Targeting Real chemical accuracy at the EXascale

Transcorrelated scheme for CI wavecunctions

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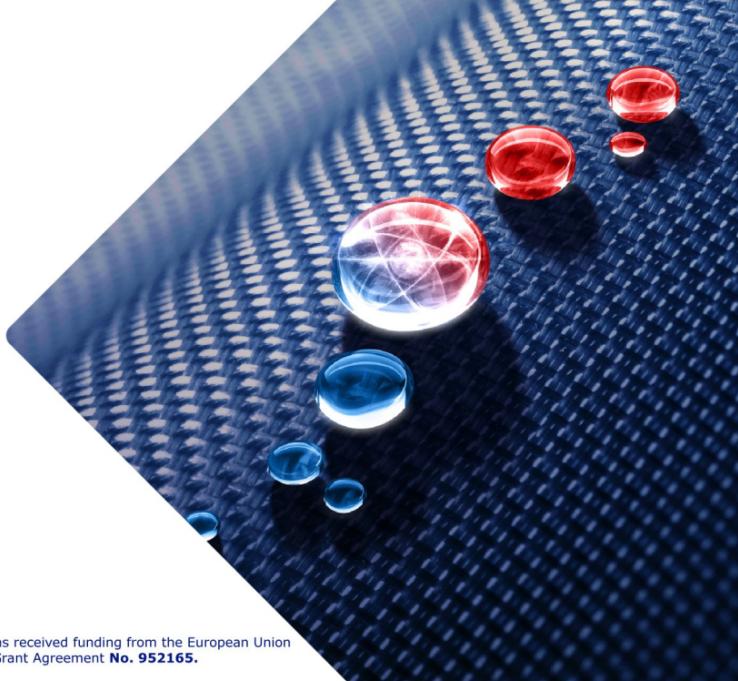

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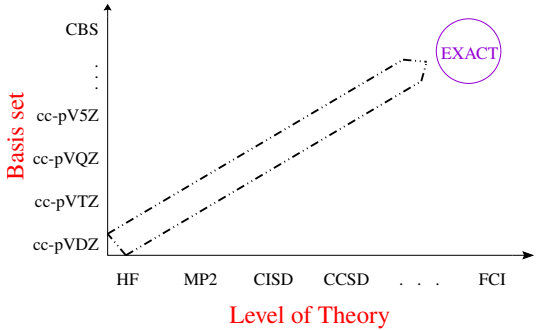
Introduction

➙ Wavefunction theory provide a systematic way to improve the accuracy



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

😎 selected CI (**CIPSI**, QMCFCI,...) are powerful methods to approximate & compactify the **FCI** space

🤔 What about the convergence with respect to the size of the basis set ❓

Basis set convergence: understanding the sluggishness

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

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

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

➙ The use of truncated basis sets $\mathcal{B}$ of one-electron functions leads to a poor representation of the "dynamical correlation" in many-electron systems. A large $\mathcal{B}$ is required to cover these effects

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

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

Basis set convergence: understanding the sluggishness

➥ To illustrate the effect of including explicit 2-electron terms we consider the exemple of the Helium atom

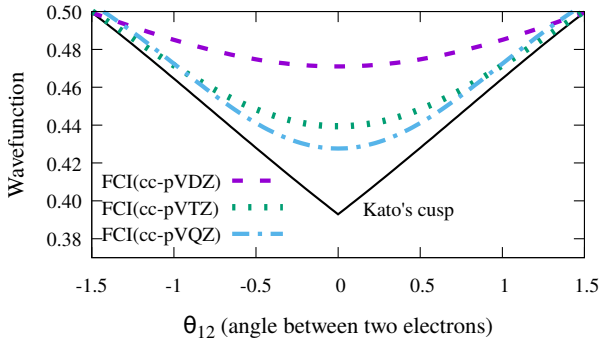
	nb of parameters	Energy (a.u.)
exact		-2.9037
FCI(cc-pVDZ)	196	-2.8876
FCI(cc-pVTZ)	900	-2.9002
FCI(cc-pVQZ)	3 025	-2.9024
FCI(cc-pV5Z)	8 281	-2.9032
FCI(cc-pV6Z)	19 600	-2.9034
Hylleraas (1928)	6	-2.9033

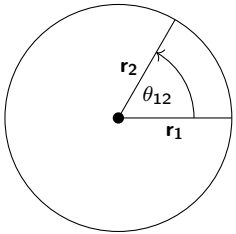
Basis set convergence: understanding the sluggishness

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

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

Exemple of Helium





- Hylleraas-like approaches $r_{12}^{\nu}, e^{-\gamma r_{12}^2}, e^{-\gamma r_{12}}, \ldots$
  - very high accuracy but feasible only for systems with at most 3-4 electrons

- R12/F12 methods:

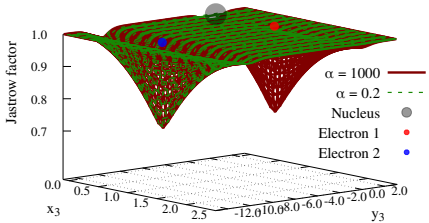
$$\Psi = \Phi_{\mathrm{CI}} + \hat{F}_{12}\,\Phi_{\mathrm{ref}}$$

  - accelerate convergence with $\mathcal{B}$, for exemple 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-Jatrow Ansatz:

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

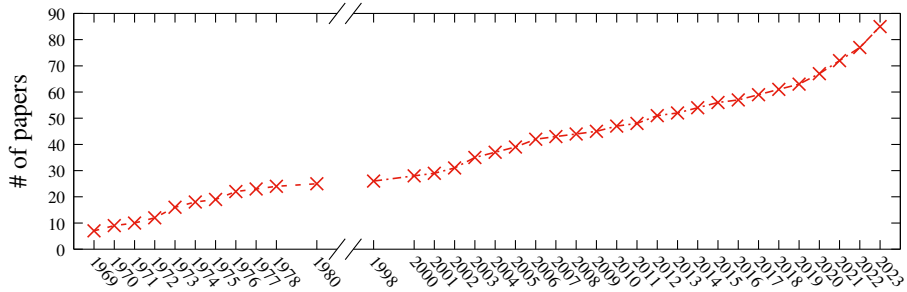
  - accelerates convergence with respect to $\mathcal{B}$
  - compacted wavefunction ($\times$ instead of $+$)
  - very complex integrals $\langle D_I\, e^{+\tau} | \widehat{O} | D_J\, e^{+\tau} \rangle$ (Monte Carlo)
    - statistical noise
    - computationally expensive algorithms



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

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

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

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

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

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

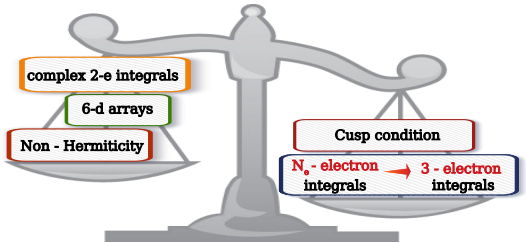
$$\hat{H}_{\text{TC}} = \hat{H} + \hat{K}_{12} + \hat{L}_{123}$$

$$\hat{H} \, |\xi\rangle = E \, |\xi\rangle \qquad \hat{H}_{\text{TC}} \, |\xi_R\rangle = E_{\text{TC}} \, |\xi_R\rangle$$

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

- 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 τ, there is no local divergences $1/r_{12}$ in $\hat{H}_{\text{TC}}$ and Φ_{CI} is **cuspless**

- $\hat{H}_{\text{TC}}$ is **non-Hermitian** (~~Variational principle~~): $\langle f \,|\, \hat{K}_{12}^{\dagger}\, g\rangle \neq \langle f \,|\, \hat{K}_{12}\, g\rangle$
- $\hat{H}_{\text{TC}}$ is a **3-electron operator**: we need 6d tables for $\langle\phi_i\phi_j\phi_k|\hat{L}_{123}|\phi_l\phi_m\phi_n\rangle$
- $\langle\phi_i\,\phi_j|\,\hat{K}_{12}|\phi_k\,\phi_l\rangle$ 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 $<$ 1mH bias

✺ For our Jastrow, the integrals $\langle \phi_i \, \phi_j | \, \hat{K}_{12} | \phi_k \, \phi_l \rangle$ 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

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

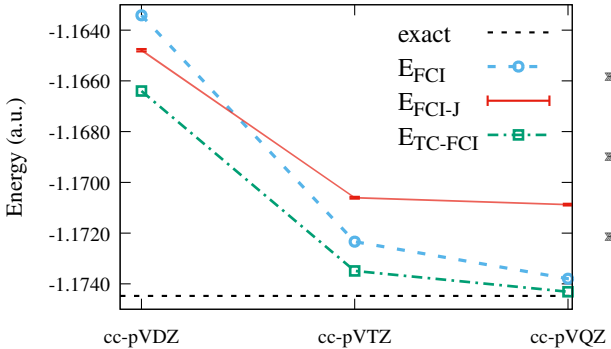
➙ For a CI-Jastow wavefunction $\Phi_{\text{CI-J}} = \sum_I c_I D_I \times e^{+\tau}$, the eigenproblem **in the variational scheme** becomes

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

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

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

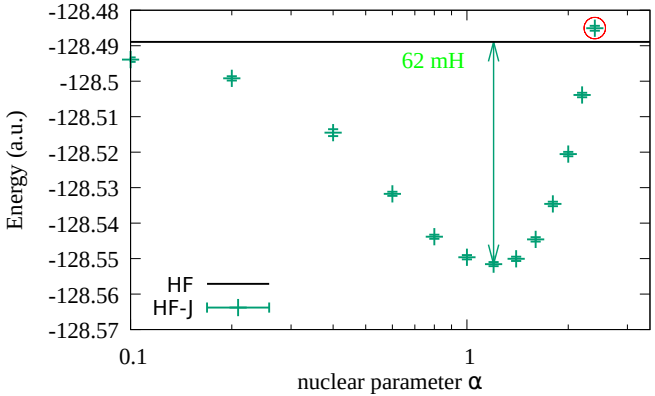
Illustration: H_2 with **FCI** wavefunctions



- FCI: $\frac{\langle \Phi_{\text{FCI}} | \hat{H} | \Phi_{\text{FCI}} \rangle}{\langle \Phi_{\text{FCI}} | \Phi_{\text{FCI}} \rangle}$
- FCI-J (whithout opt) : $\frac{\langle \Phi_{\text{FCI}}\, e^{+\tau} | \hat{H} | \Phi_{\text{FCI}}\, e^{+\tau} \rangle}{\langle \Phi_{\text{FCI}}\, e^{+\tau} | \Phi_{\text{FCI}}\, e^{+\tau} \rangle}$
- TC-FCI (whith TC opt): $\frac{\langle X_{\text{TC-FCI}} | \hat{H}_{\text{TC}} | \Phi_{\text{TC-FCI}} \rangle}{\langle X_{\text{TC-FCI}} | \Phi_{\text{TC-FCI}} \rangle}$

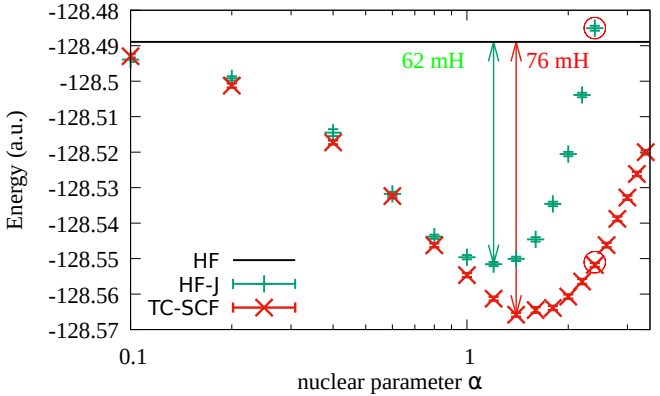
- ⇝ Hartree-Fock are widely used as start point for post-HF methods
- ⇝ TC canonical orbitals
  - ⇝ left & right orbitals: $\{\chi\}$ & $\{\phi\}$
  - ⇝ left & right Slater determinants: D^{χ} & D^{ϕ}
  - ⇝ stationary point of the TC energy ➜ generalized Brillouin theorem
- ⇝ TC self consistent field (TC-SCF)
  1. select an orthogonal orbitals C^0 as a first guess $C^{\chi} = C^{\phi} = C^0$
  2. built 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 ($\mu = 0.87$)



- HF $\quad \dfrac{\langle D^{(\mathrm{HF})} | \hat{H} | D^{(\mathrm{HF})} \rangle}{\langle D^{(\mathrm{HF})} | D^{(\mathrm{HF})} \rangle}$
- HF-J $\quad \dfrac{\langle D^{(\mathrm{HF})} e^{\tau} | \hat{H} | D^{(\mathrm{HF})} e^{\tau} \rangle}{\langle D^{(\mathrm{HF})} e^{\tau} | D^{(\mathrm{HF})} e^{\tau} \rangle}$
- TC−SCF $\quad \dfrac{\langle D^{\phi} e^{\tau} | \hat{H} | D^{\phi} e^{\tau} \rangle}{\langle D^{\phi} e^{\tau} | D^{\phi} e^{\tau} \rangle}$

Illustration: Ne in cc-pCVDZ ($\mu = 0.87$)



- HF $\quad \dfrac{\langle D^{(\mathrm{HF})}|\hat{H}|D^{(\mathrm{HF})}\rangle}{\langle D^{(\mathrm{HF})}|D^{(\mathrm{HF})}\rangle}$
- HF-J $\quad \dfrac{\langle D^{(\mathrm{HF})}e^{\tau}|\hat{H}|D^{(\mathrm{HF})}e^{\tau}\rangle}{\langle D^{(\mathrm{HF})}e^{\tau}|D^{(\mathrm{HF})}e^{\tau}\rangle}$
- TC−SCF $\quad \dfrac{\langle D^{\phi}e^{\tau}|\hat{H}|D^{\phi}e^{\tau}\rangle}{\langle D^{\phi}e^{\tau}|D^{\phi}e^{\tau}\rangle}$

selected CI for explicitly correlated wavefunction

CI using a Perturbative Selection made Iteratively (CIPSI)

➙ **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

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

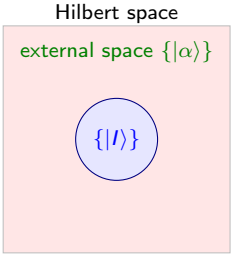
⑤ estimate the **TC-FCI** energy: $E_{\text{TC-FCI}} \approx E_{\text{TC}}^{(0)} + E_{\text{TC}}^{(2)}$

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**

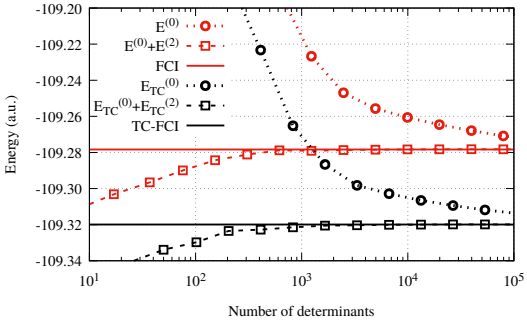
⑧ if not converged, go to ③

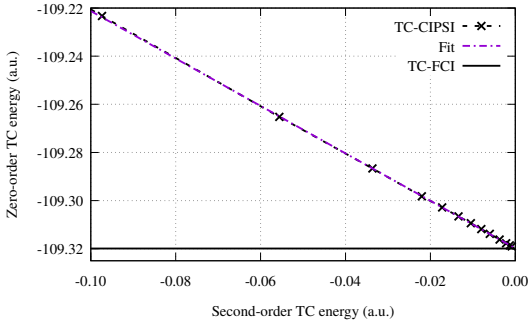
➙ **TC-CIPSI** $\rightarrow$ **TC-FCI** when $E_{\text{TC}}^{(2)} \rightarrow 0$



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 $\Phi^{(0)}, X^{(0)}, E^{(0)}_{\text{TC}}$
$e^{(2)}_{\alpha} = \dfrac{\left\lvert \langle \alpha \lvert \hat{H} \rvert \Phi^{(0)} \rangle \right\rvert^2}{E^{(0)} - \langle \alpha \lvert \hat{H} \rvert \alpha \rangle} < 0$		$e^{(2)}_{\alpha} = \dfrac{\langle X^{(0)} \lvert \hat{H}_{\text{TC}} \rvert \alpha \rangle \, \langle \alpha \lvert \hat{H}_{\text{TC}} \rvert \Phi^{(0)} \rangle}{E^{(0)}_{\text{TC}} - \langle \alpha \lvert \hat{H}_{\text{TC}} \rvert \alpha \rangle}$
symmetric Davidson to update $\Phi^{(0)}, E^{(0)}$		non-symmetric Davidson to update $\Phi^{(0)}, X^{(0)}, E^{(0)}_{\text{TC}}$

illustration N2 in cc-pVDZ





↣ CI-Jastrow wavefunction:
- compacted excplicitly correlated wavefunction
- target highly accurate calculation
- accelerate the convergence with respect to the basis set

↣ TC theory allows to avoid the high-dimensional integrals via a similarity transformation

↣ Biorthogonal Quantum Mechanics combined to TC theory allows to do Quantum Chemistry in an efficient way

↣ **TC-CIPSI** allows to select the most relevant determinants in the CI-Jastrow wavefunction and gives near-**TC-FCI** quality

Emmanuel Giner

Thank you for your attention

Targeting Real chemical accuracy at the EXascale

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