

Excited-state calculations in quantum Monte Carlo

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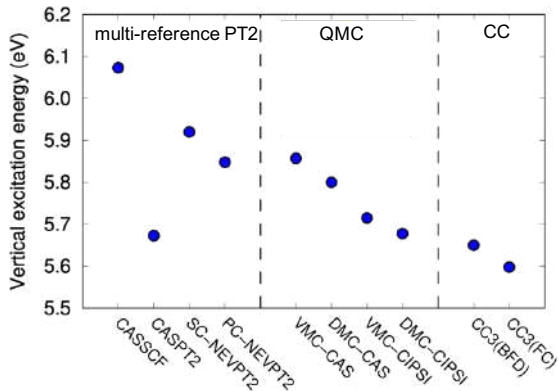
TREX - CECAM Webinar, 25 January 2024



Establishing QMC as a reliable method for excited states

Excited states → Describing absorption already complicated

Example: Vertical excitation energy of thiophene



aug-cc-pVTZ

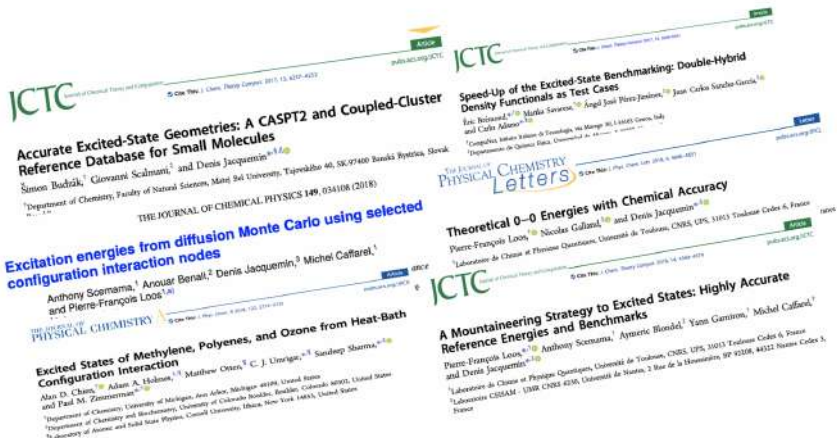
Not an unusual situation!

Dash, Moroni, Filippi, Scemama, JCTC (2021)

Needed accuracy for QMC and excited states

Surge of benchmarking studies for excited states

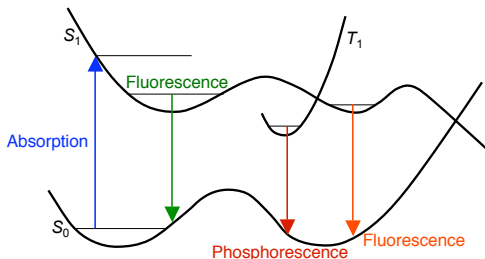
Main focus: absorption and fluorescence



... for example, mean absolute error of CC3 excitations < 0.03 eV

Why are excited states particularly demanding?

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



- Structural relaxation? Density functional theory often fails
Not many methods available/suitable for this purpose!

Quick reminder: Variational Monte Carlo

Use Monte Carlo to compute expectation values

$$\begin{aligned} E &= \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \int d\mathbf{R}^{3N} \frac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \frac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R}^{3N} |\Psi(\mathbf{R})|^2} \\ &= \int d\mathbf{R}^{3N} E_L(\mathbf{R}) P(\mathbf{R}) \\ &= \langle E_L(\mathbf{R}) \rangle \approx \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{R}_i) \end{aligned}$$



$\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ sampled from $P(\mathbf{R})$ via Metropolis algorithm

Just a trick to compute integrals in many dimensions

→ Beyond VMC with projection Monte Carlo (e.g. DMC)

QMC: Ready to explore its performance for excited states

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

Why? What about energy derivatives?

Standard approach: cost of $\partial E \gg$ cost of E : $O(N^4) \rightarrow O(N^5)$

Progress in the last decade

Efficient calculation of analytical derivatives of energy
... also for multi-determinantal expansions



Structural + variational optimization in ground and excited states!

What do we need to perform an energy optimization?

Interatomic forces \rightarrow derivatives wrt nuclear coordinates

We employ low-variance estimators of forces, $F = -\partial_\alpha E$

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

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

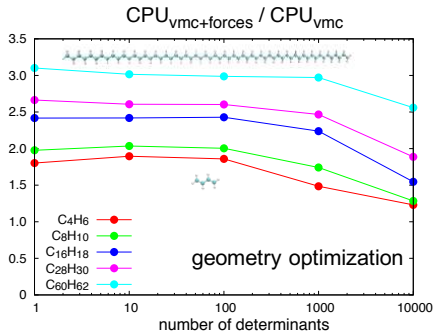
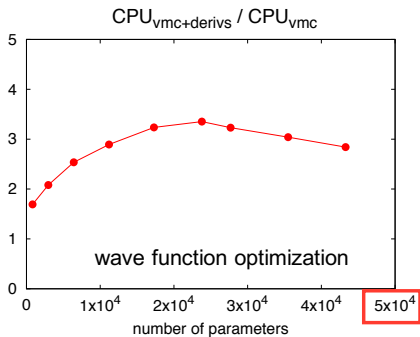
Lower fluctuations $\rightarrow 0$ as $\Psi \rightarrow \Psi_0$

Then, $\partial_\alpha E$ requires $\partial_\alpha \Psi$ and $\partial_\alpha E_L \rightarrow$ Computationally costly!

QMC: Ready to explore its performance for excited states

Efficient derivatives of energy for many parameters + determinants

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



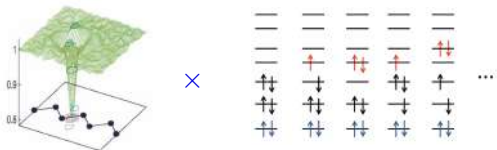
+ Optimization tools \rightarrow QMC “internally consistent”

Filippi, Assaraf, Moroni, JCP (2016); JCTC (2017)

Key is the choice of many-body wave function

Here, we use Jastrow-Slater wave functions

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



Open questions for calculations in (ground and) excited state:

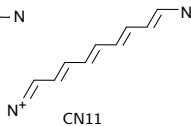
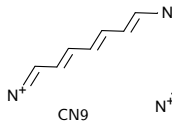
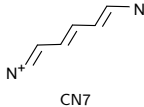
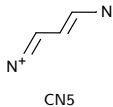
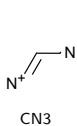
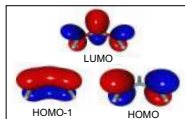
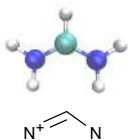
- How do we choose the determinant component?
- How compact can the wave function be?

→ Obtain competitive accuracy

A complete active space (quickly unmanageable) wave function

Example: Cyanine dyes

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



CAS (4,3) (6,5) (8,7) (10,9) (12,11)

Det. 5 52 625 7958 106772

We are only correlating a subset of electrons/orbitals!

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

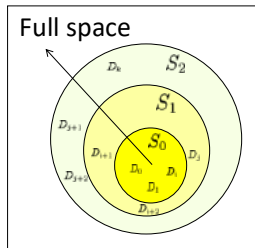
A better scheme to build the determinantal expansion

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 compact QMC expansions?

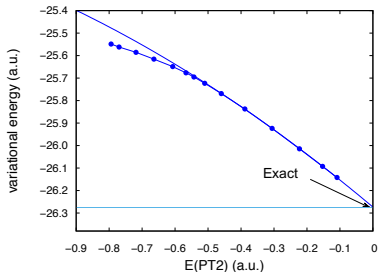
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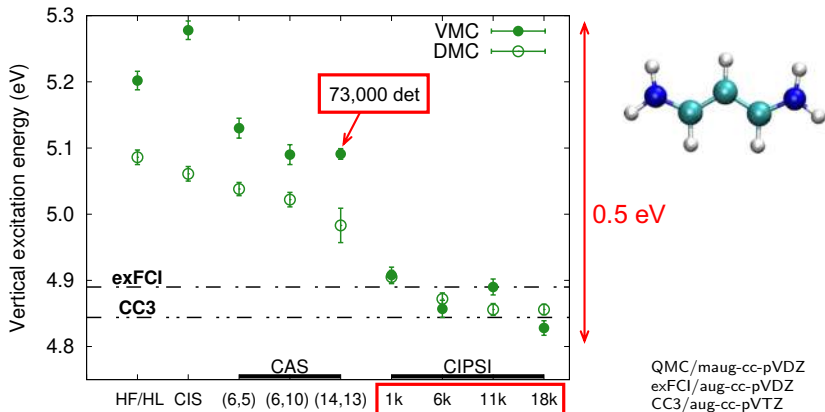
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Can this lead to compact QMC expansions?

Excited states and wave function dependence in QMC

Cyanine dye: Ground and excited states of different symmetries

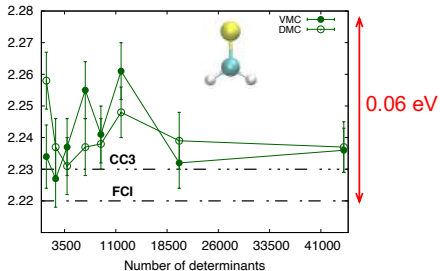
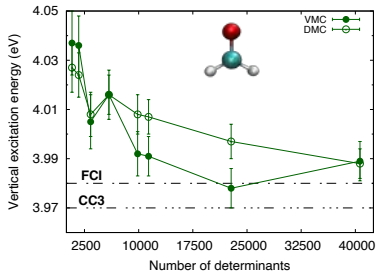


Strong dependence but automated expansions compact + accurate

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

Other examples: Formaldehyde and thioformaldehyde

Vertical excitation energy with QMC-CIPSI



QMC/maug-cc-pVDZ
FCI,CC3/aug-cc-pVTZ

We have nearly exact values with handful of determinants!

DMC is not needed

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

Computation of excitation energies

Two ingredients for a robust protocol:

1) **Balanced expansions** for multiple states

→ generate expansions of similar quality (e.g. δE_{PT2} or σ_{CI})

2) **Full optimization** of the Jastrow-Slater wave function

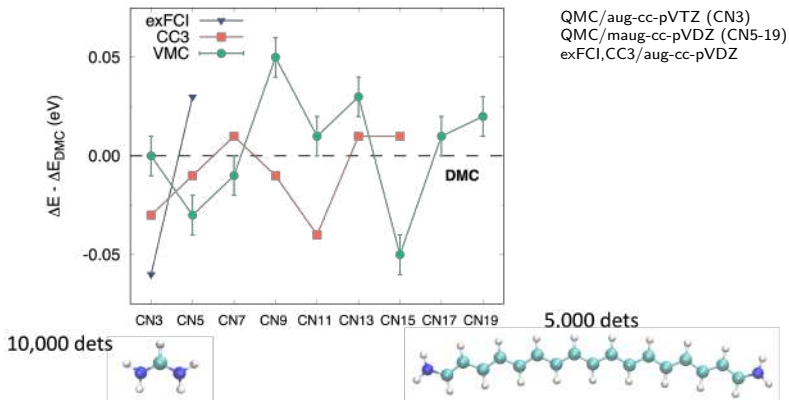
→ Chemically accurate excitations (error < 0.04 eV)
and with very few determinants

→ Already with VMC!

Validation criterion → closeness of VMC and DMC excitations!

Establishing QMC as reference method: larger systems

Larger cyanine dyes



QMC chemically accurate and applicable to all sizes

→ Coupled cluster prohibitive beyond model with 15 C+N atoms!

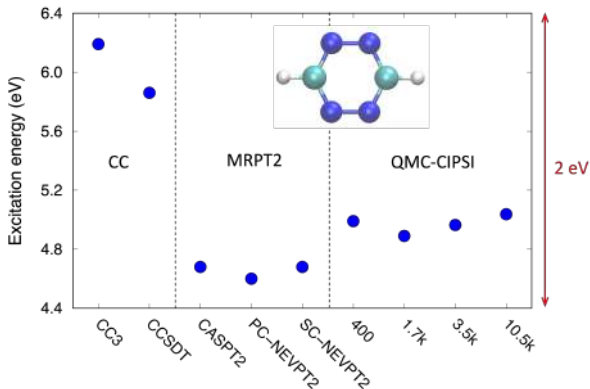
Cuzzocrea, Moroni, Scemama, Filippi, JCTC (2022)

Establishing QMC as reference method: double excitations

Double excitations → Generally problematic

Also ... for high-level coupled cluster (e.g. CC3, CCSDT)

Example: Vertical (double) excitation energy of tetrazine



Establishing QMC as reference method: double excitations

Double excitations → Problematic also for coupled cluster

Let us assess performance of QMC!



	ΔE_{VMC}	ΔE_{DMC}	(eV)
QMC	4.35(1)	4.33(1)	
CC3		5.25	
exFCI		4.32	

QMC/aug-cc-pVDZ
CC3,exFCI/aug-cc-pVQZ

Shepard, Panades-Barrueta, Moroni, Scemama, Filippi, JCTC (2022)

Establishing QMC as reference method: double excitations

Double excitations → Problematic also for coupled cluster

Let us assess performance of QMC!



	ΔE_{VMC}	ΔE_{DMC}	(eV)
QMC	5.70(1)	5.63(1)	
CC3		6.76	
exFCI		5.56(11)	

QMC/aug-cc-pVDZ
CC3/aug-cc-pVQZ
exFCI/aug-cc-pVDZ

Shepard, Panades-Barrueta, Moroni, Scemama, Filippi, JCTC (2022)

Establishing QMC as reference method: double excitations

Double excitations → Problematic also for coupled cluster

Let us assess performance of QMC!



	$\Delta E_{\text{VMC}}(\text{S1})$	$\Delta E_{\text{VMC}}(\text{S2})$	$\Delta\Delta E$	(eV)
QMC	6.10(4)	7.08(4)	1.02(5)	
CC3	7.10	6.21	-0.89	
exFCI	5.8(4)	6.9(2)	1.10(13)	

QMC/aug-cc-pVDZ
CC3/aug-cc-pVTZ
exFCI/aug-cc-pVDZ

We trust QMC as the reference!

Shepard, Panades-Barrueta, Moroni, Scemama, Filippi, JCTC (2022)

Excited state in QMC: which variational principle?

We compute total energies of multiple states

Energy minimization is the method of choice

If states have different symmetry, easy state-specific optimization!

If states have same symmetry

State-specific optimization with orthogonality constraint

$$E_{\text{SS}}[\Psi_I] = E[\Psi_I] + \sum_{J < I} \lambda_{IJ} \frac{\langle \Psi_I | \Psi_J \rangle^2}{\langle \Psi_I | \Psi_I \rangle \langle \Psi_J | \Psi_J \rangle}$$

Blunt *et al.* (2015), Choo *et al.* (2018), Pathak *et al.* (2021)

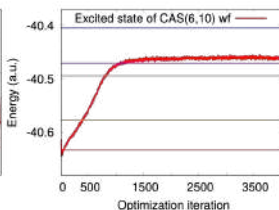
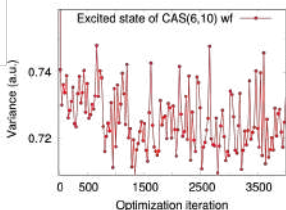
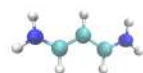
Another approach: Variance minimization

State-specific variance minimization for excited states?

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

In the limit of exact wave functions, variance must have minima!

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



→ Energy minimization safer and more robust

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

Geometry optimization in ground and excited states

So far, efficient variational optimization + compact wave functions

→ Chemically accurate excitation energies

What about structural optimization?

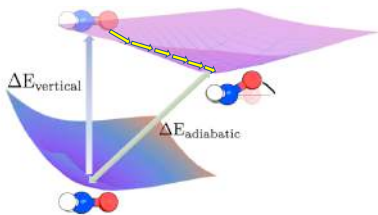
$$E = \int d\mathbf{R} E_L(\mathbf{R}) P(\mathbf{R}) = \langle E_L \rangle \rightarrow F = -\partial_\alpha \langle E_L \rangle$$

In variational Monte Carlo, $P = \Psi^2$

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

→ VMC forces are ready for use!

Relax geometry in the excited state



Need of consistent wave functions for different geometries/states!

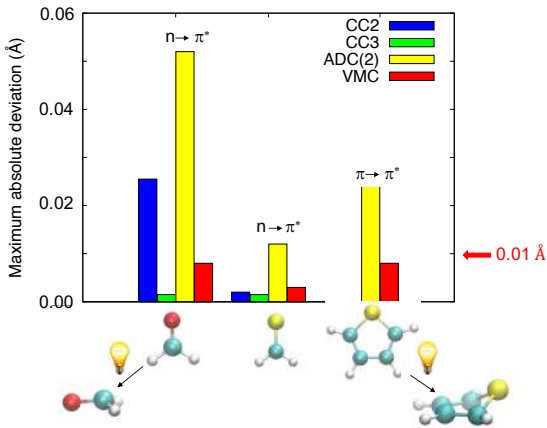
Generate “smart” expansions of similar quality

... for all geometries/states

Dash, Moroni, Filippi, Scemama, JCTC (2021)

Excited-state relaxation: some examples

Optimal excited-state geometries: MAD on bond lengths



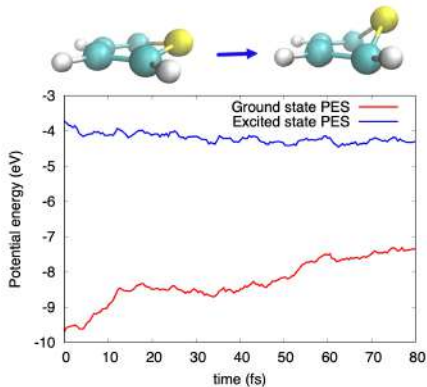
Dash *et al.* JCTC (2020); JCTC (2021)

In progress: using QMC forces for molecular dynamics

Exploring strategies to follow dynamics in excited state

→ Reducing impact of noise

→ Improving convergence of variational optimization



Cuzzocrea, Briels, Filippi (2023)

TREX flagship code CHAMP-EU

These and other developments in CHAMP code



→ Employing **TREXIO** and high-performance **QMCKI** libraries

We have very efficient algorithms for:

- Computation of observables → derivatives of the energy
- Variational and structural optimization for molecules+solids
- Treatment of excited states

<https://github.com/filippi-claudia/champ>

Summary

Robust QMC protocol for modeling ground and excited states

- Efficient computation of accurate energy derivatives
 - QMC “internally consistent” method
 - with geometries and wave functions determined in QMC
- Automated generation of accurate/compact wave functions
- Balanced description of multiple states
 - Accurate vertical excitations and excited-state geometries
- We can handle “difficult” systems and excitations, e.g. doubles

All these (and more) developments in TREX CHAMP code!

Collaborators



Monika Dash



Alice Cuzzocrea



Ravindra Shinde



Stuart Shepard



Edgar Landinez



Saverio Moroni
SISSA, Italy



Anthony Scemama
Toulouse



Wim Briels
UTwente