Optimization of large CI wave functions in QMC

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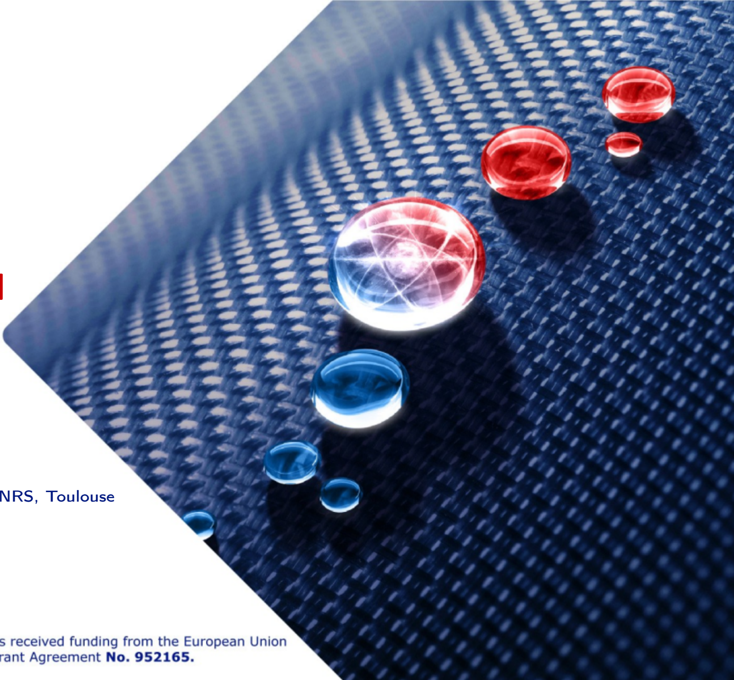

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- CI wavefunction: linear combination of Slater determinants $\{D_I\}$

$$\Phi(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \sum_{I=1}^{N_{\text{det}}} C_I \, D_I(\mathbf{r}_1, \cdots, \mathbf{r}_N)$$

- Usually, $N_{\text{det}} \ll N_{\text{FCI}}$. We improve Φ by adding a Jastrow factor:

$$\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \underbrace{\sum_{I=1}^{N_{\text{det}}} C_I \, D_I(\mathbf{r}_1, \cdots, \mathbf{r}_N)}_{\Phi(\mathbf{r}_1, \cdots, \mathbf{r}_N)} \exp\left[J\right]$$

- goal: optimize $\{C_I\}$ in the presence of Jastrow factor for large N_{det} $(\sim 10^6)$

- Common formulation of the problem:

$$\widehat{H}\left(e^{J}\Phi\right) = E\left(e^{J}\Phi\right)$$

- Transcorrelated formalism:

$$\underbrace{\left(e^{-J}\widehat{H}e^{J}\right)}_{\widehat{H}_{\mathrm{TC}}}\Phi = E\Phi$$

- In practice, we end up with integrals involving $e^{-J}\widehat{H}e^{J}$ instead of $e^{J}\widehat{H}e^{J}$
- we will optimize the coefficients by solving the TC eigenproblem in the $\{D_I\}$ basis

$$\widehat{H}_{\text{TC}}\,\Phi = E_{\text{TC}}\,\Phi \Rightarrow \sum_{K=1}^{N_{\text{det}}} \left\langle D_I \middle| \widehat{H}_{\text{TC}} - \widehat{H} + \widehat{H} \middle| D_K \right\rangle c_K^{(i)} = E_{\text{TC}}\, c_I^{(i)}$$

$$\sum_{K \neq I} \mathbf{H}_{IK}\, c_K^{(i)} + \left(\mathbf{H}_{II} + \underbrace{\boxed{\frac{1}{c_I^{(i-1)}} \left\langle D_I \middle| \widehat{H}_{\text{TC}} - \widehat{H} \middle| \Phi^{(i-1)} \right\rangle}}_{\textbf{dressing elements}} \right) c_I^{(i)} \approx E_{\text{TC}}\, c_I^{(i)}$$

$$\begin{pmatrix} x & & \\ & \ddots & \\ & & x \end{pmatrix}$$

① we build the diagonal dressing matrix $\Delta^{(i-1)}$:

$$\Delta_{IK}^{(i-1)} = \begin{cases} \dfrac{1}{c_I^{(i-1)}} \left[\underbrace{\boxed{\left\langle D_I \middle| \widehat{H}_{\text{TC}} \middle| \Phi^{(i-1)} \right\rangle}}_{\textbf{VMC}} - \left\langle D_I \middle| \widehat{H} \middle| \Phi^{(i-1)} \right\rangle \right] & \text{if } I = K \\ 0 & \text{otherwise} \end{cases}$$

② we apply Davidson to extract the new ground state

③ iterate until convergence

Advantages of this TC-VMC approach:

- memory scale: $\mathcal{O}(N_{\text{det}})$
- fast convergence ($\sim 2 - 3$ iterations)

we have applied this approach to optimize $\sim 400\,000$ coefficients with only one iteration.

- small fluctuations on the involved integrals (compared to $e^J \widehat{H} e^J$)

We need to calculate N_{det} integrals: $A_I = \left\langle D_I \middle| \widehat{H}_{\text{TC}} \middle| \Phi \right\rangle$

- first estimator:

$$a_I = \frac{D_I}{\Phi \eta^2} E_{\text{loc}}^J \quad \text{with } E_{\text{loc}}^J \equiv \frac{\widehat{H}\left(\Phi e^J\right)}{\Phi e^J}. \qquad \Rightarrow \langle a_I \rangle_{(\eta\,\Phi)^2} \equiv \frac{1}{M} \sum_{i=1}^{M} a_I\left(\mathbf{R}_i\right) \to A_I$$

- improved estimator:

$$a_I = \frac{D_I}{\Phi \eta^2}\left(E_{\text{loc}}^J - E_{\text{loc}}\right) + \left\langle D_I \middle| \widehat{H} \middle| \Phi \right\rangle \quad \text{with } E_{\text{loc}} \equiv \frac{\widehat{H}\Phi}{\Phi}.$$

- more improved estimator:

$$a_I = \frac{D_I}{\Phi \eta^2}\left(E_{\text{loc}}^J - E_{\text{loc}}^{\mathcal{J}}\right) + \left\langle D_I \middle| e^{-\mathcal{J}} \widehat{H} e^{\mathcal{J}} \middle| \Phi \right\rangle \quad \text{with } E_{\text{loc}}^{\mathcal{J}} \equiv \frac{\widehat{H}\left(\Phi e^{\mathcal{J}}\right)}{\Phi e^{\mathcal{J}}}.$$

Statistical fluctuations: illustration for N_2 in cc-pvtz