

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

James C. Womack and Fred R. Manby

University of Bristol

24<sup>th</sup> September 2013

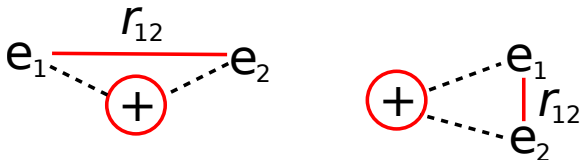


# Electron correlation

$$\hat{H}\Psi = E\Psi$$

$$E_{\text{exact}} = E_{\text{HF}} + E_{\text{corr}}$$

- Electronic repulsive interaction  $\sim \frac{1}{r_{12}}$ .
- Electronic motion is “correlated”.

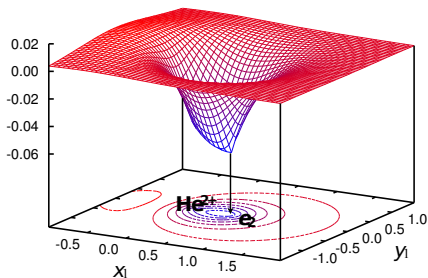


- Electron correlation is important to describe chemistry!
  - Bond dissociation
  - Dispersion interactions

e.g.  $E_{\text{corr}}$  for  $\text{H}_2$  is  $\sim -100 \text{ kJ mol}^{-1}$ .

The manifestation of electron correlation in the wavefunction [1].

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



[Figure: David Tew]

**Born interpretation:** probability density =  $|\Psi|^2$

1. Hättig, C., Klopper, W., Köhn, A. & Tew, D. P. *Chemical Reviews*. 112, 4-74 (2011).

# “Conventional” methods

## Correlated wavefunctions

Built from 1-electron, nucleus-centred HF MOs,

$$|\Psi_{\text{FCI}}\rangle = |\Psi_{\text{HF}}\rangle + \sum_{ia} c_i^a |\Psi_i^a\rangle + \frac{1}{4} \sum_{ijab} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \dots$$

e.g. CI, CC, MPPT

## The convergence problem

Poor scaling of  $\varepsilon$ , error in  $E_{\text{corr}}$ , wrt AO basis size  $m$  [1].

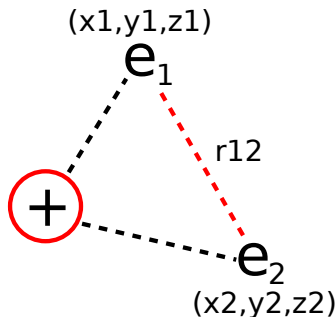
$$\varepsilon = \mathcal{O}(m^{-1}) \quad t = \mathcal{O}(m^4) \quad \varepsilon = \mathcal{O}(t^{-1/4})$$

*Reducing the error by a factor of 10 requires a 10,000-fold increase in computational work – **Poor at fitting the Coulomb hole.***

1. Klopper, W., Manby, F. R., Ten-No, S. & Valeev, E. F. *Int. Rev. Phys. Chem.* 25, 427 (2006).

# Explicitly-correlated methods

- Introduce 2-electron basis functions with explicit dependence on  $r_{12}$ .
- Improved fit of the Coulomb hole.
- Improved scaling of  $\varepsilon$  wrt  $m$ .
- Efficient description of electron correlation.



**More accurate  $E_{\text{corr}}$  with a smaller basis set.**

**BUT:** Complicated “many-electron” integrals arise.

$$\langle ijm | r_{12}^{-1} F_{23} | mlk \rangle \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \phi_i^*(1) \phi_j^*(2) \phi_m^*(3) r_{12}^{-1} F_{23} \phi_m(1) \phi_l(2) \phi_k(3)$$

# Tricky integrals

- All methods require 1- and 2- electron integrals.

$$\langle i|j\rangle \quad \langle i|\hat{h}_1|j\rangle \quad \langle ij|r_{12}^{-1}|kl\rangle$$

- There are efficient methods for computing these.
- Many-electron ( $> 2$ ) integrals in explicitly-correlated methods are numerous and complicated to evaluate.

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

- Arise due to presence of correlation factor,  $F_{12} = f(r_{12})$ .

**Approximations are required for practical calculations!**

## Resolutions of the identity (RIs)

- Widely used (R12/F12 methods).
- Introduces an additional set of functions (RI basis).
- Many electron integrals are factorised into more manageable 2-electron integrals, e.g.

$$\hat{1} \approx \sum_p |p\rangle\langle p|$$

$$\langle ijm|r_{12}^{-1}F_{23}|mlk\rangle \approx \sum_p \langle ij|r_{12}^{-1}|mp\rangle \langle mp|F_{12}|kl\rangle$$

**Problem:** A good approximation requires RI basis functions with up to at least  $3L_{\text{occ}}$  units of angular momentum.

---

Kutzelnigg, W. *Theor. Chim. Acta.* 68, 445-469 (1985).

Kutzelnigg, W. & Klopper, W. *J. Chem. Phys.* 94, 1985 (1991).

## Density-fitting (DF)

- Established technique in other contexts.
- Introduces an additional set of functions (DF basis).
- Complicated many-electron integrals are approximated as sums over simpler many-electron integrals, e.g.

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

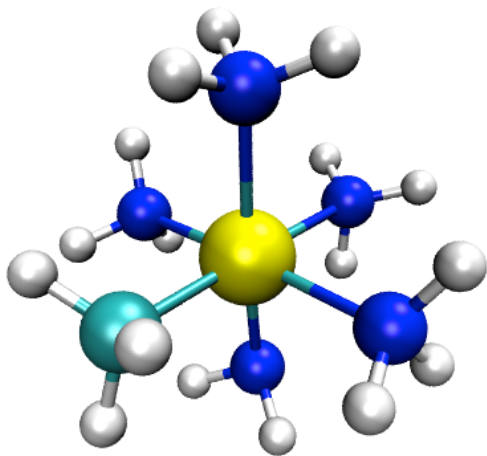
$$(im|r_{12}^{-1}|jl|F_{23}|mk) \approx \sum_{A,B,C} D_{im}^A D_{jl}^B D_{mk}^C (A|r_{12}^{-1}|B|F_{23}|C)$$

**Advantage:** Only functions with angular momentum up to  $2L_{\text{occ}}$  are required in the DF basis [1].

---

1. Manby, F.R. Explicitly correlated electronic structure theory. In *Solving the Schrodinger equation: has everything been tried?* (2011), ed. Paul Popelier, Imperial College Press.





$l$	Type	Func <sup>n</sup>
0	<i>s</i>	1
1	<i>p</i>	3
2	<i>d</i>	5
3	<i>f</i>	7
4	<i>g</i>	9
5	<i>h</i>	11
6	<i>i</i>	13

Image: Vitamin B12 model,  $[\text{Co(III)}(\text{NH}_3)_4\text{NH}_2\text{CH}_3]^+$ , Patrick von Glehn.

# Robust density-fitting

Minimize  $\Delta_{pq}$  to obtain  $D_{pq}^A$ .

$$\Delta_{pq} = (pq - \widetilde{pq} | r_{12}^{-1} | pq - \widetilde{pq})$$

$$\phi_p(\mathbf{r})\phi_q(\mathbf{r}) \equiv |pq) \approx |\widetilde{pq}) = \sum_A D_{pq}^A |A)$$

Avoid linear dependence on  $|pq - \widetilde{pq})$ , in the error in the fitted integral, use **robust density-fitted** forms of the integrals:

$$\begin{aligned} (pq|rs|tu)_{\text{robust}} &= (pq|\widetilde{rs}|\widetilde{tu}) + (\widetilde{pq}|rs|\widetilde{tu}) \\ &\quad + (\widetilde{pq}|\widetilde{rs}|tu) - 2(\widetilde{pq}|\widetilde{rs}|\widetilde{tu}) \end{aligned}$$

$$\begin{aligned} &(pq|rs|tu) - (pq|rs|tu)_{\text{robust}} \\ &= (pq - \widetilde{pq}|rs - \widetilde{rs}|tu - \widetilde{tu}) + (pq - \widetilde{pq}|rs - \widetilde{rs}|\widetilde{tu}) \\ &\quad + (\widetilde{pq}|rs - \widetilde{rs}|tu - \widetilde{tu}) + (pq - \widetilde{pq}|\widetilde{rs}|tu - \widetilde{tu}). \end{aligned}$$

---

Dunlap, B. I. *Phys. Chem. Chem. Phys.* 2, 2113-2116 (2000).

Manby, F. R. *J. Chem. Phys.* 119, 4607 (2003).

## Aim

Compare integral approximation via robust density-fitting with resolutions of the identity in MP2-F12/3\*A(D) theory.

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

- The 3\*A(D) approximation scheme was used, avoiding integrals over  $> 3$ -electron coordinates [1].
- Robust density-fitted forms of 3-electron integral classes implemented in **MOLPRO** [2].

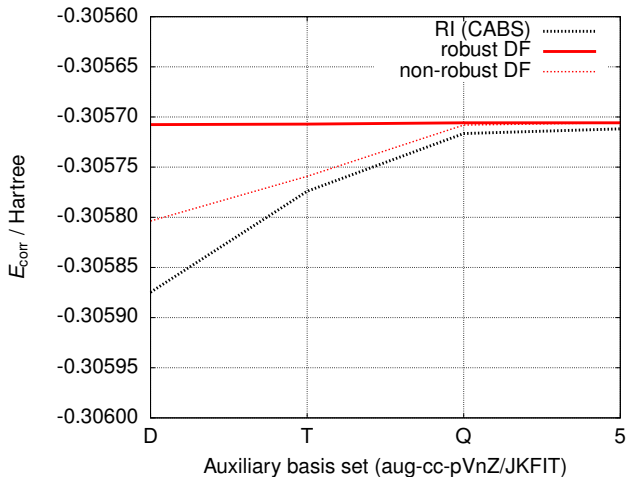
$$\langle ijm|r_{12}^{-1}F_{23}|mlk\rangle \quad \langle kli|[F_{12}, \hat{t}_1]F_{23}|inm\rangle \quad \langle kli|[F_{12}, \hat{t}_2]F_{23}|inm\rangle$$

- Existing MP2-F12 code used to produce a proof-of-concept implementation of RI-free MP2-F12/3\*A(D).

1. Werner, H.-J., Adler, T. B. & Manby, F. R. *J. Chem. Phys.* 126, 164102 (2007).

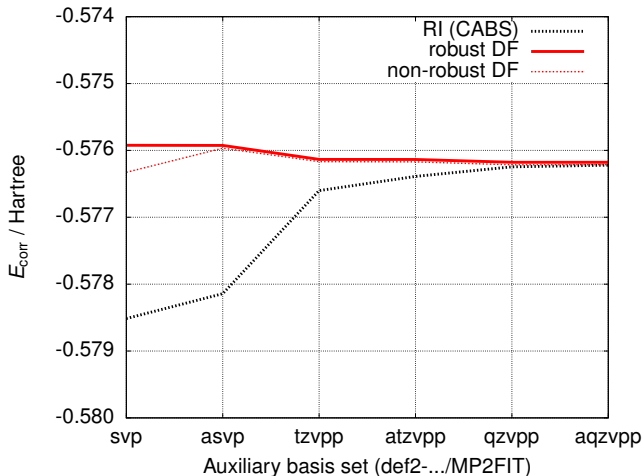
2. Werner, H.-J., Knowles, P. J., Knizia, G., Manby, F. R., Schütz, M. *et al*, <http://www.molpro.net>.

# H<sub>2</sub>O MP2-F12/3\*A correlation energy



DF-MP2-F12/3\*A(FIX) correlation energy of H<sub>2</sub>O for increasing auxiliary basis set size. The AO basis was aug-cc-pVDZ. The auxiliary basis sets used for RI, and DF-3 integral approximations were aug-cc-pVnZ/JKFIT type.

# Zn atom MP2-F12/3\*A correlation energy



DF-MP2-F12/3\*A(FIX) correlation energy calculated using RI (CABS) and robust/non-robust DF to approximate 3-electron integrals for increasing auxiliary basis set size. Auxiliary basis sets were MP2FIT basis sets optimized for the def2 family of AO basis sets. AO basis set was def2-tzvpp for all calculations.

## Conclusions

Robust density-fitting of many-electron integrals:

- Rapid convergence wrt auxiliary basis set size.
- High accuracy with comparatively small auxiliary basis set.
- Competitive with resolution of the identity.

## Further work

- Optimize implementation in MOLPRO.
- Other applications of robust density-fitted 3-electron integrals.

**... Paper currently being written!**

# Acknowledgements

I would like to thank the following people and organizations:

- Prof Fred Manby
- Dr David Tew
- Centre for Computational Chemistry
- EPSRC
- University of Bristol



# Appendix: Zn atom MP2-F12/3\*A correlation energy

Basis set (MP2FIT)	$E_{\text{CORR}}$ , RI (CABS) / Hartree	$E_{\text{CORR}}$ ,robust DF / Hartree	$E_{\text{CORR}}$ ,non-robust DF / Hartree
def2-svp	-0.578513893639	-0.575923643166	-0.576326961209
def2-asvp	-0.578142952901	-0.575925198026	-0.575966307431
def2-tzvpp	-0.576601056036	-0.576134316390	-0.576168195099
def2-atzvpp	-0.576388569981	-0.576135806852	-0.576170498453
def2-qzvpp	-0.576245605132	-0.576176920547	-0.576215031938
def2-aqvpp	-0.576220815812	-0.576177162044	-0.576212335203

DF-MP2-F12/3\*A(FIX) correlation energy calculated using RI (CABS) and robust/non-robust DF (DF-3) to approximate 3-electron integrals for increasing auxiliary basis set size. Auxiliary basis sets were MP2FIT basis sets optimized for the def2 family of AO basis sets. AO basis set was def2-tzvpp for all calculations.

- $E_{\text{Corr}}(\text{DF-MP2}) = -488.50$  millihartree
- $E_{\text{Corr}}(\text{FEM-MP2}) = -599.32$  millihartree [1]