-2} = + \frac{L(L+2)}{2(L+1)^2} \xrightarrow[L\to\infty]{} + \frac{1}{2} \quad \checkmark$$

$$\varepsilon_{-1} = - \frac{1}{\sqrt{2}} F \left[\begin{matrix} -L, & L+2, & \frac{1}{2}, & -\frac{1}{2} \\ -L-\frac{1}{2}, & L+\frac{3}{2}, & 2 & \end{matrix} \right] \xrightarrow[L\to\infty]{} - \frac{4\sqrt{2}}{3\pi} \quad \checkmark$$

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$$\varepsilon_{0,\text{K}} = \frac{1}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle\langle ba|ij\rangle}{\kappa_a + \kappa_b - \kappa_i - \kappa_j} \xrightarrow[L\to\infty]{} G - \frac{8}{\pi^2}\beta(4) \quad \checkmark$$

$$\lambda_1 = (\text{resummation}) \xrightarrow[L\to\infty]{} - \sqrt{2}\left(\frac{10}{3\pi} - 1\right) \quad \checkmark$$

Loos & Gill, PRB 83 (2011) 233102; ibid 84 (2011) 033103

High-density ($r_s \to 0$) limit: L-glomium vs 3D jellium

$$\boxed{e_{\text{jellium}}^{\text{3D}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + \lambda_0 \ln r_s + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + O(r_s \ln r_s)}$$

ε_{-2}

ε_{-1}

λ_0

$\varepsilon_{0,\text{J}}$

$\varepsilon_{0,\text{K}}$

High-density ($r_s \to 0$) limit: L-glomium vs 3D jellium

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$$\varepsilon_{-2} \xrightarrow[L\to\infty]{} +\frac{3}{10}\left(\frac{9\pi}{4}\right)^{2/3}$$

$$\varepsilon_{-1} \xrightarrow[L\to\infty]{} -\frac{3}{4\pi}\left(\frac{9\pi}{4}\right)^{1/3}$$

$$\lambda_0 \xrightarrow[L\to\infty]{\text{resum.}} \frac{1-\ln 2}{\pi^2}$$

$$\varepsilon_{0,\text{J}} \xrightarrow[L\to\infty]{\text{resum.}} -0.071099$$

$$\varepsilon_{0,\text{K}} \xrightarrow[L\to\infty]{} \frac{\ln 2}{6} - \frac{3}{4\pi^2}\zeta(3)$$

High-density ($r_s \to 0$) limit: L-glomium vs 3D jellium

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ε_{-2}	$\xrightarrow[L\to\infty]{}$	$+\frac{3}{10}\left(\frac{9\pi}{4}\right)^{2/3}$	✓
ε_{-1}	$\xrightarrow[L\to\infty]{}$	$-\frac{3}{4\pi}\left(\frac{9\pi}{4}\right)^{1/3}$	✓
λ_0	$\xrightarrow[L\to\infty]{\text{resum.}}$	$\frac{1-\ln 2}{\pi^2}$	✓
$\varepsilon_{0,\text{J}}$	$\xrightarrow[L\to\infty]{\text{resum.}}$	-0.071099	✓
$\varepsilon_{0,\text{K}}$	$\xrightarrow[L\to\infty]{}$	$\frac{\ln 2}{6} - \frac{3}{4\pi^2}\zeta(3)$	✓

Our conjecture

$$e(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + \sum_{\ell=0}^{\infty} [\lambda_\ell \ln r_s + \varepsilon_\ell] r_s^\ell$$

"[. . .] the high-density expansions are identical to all order"

$\Leftrightarrow$ "short-sightedness" of electronic matter
Kohn PRL 76 (1996) 3168

Loos & Gill, JCP 135 (2011) 214111

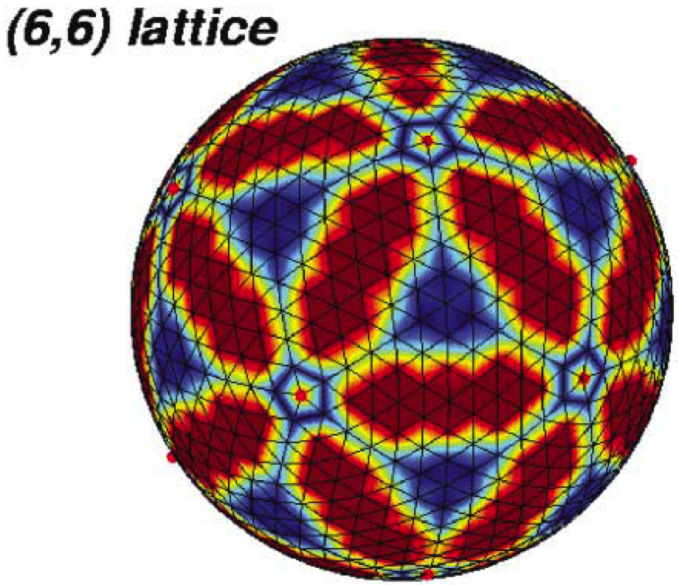
Low-density ($r_s \to \infty$) limit of L-spherium

$$e^{\text{2D}}_{\text{jellium}}(r_s) = \frac{\eta_1}{r_s} + \frac{\eta_{3/2}}{r_s^{3/2}} + \frac{\eta_2}{r_s^2} + \dots$$

Thomson problem

"determine the minimum energy configuration of n electrons on the surface of a sphere that repel each other with a force given by Coulomb's law"

$$e_{\text{sph.}}(r_s) \sim -\frac{1.10494}{r_s} \quad \text{(large-}n\text{ limit)}$$



Note: identical to the Wigner crystal phase of 2D jellium (hexagonal lattice)

Bowick et al. PRL 89 (2002) 185502
Agboola, Knol, Gill & Loos, JCP 143 (2015) 084114

Section 5

Many-electron integrals

Why?! Just why do we want to calculate these nasty integrals?!

#balance ta resolution de l'identité (RI)

- Uncontrolled RI error in F12 methods
- (Huge) auxiliary basis set
- In 1991, Kutzelnigg wrote:
  "Even if fast procedures for the evaluation of these interals were available, one would have to face the problem of the large number of these integrals; while that of two-electron integrals is $\sim N^4$*, there are* $\sim N^6$ *three-electron and* $\sim N^8$ *four-electron integrals. The storing and manipulating of these integrals could be handled only for extremely small basis sets."*
- Still, integral algorithms are much faster these days...
- Moreover, (if you screen the hell out of them) the number of significant integrals isn't that bad...

What do we want to calculate?

Three-electron integral

$$\langle \boldsymbol{a}_1 \boldsymbol{a}_2 \boldsymbol{a}_3 | \boldsymbol{b}_1 \boldsymbol{b}_2 \boldsymbol{b}_3 \rangle \equiv \langle \boldsymbol{a}_1 \boldsymbol{a}_2 \boldsymbol{a}_3 | f_{123} | \boldsymbol{b}_1 \boldsymbol{b}_2 \boldsymbol{b}_3 \rangle$$
$$= \iiint \psi_{\boldsymbol{a}_1}^{\mathbf{A}_1}(\boldsymbol{r}_1) \psi_{\boldsymbol{a}_2}^{\mathbf{A}_2}(\boldsymbol{r}_2) \psi_{\boldsymbol{a}_3}^{\mathbf{A}_3}(\boldsymbol{r}_3) \, f_{123} \, \psi_{\boldsymbol{b}_1}^{\mathbf{B}_1}(\boldsymbol{r}_1) \psi_{\boldsymbol{b}_2}^{\mathbf{B}_2}(\boldsymbol{r}_2) \psi_{\boldsymbol{b}_3}^{\mathbf{B}_3}(\boldsymbol{r}_3) d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3$$

Gaussian-type orbital (GTO)

$$\text{Primitive GTO} = |\boldsymbol{a}] = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} e^{-\alpha |\boldsymbol{r} - \mathbf{A}|^2}$$

$$\text{Contracted GTO} = |\boldsymbol{a}\rangle \equiv \psi_{\boldsymbol{a}}^{\mathbf{A}}(\boldsymbol{r}) = \sum_i^K D_i |\boldsymbol{a}]_i$$

- Exponent α
- Center $\mathbf{A} = (A_x, A_y, A_z)$
- Angular momentum $\boldsymbol{a} = (a_x, a_y, a_z)$ and total angular momentum $a = a_x + a_y + a_z$

Three-electron operator

Three-electron operators

$$f_{123} = f_{12} g_{13} h_{23}$$

Two-electron operators

- Long-range Coulomb operator

$$\mathcal{C}_{12} = r_{12}^{-1}$$

- Short-range Slater geminal

$$\mathcal{S}_{12} = \exp(-\lambda r_{12})$$

- Short-range Gaussian geminal

$$\mathcal{G}_{12} = \exp(-\lambda r_{12}^2)$$

- Short-range operator

$$\mathcal{E}_{12} = r_{12} \operatorname{erfc}(\sqrt{\lambda} r_{12})$$

Asymptotic scaling

Operator		Scaling
Two-electron	Three-electron	
S	SS, SSS, SSL	$\mathcal{O}(N)$
L	SL, SLL	$\mathcal{O}(N^2)$
—	LL, LLL	$\mathcal{O}(N^3)$

S = short range
L = long range

Asymptotic scaling of two-electron integrals

Number of significant two-electron integrals for polyenes

$$N_{\text{sig}} = c\, N^{\alpha}$$

Molecule	N	$\mathcal{C}_{12}$		$\mathcal{G}_{12}$	
		N_{sig}	α	N_{sig}	α
propene	12	1 625	—	1 650	—
butadiene	16	5 020	3.9	5 020	3.9
hexatriene	24	24 034	3.9	23 670	3.8
octatetraene	32	63 818	3.4	52 808	2.8
decapentaene	40	119 948	2.8	81 404	1.9
dodecaexaene	48	192 059	2.6	109 965	1.6

Helgaker, Jorgensen & Olsen, Molecular Electronic-Structure Theory

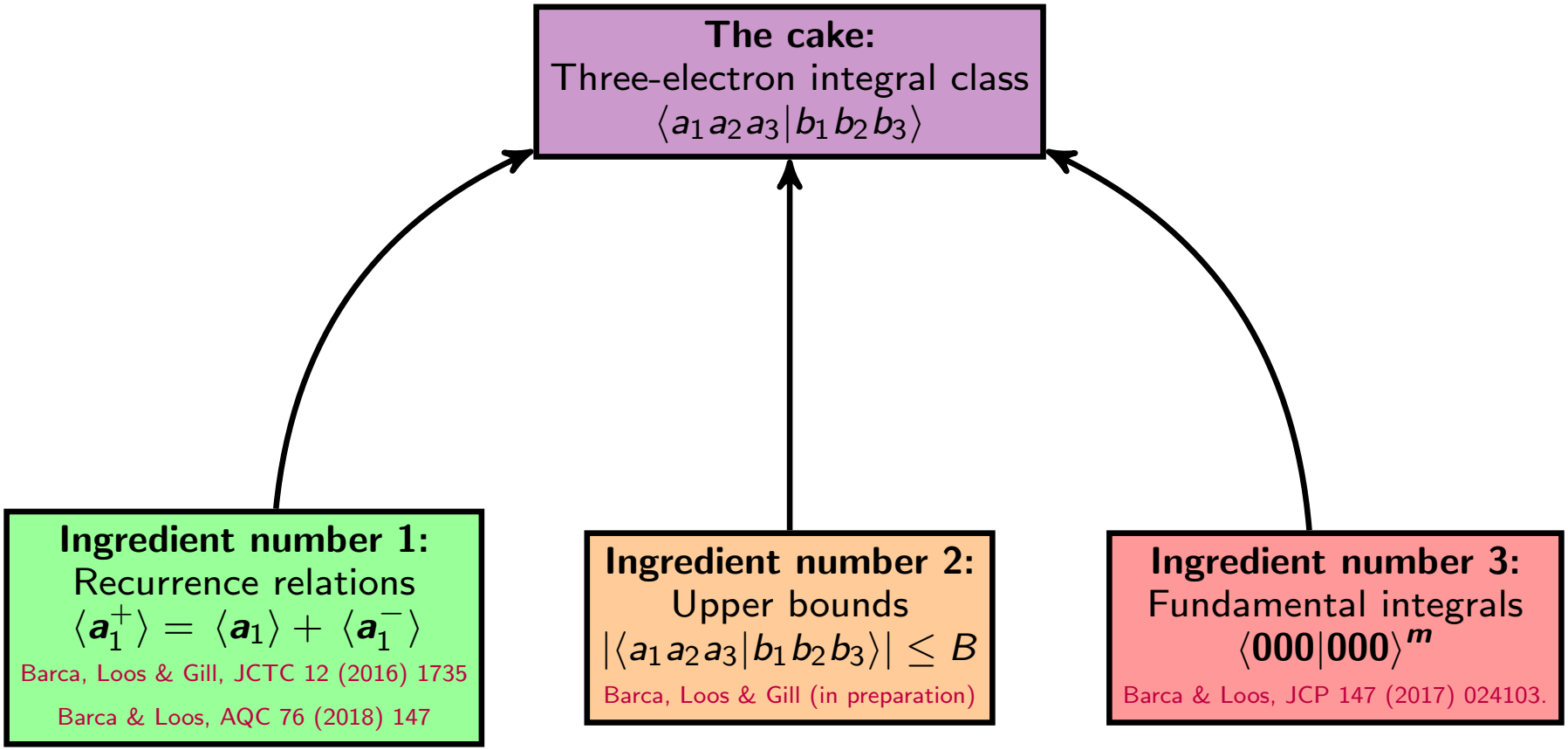
Asymptotic scaling of three-electron integrals

Number of significant three-electron integrals for polyenes

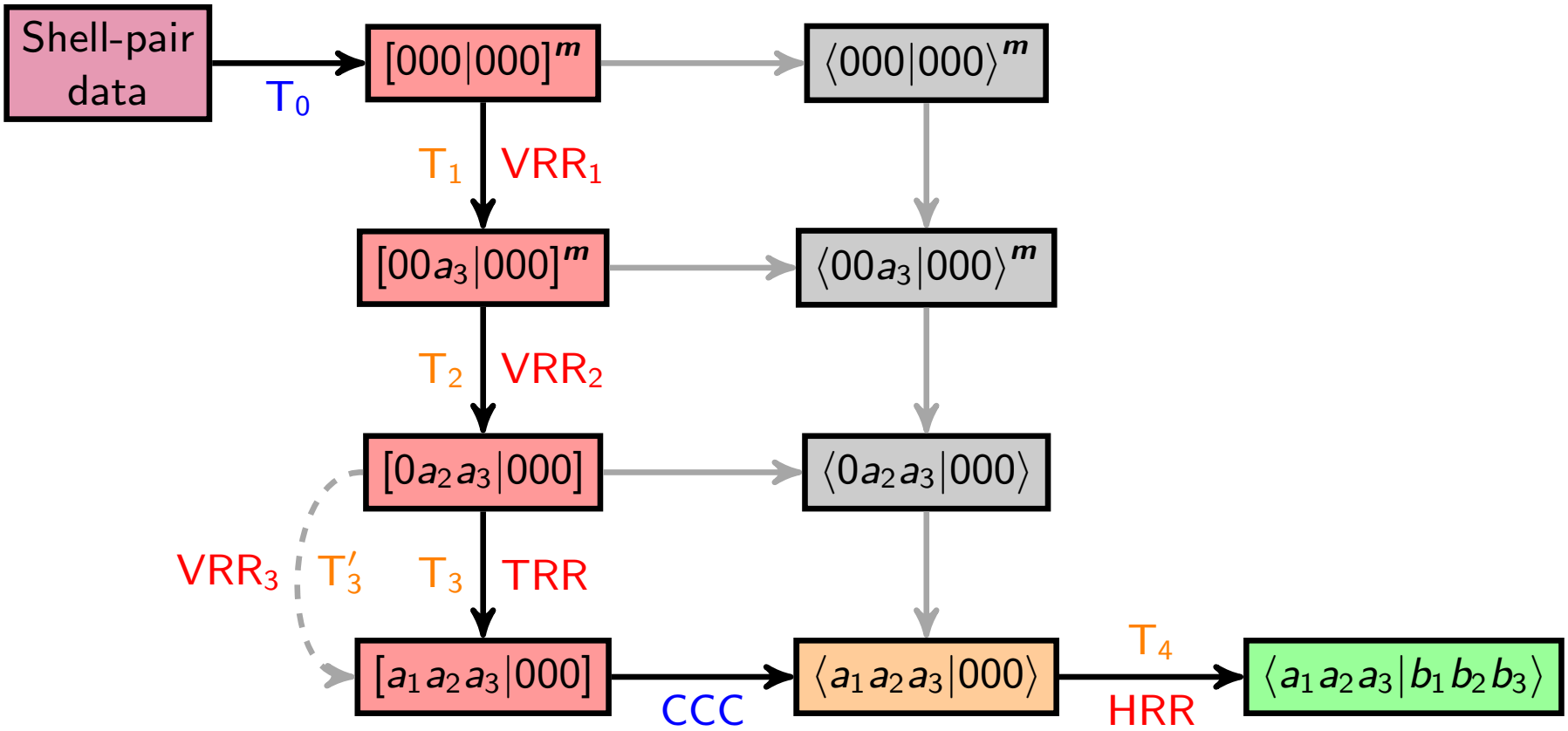
$$N_{\text{sig}} = c\, N^{\alpha}$$

Molecule	N	$\mathcal{C}_{12}\mathcal{C}_{13}$		$\mathcal{G}_{12}\mathcal{C}_{13}$		$\mathcal{G}_{12}\mathcal{G}_{13}$	
		N_{sig}	α	N_{sig}	α	N_{sig}	α
propene	12	123 480	—	243 071	—	123 480	—
butadiene	16	650 034	5.8	1 288 614	5.8	649 796	5.8
hexatriene	24	6 259 263	5.6	10 992 400	5.3	4 436 162	4.7
octatetraene	32	22 875 778	4.5	31 511 030	3.7	9 273 218	2.6
decapentaene	40	53 576 923	3.8	59 315 069	2.8	14 101 575	1.9
dodecaexaene	48	101 224 185	3.5	94 176 325	2.5	18 927 362	1.6

Recipe for three-electron integrals

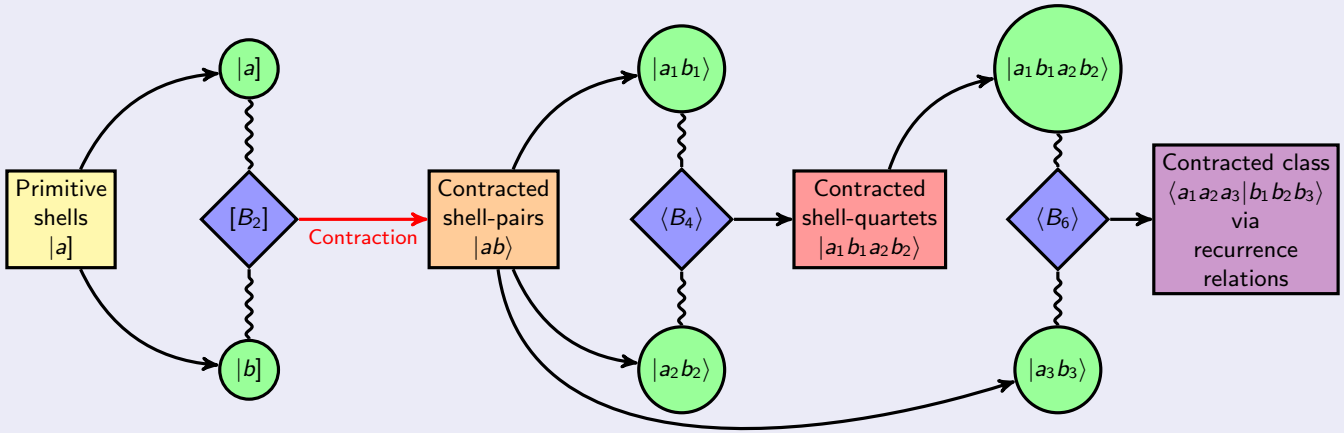


Late-contraction path algorithm (Head-Gordon-Pople & PRISM inspired)

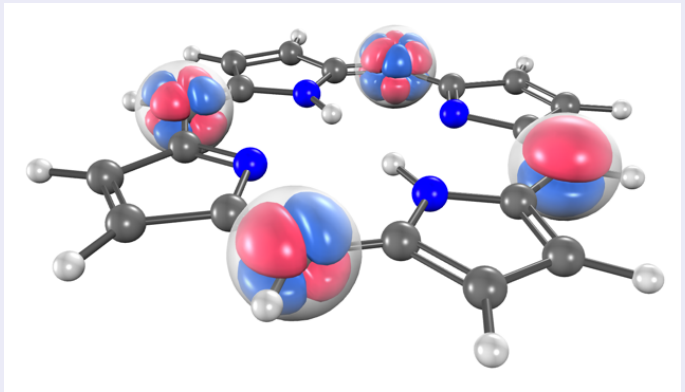


Screening algorithm for three-electron integrals

Screening algorithm



Bounding Gaussians



Section 6

QMC@FCI: QMC as a post-FCI method

QMC without "Gastrow"

Trial wave function for QMC

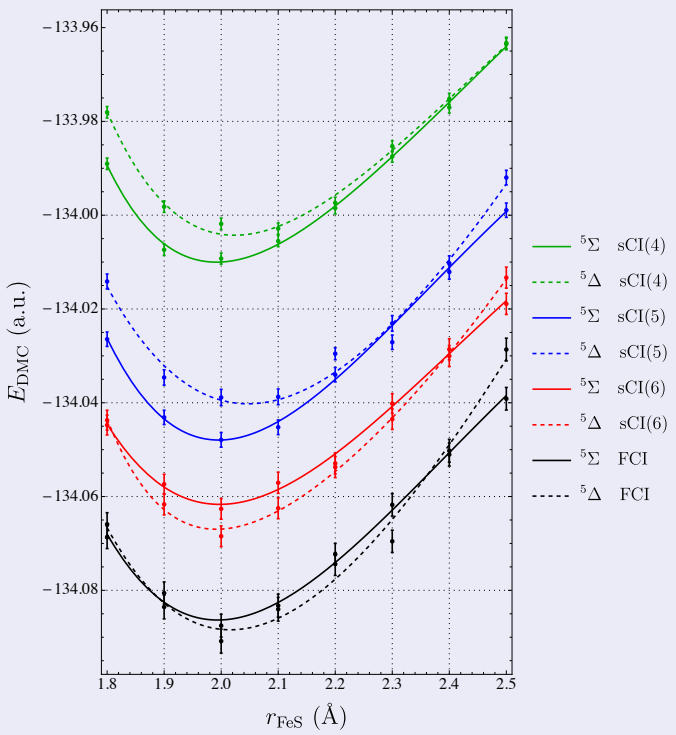
$$\Psi_T(\boldsymbol{R}) = e^{J(\boldsymbol{R})} \sum_I c_I D_I^{\uparrow}(\boldsymbol{R}^{\uparrow}) D_I^{\downarrow}(\boldsymbol{R}^{\downarrow})$$

- The multideterminant part is obtained via the (selected FCI) CIPSI algorithm
  Giner et al. CJC 91 (2013) 879
  Giner et al. JCP 142 (2015) 044115
  Caffarel et al. JCP 144 (2016) 151103

- We may or may not use a "minimal" (nodeless) Jastrow $J(\boldsymbol{R})$

QMC@FCI without Jastrow: dissociation of FeS

Dissociation profile



Method	ϵ	N_{det}	$N_{\mathrm{det}}^{\uparrow}$	$N_{\mathrm{det}}^{\downarrow}$	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(∞)
FCI	—	$\sim 10^{27}$	$\sim 10^{16}$	$\sim 10^{11}$	FCI

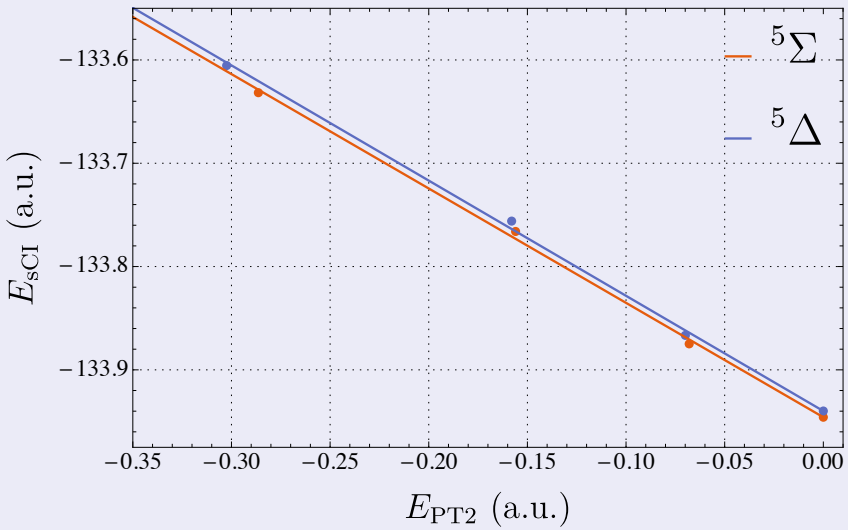
What	Who	D_0 (in eV)
Exp.	Matthew et al.	3.240 ± 0.003
CAS/Jastrow/opt	Hagagi-Mood/Luchow	3.159 ± 0.015
FCI/DMC/extrap	Scemama and co	3.271 ± 0.077

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

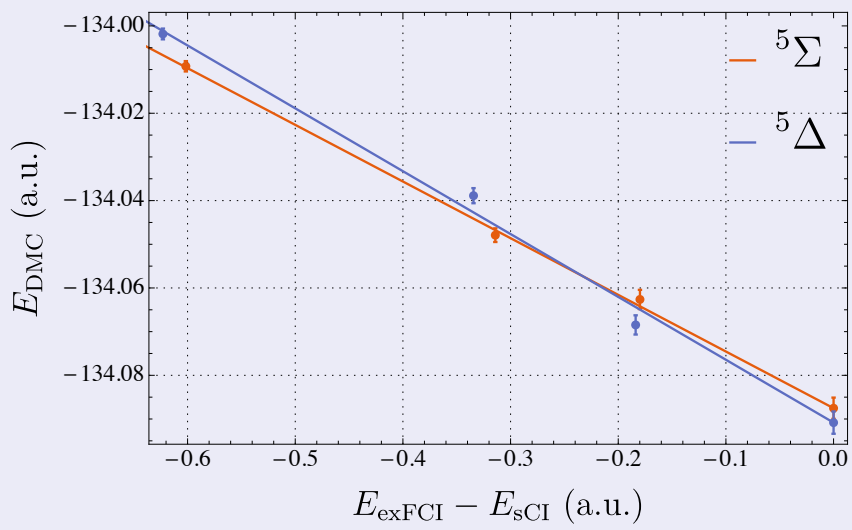
Scemama, Garniron, Caffarel & Loos, JCTC (almost in press), arXiv:1712.05034

The protocol: extrapolation to FCI nodes

Extrapolation to FCI **limit**



Extrapolation to FCI **nodes**

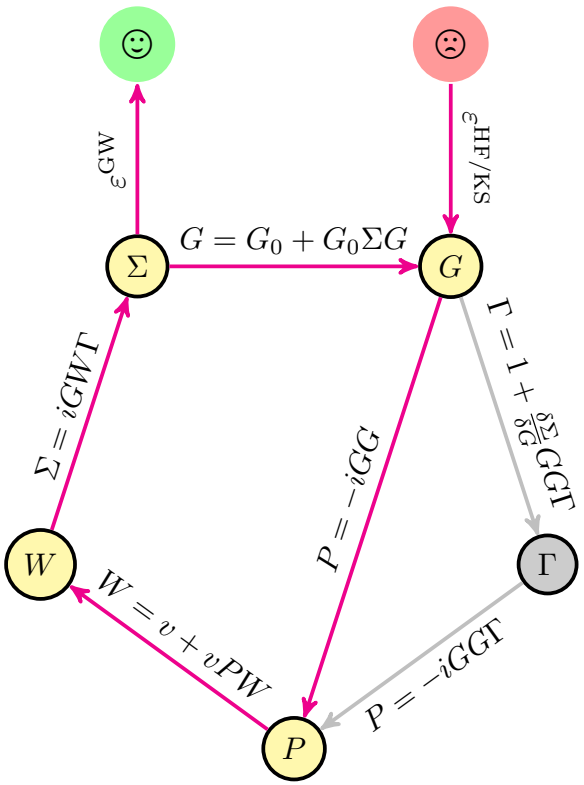


Holmes, Umrigar, Sharma, JCP 147 (2017) 164111
Scemama, Garniron, Caffarel & Loos, JCTC (almost in press), arXiv:1712.05034

Section 7

GW methods

Hedin's pentagon



Flavors of GW

- G0W0 or one-shot GW
- evGW or eigenvalue-only self-consistent GW
- qsGW or quasiparticle self-consistent GW
- scGW or fully self-consistent GW
- BSE($\equiv$ TD-DFT) or Bethe-Salpeter equation

Hedin, Phys Rev 139 (1965) A796

Hedin's pentagon

Questions we are trying to answer...

- Which method is the most suitable in the strongly-correlated regime?
- What is the effect of self-consistency (qs, ev, full, etc)?
- How GF methods compare to GW methods?
- Can we calculate vertex corrections cleanly?
- How good are GW nodes?

Berger & Loos, (in preparation).

Acknowledgements

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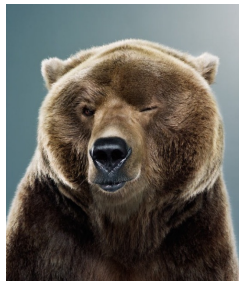
- **Toulouse crew**

Anthony Scemama



Yann Garniron

Michel Caffarel

Arjan Berger

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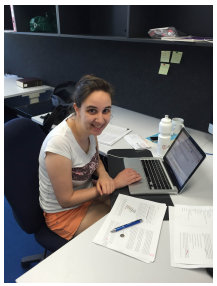
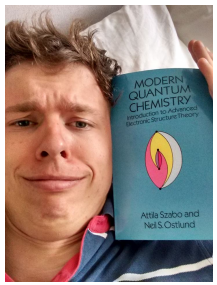
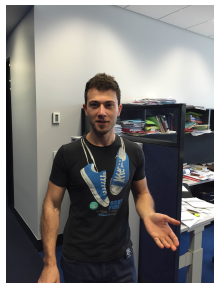


Anneke Knol



Fergus Rogers



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