

# A new approach to density-fitting in explicitly-correlated electronic structure theories



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Can we use **density-fitted orbital pairs** to devise a **competitive** explicitly-correlated electronic structure method, without using **resolutions of the identity**?

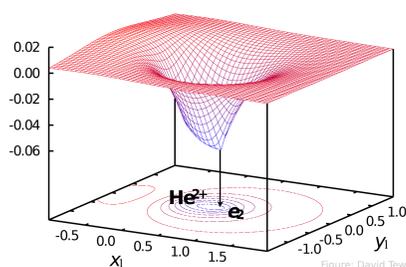
## Explicitly-correlated methods

### The basis-set convergence problem for conventional methods

- Slow convergence in the electron correlation energy with basis set size.
- The error in the electron correlation energy in cc-pVXZ basis sets:
 
$$\varepsilon = \mathcal{O}(X^{-3})$$
- Number of basis functions  $m = \mathcal{O}(X^3)$ , computer time  $t = \mathcal{O}(m^4)$ , computational cost:
 
$$\varepsilon = \mathcal{O}(t^{-1/4})$$
- Reducing the error by a factor of 10 requires a 10,000-fold increase in computational work.

### The Coulomb hole

- The slow convergence is due to poor reproduction of the Coulomb hole (where interelectronic distance,  $r_{12}$ , approaches zero) by conventional wavefunctions.
- These wavefunctions are built from nucleus-centred 1-electron basis functions and a large basis-set expansion is necessary to fit the electron-centred Coulomb hole.



- 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 basis set convergence [1].

### The many-electron integral problem

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

$$\langle ij|f_{12}f_{23}|mlk\rangle \equiv \langle im|f_{12}|j|f_{23}|mk\rangle$$

- These are numerous and complicated to evaluate.
- Calculations on systems larger than a few atoms require approximation of these integrals.
- A variety of strategies for dealing with these integrals have been tried (see ref. [1]).
- The resolution of the identity approach of Kutzelnigg and Klopper [2] (as used in modern R12 and F12 methods) remains the only practical approach for larger systems.

### R12 and F12 methods

Originally proposed by Kutzelnigg in 1985 [3], R12 and F12 methods are characterised by:

- The augmentation of the conventional first-order wavefunction with a small set of explicitly-correlated configurations, depending on the correlation factor,  $f_{12}$ .
- The use of resolutions of the identity to approximate the many-electron integrals arising from this augmentation.

### MP2-R12/F12 methods:

- First-order pair functions are expanded in a basis of 2-electron basis functions,  $\chi_{ij}(1,2) = Q_{12}f_{12}|ij\rangle$ , as well as conventional 1-electron orbital-products.
- Introduction of these 2-electron basis functions into the equations of MP2 theory results in the need to evaluate 3- and 4-electron integrals.

## Resolutions of the identity

R12 and F12 methods avoid 3- or more electron integrals by insertion of an approximation to the identity,  $1 \approx \sum_p |p\rangle\langle p|$ , e.g.

$$\langle ij|f_{12}f_{23}|mlk\rangle \approx \sum_p \langle ij|f_{12}|mp\rangle \langle mp|f_{12}|kl\rangle$$

1 × 3-electron integral → 2 × 2-electron integral

- $\hat{O}(N^6)$  scaling for approximation of the above 3-electron integral.
- Functions with  $3l_{occ}$  needed to saturate the RI basis [4].

## Density-fitted orbital pairs

The product of two 1-centre, 1-electron orbitals can be approximated as a sum of 1-center densities [5], e.g.

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

This suggests an alternative strategy for approximating many-electron integrals [4].

$$\langle im|f_{12}|j|f_{23}|mk\rangle \approx \sum_{A,B,C} D_A^{im} D_B^{jl} D_C^{mk} \langle A|f_{12}|B\rangle \langle B|f_{23}|C\rangle$$

3-electron, 6-index integral → 3-electron, 3-index integrals

- $\hat{O}(N^5)$  scaling for approximation of robust-fitted 3-electron integrals.
- Functions with  $2l_{occ}$  needed to saturate the DF basis [4].

## Robust-fitted 3-electron integrals

We find the DF coefficients,  $D_A^{ab}$ , by minimizing the error in the fitting procedure, as measured by the Coulomb energy of the fitting residual,  $|ab - \tilde{ab}\rangle$  [5]:

$$\Delta_{ab} = \langle ab - \tilde{ab}|r_{12}^{-1}|ab - \tilde{ab}\rangle.$$

The error in  $\langle \tilde{ab}|\tilde{cd}|\tilde{ef}\rangle$  is linear in the error in fitting,  $\Delta_{ij}$ .

$$\langle ab|cd|ef\rangle - \langle \tilde{ab}|\tilde{cd}|\tilde{ef}\rangle = \langle ab - \tilde{ab}|cd - \tilde{cd}|ef - \tilde{ef}\rangle + \langle ab - \tilde{ab}|\tilde{cd}|ef\rangle + \langle \tilde{ab}|\tilde{cd}|ef - \tilde{ef}\rangle + \langle ab|cd - \tilde{cd}|\tilde{ef}\rangle$$

To overcome this problem, we use the robust fitted [5, 6] form of the integral :

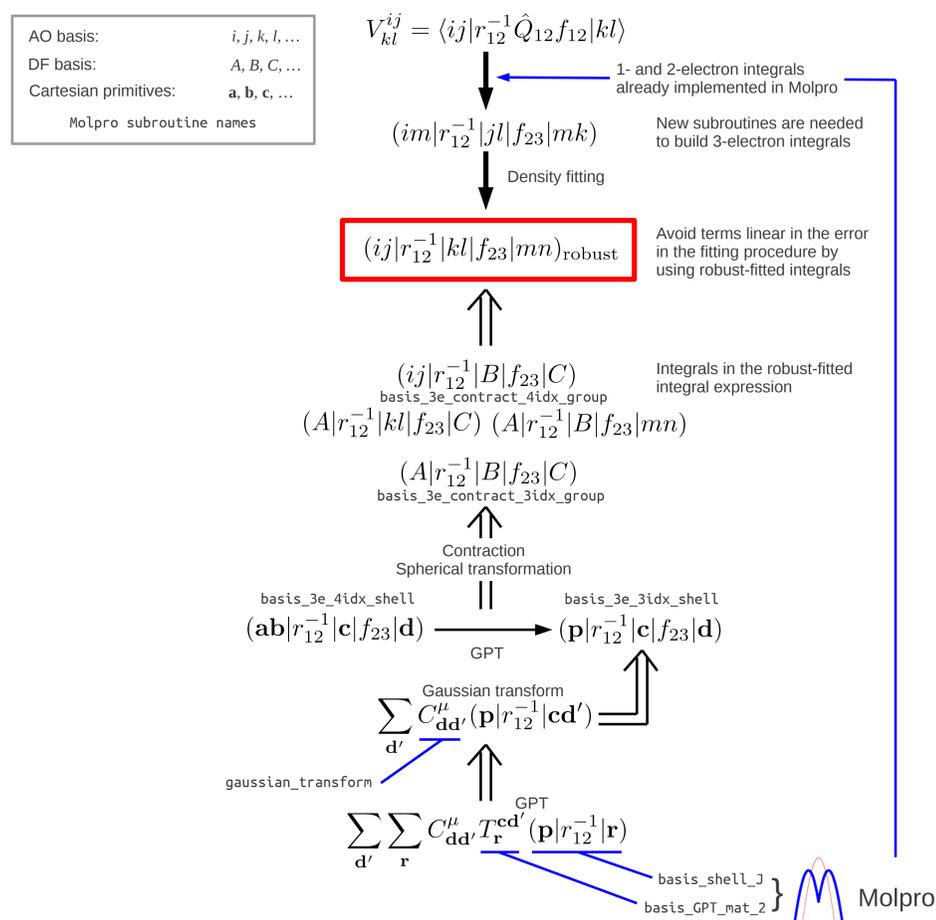
$$\langle ab|cd|ef\rangle_{\text{robust}} = \langle ab|\tilde{cd}|\tilde{ef}\rangle + \langle \tilde{ab}|\tilde{cd}|ef\rangle + \langle \tilde{ab}|\tilde{cd}|\tilde{ef}\rangle - 2\langle \tilde{ab}|\tilde{cd}|\tilde{ef}\rangle$$

The resulting error in the integral  $\langle ab|cd|ef\rangle_{\text{robust}}$  has no linear terms in  $\Delta_{ij}$ :

$$\langle ab|cd|ef\rangle - \langle ab|cd|ef\rangle_{\text{robust}} = \langle ab - \tilde{ab}|cd - \tilde{cd}|ef - \tilde{ef}\rangle + \langle ab - \tilde{ab}|cd - \tilde{cd}|\tilde{ef}\rangle + \langle \tilde{ab}|\tilde{cd} - \tilde{cd}|ef - \tilde{ef}\rangle + \langle ab - \tilde{ab}|\tilde{cd}|ef - \tilde{ef}\rangle.$$

## Integral retrosynthesis

The generation of one class of 3-electron integrals arising in MP2-F12/3\*A theory:



### Gaussian product theory (GPT):

$$g(\vec{r}_1; \alpha, \vec{A}, \mathbf{a})g(\vec{r}_1; \beta, \vec{B}, \mathbf{b}) = \sum_{\mathbf{p}} T_{\mathbf{p}}^{\alpha\beta} g(\vec{r}_1; \zeta, \vec{P}, \mathbf{p})$$

### Gaussian transform of a Cartesian Gaussian:

$$\int d\vec{r}_2 g(\vec{r}_2; \mu, \vec{r}_1, \mathbf{0})g(\vec{r}_2; \alpha, \vec{A}, \mathbf{a}) = \sum_{\mathbf{a}'} C_{\mathbf{a}\mathbf{a}'}^{\mu} g(\vec{r}_1; \xi, \vec{A}, \mathbf{a}')$$

### MP2-F12/3\*A:

"3\*A" describes the set of approximations used in deriving the integrals required. We also use the diagonal approximation. See ref. [7] for details.

## References

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