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-pV\(X\)Z basis sets:
    \[ \varepsilon = C(X^{-2}) \]
  - Number of basis functions \(m = C(X^3)\), computer time \(\varepsilon = C(m^3)\), computational cost:
    \[ \varepsilon = C(X^{-1/2}) \]
  - 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, \(r_{ij}\), 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 \(r_{ij}\).
- 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**
  - 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:
      1. The augmentation of the conventional first-order wavefunction with a small set of explicitly-correlated configurations, depending on the correlation factor, \(f_{12}\).
      2. The use of resolutions of the identity to approximate the many-electron integrals arising from this augmentation.

### MP2-12/R12/F12 methods:

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

- First-order pair functions are expanded in a basis of 2-electron basis functions, \(\chi_{abc} = \hat{Q}(\mathbf{r}_{ab}; \mathbf{r}_{bc})\), 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.

### Robustly fitted 3-electron integrals

We find the DF coefficients, \(\Delta_{\alpha\beta}\), by minimizing the error in the fitting procedure, as measured by the Coulomb energy of the fitting residual, \((\omega - \omega_\alpha)\) [5].

\[ \Delta_{\alpha\beta} = (\omega - \omega_{\alpha\beta})^2 \]

The error in \(\Delta_{\alpha\beta}\) is linear in the error in fitting, \(\Delta_{\beta\gamma}\) [5, 6].

\[ \Delta_{\alpha\beta} = (\omega - \omega_{\alpha\beta}) (\Delta_{\alpha\beta} - \Delta_{\beta\gamma}) \]

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

\[ \Delta_{\alpha\beta} = (\omega - \omega_{\alpha\beta}) \left( \Delta_{\alpha\beta} + \Delta_{\beta\gamma} \right) - 2 \Delta_{\beta\gamma} \]

The resulting error in the integral \((\omega - \omega_{\alpha\beta})\) has no linear terms in \(\Delta_{\beta\gamma}\):

\[ (\omega - \omega_{\alpha\beta}) = (\omega - \omega_{\alpha\beta}) \left( \Delta_{\alpha\beta} + \Delta_{\beta\gamma} \right) - 2 \Delta_{\beta\gamma} \]

### Integral retro synthesis

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

- 3-electron, 6-index integral \(3\epsilon_{ijklm}(\mathbf{r}_{ij}, \mathbf{r}_{jk}, \mathbf{r}_{km})\) is needed to saturate the RI basis [4].

### Density-fitted orbital pairs

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

\[ \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) \approx \langle \mathbf{r} | \mathbf{r} \rangle = \sum_{k} D_k(\mathbf{r}) \]

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

\[ (\omega_{ijlm}) = \sum_{k} D_k(\mathbf{r}) \]

3-electron, 6-index integral \(3\epsilon_{ijklm}(\mathbf{r}_{ij}, \mathbf{r}_{jk}, \mathbf{r}_{km})\) is needed to saturate the DF basis [4].

### References