

# Recent developments in (real-space) quantum Monte Carlo

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Wave-function methods in quantum chemistry and nuclear physics, 8-12  
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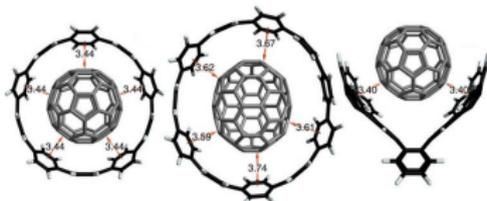
## Real-space quantum Monte Carlo methods

Stochastically solve interacting Schrödinger equation

Why (real-space) quantum Monte Carlo?

- Favorable scaling  $\rightarrow$  Energy is  $O(N^4)$
- Flexibility in choice of functional form of wave function
- Easy parallelization
- Among most accurate calculations for medium-large systems

Routinely, molecules of up to 100 (mainly 1st/2nd-row) atoms



upto C<sub>136</sub>H<sub>44</sub> (Alfé 2017)

## Simplest flavor: Variational Monte Carlo

Quantum observables  $\rightarrow$  expectations values  $\rightarrow$  integrals

Use Monte Carlo to compute expectation values

$$E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \int d\mathbf{R}^{3N} \frac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \frac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R}^{3N} |\Psi(\mathbf{R})|^2}$$

$$\approx \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{R}_i)$$

$\leftarrow$  Sampled by Metropolis



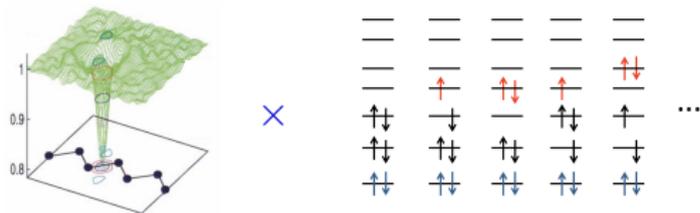
Random walk in  $3N$  dimensions,  $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$

Just a trick to compute integrals in many dimensions

## Key role of many-body wave function

Commonly employed compact Jastrow-Slater wave functions

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \mathcal{J}(\mathbf{r}_1, \dots, \mathbf{r}_N) \times \sum_i c_i D_i(\mathbf{r}_1, \dots, \mathbf{r}_N)$$



$\mathcal{J}$   $\longrightarrow$  Jastrow correlation factor

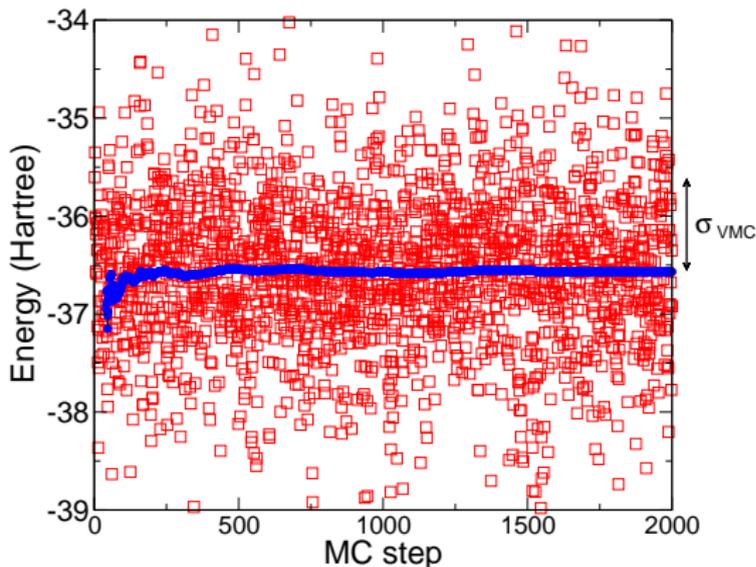
- Explicit dependence on electron-electron distances  $r_{ij}$

$\sum_i c_i D_i$   $\longrightarrow$  Determinants of single-particle orbitals

- **Few** and not millions of determinants

## Typical variational Monte Carlo run

Example: Local energy and average energy of acetone ( $C_3H_6O$ )



$$E = \langle E_L(\mathbf{R}) \rangle = -36.542 \pm 0.001 \text{ Hartree (40} \times \text{20000 steps)}$$

$$\sigma_E^2 = \langle (E_L(\mathbf{R}) - E)^2 \rangle = 0.90 \text{ Hartree}$$

## Beyond variational Monte Carlo

What goes in, comes out! Can we remove wave function bias?

## Projector Monte Carlo method

▷ Construct an operator which inverts spectrum of  $\mathcal{H}$

Diffusion Monte Carlo  $\rightarrow e^{-\tau(\mathcal{H}-E_T)}$

▷ Apply operator to initial  $\Psi$

$$\Psi_0 = \lim_{\tau \rightarrow \infty} e^{-\tau(\mathcal{H}-E_T)}\Psi$$

if we choose  $E_T \approx E_0$

## How do we perform the projection stochastically?

$$\Psi_0 = \lim_{\tau \rightarrow \infty} e^{-\tau(\mathcal{H} - E_T)} \Psi$$

Rewrite projection equation in integral form

$$\Psi(\mathbf{R}', t + \tau) = \int d\mathbf{R} \langle \mathbf{R}' | e^{-\tau(\mathcal{H} - E_T)} | \mathbf{R} \rangle \Psi(\mathbf{R}, t)$$

Perform this integral by Monte Carlo integration

- ▷ Represent  $\Psi(\mathbf{R}, t)$  as an ensemble of walkers
- ▷ Generate random walk by iterating integral equation

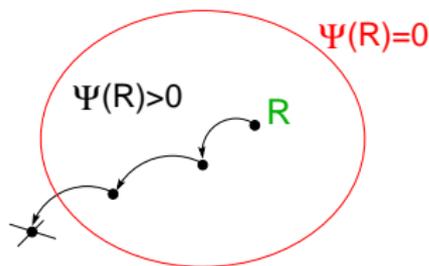


Note: Projection with other basis, e.g. determinants  $\rightarrow$  FCIQMC

## Diffusion Monte Carlo and the fermionic sign problem

$\Psi$  is positive/negative  $\Rightarrow \Psi$  is not a probability distribution

$\rightarrow$  Fixed-node approximation



Find best solution with same nodes as trial wave function  $\Psi$

Is fixed-node diffusion Monte Carlo variational?

- For the ground state and each lowest state in its symmetry class
- What about “real” excited states?

In general, exact excited state for exact nodal structure

Have we solved all our problems?

Results depend on the nodes of the trial wave function  $\Psi$

Diffusion Monte Carlo as a black-box approach?

$\epsilon_{\text{MAD}}$  for atomization energy of the G2 set

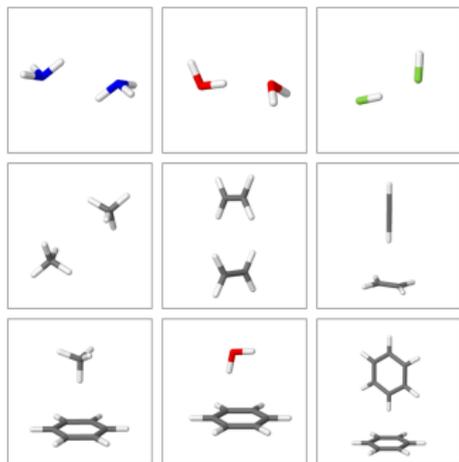
	DMC			CCSD(T)/aug-cc-pVQZ
	HF orb	Optimized orb	CAS	
$\epsilon_{\text{MAD}}$	3.1	2.1	1.2	2.8 kcal/mol

Petruzielo, Toulouse, Umrigar, J. Chem. Phys. **136**, 124116 (2012)

With “some” effort on  $\Psi$ , we can do rather well

## Diffusion Monte Carlo as a black-box approach?

Non-covalent interaction energies for 9 compounds from S22 set  
DMC with B3LYP/aug-cc-pVTZ orbitals versus CCSD(T)/CBS



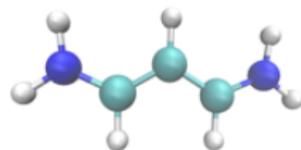
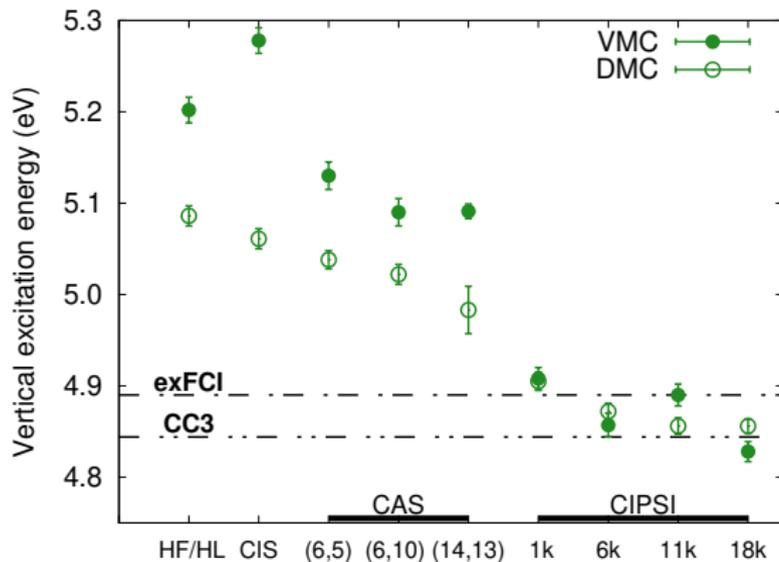
$$\Delta_{\text{MAD}} = 0.058 \text{ kcal/mol}$$

Dubecky *et al.*, JCTC **9**, 4287 (2013)

With “practically no” effort on  $\Psi$ , we can do rather well

## Diffusion Monte Carlo as a black-box approach?

Not really! Excitation energy and wave function dependence:



Cuzzocrea, Scemama, Briels, Moroni, Filippi, JCTC **16**, 4203 (2020)

DMC is not a panacea but effort on  $\Psi$  pays off!

## Optimization in QMC

In QMC literature, a lot of total (ground state) energy calculations  
... with “borrowed” geometries and/or wave functions

Why? What about energy derivatives?

Cost of forces is much larger than cost of  $E$ :  $O(N^4) \rightarrow O(N^5)$

## Recent developments

Formalism to compute many derivatives as efficiently as the energy  
... also for multi-determinantal expansions

→ Optimize the energy of ground and excited states!

What do we need to perform an energy optimization?

(1)

Interatomic forces  $\rightarrow$  derivatives wrt nuclear coordinates

We employ low-variance estimators of forces

$$F = -\partial_{\alpha} E = -\langle \partial_{\alpha} E_L + 2(E_L - E) \frac{\partial_{\alpha} \Psi}{\Psi} \rangle$$

$$\Rightarrow F = \langle \partial_{\alpha} \mathcal{H} + \underbrace{\frac{(\mathcal{H} - E_L) \partial_{\alpha} \Psi}{\Psi}}_{\text{zero expectation value}} + 2 \overbrace{(E_L - E) \frac{\partial_{\alpha} \Psi}{\Psi}}^{\text{"Pulay" term}} \rangle$$

Why using such an expression?

Lower fluctuations  $\rightarrow 0$  as  $\Psi \rightarrow \Psi_0$

## What do we need to perform an energy optimization?

(2)

Low-variance estimator of interatomic forces

$$F = -\nabla_{\alpha} E = -\left\langle \nabla_{\alpha} E_L + \underbrace{2(E_L - E) \frac{\nabla_{\alpha} \Psi}{\Psi}}_{\text{"Pulay" term}} \right\rangle$$

We need the following quantities:

–  $\Psi$  in the sampling process

$$– E \rightarrow E_L = \frac{1}{2} \frac{\Delta \Psi}{\Psi} + \frac{V \Psi}{\Psi}$$

$$– \frac{\partial E}{\partial \alpha} \rightarrow \frac{\partial \Psi}{\partial \alpha} \text{ and } \frac{\partial E_L}{\partial \alpha} \rightarrow \text{Computationally costly!}$$

Wave function optimization  $\rightarrow \frac{\partial \Psi}{\partial p}$  and  $\frac{\partial E_L}{\partial p}$  might be needed

## Efficient computation of derivatives of $E$

Simple formalism for the efficient computation of  $\Psi$ ,  $E_L$ ,  $\partial\Psi$ ,  $\partial E_L$   
for general multi-determinant Jastrow-Slater wave functions

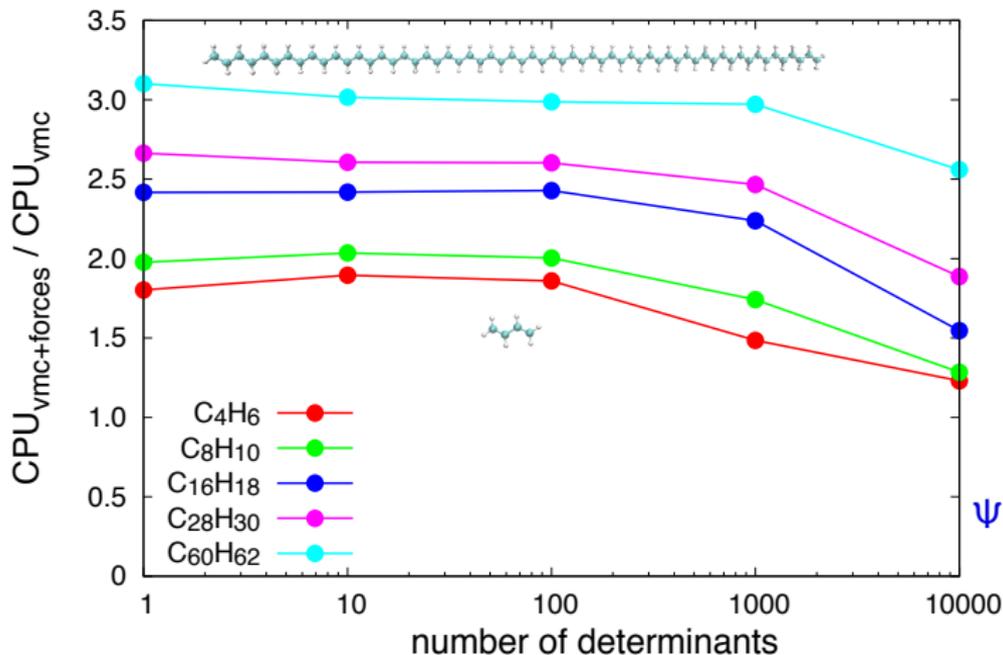
→ Cost of derivatives is the same cost as computing  $E$

C. Filippi, R. Assaraf and S. Moroni, JCP (2016)

R. Assaraf, S. Moroni, and C. Filippi, JCTC (2017)

# Interatomic forces for multi-determinant wave functions

Example: Polyenes  $C_nH_{n+2} \rightarrow$  from  $C_4H_6$  to  $C_{60}H_{62}$



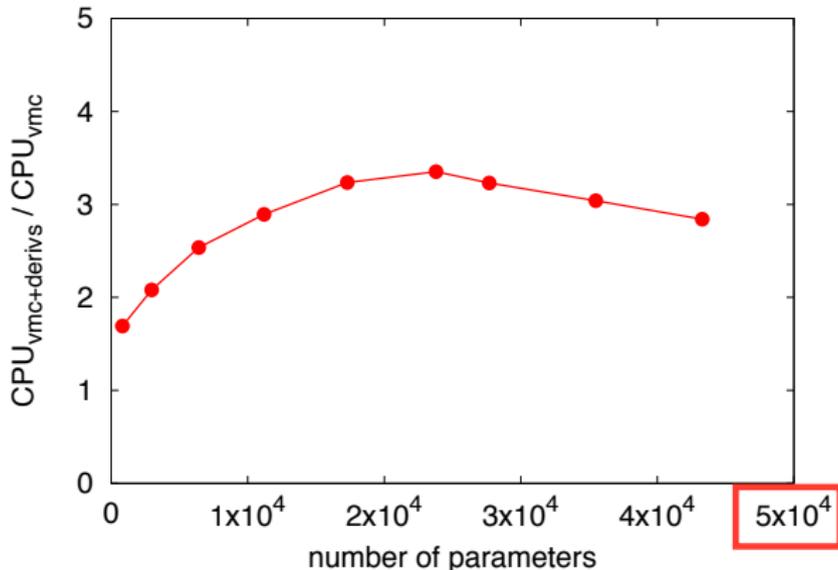
$$\Psi = \mathcal{J} \left[ \sum c_i D_i \right]$$

Cost of forces is less than 4 times the cost of the energy

## Wave function optimization

Example: Polyenes  $C_nH_{n+2} \rightarrow$  from  $C_4H_6$  to  $C_{60}H_{62}$

Derivatives with respect to parameters in  $\Psi = \mathcal{J} D$



$O(N^2)$  derivatives of  $\Psi$  and  $E_L$  cost less than 4 times cost of  $E_L$

## Origin of magic?

(1)

Recall: We want efficient computation of  $\Psi$ ,  $E_L$ ,  $\partial\Psi$ ,  $\partial E_L$

Consider simple one-determinant wave functions

$$\Psi = \mathcal{J} \det(A) \quad \text{where} \quad A_{ij} = \phi_j(\mathbf{r}_i)$$

For the derivatives, use that

$$\frac{\partial_\mu \det(A)}{\det(A)} = \text{tr}(A^{-1} \partial_\mu A)$$

Rewrite one-body operators acting on  $\Psi$  in a similar manner!

For instance, the local energy  $\rightarrow$  
$$E_L = \frac{H\Psi}{\Psi} = \text{tr}(A^{-1}B)$$

where  $B$  depends on orbitals, Jastrow, and their derivatives

## Simple rewriting of one-body operators

Consider a one-body operator  $\hat{O} = O(\mathbf{r}_1) + \dots O(\mathbf{r}_N)$

and  $\Psi = \det(A)$  with  $A_{ij} = \phi_j(\mathbf{r}_i)$

$$\begin{aligned}\hat{O} \det(A) &= \sum_i O(\mathbf{r}_i) \det(A) \\ &= \sum_i \sum_j (O\phi_j)(\mathbf{r}_i) (A^{-1})_{ji} \det(A) \\ &= \sum_i \sum_j B_{ij} (A^{-1})_{ji} \det(A) \\ &= \text{tr}(A^{-1}B) \det(A)\end{aligned}$$

$$\frac{\hat{O}\Psi}{\Psi} = \text{tr}(A^{-1}B) \quad \text{with} \quad B_{ij} = (O\phi_j)(\mathbf{r}_i)$$

## Simple example: the local kinetic energy

$$\hat{T} = -\frac{1}{2} \sum_i \Delta_i \Rightarrow O(\mathbf{r}_i) = -\frac{1}{2} \Delta_i = -\frac{1}{2} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$$

Let us compute the local kinetic energy of  $\Psi = \det(A)$

$$\frac{\hat{T} \det(A)}{\det(A)} = \text{tr}(A^{-1} B^{\text{kin}})$$

where

$$B_{ij}^{\text{kin}} = -\frac{1}{2} \Delta_i A_{ij} = -\frac{1}{2} \Delta \phi_j(\mathbf{r}_i)$$

## Origin of the magic?

(2)

Given  $\Psi = \mathcal{J} \det(A)$  where  $A_{ij} = \phi_j(\mathbf{r}_i)$

$$E_L = \frac{\mathcal{H}\Psi}{\Psi} = \text{tr}(A^{-1}B)$$

Advantage in computing the derivatives?

$$\partial_\mu E_L = \text{tr}(A^{-1}\partial_\mu B - X\partial_\mu A)$$

- Compute and store  $X = A^{-1}BA^{-1}$
- Compute each derivatives at a cost  $O(N^2)$
- Forces will cost  $O(N^3)$  like the energy!

## What about multi-determinant wave functions?

Simple formulas to compute all derivatives of  $E$

---

$$\Psi \quad \mathcal{J} \det(A) \quad \rightarrow \quad \mathcal{J} \sum_I^{N_e} c_I \det(A_I)$$

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Simple formulas to compute all derivatives of  $E$

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$$\Psi \quad \mathcal{J} \det(A) \quad \rightarrow \quad \mathcal{J} \sum_I^{N_e} c_I \det(A_I)$$

$$\text{Matrix} \quad A \quad \rightarrow \quad \tilde{A} \quad (\text{extension to virtual orbitals})$$

$$B \quad \rightarrow \quad \tilde{B}$$

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$$B \quad \rightarrow \quad \tilde{B}$$

$$E_L \quad \text{tr}(A^{-1}B) \quad \rightarrow \quad \text{tr}(\Gamma \tilde{B})$$

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Simple formulas to compute all derivatives of  $E$

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$$B \quad \rightarrow \quad \tilde{B}$$

$$E_L \quad \text{tr}(A^{-1}B) \quad \rightarrow \quad \text{tr}(\Gamma \tilde{B})$$

---

Similar expression for derivatives as in single-determinant case

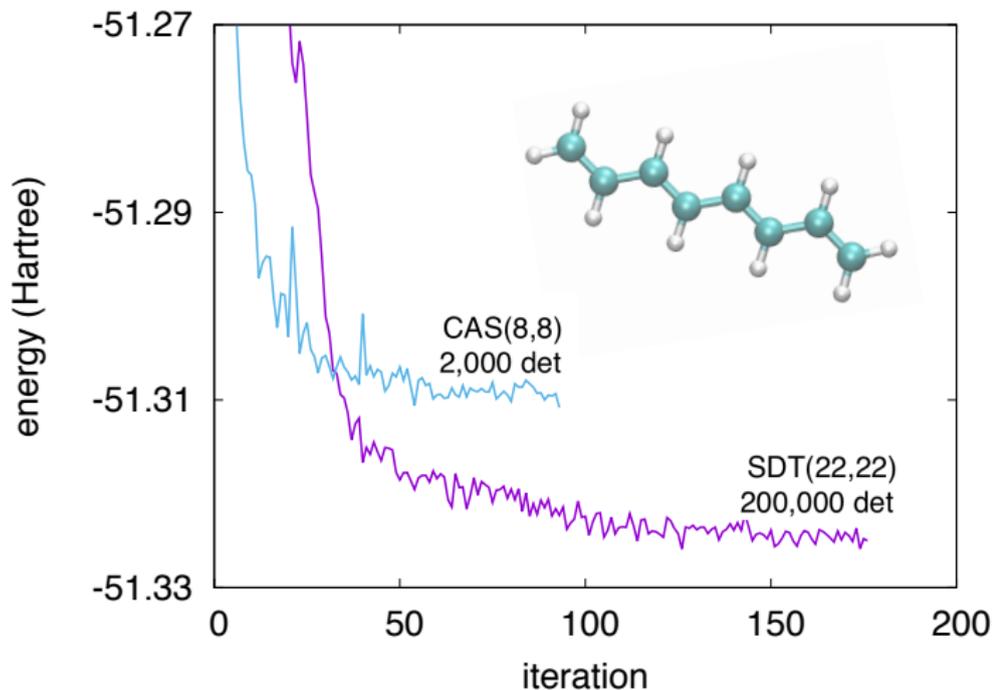
$$\partial_\mu E_L = \text{tr}(\Gamma \partial_\mu \tilde{B} - \Omega \partial_\mu \tilde{A})$$

Compute  $\Gamma$  and  $\Omega$ , evaluate all derivatives at cost  $O(N^3) + O(N_e)$

## Full optimization of octatetraene

$C_8H_{10}$  with a SDT(22,22)  $\rightarrow$  200 000 determinants

Optimize geometry and all 65 000 parameters in wave function



## Wave function optimization: stochastic reconfiguration

Efficient computation of  $\partial_\mu \Psi$  and  $\partial_\mu E_L$

but we are typically optimizing many parameters, 50k-100k

→ Energy minimization with which approach?

We have been using the SR method to optimize parameters,  $\mathbf{p}$

$$\Delta \mathbf{p} = -\tau \bar{\mathbf{S}}^{-1} \mathbf{g}$$

where the “poor-man” Hessian is

$$\bar{S}_{ij} = \left\langle \frac{\Psi_i}{\Psi} \frac{\Psi_j}{\Psi} \right\rangle - \left\langle \frac{\Psi_i}{\Psi} \right\rangle \left\langle \frac{\Psi_j}{\Psi} \right\rangle$$

with  $\Psi_i = \partial_{p_i} \Psi$

## Stochastic reconfiguration

We use low-memory implementation of the SR method

$$\Delta \mathbf{p} = -\tau \bar{\mathbf{S}}^{-1} \mathbf{g}$$

$$\rightarrow S_{ij} = \left\langle \frac{\Psi_i}{\Psi} \frac{\Psi_j}{\Psi} \right\rangle = \frac{1}{M} \sum_{k=1}^{M_{\text{MC}}} \frac{\Psi_i(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)} \frac{\Psi_j(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)}$$

In conjugate-gradient method, we compute  $\bar{\mathbf{S}} \Delta \mathbf{p}$

$$\sum_{j=1}^{N_p} S_{ij} \delta p_j = \frac{1}{M} \sum_{k=1}^{M_{\text{MC}}} \frac{\Psi_i(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)} \sum_{j=1}^{N_p} \frac{\Psi_j(\mathbf{R}_k)}{\Psi(\mathbf{R}_k)} \delta p_j,$$

Store  $\Psi_i/\Psi$  along the run  $\rightarrow$  cost  $\mathcal{O}(N_{\text{CG}} M N_p)$

## Alternative optimization approaches

Linear method (Toulouse, Umrigar, 2007)

$$\Psi(p) \approx \Psi(p^0) + \sum_i \frac{\partial \Psi(p^0)}{\partial p_i} \Delta p_i$$

Solution of generalized eigenvalue problem

$$\mathbf{H} \Delta p = E \mathbf{S} \Delta p$$

in the basis of  $\left\{ \Psi(p^0), \frac{\partial \Psi(p^0)}{\partial p_i} \right\}$

→ Low-memory implementation with Davidson

In principle, faster converging but SR much more robust to noise

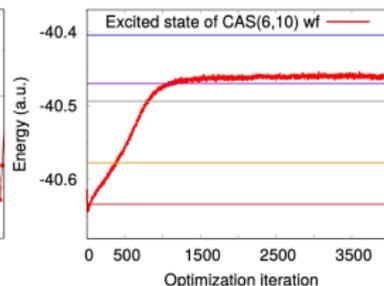
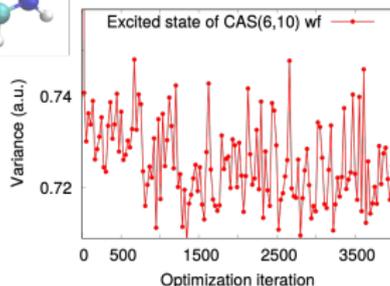
Method of choice is energy minimization !

State-specific variance minimization also for excited states?

$$\sigma_{\omega}^2 = \frac{\langle \Psi | (\hat{\mathcal{H}} - \omega)^2 | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

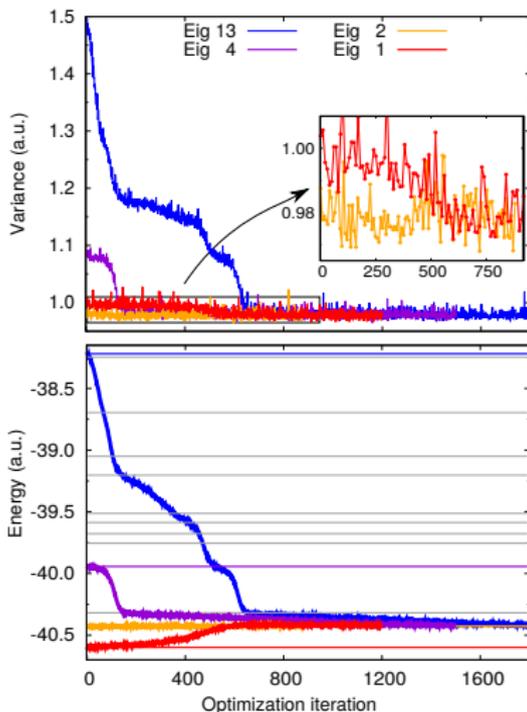
where  $\omega$  is modified to follow average energy

Often, optimization escapes target state, finding little or no barrier



Cuzzocrea, Scemama, Briels, Moroni, Filippi, JCTC (2020)

Toy problem:  $\Psi = \sum_i c_i \mathcal{J} D_i$  with 13 linear parameters/eigenstates



Lowest-variance state is not lowest-energy state

## Treating excited states

For multiple states of same symmetry  $\rightarrow \Psi^K = \sum_I c_I^K \mathcal{J} D_I$

Common parameters in  $\mathcal{J}$  and  $D_I$  but different coefficients  $c_I^K$

Optimize parameters in  $\mathcal{J}$  and  $D_I$  by minimizing state-average  $E_{SA}$

$$E^{SA} = \sum_K w_K \frac{\langle \Psi^K | \mathcal{H} | \Psi^K \rangle}{\langle \Psi^K | \Psi^K \rangle} \quad \text{with} \quad \sum_K w_K = 1$$

and preserve orthogonality through coefficients  $c_I^K$

Ready to explore new territories

Efficient derivatives of  $E$  for many parameters and determinants

+ Toolbox of optimization tools

→ QMC “internally consistent” (geometry and wave function)

→ Explore sensitivity of QMC to choice of Slater expansion

→ Answer some open questions:

Do we really need a multi-determinant expansion in QMC?

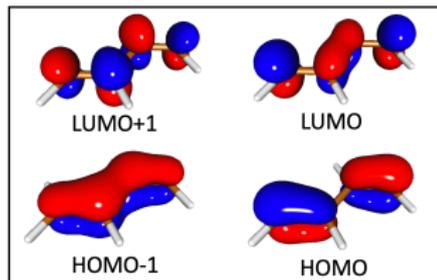
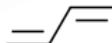
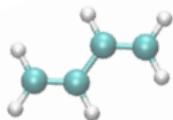
How do we choose the expansion in  $\Psi = \mathcal{J} \sum_I c_I D_I$  ?

What do we gain from a DMC calculation?

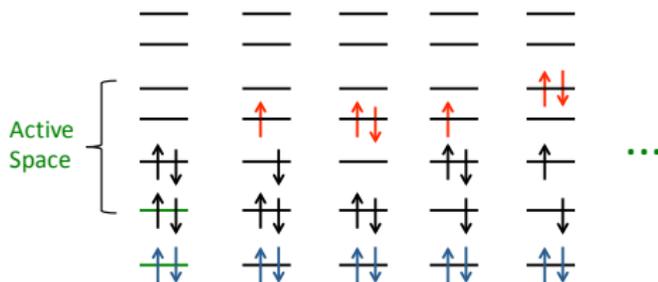
# Determinantal expansion in QMC wave functions

## Example: Polyenes

$$\Psi = \mathcal{J} \left[ \sum_i c_i D_i \right] \rightarrow$$



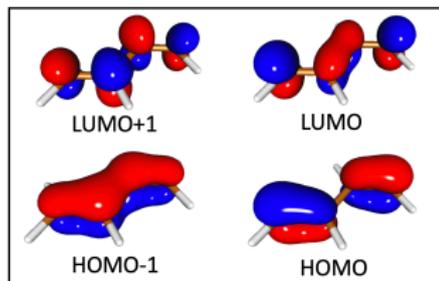
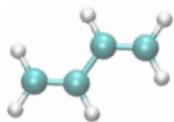
Possible choice: Correlate electrons in active orbitals  $\rightarrow$  CAS(4,4)



# A quickly unmanageable wave function

Example: Polyenes

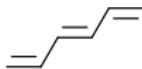
$$\Psi = \mathcal{J} \left[ \sum_i c_i D_i \right] \rightarrow$$



C<sub>4</sub>H<sub>6</sub>

CAS (4,4)

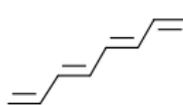
Det. 36



C<sub>6</sub>H<sub>8</sub>

(6,6)

400



C<sub>8</sub>H<sub>10</sub>

(8,8)

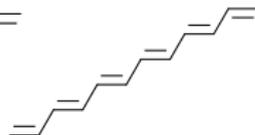
4900



C<sub>10</sub>H<sub>12</sub>

(10,10)

63504



C<sub>12</sub>H<sub>14</sub>

(12,12)

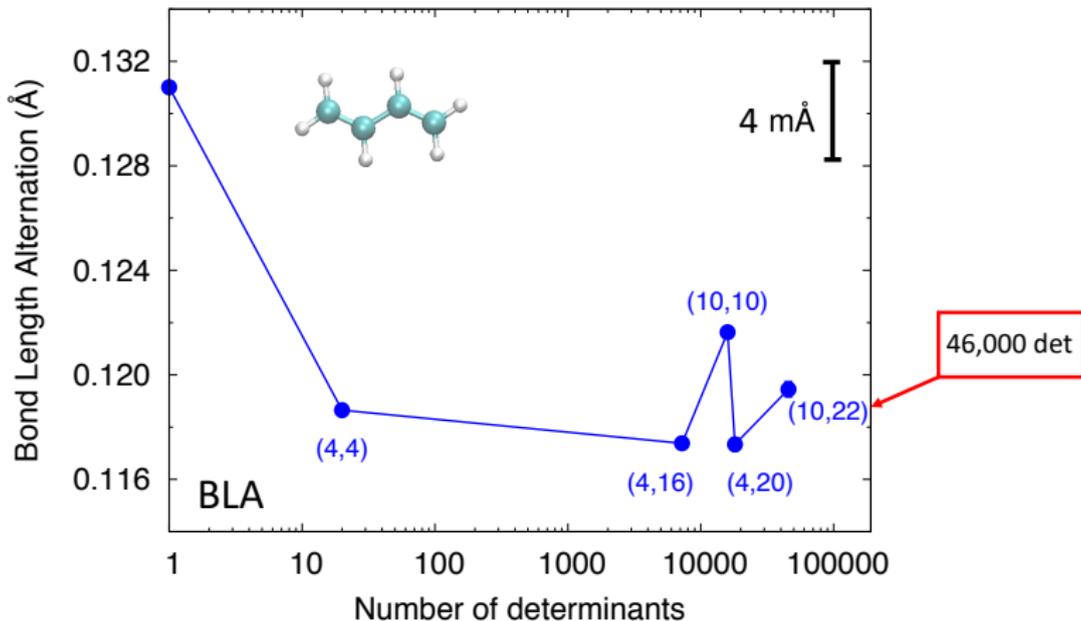
853776

We are only correlating a subset of electrons/orbitals!

... and some sort of truncation of expansion is clearly needed

## Example: Geometry optimization of butadiene

Optimal bond length alternation with  $\Psi = \mathcal{J} \times \text{CAS}$



Surprisingly large number of determinants!

## A better scheme to build the wave function

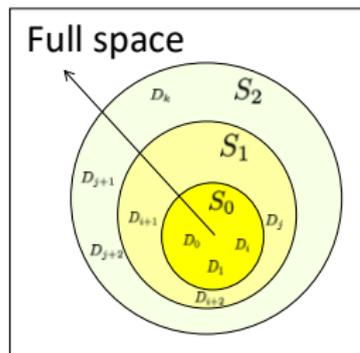
Butadiene: significant variations in QMC geometry/energy with  $\Psi$

Selected CI  $\rightarrow$  Automated approach for wave function generation

$$\Psi_{\text{CIPSI}} = \sum_{D_i \in S} c_i D_i$$

$$S_0 \rightarrow S_1 \cdots \rightarrow S_n$$

$$\delta E_j^{(2)} = \frac{|\langle D_j | \mathcal{H} | \psi_{\text{CIPSI}} \rangle|^2}{E(\text{CI}) - \langle D_j | \mathcal{H} | D_j \rangle}$$



Can this lead to optimal QMC geometries with few determinants?

## A better scheme to build the wave function

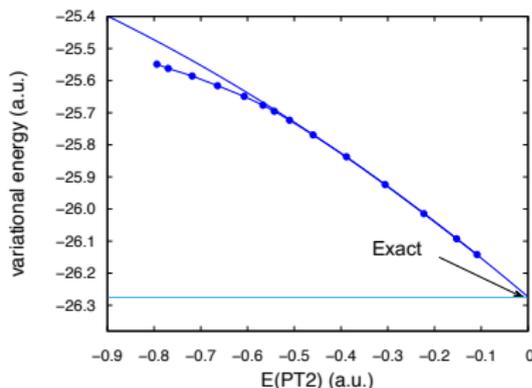
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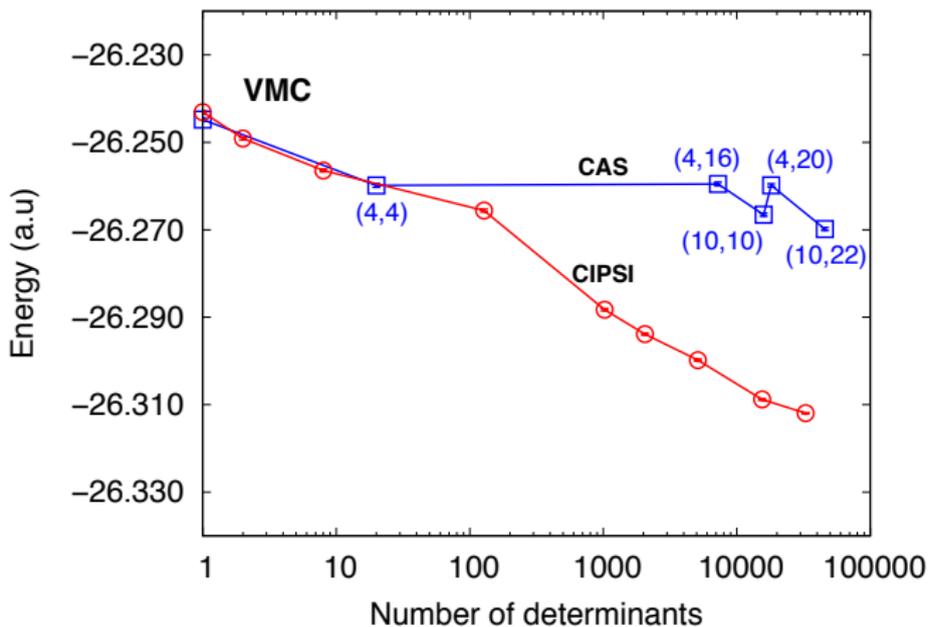


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# Optimal geometries and energies with Jastrow-CIPSI

Revisit geometry optimization of butadiene

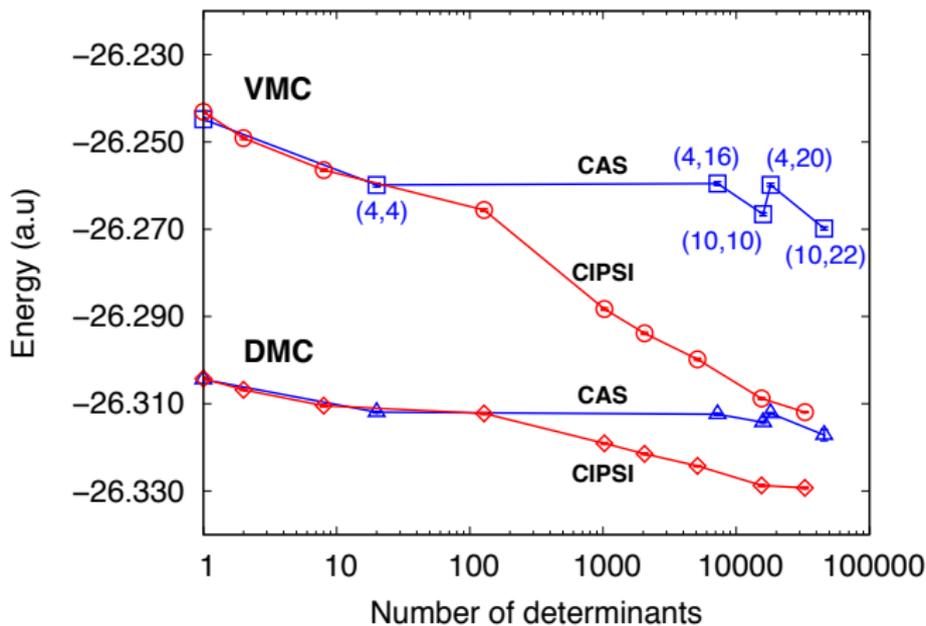
Jastrow-CIPSI: Great energies both in VMC and in DMC!



# Optimal geometries and energies with Jastrow-CIPSI

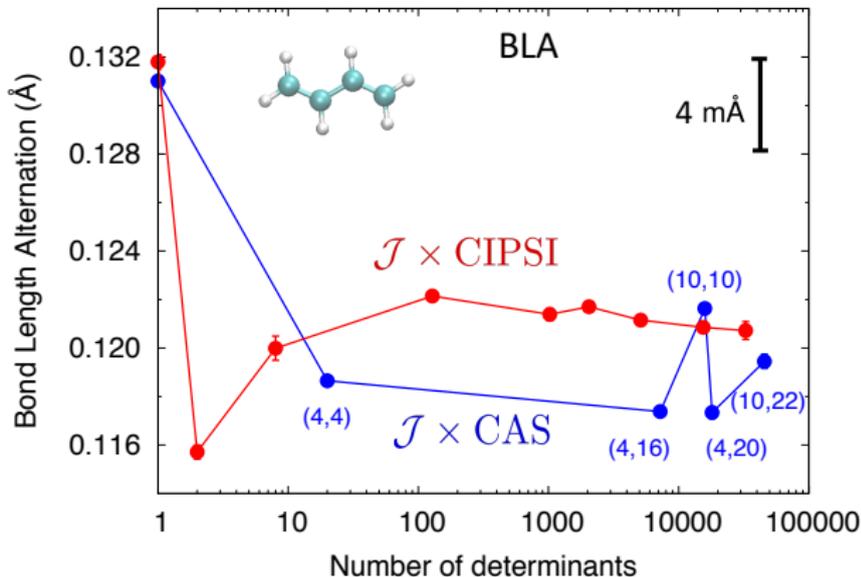
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Jastrow-CIPSI: Great energies both in VMC and in DMC!



## Jastrow-CIPSI: QMC geometries with few determinants

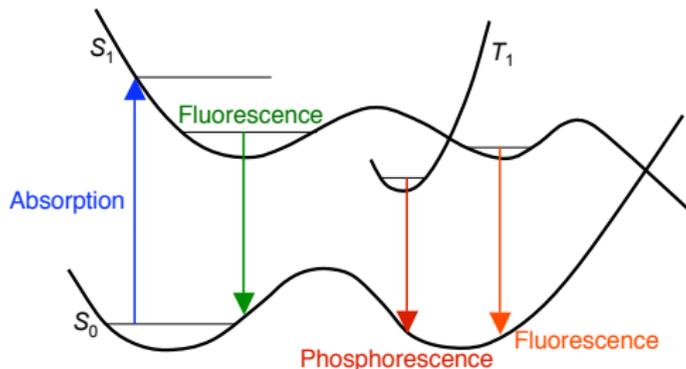
Convergence with about 5000 determinants to better than 0.5 mÅ



Dash, Moroni, Scemama, Filippi, JCTC (2018)

## More demanding application: excited states

- Often stronger electronic correlations than in the ground states
- One needs uniformly good description of multiple energy surfaces



Difficult ... already describing absorption

Structural relaxation? Not many methods suitable for this purpose!

# Needed accuracy for QMC and excited states

Surge of benchmarking studies for excited states

Main focus: absorption and fluorescence

**Accurate Excited-State Geometries: A CASPT2 and Coupled-Cluster Reference Database for Small Molecules**  
Šimon Budžák,<sup>†</sup> Giovanni Scalmani,<sup>‡</sup> and Denis Jacquemin<sup>\*,§,||</sup>  
<sup>†</sup>Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, SK-97400 Banská Bystrica, Slovakia  
Cite This: *J. Chem. Theory Comput.* 2017, 13, 6237–6252  
pubs.acs.org/JCTC

**Excitation energies from diffusion Monte Carlo using selected configuration interaction nodes**  
Anthony Scemama,<sup>†</sup> Anouar Benali,<sup>‡</sup> Denis Jacquemin,<sup>‡</sup> Michel Caffarel,<sup>†</sup> and Pierre-François Loos<sup>†,§</sup>  
Cite This: *J. Phys. Chem. A* 2018, 122, 2714–2723  
pubs.acs.org/JPCA

**Excited States of Methylene, Polyenes, and Ozone from Heat-Bath Configuration Interaction**  
Alan D. Chien,<sup>†</sup> Adam A. Holmes,<sup>‡,§</sup> Matthew Otten,<sup>¶</sup> C. J. Umrigar,<sup>\*,||</sup> Sandeep Sharma,<sup>\*,||</sup> and Paul M. Zimmerman<sup>\*,||</sup>  
<sup>†</sup>Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, United States  
<sup>‡</sup>Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado 80302, United States  
<sup>§</sup>Department of Chemistry and Biochemistry, Cornell University, Ithaca, New York 14853, United States  
<sup>||</sup>Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, United States

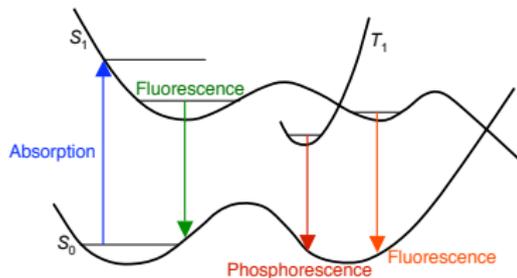
**Theoretical 0–0 Energies with Chemical Accuracy**  
Pierre-François Loos,<sup>†</sup> Nicolas Galland,<sup>‡</sup> and Denis Jacquemin<sup>\*,†,§</sup>  
<sup>†</sup>Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, 31013 Toulouse Cedex 6, France  
Cite This: *J. Phys. Chem. Lett.* 2018, 9, 4646–4651  
pubs.acs.org/JPCA

**A Mountaineering Strategy to Excited States: Highly Accurate Reference Energies and Benchmarks**  
Pierre-François Loos,<sup>†,§</sup> Anthony Scemama,<sup>†</sup> Aymeric Blondel,<sup>‡</sup> Yann Gamiron,<sup>†</sup> Michel Caffarel,<sup>†</sup> and Denis Jacquemin<sup>\*,†,§</sup>  
<sup>†</sup>Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, 31013 Toulouse Cedex 6, France  
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Cite This: *J. Chem. Theory Comput.* 2018, 14, 4360–4374  
pubs.acs.org/JCTC

**Speed-Up of the Excited-State Benchmarking: Double-Hybrid Density Functionals as Test Cases**  
Éric Brémond,<sup>\*,†</sup> Marka Savarese,<sup>‡</sup> Ángel José Pérez-Jiménez,<sup>‡</sup> Juan Carlos Sancho-García,<sup>‡</sup> and Carlo Adamo<sup>\*,†,§</sup>  
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Cite This: *J. Chem. Theory Comput.* 2017, 13, 5558–5571  
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... for example, mean absolute error of CC3 excitations < 0.03 eV

With this in mind, what do we have so far?



So far, we achieved

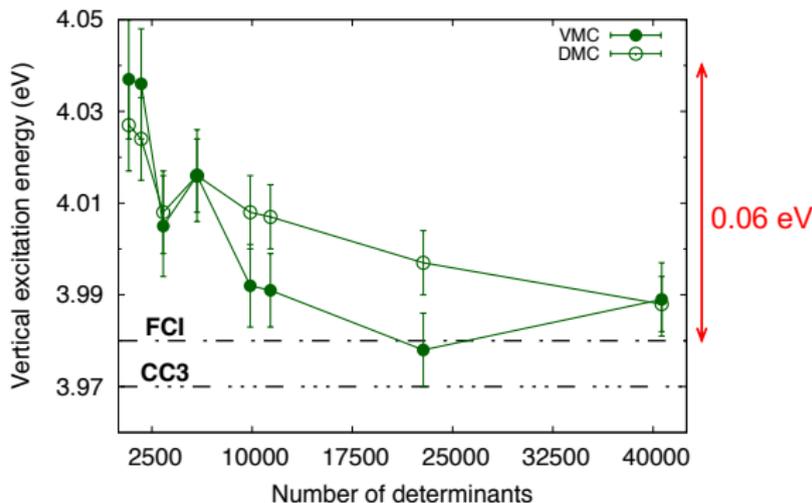
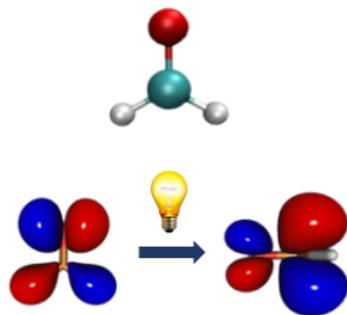
- ✓ Cheap VMC forces
  - ✓ Automatic generation of compact wave functions
  - ✓ Accurate ground-state geometries
- Test our scheme for excited states on “problematic” cases



## Photo-excitations with QMC and CIPSI wave functions

Formaldehyde: Vertical excitation energy

Literature: DMC with CIPSI  $\rightarrow$  300,000 dets for error  $<$  0.1 eV !

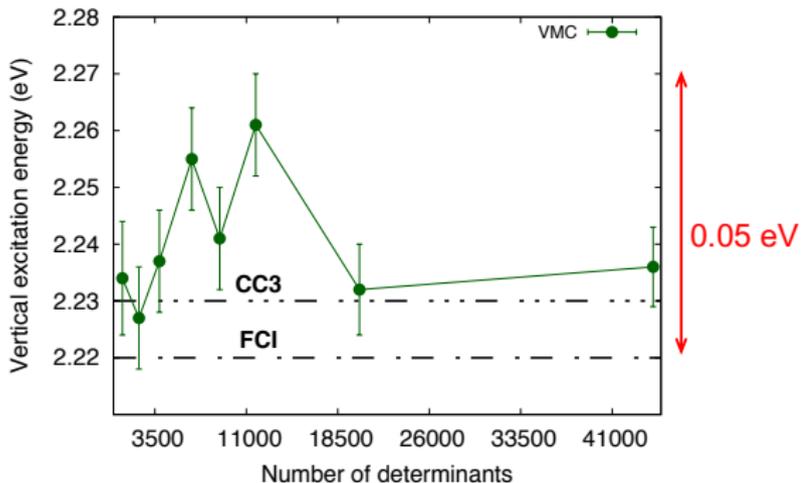
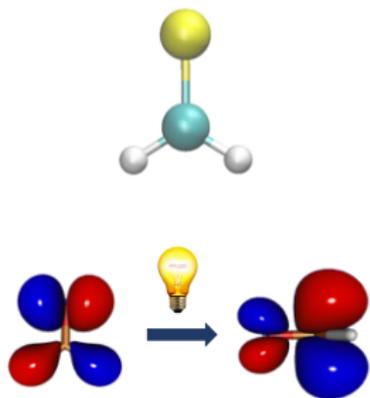


We have nearly exact values with handful of determinants!

## Another example: Thioformaldehyde

Thioformaldehyde: Vertical excitation energy

Literature: VMC with CIPSI  $\rightarrow$  error of 0.2 eV !

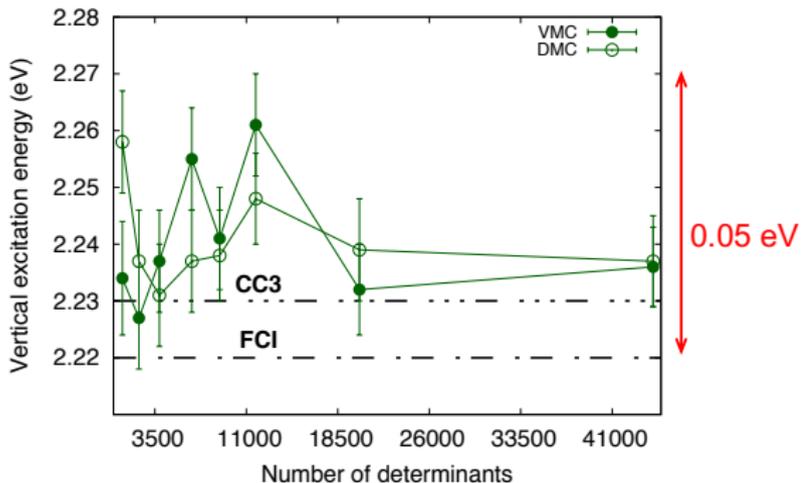
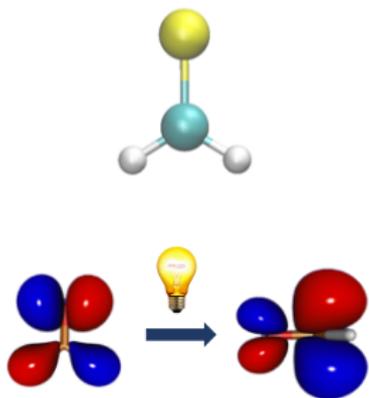


Again, we are within 0.04 eV of reference value

## Another example: Thioformaldehyde

Thioformaldehyde: Vertical excitation energy

Literature: VMC with CIPSI  $\rightarrow$  error of 0.2 eV !



Again, we are within 0.04 eV of reference value

## Computation of excitation energies

Two ingredients for a robust protocol:

1) Balanced determinantal expansions for multiple states

→ CIPSI selection targets similar  $\delta E_{\text{PT2}}$  or  $\sigma_{\text{CI}}$  for all states

2) Fully optimize the Jastrow-Slater wave function

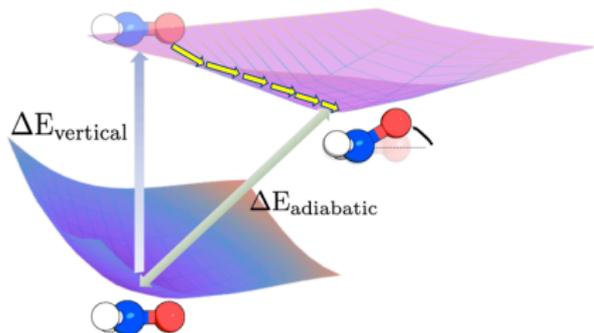
With **balanced generation + VMC optimization**

→ Chemically accurate excitations (error  $< 0.04$  eV)

and with very few determinants

→ No need to perform a DMC calculation!

## Next step: Relax excited-state geometries



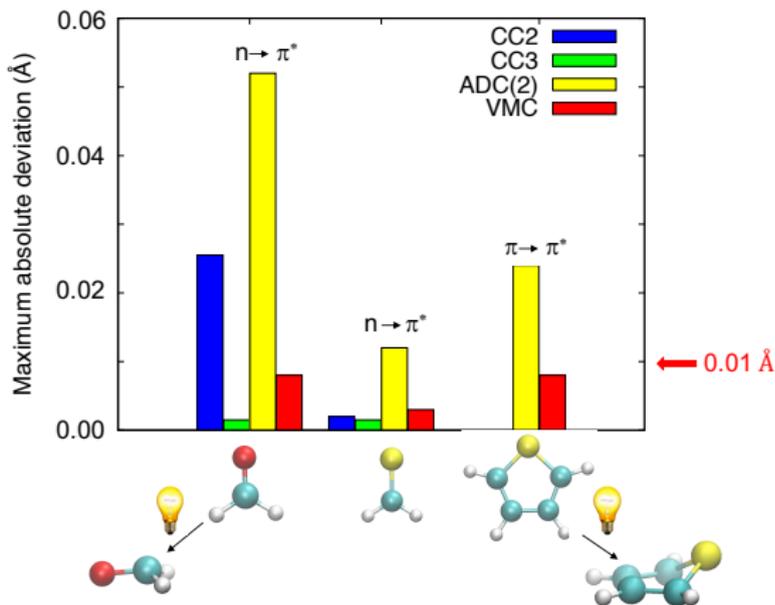
Need of consistent wave functions for different geometries/states!

Generate CIPSI expansions targeting

- Similar  $\delta E_{\text{PT2}}$  for all geometries/states
- Similar  $\sigma_{\text{CI}}$  for all geometries/states

## Excited-state relaxation: some examples

### Optimal excited-state geometries: MAD on bond lengths



Promising ... more work in progress for larger systems

Dash, Feldt, Moroni, Scemama, Filippi, JCTC (2020)

## Summary

Efficient computation of derivatives + optimization toolbox

→ QMC “internally consistent” method

with geometries and wave functions determined in QMC

With some work on wave functions → DMC just not “needed”

Searching for robust QMC protocol for modeling photo-excitations

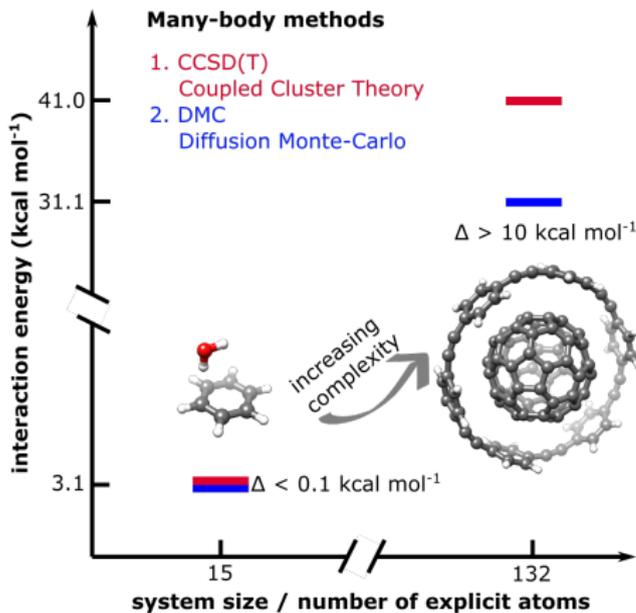
– Automated generation of accurate/compact wave functions

– Balanced description of multiple states

→ Accurate vertical excitations and excited-state geometries

Larger systems?

## Larger systems pose new problems



Y.S. Al-Hamdani *et al.* arXiv:2009.08927v1 (2020)

## To conclude: ongoing research in QMC

- ▶ Search for different forms of trial wave function
- ▶ Push optimization techniques to larger systems
- ▶ More work on transition metals
- ▶ Alternatives to fixed-node diffusion Monte Carlo

## Collaborators



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Paris



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