

Density-fitted many-electron integrals in explicitly-correlated methods

The basis set convergence problem

For conventional wavefunction-based methods:

$$\begin{aligned} \text{Error in } E_{\text{corr}} \text{ (cc-pVXZ)} \quad \varepsilon &= \mathcal{O}(X^{-3}) \\ \text{Number of basis functions } m &= \mathcal{O}(X^3) \\ \text{Computer time } t &= \mathcal{O}(m^4) \end{aligned}$$

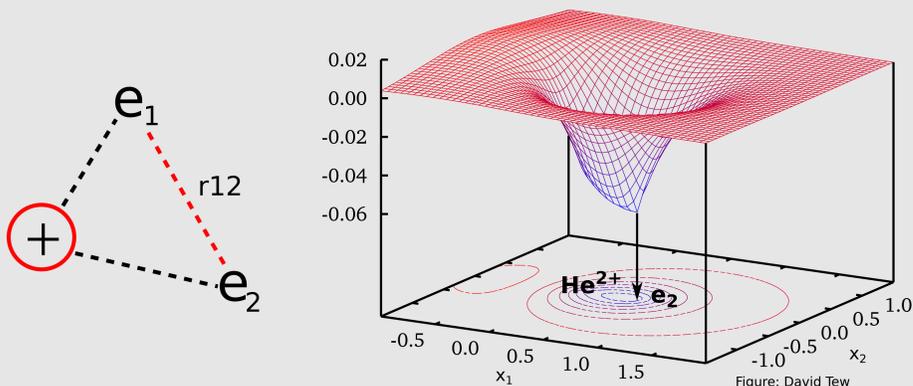
$$\varepsilon = \mathcal{O}(t^{-1/4})$$

Reducing the error in E_{corr} , ε , by a factor of 10 requires a 10,000-fold increase in computational work [1].

Explicitly-correlated methods

Conventional wavefunctions are inaccurate where $r_{12} \rightarrow 0$. A large basis set of nucleus-centred 1-electron basis functions is necessary to fit the electron-centred Coulomb hole, resulting in slow convergence of ε wrt basis set size.

$$h_c = \Psi_{\text{exact}} - \Psi_{\text{HF}}$$



Explicitly correlated methods address this issue by introducing 2-electron basis functions with explicit dependence on r_{12} . Wavefunctions incorporating these functions give a better reproduction of the Coulomb hole, greatly accelerating convergence of ε wrt basis set size [1].

MP2-F12 theory

Augment the conventional MP2 first-order pair function with a set of explicitly-correlated configurations which depend on $F_{12} = f(r_{12})$ [2],

$$|u_{ij}\rangle = \frac{1}{2} \sum_{ab} T_{ab}^{ij} |ab\rangle + \frac{1}{2} \hat{Q}_{12} \sum_{kl} T_{kl}^{ij} F_{12} |kl\rangle$$

and minimize the Hylleraas pair function,

$$H[u_{ij}] = \langle u_{ij} | \hat{Q}_{12} (\hat{f}_1 + \hat{f}_2 - \epsilon_i - \epsilon_j) \hat{Q}_{12} | u_{ij} \rangle + 2 \langle u_{ij} | \hat{Q}_{12} r_{12}^{-1} | ij \rangle \geq \epsilon_{ij}^{(2)}$$

to optimize the amplitudes T_{ab}^{ij} , T_{kl}^{ij} and obtain MP2 pair energies, $\epsilon_{ij}^{(2)}$ [3].

The projection operator \hat{Q}_{12} ensures strong orthogonality of $|u_{ij}\rangle$ to the occupied orbital space, $\langle u_{ij} | k \rangle$, enabling decomposition of $E^{(2)}$ into pair contributions.

Many-electron integrals

Introduction of 2-electron pair functions results in many-electron integrals, e.g.

$$\langle ij | r_{12}^{-1} F_{23} | mlk \rangle \equiv (im | r_{12}^{-1} | j | F_{23} | mk)$$

These are numerous and complicated to evaluate, requiring approximation. R12 and F12 methods use approximate resolutions of the identity (RIs) [4, 5, 6], e.g.

$$\langle ij | r_{12}^{-1} F_{23} | mlk \rangle \approx \sum_x \langle ij | r_{12}^{-1} | mx \rangle \langle mx | F_{23} | kl \rangle$$

where $\hat{X} = \sum_x |x\rangle \langle x| \approx \hat{1}$ to simplify many-electron integrals.

The RI basis must contain functions with up to at least $3L_{\text{occ}}$, which may be problematic where the highest angular momentum of the occupied orbitals, L_{occ} , is large [1, 7].

Robust density-fitting

The product of two 1-centre, 1-electron orbitals can be approximated as a sum of 1-center densities, e.g.

$$\phi_i(\mathbf{r})\phi_j(\mathbf{r}) \equiv |ij\rangle \approx |\tilde{ij}\rangle = \sum_A D_A^{ij} |A\rangle$$

where the density-fitting (DF) coefficients, D_A^{ij} , are determined by minimization of the Coulomb energy of the fitting residuals,

$$\Delta_{ij} = (ij - \tilde{ij} | r_{12}^{-1} | ij - \tilde{ij}).$$

This suggests an alternative for approximating many-electron integrals [7]:

$$(im | r_{12}^{-1} | j | F_{23} | mk) \approx \sum_{A,B,C} D_A^{im} D_B^{jl} D_C^{mk} (A | r_{12}^{-1} | B | F_{23} | C) = (\tilde{im} | r_{12}^{-1} | \tilde{j} | F_{23} | \tilde{mk})$$

To avoid linear dependence on the error in the fitted densities, $|ij - \tilde{ij}\rangle$, in the error in the fitted integral, we use robust fitted forms of the integrals [8, 9]:

$$\begin{aligned} (im | r_{12}^{-1} | j | F_{23} | mk)_{\text{robust}} &= (im | r_{12}^{-1} | \tilde{j} | F_{23} | \tilde{mk}) + (\tilde{im} | r_{12}^{-1} | j | F_{23} | \tilde{mk}) \\ &\quad + (\tilde{im} | r_{12}^{-1} | \tilde{j} | F_{23} | mk) - 2(\tilde{im} | r_{12}^{-1} | \tilde{j} | F_{23} | \tilde{mk}) \end{aligned}$$

The DF basis for fitting a product of 1-electron functions requires functions with up to $2L_{\text{occ}}$, lower than the at least $3L_{\text{occ}}$ required for approximating a 3-electron integral with RI.

MP2-F12/3*A(D) without RIs

To compare integral approximation via robust density-fitting with resolution of the identity, we have implemented an RI-free version of MP2-F12/3*A(D) theory in MOLPRO [10].

In the 3*A(D) scheme [11], the Ansatz 3 projector,

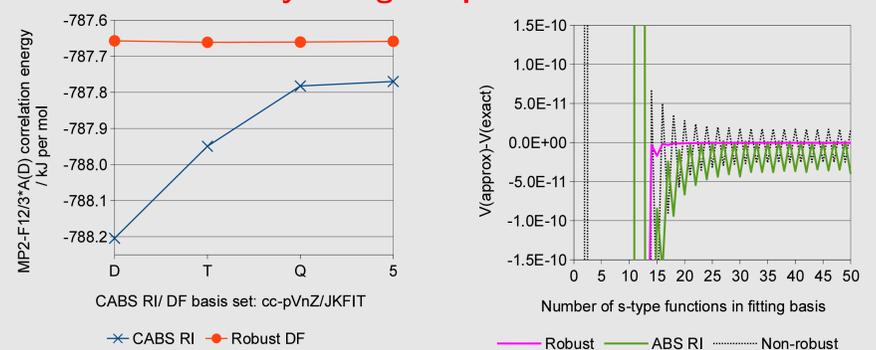
$$\hat{Q}_{12} = (1 - \hat{o}_1)(1 - \hat{o}_2)(1 - \hat{v}_1\hat{v}_2)$$

is used and the set of approximations used avoids integrals over > 3 -electron coordinates. In our RI-free implementation the 3-electron components of the V_{kl}^{ij} and $A_{kl,mn}$ matrix elements are robust density-fitted:

$$\langle ij | r_{12}^{-1} F_{23} | mlk \rangle \quad \langle kli | [F_{12}, \hat{t}_1] F_{23} | inm \rangle \quad \langle kli | [F_{12}, \hat{t}_2] F_{23} | inm \rangle$$

Results

Fast convergence of the error in the integrals with fitting basis set size for robust density-fitting compared to resolution of the identity.



MP2-F12/3*A(D) correlation energies for H₂O calculated using CABS RI [6] and robust DF for the 3-electron integrals for increasing fitting basis size. The difference between the two schemes at cc-pV5Z/JKFIT is $\sim 0.1 \text{ kJ mol}^{-1}$.

Comparison of the integral $\langle 111 | r_{12}^{-1} F_{23} | 111 \rangle$ approximated using robust DF, non-robust DF and ABS RI [5] to the exact integral for the He atom. The fitting basis used is an even-tempered set of s-type primitives which can be systematically grown.

References

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