

Density-fitted many-electron integrals in explicitly correlated methods

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The basis set convergence problem

For conventional wavefunction-based methods (e.g. MP2, CI, CC):

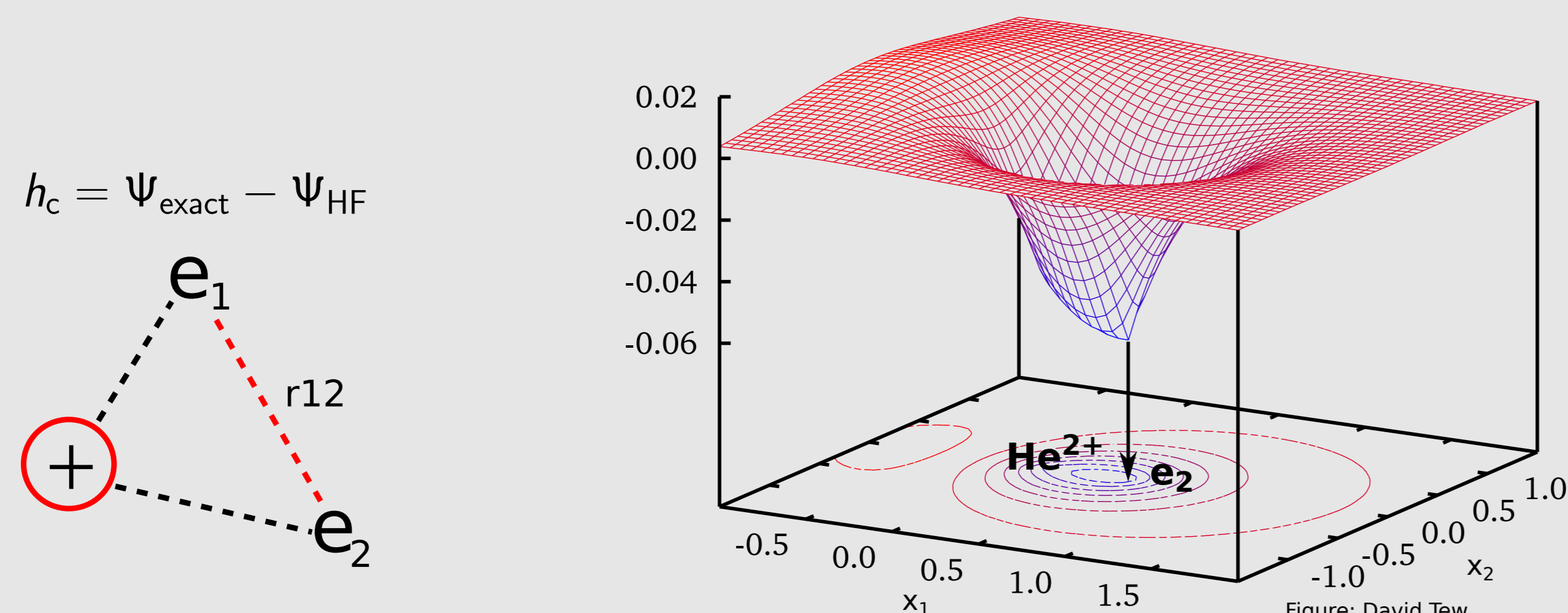
$$\begin{aligned} \text{Error in } E_{\text{corr}} \text{ (cc-pVXZ)} & \quad \varepsilon = \mathcal{O}(X^{-3}) \\ \text{Number of basis functions} & \quad m = \mathcal{O}(X^3) \\ \text{Computer time} & \quad t = \mathcal{O}(m^4) \end{aligned}$$

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

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.



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, 2].

MP2-F12 theory

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

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

and minimize the Hylleraas pair functional,

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

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. RI and F12 methods use approximate resolutions of the identity (RIs) [4], 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 $3\ell_{\text{occ}}$, which may be problematic where the highest angular momentum of the occupied orbitals, ℓ_{occ} is large [1, 5].

Density-fitting orbital products

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 is a well-established method for approximating 4-index, 2-electron electron repulsion integrals in terms of 2- and 3-index objects, used in a variety of methods (e.g. DF-MP2 [6] and DF-MP2-F12 [3, 7]):

$$(\tilde{pq} | r_{12}^{-1} | \tilde{rs}) = D_A^{pq} J_{AB} D_B^{rs} = J_{pq}^A [J^{-1}]_{AB} J_{rs}^B.$$

Robust density fitting

Density fitting can also be used for approximating many-electron integrals [5]:

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

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 [7, 8]:

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

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

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 [9].

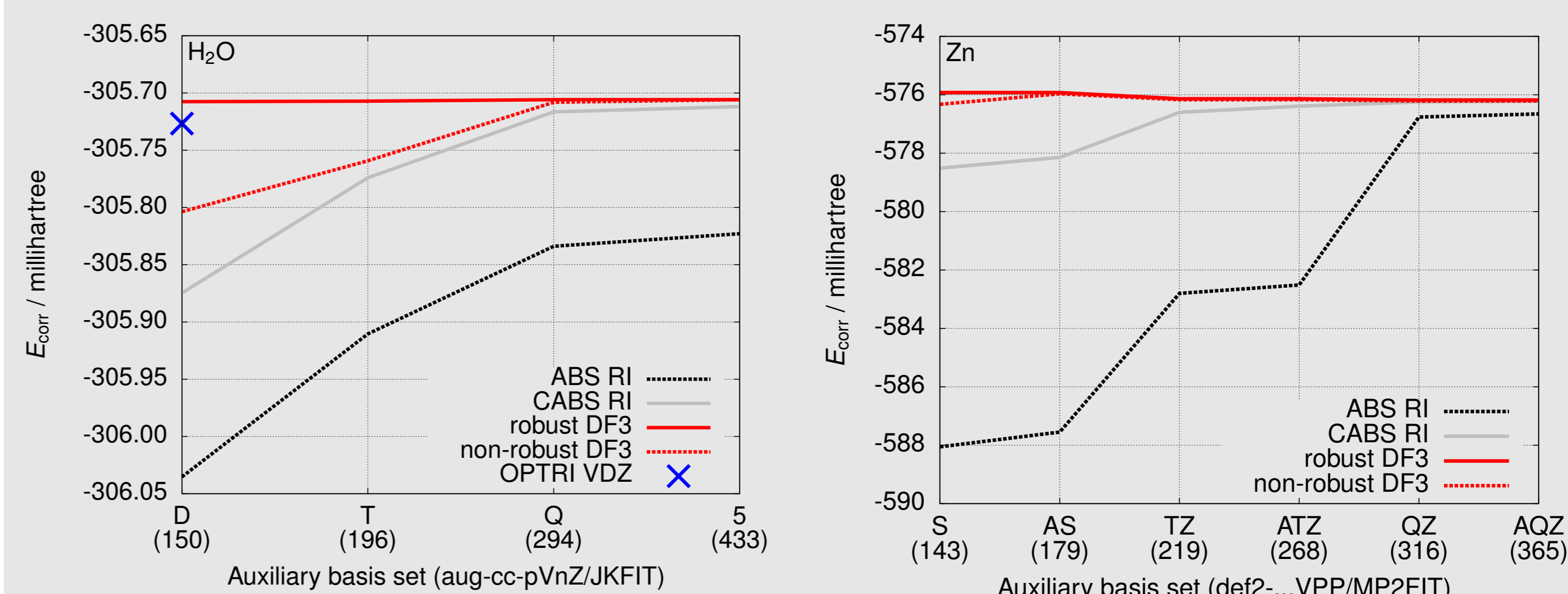
In the 3*A(D) scheme [10], the Ansatz 3 projector,

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

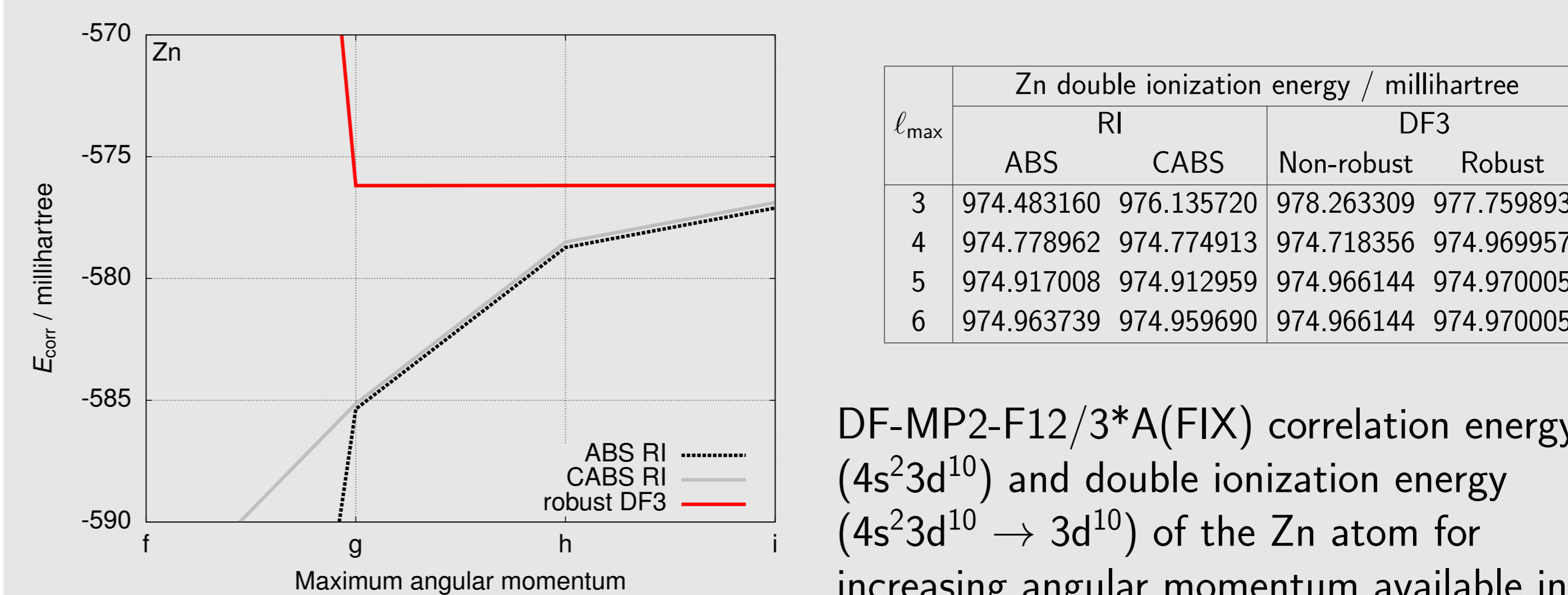
is used and the set of approximations used avoids integrals over > 3 -electron coordinates. In our RI-free implementation the 3-electron components of the V_{kl}^{ij} and $A_{kl,mn}$ matrix elements are robust density-fitted (robust DF3):

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

Results



DF-MP2-F12/3*A(FIX) correlation energy of H₂O and Zn for increasing auxiliary basis set size using variants of RI and DF3 to approximate the 3-electron integrals. Numbers in parentheses are the total numbers of basis functions in the auxiliary basis sets.



DF-MP2-F12/3*A(FIX) correlation energy ($4s^2 3d^{10}$) and double ionization energy ($4s^2 3d^{10} \rightarrow 3d^{10}$) of the Zn atom for increasing angular momentum available in the auxiliary basis set.

Robust DF3-based MP2-F12/3*A demonstrates rapid convergence of the correlation energy wrt auxiliary basis set size. The maximum angular momentum required in the DF3 auxiliary basis set for submillihartree accuracy is lower than that required in a corresponding RI basis. These are attractive features for explicitly correlated calculations on systems with high-angular momentum occupied orbitals, such as transition metal complexes.

References

- [1] Klopper, W., Manby, F.R., Ten-No, S. & Valeev, E.F. *Int. Rev. Phys. Chem.* **25**, 427 (2006).
- [2] Hättig, C., Klopper, W., Köhn, A. & Tew, D. P. *Chem. Rev.* **112**, 4 (2012).
- [3] May, A. J. & Manby, F. R. *J. Chem. Phys.* **121**, 4479 (2004).
- [4] Kutzelnigg, W. & Klopper, W. *J. Chem. Phys.* **94**, 1985 (1991).
- [5] Manby, F.R. Explicitly correlated electronic structure theory. In *Solving the Schrodinger equation: has everything been tried?* (2011), ed. Paul Popelier, Imperial College Press, pp. 25–42.
- [6] Werner, H.-J., Manby, F. R. & Knowles, P. J. *J. Chem. Phys.* **118**, 8149 (2003).
- [7] Manby, F.R. *J. Chem. Phys.* **119**, 4607 (2003).
- [8] Dunlap, B. I. *Phys. Chem. Chem. Phys.* **2**, 2113 (2000).
- [9] MOLPRO, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others, see <http://www.molpro.net>.
- [10] Werner, H.-J., Adler, T. B. & Manby, F. R. *J. Chem. Phys.* **126**, 164102 (2007).

Publication: Womack, J. C. & Manby, F. R. *J. Chem. Phys.* **140**, 044118 (2014).