EXPLICITLY CORRELATED FULL CI

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Full-CI

- Only approximation : one-electron basis set
- Can be computed exactly for small systems
- Can be computed with FCI-QMC for larger systems
- Can be approached with selected-CI methods (CIPSI, SHCI, etc) + PT2 and extrapolation

Main difficulties with Full-CI

- Exponential scaling with the size of the basis set
- Slow convergence of the energy with the basis set

Three directions to reduce the basis set incompleteness bias

- QMC : Solve Schrödinger's eq. in a complete basis set, with the nodes of a quasi-FCI in a smaller basis set (post-Full-CI)
- Combine FCI with DFT : range-separated DFT/FCI. (Giner & Toulouse, Paris)
- Use a F_{12} correlation factor.

F_{12}

- Linear combinations of Slater determinants are unable to represent properly the electron-electron cusp when $r_{ij} \to 0$.
- Kutzelnigg (1985) introduced linear terms which depend *explicitly* on r_{ij} to impose the cusp
- Ten-no proposed a short-range Slater geminal as a better approximation:

$$F_{12}(r_{12}) = -\frac{1}{\lambda} e^{-\lambda r_{12}} \tag{1}$$

- Similar to the two-body Jastrow factor in QMC

$$J_{12}(r_{12}) = \exp\left(\frac{\alpha r_{12}}{1+\beta r_{12}}\right) \tag{2}$$

Target

- A general F_{12} scheme, applicable to *any* CI method
- Use the F_{12} scheme with CISPI to keep basis sets small
- CISPI is expected to converge faster
- Use QMC on top of these compact wave functions
  - The F_{12} term replaces the Jastrow factor. It reduces the variance and the cost of the QMC calculations.
  - No need to optimize a Jastrow factor and re-optimize stochastically the wave function
  - $\Longrightarrow$ Use QMC as a black box

Ansatz

$$|\Psi\rangle = (1 + \hat{Q} f) |\Psi_{\text{FCI}}\rangle \tag{3}$$

- Conventional part (Full-CI) : $|\Psi_{\text{FCI}}\rangle = \sum_I c_I |I\rangle$
- Explicitly correlated part : $|F\rangle = \hat{Q} f |\Psi_{\text{FCI}}\rangle$
- $f = \sum_{i<j} \left(\gamma_{ij} \times f_{12}(r_{ij})\right)$.
- γ_{ij} is chosen to impose the cusp conditions.
- $\hat{Q} = \hat{1} - \sum_I |I\rangle\langle I|$ ensuring that $\langle \Psi_{\text{FCI}} | F \rangle = 0$

Ansatz

$$|\Psi\rangle = (1 + \hat{Q}f)\,|\Psi_{\mathrm{FCI}}\rangle \qquad f(r_{12}) = -\tfrac{1}{\lambda}e^{-\lambda r_{12}}$$

Difficulties

- Using a Slater geminal involves very expensive integrals
- Computing $\langle I|\hat{H}|fJ\rangle$ requires three-electron integrals.
- Computing $\langle\Psi|\hat{H}|\Psi\rangle$ requires $\langle If|\hat{H}|fJ\rangle$ which requires three- and four-electron integrals.
- Using those integrals would involve 6-index and 8-index transformations

Ansatz

$$|\Psi\rangle = (1 + \hat{Q} f) |\Psi_{\text{FCI}}\rangle \qquad f(r_{12}) = -\frac{1}{\lambda} e^{-\lambda r_{12}}$$

Conventional solutions

1. Introduce an auxiliary basis set :

$$\langle I|\hat{H}|fJ\rangle = \langle I|\hat{H}\hat{f}|J\rangle = \sum_{\alpha} \langle I|\hat{H}|\alpha\rangle \langle \alpha|\hat{f}|J\rangle \tag{4}$$

2. Use a Gaussian fit of the Slater geminal : all integrals involve only Gaussians and are separable in x, y, z

For now, we will adopt these solutions.

Our F_{12}-FCI strategy

- Compute the energy by projection on the Full-CI wave function to avoid four-electron integrals. Cheaper, but loss of variational principle.
- Consider the explicitly correlated term as a dressing of the conventional Hamiltonian
- Iteratively diagonalize the dressed Hamiltonian to vary the c_I to minimize the energy
- Close to MR-CCSD of Malrieu, Garniron, David, Giner, AS.

f_{12}-DRESSED HAMILTONIAN

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle \tag{5}$$

$$\langle I|\hat{H}|\Psi\rangle = Ec_I \tag{6}$$

$$0 = \sum_K \langle I|\hat{H}|K\rangle\, c_K + \langle I|\hat{H}|F\rangle - Ec_I \tag{7}$$

$$0 = \left(\langle I|\hat{H}|I\rangle + \frac{1}{c_I}\langle I|\hat{H}|F\rangle - E\right)c_I + \tag{8}$$

$$\sum_{K\neq I} \langle I|\hat{H}|K\rangle\, c_K \tag{9}$$

$$\tag{10}$$

(To avoid numerical instabilities due to $1/c_I$ in the diagonal dressing, we use a column dressing in the column of the determinant with the largest c_I.)

Helium atom

Method	Basis	Total energy (au)
FCI	cc-pVDZ	-2.887 595
	cc-pVTZ	-2.900 232
	cc-pVQZ	-2.902 411
	∞	-2.903 724
CCSD-F12b	cc-pVDZ-F12	-2.902 251
	cc-pVTZ-F12	-2.903 380
FCI-F12	cc-pVDZ-F12	-2.901 897
	cc-pVTZ-F12	-2.902 643

- Implement F12 in Quantum Package to perform F12-CIPSI
- Modify stochastic PT2 algorithm of Yann Garniron to compute

$$\sum_{\alpha} \langle I|\hat{H}|\alpha\rangle \ \langle\alpha|\hat{F}|J\rangle \tag{11}$$

- Implement three-electron integrals to remove the auxiliary basis set
- Implement F_{12} correlation factor in QMC=Chem