



Targeting Real chemical accuracy at the EXascale

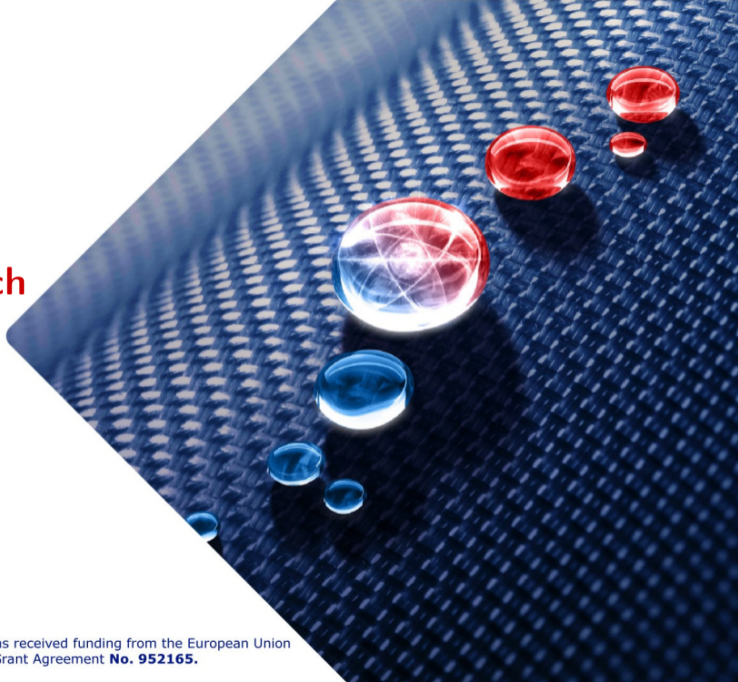
## Transcorrelated approach for CI methods

A Ammar<sup>1</sup>, E Giner<sup>2</sup>, P F Loos<sup>1</sup>  
& A Scemama<sup>1</sup>

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<sup>1</sup> LCPQ, IRSAMC, UPS/CNRS, Toulouse, France

<sup>2</sup> LCT, Sorbonne Université/CNRS, Paris, France



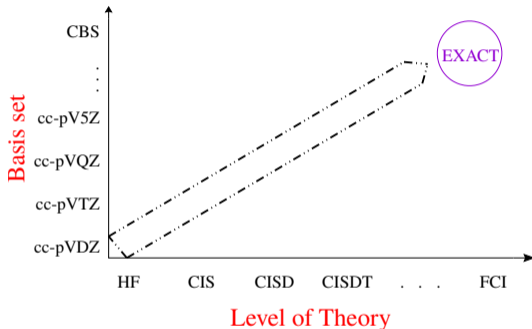
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## Introduction



→ Wavefunction theory provides a systematic way to improve the accuracy



→ **FCI** calculation in a **CBS** gives the **exact** solution

- 🧐 selected CI (**CIPSI**, QMCFI, ...) are powerful methods to approximate & compactify the **FCI** space
- 🤔 What about the convergence with respect to the size of the basis set ?

→ If we have a **CBS**  $\{\phi_1(\mathbf{r}), \phi_2(\mathbf{r}), \dots\}$ , we can expand **exactly** the wavefunction in this basis

$$\text{For 1 electron: } \Psi(\mathbf{r}) = \sum_i^{\infty} c_i \phi_i(\mathbf{r})$$

$$\text{For 2 electrons: } \Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_i^{\infty} c_i(\mathbf{r}_2) \phi_i(\mathbf{r}_1) = \sum_{i,j}^{\infty} a_{ij} \phi_j(\mathbf{r}_2) \phi_i(\mathbf{r}_1) = \frac{1}{2} \sum_{i,j}^{\infty} a_{ij} \begin{vmatrix} \phi_i(\mathbf{r}_1) & \phi_j(\mathbf{r}_1) \\ \phi_i(\mathbf{r}_2) & \phi_j(\mathbf{r}_2) \end{vmatrix}$$

→ The use of truncated basis sets **B** of one-electron functions leads to a poor representation of the “dynamical correlation” in many-electron systems. A large **B** is required to cover these effects

→ Alternatively, one may expect to converge faster by including **explicit two-electron functions**

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \approx \left( \sum_{i,j}^{<\infty} a_{ij} \phi_j(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \right) \mathcal{J}(\mathbf{r}_1, \mathbf{r}_2)$$

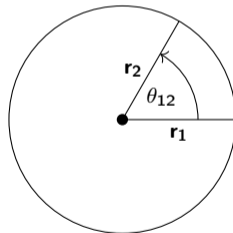
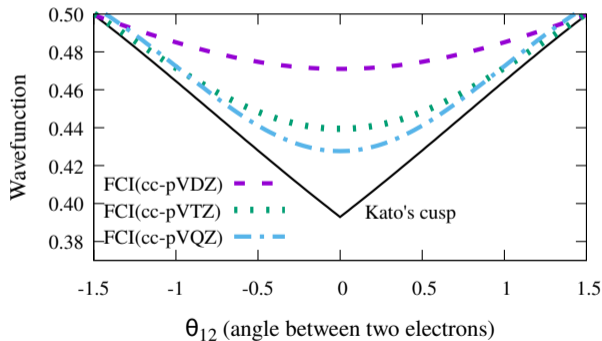
→ To illustrate the effect of including explicit 2-electron terms we consider the example of the Helium atom

	nb of parameters	Energy (a.u.)
exact		<b>-2.9037</b>
<b>FCI(cc-pVDZ)</b>	196	-2.8876
<b>FCI(cc-pVTZ)</b>	900	<b>-2.9002</b>
<b>FCI(cc-pVQZ)</b>	3 025	<b>-2.9024</b>
<b>FCI(cc-pV5Z)</b>	8 281	<b>-2.9032</b>
<b>FCI(cc-pV6Z)</b>	19 600	<b>-2.9034</b>
Hylleraas (1928)	6	<b>-2.9033</b>

→ On the other hand, exact wavefunction must satisfies the Kato's cusp

$$\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}} \Big|_{r_{12}=0} = \frac{1}{2}$$

Exemple of Helium



→ Hylleraas-like approaches  $r_{12}^\nu, e^{-\gamma r_{12}^2}, e^{-\gamma r_{12}}, \dots$

- ▶ very high accuracy but feasible only for systems with at most 3-4 electrons

→ R12/F12 methods:

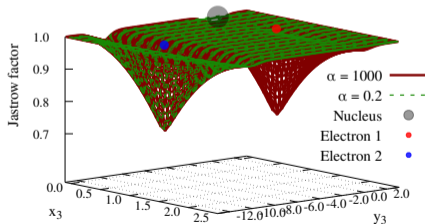
$$\Psi = \Phi_{\text{CI}} + \hat{F}_{12} \Phi_{\text{ref}}$$

- ▶ accelerate convergence with respect to  $\mathcal{B}$  (for example CCSD-R12 in cc-pVTZ  $\approx$  CCSD in cc-pV5Z)
- ▶ but, the wavefunction is expanded instead of being compacted
- ▶ involves 3- and 4-electron integrals, auxiliary bases, simple 2-electron geminals, many approximations ...

→ CI-Jastrow Ansatz:

$$\Psi = \Phi_{\text{CI}} \times e^{+\tau} = \sum_I c_I D_I \times e^{+\tau} \quad \text{with } \tau = \sum_{i,j} u(\mathbf{r}_i, \mathbf{r}_j)$$

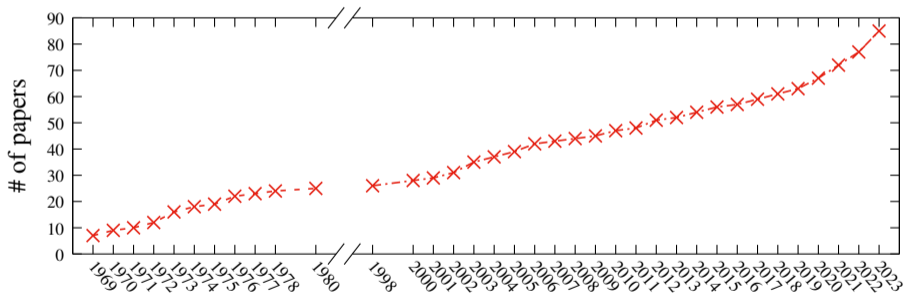
- ▶ accelerates convergence with respect to  $\mathcal{B}$
- ▶ compacted wavefunction ( $\times$  instead of  $+$ )
- ▶ very complex integrals  $\langle D_I e^{+\tau} | \hat{O} | D_J e^{+\tau} \rangle$  (Monte Carlo)
  - ⚡ statistical noise
  - ⚡ computationally expensive algorithms



## Transcorrelated approach



- introduced by Boys & Handy in 1979 and resurrected in 2000 by Ten-no and coworkers
- from 2000 → 2023: **TC** has been combined with PT, CI, CC, DMRG, DFT, Quantum computing, ...



→ The aim of the **TC** theory is nothing but to solve the Schrödinger equation for the Ansatz

$$\Psi = \Phi_{\text{CI}} \times e^{+\tau} \quad \text{with} \quad \begin{cases} \Phi_{\text{CI}} = \sum_l c_l D_l \\ \tau = \sum_{i,j} u(\mathbf{r}_i, \mathbf{r}_j) \end{cases}$$

$$\hat{H} (e^{+\tau} \Phi_{\text{CI}}) = E (e^{+\tau} \Phi_{\text{CI}}) \Rightarrow e^{-\tau} \hat{H} (e^{+\tau} \Phi_{\text{CI}}) = E \Phi_{\text{CI}}$$

$$\Rightarrow \boxed{\hat{H}_{\text{TC}} \Phi_{\text{CI}} = E \Phi_{\text{CI}}} \quad \text{with} \quad \boxed{\hat{H}_{\text{TC}} \equiv e^{-\hat{\tau}} \hat{H} e^{+\hat{\tau}}}$$

→  $\hat{H}$  and  $\hat{H}_{\text{TC}}$  share the same spectrum (**similarity-transformation**)

→ The effective **TC** Hamiltonian is **non-Hermitian** and can be written as

$$\hat{H}_{\text{TC}} = \hat{H} + \hat{K}_{12} + \hat{L}_{123}$$

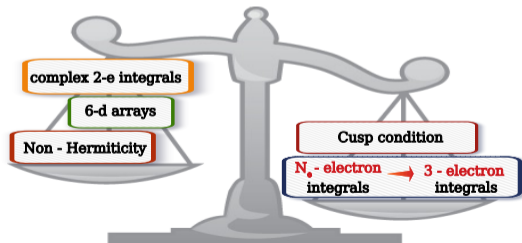
$$\hat{H} |\xi\rangle = E |\xi\rangle$$

$$\langle \xi | \hat{H}^\dagger = E \langle \xi |$$

$$\hat{H}_{\text{TC}} |\xi_R\rangle = E_{\text{TC}} |\xi_R\rangle$$

$$\langle \xi_L | \hat{H}_{\text{TC}}^\dagger = E_{\text{TC}} \langle \xi_L |$$

- 😊 restored **Slater-Condon rules**:  $\langle D_I | \hat{H} | D_J \rangle$ ,  $\langle D_I | \hat{K}_{12} | D_J \rangle$ ,  $\langle D_I | \hat{L}_{123} | D_J \rangle$
- 😊 For a good choice of  $\tau$ , there is no local divergences  $1/r_{12}$  in  $\hat{H}_{TC}$  and  $\Phi_{CI}$  is **cusplless**
- 😞  $\hat{H}_{TC}$  is **non-Hermitian** (~~Variational principle~~):  $\langle f | \hat{K}_{12}^\dagger g \rangle \neq \langle f | \hat{K}_{12} g \rangle$
- 😞  $\hat{H}_{TC}$  is a **3-electron operator**: we need 6d tables for  $\langle \phi_i \phi_j \phi_k | \hat{L}_{123} | \phi_l \phi_m \phi_n \rangle$
- 😞 2-electron integrals are **not analytical** in general (even with GTOs)



## → Biorthogonal Quantum Mechanics

\* Optimization: ~~Variational principle~~ → stationary principle

to optimize the CI parameters of  $\Phi(\mathcal{P}) \times e^{+\tau}$ , we introduce a left wavefunction  $X(\mathcal{P}') \times e^{-\tau}$

$$\boxed{\frac{\partial}{\partial \mathcal{P}'} E_{\text{TC}}[X, \Phi] = 0 \Rightarrow \text{stationary point } \mathcal{P}} \quad \text{with} \quad \boxed{E_{\text{TC}}[X, \Phi] = \frac{\langle X | \hat{H}_{\text{TC}} | \Phi \rangle}{\langle X | \Phi \rangle}}$$

\* Application: Quantum dynamics, perturbation theory, second quantization, ...

## → Integrals complexity

\* usually we can reduce the complexity of 3-e integrals from  $\mathbb{R}^9$  to  $\mathbb{R}^6$

\* data storage of the 3-e term  $\mathcal{O}(M_{\mathcal{B}}^6)$  → approximations on the 3-e term lead to small bias (xTC)

\* For our Jastrow, the involved integrals are semi-analytical



## Optimization of CI-Jastrow wavefunction

→ Recall: CI coefficients of  $\Phi_{\text{CI}} = \sum_I c_I D_I$  are optimized by solving

$$\mathbf{HC} = E \mathbf{SC} \quad \text{where} \quad \begin{cases} H_{IK} = \langle D_I | \hat{H} | D_K \rangle, & \sum \text{ over 2-electron integrals thanks to Slater-Condon rules} \\ S_{IK} = \langle D_I | D_K \rangle = \delta_{IK} \end{cases}$$

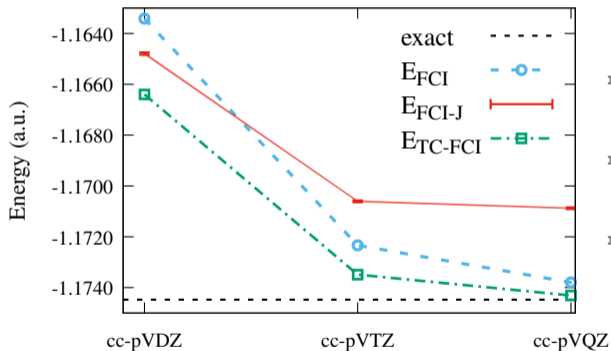
→ For a CI-Jastow wavefunction  $\Phi_{\text{CI-J}} = \sum_I c_I D_I \times e^{+\tau}$ , the eigenproblem **in the variational scheme** becomes

$$\mathbf{HC} = E \mathbf{SC} \quad \text{where} \quad \begin{cases} H_{IK} = \langle D_I e^{+\tau} | \hat{H} | D_K e^{+\tau} \rangle, & \text{Monte Carlo technics} \\ S_{IK} = \langle D_I e^{+\tau} | D_K e^{+\tau} \rangle \neq \delta_{IK}, & \text{Monte Carlo technics} \end{cases}$$

→ In the **TC** framework, we solve rather a **non-variational (stationary) eigenproblem**

$$\mathbf{HC} = E \mathbf{SC} \quad \text{where} \quad \begin{cases} H_{IK} = \langle D_I e^{-\tau} | \hat{H} | D_K e^{+\tau} \rangle = \langle D_I | \hat{H}_{\text{TC}} | D_K \rangle, & \sum \text{ over 2- \& 3-electron integrals} \\ S_{IK} = \langle D_I e^{-\tau} | D_K e^{+\tau} \rangle = \delta_{IK} \end{cases}$$

Illustration: H<sub>2</sub> with FCI wavefunctions



⇒ FCI:

⇒ FCI-J (whithout opt) :

⇒ TC-FCI (whith TC opt):

$$\frac{\langle \Phi_{\text{FCI}} | \hat{H} | \Phi_{\text{FCI}} \rangle}{\langle \Phi_{\text{FCI}} | \Phi_{\text{FCI}} \rangle}$$

$$\frac{\langle \Phi_{\text{FCI}} e^{+\tau} | \hat{H} | \Phi_{\text{FCI}} e^{+\tau} \rangle}{\langle \Phi_{\text{FCI}} e^{+\tau} | \Phi_{\text{FCI}} e^{+\tau} \rangle}$$

$$\frac{\langle X_{\text{TC-FCI}} | \hat{H}_{\text{TC}} | \Phi_{\text{TC-FCI}} \rangle}{\langle X_{\text{TC-FCI}} | \Phi_{\text{TC-FCI}} \rangle}$$

→ Hartree-Fock are widely used as start point for post-HF methods

→ **TC** canonical orbitals

→ left & right orbitals:  $\{\chi\}$  &  $\{\phi\}$

→ left & right Slater determinants:  $D^\chi$  &  $D^\phi$

→ stationary point of the **TC** energy → generalized Brillouin theorem

→ **TC** self consistent field (**TC-SCF**)

① select an orthogonal orbitals  $C^0$  as a first guess  $C^\chi = C^\phi = C^0$

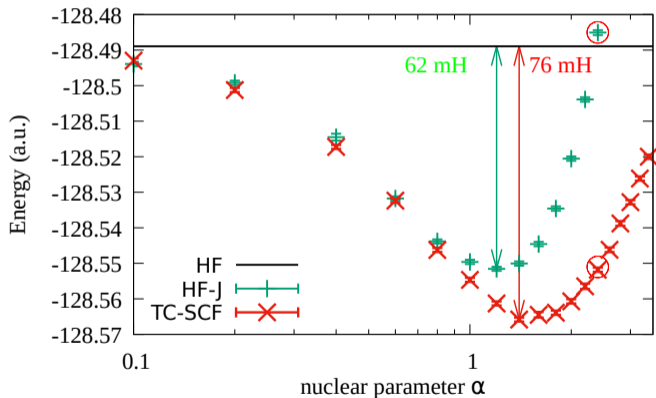
② build and diagonalize the TC-Fock matrix to get new biorthogonal vectors  $\{V_L, V_R\}$ ,  $V_L^t \times V_R = \mathcal{I}$

③ update orbitals:  $C^\chi \leftarrow C^\chi \times V_L$ ,  $C^\phi \leftarrow C^\phi \times V_R$

④ **if(.not.converged)** go to ②



Illustration: Ne in cc-pCVDZ



$\Rightarrow$  HF  $\frac{\langle D^{(\text{HF})} | \hat{H} | D^{(\text{HF})} \rangle}{\langle D^{(\text{HF})} | D^{(\text{HF})} \rangle}$

$\Rightarrow$  HF-J  $\frac{\langle D^{(\text{HF})} e^{\tau} | \hat{H} | D^{(\text{HF})} e^{\tau} \rangle}{\langle D^{(\text{HF})} e^{\tau} | D^{(\text{HF})} e^{\tau} \rangle}$

$\Rightarrow$  TC-SCF  $\frac{\langle D^{\phi} e^{\tau} | \hat{H} | D^{\phi} e^{\tau} \rangle}{\langle D^{\phi} e^{\tau} | D^{\phi} e^{\tau} \rangle}$

selected CI for explicitly correlated  
wavefunction

→ **TC-CIPSI** algorithm

① start with a selected CI space  $\mathcal{I}$

② diagonalize  $\hat{H}_{\text{TC}}$  in  $\mathcal{I}$ :  $X^{(0)}$ ,  $\Phi^{(0)}$ ,  $E_{\text{TC}}^{(0)}$

③ find the connected external determinants  $\{\alpha | \langle \alpha | \hat{H}_{\text{TC}} | I \rangle \neq 0\}$

④ compute the **TC** second-order perturbative contributions (**TC-PT<sub>2</sub>**)

$$e_{\alpha}^{(2)} = \frac{\langle X^{(0)} | \hat{H}_{\text{TC}} | \alpha \rangle \langle \alpha | \hat{H}_{\text{TC}} | \Phi^{(0)} \rangle}{E_{\text{TC}}^{(0)} - \langle \alpha | \hat{H} | \alpha \rangle}, \quad E_{\text{TC}}^{(2)} = \sum_{\alpha} e_{\alpha}^{(2)}$$

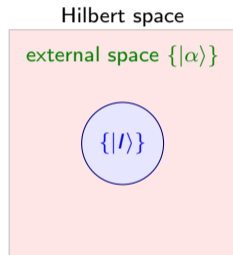
⑤ estimate the **TC-FCI** energy:  $E_{\text{TC-FCI}} \approx E_{\text{TC}}^{(0)} + E_{\text{TC}}^{(2)}$

⑥ select the most relevant external determinants  $\mathcal{A}$ :  $\mathcal{I} \leftarrow \mathcal{I} \cup \mathcal{A}$

⑦ update the zeroth-order  $X^{(0)}$ ,  $\Phi^{(0)}$  and  $E_{\text{TC}}^{(0)}$  using **Davidson**

⑧ if not converged, go to ③

→ **TC-CIPSI** → **TC-FCI** when  $E_{\text{TC}}^{(2)} \rightarrow 0$



## CIPSI

vs

## TC-CIPSI

 compactify  $\Psi_{\text{CI}} = \sum_I c_I D_I$ 

 compactify  $\Psi_{\text{CI-J}} = \sum_I c_I D_I e^{+\tau}$ 

 target the **FCI**

 target the **TC-FCI**

 start with  $\Phi^{(0)}, E^{(0)}$ 

 start with  $\Phi^{(0)}, X^{(0)}, E_{\text{TC}}^{(0)}$ 

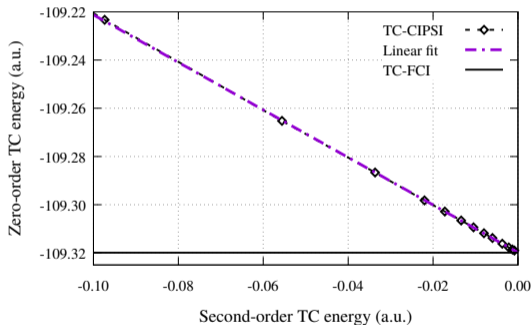
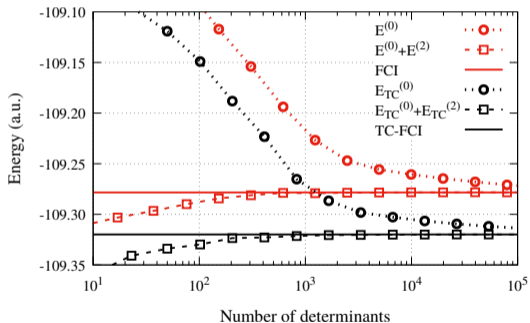
$$e_{\alpha}^{(2)} = \frac{|\langle \alpha | \hat{H} | \Phi^{(0)} \rangle|^2}{E^{(0)} - \langle \alpha | \hat{H} | \alpha \rangle} < 0$$

$$e_{\alpha}^{(2)} = \frac{\langle X^{(0)} | \hat{H}_{\text{TC}} | \alpha \rangle \langle \alpha | \hat{H}_{\text{TC}} | \Phi^{(0)} \rangle}{E_{\text{TC}}^{(0)} - \langle \alpha | \hat{H}_{\text{TC}} | \alpha \rangle}$$

 symmetric Davidson to update  $\Phi^{(0)}, E^{(0)}$ 

 non-symmetric Davidson to update  $\Phi^{(0)}, X^{(0)}, E_{\text{TC}}^{(0)}$

Exemple:  $N_2$  in cc-pVDZ



→ CI-Jastrow wavefunction

👉 provides a compacted explicitly correlated wavefunction

👉 accelerates the convergence with respect to the basis set

→ TC theory

👉 allows to avoid high-dimensional integrals via a similarity transformation

👉 combined with **Biorthogonal QM**, enables to do Quantum Chemistry in an efficient way

→ TC-CIPSI algorithm

👉 selects the most relevant determinants in the CI-Jastrow wavefunction

👉 gives near **TC-FCI** quality thanks to **TC-PT<sub>2</sub>**

Emmanuel Giner



Thank you for your attention