QMC with large CI trial wave functions

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Wave function methods

Full-CI

Chlorine atom in cc-pVDZ

- 9 $\uparrow$ and 8 $\downarrow$ electrons in 19 MOs
- Full-CI: 92378 $\uparrow$ determinants and 75582 $\downarrow$ determinants
- 6.98 10^9 possible Slater determinants
- The size of the Full-CI space is huge, but the space is empty : $\sim 10^6$ coefficients $|c_k| > 10^{-12}$

$\Longrightarrow$ Selected CI algorithm to select iteratively the most important Slater determinants

Brief history of Selected CI

1969 Bender / Davidson *et al* : one-shot selection with perturbative criterion

1969 Whitten / Ackmeyer : Independently proposed the same criterion, but with iterative selection

1973 Malrieu *et al* : Add a PT2 calculation to the selected determinants (CIPSI)

Groups using/developing CIPSI independently since then

- Angeli, Cimiraglia, Persico : Italy
- Barone : Italy
- Illas, Rubio, Ricart : Spain
- Malrieu, Daudey, Spiegelman : France

Brief history of Selected CI

Iterative selected CI has been re-invented many times.

CIPSI

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- CIPSI
- MRDCI (< 1980)

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(Evangelista,2014)

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All differ by the selection criterion and the implementation.

but they refer to the *same natural idea*

Selected CI algorithm

1. Define a *reference* wave function:

$$|\Psi\rangle = \sum_{i \in \mathcal{D}} c_i |i\rangle \qquad\qquad E_{\mathrm{var}} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

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2. Generate external determinants α:

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

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

$$\Delta E_\alpha = \frac{\langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle}{E_{\mathrm{var}} - \langle \alpha | \hat{H} | \alpha \rangle}$$

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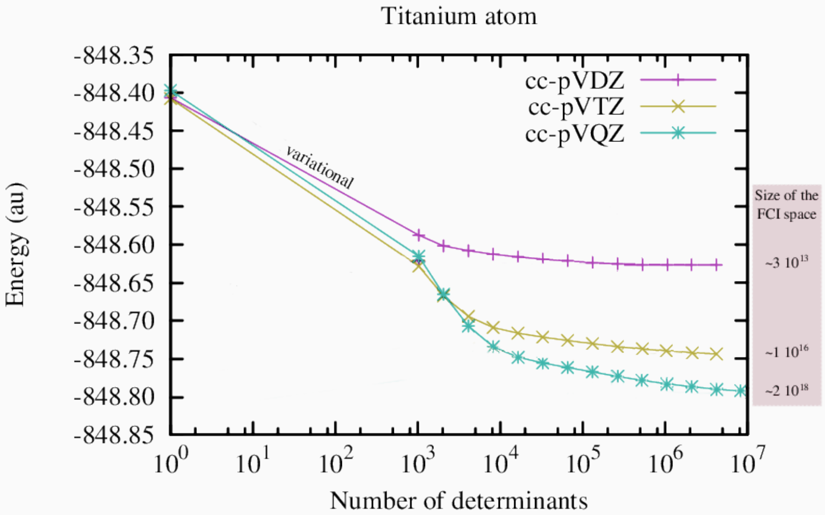
6. Iterate

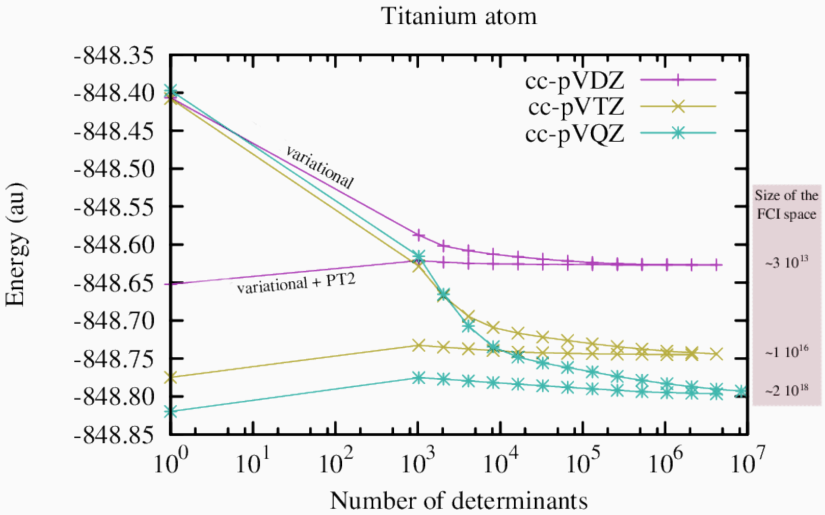
Illustration



Remarks

- When all $|\alpha\rangle$'s are selected the Full-CI is obtained
- CIPSI is more an *algorithm* than a *method*
- CIPSI can be seen as the deterministic counterpart of FCIQMC
- Any WF method can be realized with the CIPSI algorithm
- Rules on the generation of $|\alpha\rangle$'s define the wave function method (CISD, CAS, MRCI, ...)
- Rules on the selection of $|\alpha\rangle$'s define the person you need to cite for the trademark
- With the CIPSI selection, at any time $E_{\mathrm{PT2}} = \sum_\alpha \Delta E_\alpha$ estimates the distance to the solution

Illustration



Making CIPSI efficient

1. Initiator-like approximation : Generate only α determinants from the most important determinants (typically 99% of the norm) (Evangelisti, Chem. Phys., 1983). Typically $\sim$ 2 000 generators for 10^7 determinants
2. Each α determinant is connected to only a subset of determinants of the wave function $\Longrightarrow \Delta E_\alpha$ is done in *constant time* (Cimiraglia, JCP, 1985)
3. Evaluation of $H_{\alpha\alpha}$ needs 10 flops in the worst case : doesn't scale with the number of electrons (Cimiraglia, JCP, 1985)

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Our contributions:

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Our contributions:

1. Efficient implementation of Slater Condon's rules (ArXiv 2013)
2. Knowing that H_{ij} is zero can be done in 5.3 CPU cycles, $\sim 50\times$ faster than a random memory access
3. Sorting : $\mathcal{O}(N\log(N))$ for mathematicians but $\mathcal{O}(N)$ for computer scientists (radix sort algorithm)

Making CIPSI efficient

- Selection and PT2 scale *linearly* with the number of variational determinants
- Efficient hybrid stochastic PT2[1]which converges to the exact (zero error) value in *finite* time. Error convergence rate is $\mathcal{O}(1/t^{3.5})$.
- Selection is embarrassingly parallel (client/server task parallelism)
- Practical bottleneck is today the Davidson diagonalization (work in progress)

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[1] Hybrid stochastic-deterministic calculation of the MRPT2
Y. Garniron, A. Scemama, P.-F. Loos, M. Caffarel, *J. Chem. Phys.*, **147**, 034101, (2017).

What we can do today

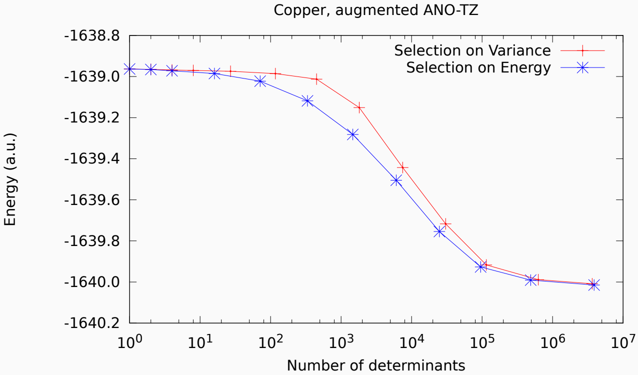
Big picture: we can address the same problems as other seleted CI methods, including FCI-QMC.

These are *not* heroic runs but large runs:

- Cr_2 cc-pVQZ, 20 million dets + PT2, (JCP 2017)
- Butadiene, 60 million dets+PT2 (work in progress)
- FeO_4, def2-TZVPP, 50 million dets +PT2 (work in progress)
- $Cu_2O_2^{2+}$, 6-31G benchmark (work in progress)
- We could not do more than 60 million because of a stupid 32-bit integer limit in a library call (will be fixed soon)

CIPSI *vs* HCI

Energy : $\sum_{\alpha \notin \mathcal{D}} \frac{\langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle}{E_{\text{var}} - \langle \alpha | \hat{H} | \alpha \rangle}$ Variance : $\sum_{\alpha \notin \mathcal{D}} \langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle$



Difference:

CIPSI : Energy minimization HCI : Variance minimization

QMC

Jastrow factors?

- Full-CI : post-Hartree-Fock method

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[2] To see what these WFs give with a Jastrow, see Anouar Benali's talk on Friday.

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- DMC : post-Full-CI method

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What else?

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What else?

So in this talk, I have used my favorite Jastrow factor[2]:

$$J = 1$$

---

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Efficient scheme for CI wave functions in QMC

Ψ can be expressed in a bi-linear form[3]:

$$\Psi(\mathbf{R}) = \sum_{k}^{N_{\text{det}}} c_k \mathcal{D}_k = \sum_{i}^{N_{\mathrm{det}\uparrow}} \sum_{j}^{N_{\mathrm{det}\downarrow}} C_{ij} D_{i\uparrow}(\mathbf{R}_\uparrow) D_{j\downarrow}(\mathbf{R}_\downarrow) \qquad (1)$$

- $\mathbf{D}_\uparrow(\mathbf{R}_\uparrow)$: vector of $N_{\mathrm{det}\uparrow}$ elements
- $\mathbf{D}_\downarrow(\mathbf{R}_\downarrow)$: vector of $N_{\mathrm{det}\downarrow}$ elements
- $\mathbf{C}$: $N_{\mathrm{det}\uparrow} \times N_{\mathrm{det}\downarrow}$ matrix. The matrix contains N_{det} elements.

C is constant in a QMC run $\Longrightarrow$ preprocessing.

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[3] QMC with very large multideterminant wavefunctions
J. Comput. Chem., **37:20**, 1866–1875, (2016).

Efficient scheme for CI wave functions in QMC

At every MC step, we need to evaluate: (↑ electrons and ↓ electrons)

$$
\begin{aligned}
\Psi &= (\mathbf{D}_{\uparrow}{}^{\dagger}(\mathbf{C})\mathbf{D}_{\downarrow}) && (2)\\
\nabla_i \Psi &= \nabla_i \mathbf{D}_{\uparrow}{}^{\dagger}.(\mathbf{C}\mathbf{D}_{\downarrow}) \text{ or } (\mathbf{D}_{\uparrow}{}^{\dagger}\mathbf{C}).\nabla_i \mathbf{D}_{\downarrow} && (3)\\
\Delta_i \Psi &= \Delta_i \mathbf{D}_{\uparrow}{}^{\dagger}.(\mathbf{C}\mathbf{D}_{\downarrow}) \text{ or } (\mathbf{D}_{\uparrow}{}^{\dagger}\mathbf{C}).\Delta_i \mathbf{D}_{\downarrow} && (4)\\
V_{\mathrm{pseudo}}^{\mathrm{non-loc}} \Psi &= V_{\mathrm{pseudo}}^{\mathrm{non-loc}} \mathbf{D}_{\uparrow}{}^{\dagger}.(\mathbf{C}\mathbf{D}_{\downarrow}) \text{ or } (\mathbf{D}_{\uparrow}{}^{\dagger}\mathbf{C}).V_{\mathrm{pseudo}}^{\mathrm{non-loc}} \mathbf{D}_{\downarrow} && (5)
\end{aligned}
$$

- Only Ψ requires $\mathcal{O}(N_{\mathrm{det}})$ operations (tiny prefactor)
- Others are $\mathcal{O}(N_{\mathrm{elec}\uparrow} \times N_{\mathrm{det}\uparrow}) \Longrightarrow$ expensive work is $\mathcal{O}(\sqrt{N_{\mathrm{det}}})$

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- **We can now use $\sim$ 2 000 000 determinants in DMC.**

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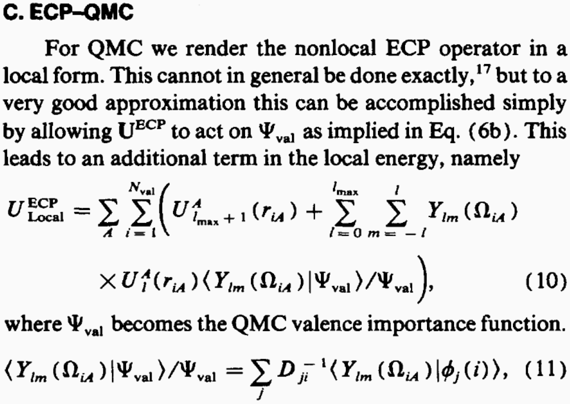
[3] QMC with very large multideterminant wavefunctions *J. Comput. Chem.*, **37:20**, 1866–1875, (2016).

Pseudo-potentials

Back 30 years ago[4]:



C. ECP–QMC

For QMC we render the nonlocal ECP operator in a local form. This cannot in general be done exactly,[17] but to a very good approximation this can be accomplished simply by allowing $\mathbf{U}^{\mathrm{ECP}}$ to act on Ψ_{val} as implied in Eq. (6b). This leads to an additional term in the local energy, namely

$$U^{\mathrm{ECP}}_{\mathrm{Local}} = \sum_{A} \sum_{i=1}^{N_{\mathrm{val}}} \Bigg(U^{A}_{l_{\max}+1}(r_{iA}) + \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} Y_{lm}(\Omega_{iA}) \times U^{A}_{l}(r_{iA}) \langle Y_{lm}(\Omega_{iA}) | \Psi_{\mathrm{val}} \rangle / \Psi_{\mathrm{val}} \Bigg), \qquad (10)$$

where Ψ_{val} becomes the QMC valence importance function.

$$\langle Y_{lm}(\Omega_{iA}) | \Psi_{\mathrm{val}} \rangle / \Psi_{\mathrm{val}} = \sum_{j} D^{-1}_{ji} \langle Y_{lm}(\Omega_{iA}) | \phi_j(i) \rangle, \qquad (11)$$

---

[4] Valence quantum Monte Carlo with abinitio effective core potentials
B. Hammond, *et al*, *J. Chem. Phys.*, **87:2**, 1130–1136, (1987).

Pseudo-potentials

- $\langle Y_{lm}(\Omega_{iA}) | \Phi_j(i) \rangle$ can be computed analytically
- For efficiency: pre-computed on a grid
- No more quadrature points to compute
- No more need for "T-moves or not T-moves"
- Cost : Same as Laplacian ($\sim 15 - 20\%$ of a MC step)
- Of course, also applicable to single-determinant for DFT trial wave functions

Some results

1. FCI/DMC — H_2O

All-electron quasi-Full-CI trial wave functions:

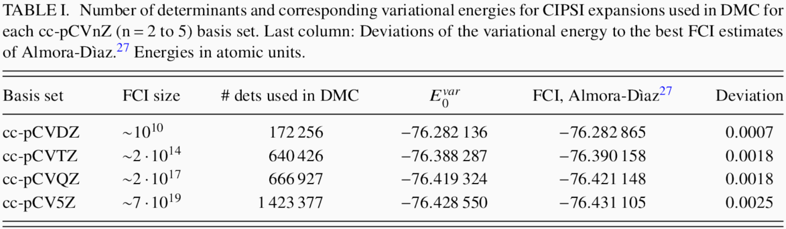
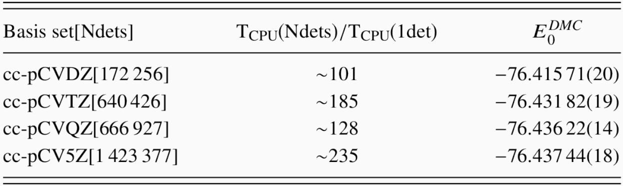


TABLE I. Number of determinants and corresponding variational energies for CIPSI expansions used in DMC for each cc-pCVnZ (n = 2 to 5) basis set. Last column: Deviations of the variational energy to the best FCI estimates of Almora-Dìaz.[27] Energies in atomic units.

Basis set	FCI size	# dets used in DMC	E_0^{var}	FCI, Almora-Dìaz[27]	Deviation
cc-pCVDZ	$\sim 10^{10}$	172 256	−76.282 136	−76.282 865	0.0007
cc-pCVTZ	$\sim 2 \cdot 10^{14}$	640 426	−76.388 287	−76.390 158	0.0018
cc-pCVQZ	$\sim 2 \cdot 10^{17}$	666 927	−76.419 324	−76.421 148	0.0018
cc-pCV5Z	$\sim 7 \cdot 10^{19}$	1 423 377	−76.428 550	−76.431 105	0.0025



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)

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[4] Toward an improved control of the FN error in QMC: The case of the water molecule, *J. Chem. Phys.*, **144**, 151103, (2016).

1. FCI/DMC — H_2O

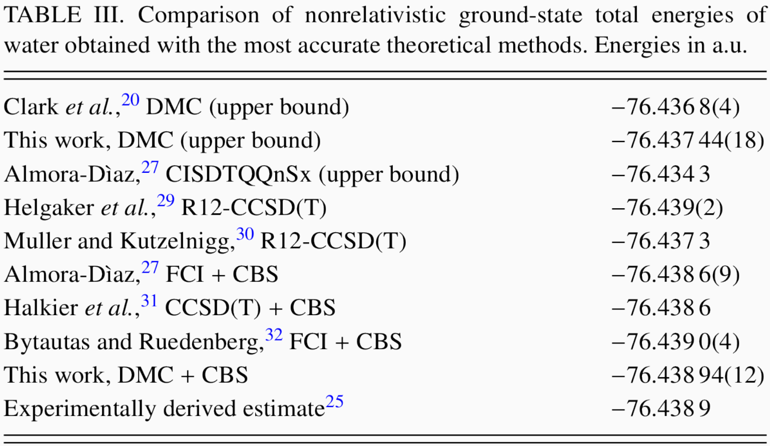

TABLE III. Comparison of nonrelativistic ground-state total energies of water obtained with the most accurate theoretical methods. Energies in a.u.

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

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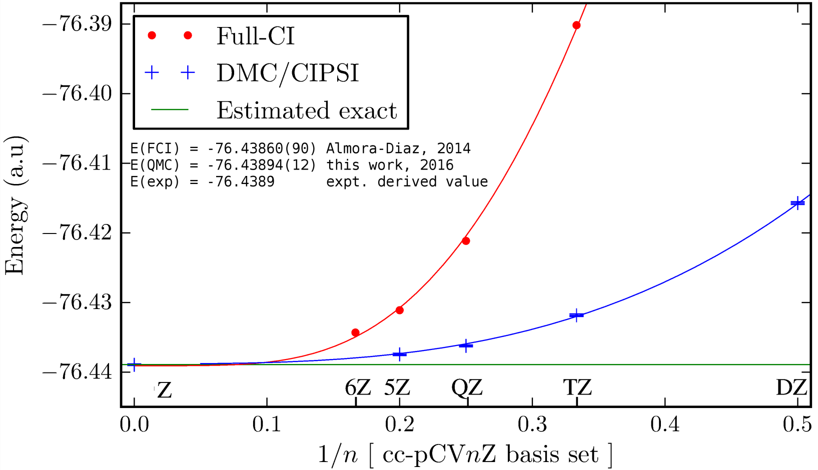

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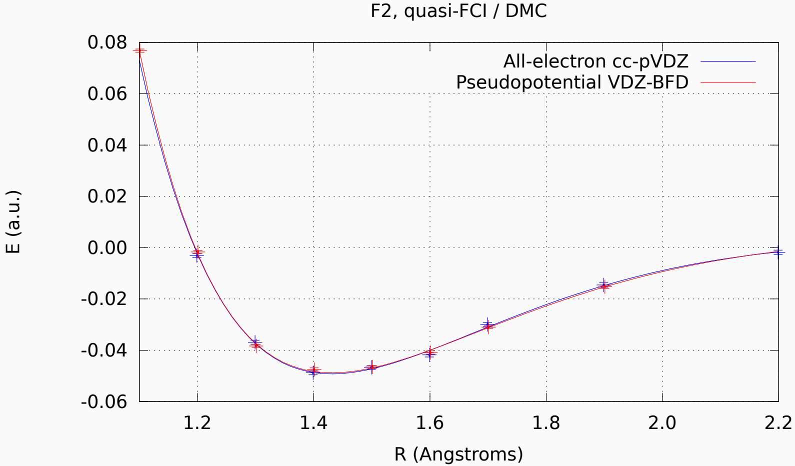
2. Pseudopotentials — C_2

C_2, cc-pVTZ and VTZ-BFD

	Energy			Number of determinants	
	C (a.u.)	C_2 (a.u.)	AE (kcal/mol)	C	C_2
Hartree-Fock					
all-*e*	-37.6867	-75.4015	17.6	1	1
pseudo-	-5.3290	-10.6880	18.8	1	1
CIPSI					
all-*e*	-37.7810	-75.7852	140.1	3796	10^6
pseudo-	-5.4280	-11.0800	140.6	3882	10^6
DMC-HF					
all-*e*	-37.8293(1)	-75.8597(3)	126.3(2)	1	1
pseudo-	-5.4167(1)	-11.0362(3)	127.2(2)	1	1
DMC-CIPSI, $\epsilon = 10^{-6}$					
all-*e*	-37.8431(2)	-75.9166(2)	144.6(2)	3497	173553
pseudo-	-5.4334(1)	-11.0969(3)	144.3(2)	3532	231991
Estimated exact AE			147±2		

2. Pseudopotentials — F_2



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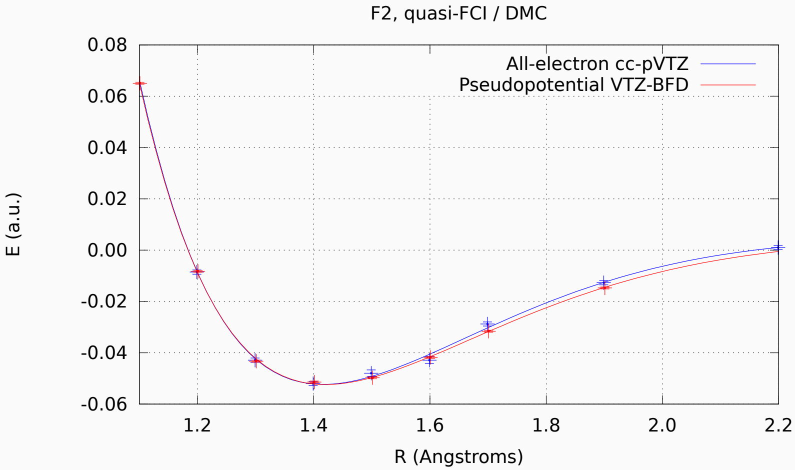

2. Pseudopotentials — Discussion

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This effect is responsible for some of the *Localization Error*.

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If the method used to generate Ψ_T is not size-consistent, the DMC will loose the property of additivity of the energies.

This effect is responsible for some of the *Localization Error*. A scheme for very large systems (low-quality Jastrow + Kohn-Sham determinant)

- Kohn-Sham determinant
- Use a Jastrow to reduce the fluctuations
- Localize the pseudopotentials only on the determinantal component
- The FN-DMC energy will no longer depend on the Jastrow, similarly to all-electron calculations
- Additivity of energies is conserved in H whatever the Jastrow
- No quadrature points to compute

3. Dissociation of FeS

Recent work of Mood and Lüchow[5]:

- Experiment: $^5\Delta$ ground state
- DFT : mostly $^5\Delta$, some $^5\Sigma$, Post-HF : $^5\Sigma$
- Single determinant DMC gives inaccurate results
- Full optimization (Jastrow, CI, MOs) + FN-DMC confirms the $^5\Delta$ ground state
- What do we get with CIPSI?
- What do we get with CIPSI+DMC?

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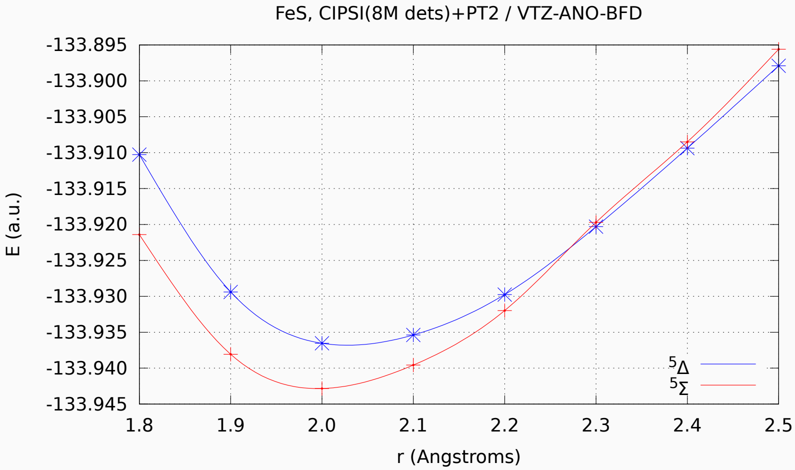
[5] Full WF optimization with QMC and its effect on the dissociation energy of FeS, K. H. Mood, A. Lüchow, *ArXiv*[physics.chem-ph]: 1702.06535v3

3. Dissociation of FeS



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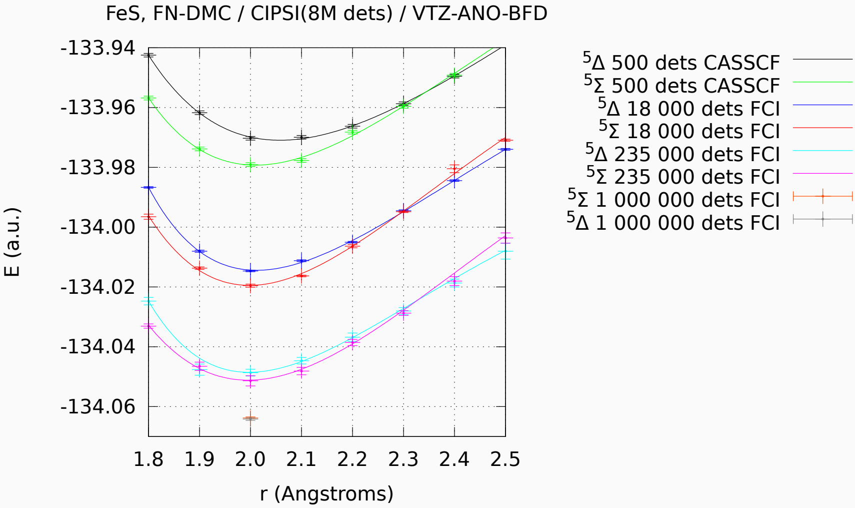

3. Dissociation of FeS

	Mood/Lüchow	This work		Exp.
Energies		$\sim$ 1M dets	Extrapolated to 8M	
$^5\Sigma$	-134.0571(4)	-134.0638(4)	-134.0696(6)	
$^5\Delta$	-134.0579(4)	-134.0642(4)	-134.0714(6)	
Fe	-123.8126(4)	-123.8321(4)		
S	-10.1314(1)	-10.1325(3)		
D_0 (eV)	3.159(15)	2.770(17)	2.965(21)	3.25(15)
Frequencies		18 000	235 000 dets	
$^5\Sigma$	518(7)	558(25)	535(38)	
$^5\Delta$	499(11)	542(37)	544(31)	518(5)
Equilibrium		18 000	235 000 dets	
$^5\Sigma$	2.00(1)	1.9882(3)	1.9933(4)	
$^5\Delta$	2.031(7)	2.0124(2)	1.9909(7)	2.017

Summary

1. quasi-Full-CI wave functions:
    - DMC can be used as a “post-Full-CI” method
    - Black-box : no need to define a CAS
    - Results are reproducible and well defined
    - FCI is orbital-invariant and size-consistent
    - Fixed-node error is systematically improvable (Water)
    - Sensitivity to the basis set: atomization energies are always underestimated because atoms are described better than molecules, but less severly than in FCI

Summary

2. Pseudopotentials:
    - No numerical integration needed
    - No need for T-moves
    - Size-consistent wave functions : localization error behaves well (F_2, FeS)

Perspectives

3. What can we do to reduce the dependence on the basis set?

- CIPSI+Jastrow (E. Giner *et al*). See Anouar's talk on Friday.
- Another old idea : basis functions at the middle of bonds
- CI with range-separated DFT (E. Giner). LDA can play the role of the Jastrow. Preliminary results on F_2 increase the atomization energy by 2 kcal/mol:

R(Å)	CIPSI	LDA/CIPSI
4.0	-199.437(1)	-199.437(1)
1.4	-199.4867(6)	-199.4899(6)

- Combining Selected CI with f_{12} (P. F. Loos) : very promising results
- These schemes are applicable to any post-HF method

Perspectives

4. What can we do for larger systems?

Quasi-Full-CI wave functions are too large. We can apply the selected CI algorithm to:

- CAS+SD: not size-consistent but very good nodes (careful with pseudos)
- MR-CCSD(T)[6]/ MR-(SC)2: PhD. thesis of Y. Garniron
- DD-CI: Excited states, magnetic systems
- B_k method method (Davidson *et al* 1981): Dress the Hamiltonian with the PT2 $\Longrightarrow$ diagonalize in the presence of the $|\alpha\rangle$
- JM-Heff-PT2: Effective Hamiltonian with a size-consistent MR-PT2 scheme (Giner, JCP 2017)
- Any other post-HF method

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[6] Alternative definition of excitation amplitudes in state-specific MRCC, Y. Garniron, E. Giner, J.-P. Malrieu, A. Scemama *J. Chem. Phys.*, **146:15**,

All calculations performed with our codes (open source, GitHub) :

- Quantum Package (Selected CI)
- QMC=Chem

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