

A new method of approximating many-electron integrals in explicitly-correlated methods

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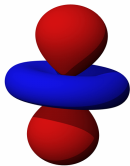
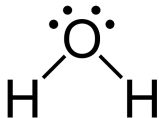


31 October 2012

Tricky electrons

Chemistry is fundamentally about the behaviour of electrons

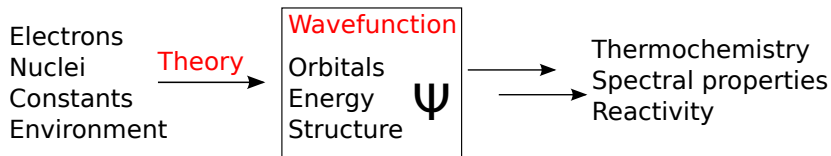
e.g. reaction, bonding, structure, catalysis



$$H\Psi = E\Psi$$

- ▶ 1-electron: can be exactly modelled, e.g. H, He⁺, H₂⁺.
- ▶ > 1-electron: approximations required, e.g. He, H₂O, glycine.
- ▶ Molecular electronic structure - **a many body problem.**

Quantum chemistry



$$\text{Solve } \hat{H}\Psi(\vec{r}_1, \dots, \vec{r}_N) = E\Psi(\vec{r}_1, \dots, \vec{r}_N) \text{ for } E$$

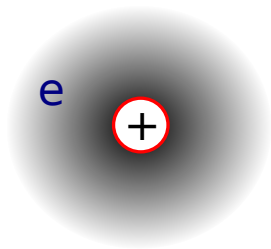
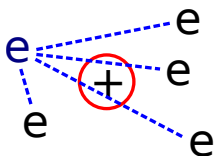
Practical calculations require approximations to $\Psi(\vec{r}_1, \dots, \vec{r}_N)$

- ▶ Theoretical method development:
 - ▶ Improve speed and accuracy of calculations.
 - ▶ Model new systems and situations.
 - ▶ Practicality vs. accuracy compromise.

Quantum chemistry

Hartree-Fock theory:

- ▶ Each electron sees an average field of all other electrons.
- ▶ N -body problem $\rightarrow N$ 1-body problems.
- ▶ Obtain an approximate wavefunction, Φ .
- ▶ Φ is constructed from m 1-electron functions, $\phi(\vec{r})$.
- ▶ Able to account for $\sim 99\%$ of E_{exact} .

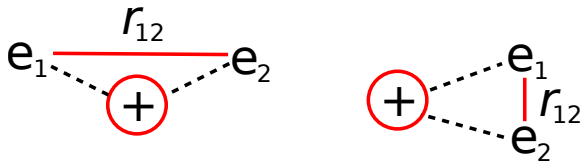


BUT some electron-electron interaction is neglected.

Electron correlation

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

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



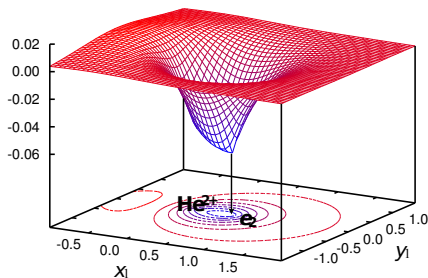
- ▶ Electron correlation is important to describe chemistry!
 - ▶ Bond dissociation
 - ▶ Dispersion interactions

e.g. E_{CORR} for H_2 is $\sim -100 \text{ kJ mol}^{-1}$.

Coulomb hole

The manifestation of electron correlation in the wavefunction.

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



[Figure: David Tew]

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

Convergence problem

Conventional wavefunction-based methods:

- ▶ Build upon HF, reintroducing some correlation.
- ▶ More complicated wavefunction constructed from nucleus-centred, 1-electron basis functions.
- ▶ Computational cost increases with basis set size, m .
- ▶ Poor scaling of ε , error in E_{corr} , wrt m .

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

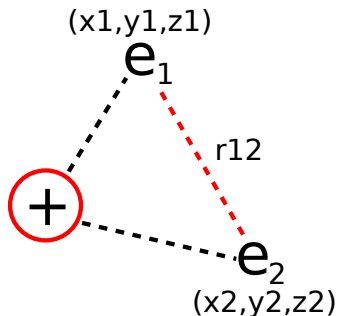
- ▶ Reducing the error by a factor of 10 requires a 10,000-fold increase in computational work.

Poor at fitting the Coulomb hole.

Convergence problem

Explicitly correlated methods:

- ▶ 2-electron basis functions with explicit dependence on r_{12} .
- ▶ Improved scaling of ε , error in E_{CORR} , wrt m , basis set size.
- ▶ More accurate E_{CORR} with fewer basis functions.



Better at fitting the Coulomb hole.

BUT: Complicated “many-electron” integrals arise.

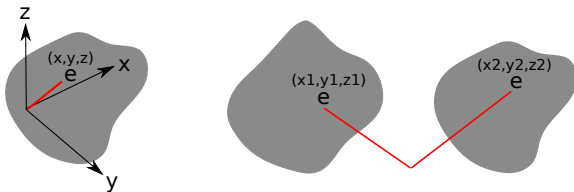
Tricky integrals

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

$$\langle i|j\rangle = \int d\vec{r} \phi_i^*(\vec{r})\phi_j(\vec{r})$$

$$\langle ij|r_{12}^{-1}|kl\rangle = \int d\vec{r}_1 d\vec{r}_2 \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)r_{12}^{-1}\phi_k(\vec{r}_1)\phi_l(\vec{r}_2)$$

- ▶ There are efficient methods for evaluating these.

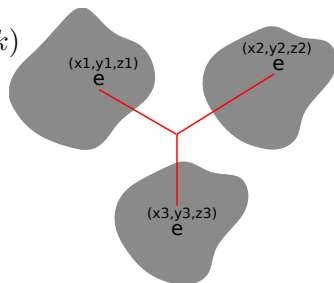


Tricky integrals

Many-electron integrals arise in explicitly-correlated methods.

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

- ▶ Numerous and complicated to evaluate.
- ▶ Practical calculations require approximations to these.



Approximating integrals

Current state of the art: Resolutions of the identity

- ▶ Currently the only practical approach for larger systems.
- ▶ Used in R12 and F12 methods.

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

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

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

Problem: A good approximation requires a large RI basis.

... Can we do better?

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

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

Approximating integrals

An alternative method: Density-fitted orbital pairs

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

$$(im|r_{12}^{-1}|jklf_{23}|ml) \approx \sum_{A,B,C} D_A^{im} D_B^{jk} D_C^{ml} (A|r_{12}^{-1}|B|f_{23}|C)$$

3-electron, 6-index integral \rightarrow sum over 3-electron, 3-index integrals

Advantage: Smaller fitting basis required for good approximation.

... Still need the fitted 3-electron integrals.

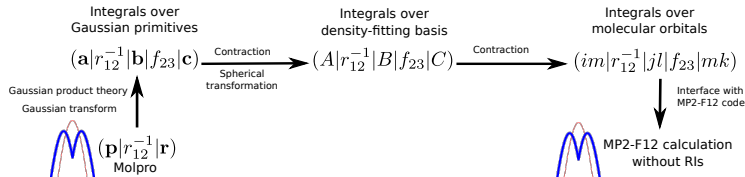
Manby, F.R. Explicitly correlated electronic structure theory. In *Solving the Schrodinger equation: has everything been tried?* (2011), ed. Paul Popelier, Imperial College Press.

Plan

- ▶ Derive many-electron integrals **without RIs** (MP2-F12/3*A).
- ▶ Derive approximate density-fitted forms of integrals.
- ▶ Write code for new many-electron integrals in **Molpro**.
- ▶ Interface with pre-existing MP2-F12 code in **Molpro**.
- ▶ Substitute our integrals into existing MP2-F12 code.
- ▶ Run test calculations to compare approximation methods.

Generating integrals

Multiple steps involved:



Must test for consistency at each step:

- ▶ No pre-existing integrals of this type to test against.
- ▶ Alternative tests must be devised!

e.g. use integrals that *are* available in Molpro:

$$\lim_{\mu \rightarrow \infty} \left(\frac{\mu}{\pi}\right)^{1/2} (\mathbf{a}|r_{12}^{-1}|\mathbf{b}|e^{-\mu r_{23}^2}|\mathbf{c}) = (\mathbf{a}|r_{12}^{-1}|\mathbf{bc})$$

Coming soon...

- ▶ **Imminent:** comparison of our approximate integrals with those generated using RIs.
- ▶ **Near future:** MP2-F12 calculations without RIs.
 - ▶ Calculations on molecular systems.
 - ▶ Quantitative comparisons of accuracy, efficiency.

Will the theoretical advantages of our integral approximation scheme translate into practical improvements?

Summary

- ▶ Accurate theoretical models account for electron correlation.
- ▶ Explicitly-correlated methods account for electron correlation efficiently but introduce many-electron integrals.
- ▶ Many-electron integrals must be approximated.
- ▶ RI is currently the only practical approximation scheme.
 - ▶ **Problem:** Requires a large RI basis set.
- ▶ We propose an alternative integral approximation scheme.
 - ▶ **Advantage:** Comparatively smaller DF basis set.
- ▶ We are close to having a full implementation of our new approximation scheme in Molpro.

Acknowledgements

I would like to thank the following people and organizations:

- ▶ Prof Fred Manby
- ▶ Colleagues at the Centre for Computational Chemistry.
- ▶ SCI College of Scholars
- ▶ EPSRC
- ▶ University of Bristol



Appendix

Why do we need theory / simulation?

- ▶ Elimination of the unprofitable or irrelevant.
 - ▶ e.g. virtual screening of drug candidates.
- ▶ Some systems inaccessible to experiment.
 - ▶ e.g. astrochemistry, radioactive decay.
- ▶ Mechanistic insight and understanding.
 - ▶ e.g. enzyme reactions, atmospheric chemistry.
- ▶ Facilitates rational design.
 - ▶ e.g. drug design, catalyst design.

Appendix

Current widely used method: **resolution of the identity (RI)** [1]

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

$$\mathcal{O}(N^6), 3l_{\text{occ}} [2]$$

Alternative method: **density fitted orbital pairs** [3]

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

$$\mathcal{O}(N^5), 2l_{\text{occ}} [2]$$

[1] Kutzelnigg, W. & Klopper, W., J. Chem. Phys. 94, 1985 (1991).

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

[3] Manby, F.R., J. Chem. Phys. 119, 4607 (2003).