

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

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

**Conventional methods:**  $|\Psi\rangle = \sum_i c_i |\Phi_i\rangle$

- Poor at reproducing the Coulomb hole.
- Correlation energy converges slowly wrt number of AOs.

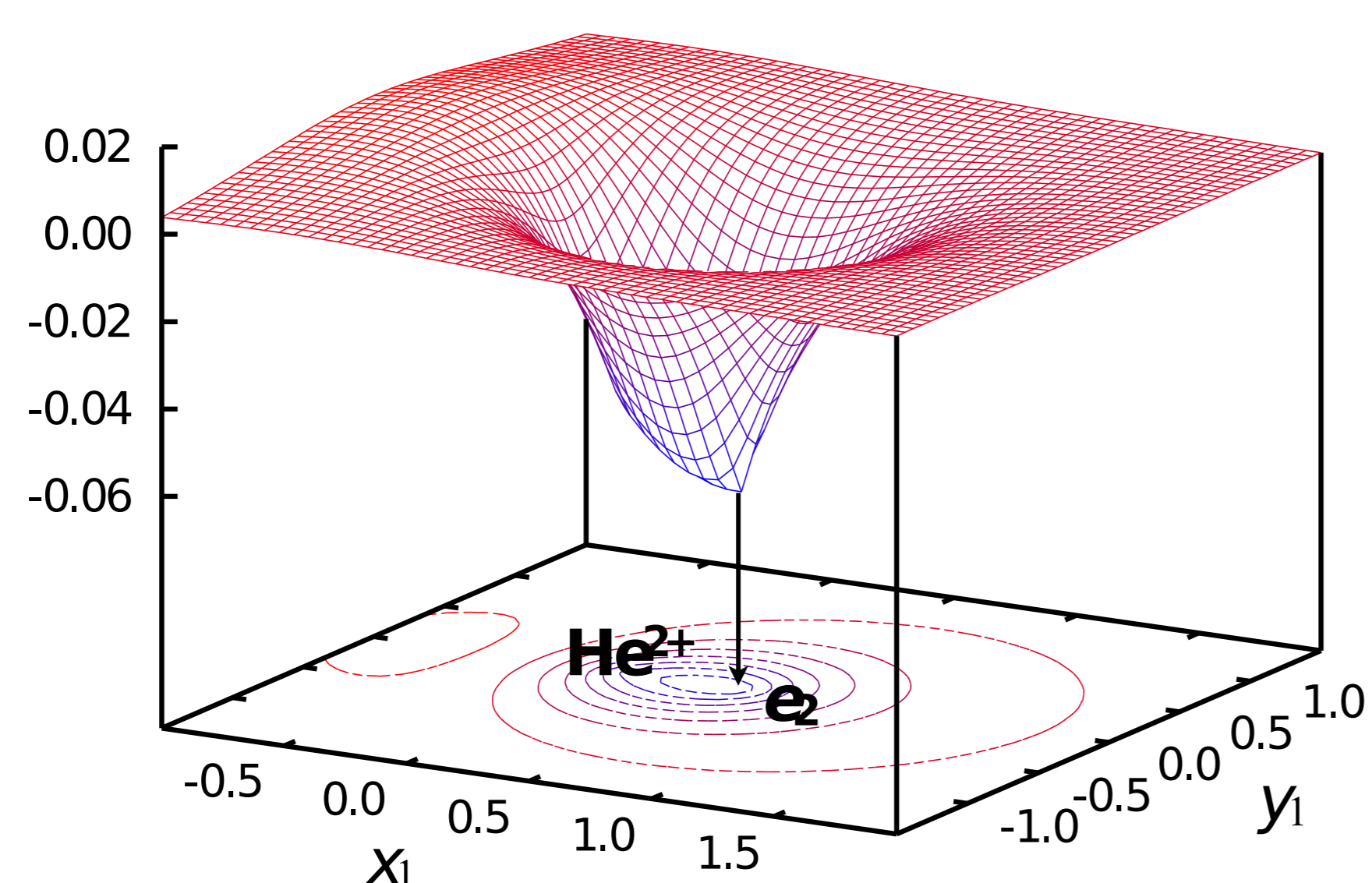
$$t = \hat{O}(m^4) \quad \varepsilon = \hat{O}(m^{-1}) = \hat{O}(t^{-1/4})$$

**Explicitly correlated methods:** [1]

- $|\Psi\rangle$  depends on  $r_{12}$  explicitly.
- Introduce electron-centred basis functions.
- Better fit of Coulomb hole. Faster convergence.
- Many-electron integrals arise, e.g.

$$\langle ijm|f_{12}f_{23}|mlk\rangle \equiv (im|f_{12}|jl|f_{23}|mk)$$

The Coulomb hole



[Figure: David Tew]

## Resolutions of the identity

- Forms the basis of R12 and F12 methods [2, 3].
- A way to approximate many-electron integrals, e.g.

$$\mathbf{1} = \sum_p |p\rangle\langle p|$$

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

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

- **Problem:** Need functions with  $3l_{occ}$  [4].
- Expense is  $\hat{O}(N^6)$  [4].

## Density-fitted orbital pairs

- An alternative strategy for approximating many-electron integrals [4,5].

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

$$(im|f_{12}|jk|f_{23}|ml) \approx \sum_{A,B,C} D_A^{im} D_B^{jk} D_C^{ml} (A|f_{12}|B|f_{23}|C)$$

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

- **Advantages:** Only  $2l_{occ}$  required, expense is  $\hat{O}(N^5)$  [4].

## Robust-fitted 3-electron integrals

- Error in the fitting procedure [5]:

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

- Error in  $(\tilde{ab}|\tilde{cd}|\tilde{ef})$  is linear in the error in  $\Delta_{ij}$ .
- Robust fitted form has no linear terms in  $\Delta_{ij}$ :

$$(ab|cd|ef)_{\text{robust}} = (ab|\tilde{cd}|\tilde{ef}) + (\tilde{ab}|cd|\tilde{ef}) + (\tilde{ab}|\tilde{cd}|ef) - 2(\tilde{ab}|\tilde{cd}|\tilde{ef})$$

- Error in the integral  $(ab|cd|ef)_{\text{robust}}$ :

$$\begin{aligned} & (ab|cd|ef) - (ab|cd|ef)_{\text{robust}} \\ &= (ab - \tilde{ab}|cd - \tilde{cd}|ef - \tilde{ef}) + (ab - \tilde{ab}|cd - \tilde{cd}|\tilde{ef}) \\ &+ (\tilde{ab}|cd - \tilde{cd}|ef - \tilde{ef}) + (ab - \tilde{ab}|\tilde{cd}|ef - \tilde{ef}). \end{aligned}$$

## Integral retrosynthesis

$$V_{kl}^{ij} = \langle ij|r_{12}^{-1}\hat{Q}_{12}f_{12}|kl\rangle = \sum_m (im|r_{12}^{-1}|jl|f_{23}|mk)$$

↑

General integral form:  $(ij|r_{12}^{-1}|kl|f_{23}|mn)_{\text{robust}}$

↑

Integrals over DF and MO bases:

$$\begin{aligned} & (ij|r_{12}^{-1}|B|f_{23}|C) \quad (A|r_{12}^{-1}|kl|f_{23}|C) \\ & (A|r_{12}^{-1}|B|f_{23}|mn) \quad (A|r_{12}^{-1}|B|f_{23}|C) \end{aligned}$$

$$(ij|r_{12}^{-1}|B|f_{23}|C)$$

↑

Integral over primitives:  $(\mathbf{ab}|r_{12}^{-1}|\mathbf{c}|f_{23}|\mathbf{d})$

↑

3-index integral over primitives:  $(\mathbf{p}|r_{12}^{-1}|\mathbf{c}|f_{23}|\mathbf{d})$

↑

$$(\mathbf{p}|r_{12}^{-1}|\mathbf{c}|g_{23}^{\mu}|\mathbf{d}) = \sum_{\mathbf{d}'} C_{\mathbf{d}\mathbf{d}'}^{\mu} (\mathbf{p}|r_{12}^{-1}|\mathbf{c}\mathbf{d}') = \sum_{\mathbf{d}'} \sum_{\mathbf{r}} C_{\mathbf{d}\mathbf{d}'}^{\mu} T_{\mathbf{r}}^{\mathbf{c}\mathbf{d}'} (\mathbf{p}|r_{12}^{-1}|\mathbf{r})$$

## References

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4. Manby, F.R. Explicitly correlated electronic structure theory. Solving the Schrodinger equation: has everything been tried? (2011), ed. Paul Popelier, Imperial College Press.
5. Manby, F.R., J. Chem. Phys. 119, 4607 (2003).