Correlated electrons and complicated integrals

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Chemistry is fundamentally about the behaviour of electrons
e.g. reaction, bonding, structure, catalysis

Atoms and molecules - lots of electrons.
Negatively charged electrons repel one another.
Molecular electronic structure - a many body problem.
Many-body problems

**Definition**

“the study of the effects of interactions between bodies on the behaviour of a many-body system”

Many non-interacting particles $\rightarrow$ many 1-body problems. **BUT** interactions are often important to describe properties.

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Hartree-Fock theory

- Each electron sees an average field of all other electrons.
- Approximate solution of the Schrödinger equation.
- Account for $\sim 99\%$ of $E_{\text{exact}}$.

**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

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

We want to find $\Psi$, but this is hard!

$$\hat{H} \psi(x_1, x_2, \ldots, x_N) = E \psi(x_1, x_2, \ldots, x_N)$$

Build approximate $\Psi$ from a **basis set** of simpler functions.

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Explicitly-correlated methods

- Build upon Hartree-Fock theory.
- Efficiently describe electron correlation.
- Introduce functions with explicit dependence on $r_{12}$.
- More accurate $E_{\text{corr}}$ with a smaller basis set.

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

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

There are efficient methods for computing these.

Many-electron (> 2) integrals in explicitly correlated methods are numerous and complicated to evaluate.

Approximations are required for practical calculations!
**Integral approximations**

### Resolutions of the identity (RIs)

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

\[
\langle ijm | r_{12}^{-1} F_{23} | mkl \rangle \approx \sum_p \langle ij | r_{12}^{-1} | mp \rangle \langle mp | F_{23} | kl \rangle
\]

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

**Problem:** A good approximation may require a large RI basis with unwieldy high-angular momentum functions.

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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.

\[
(\text{i}m|\text{r}_{12}^{-1}|\text{j}k|\text{F}_{23}|\text{m}l) \approx \sum_{A,B,C} D_{A}^{im} D_{B}^{jk} D_{C}^{ml} (A|\text{r}_{12}^{-1}|B|\text{F}_{23}|C)
\]

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

**Advantage:** A good approximation with a smaller DF basis.

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Vitamin B12 model, \([\text{Co(III)}(\text{NH}_3)_4\text{NH}_2\text{CH}_3]^+\), Patrick von Glehn.
CCSD vs CCSD-F12 reaction energy errors for a set of 50 test reactions.

Plot: Dr. David Tew, University of Bristol
Implementation

Aim

Perform explicitly-correlated (MP2-F12) calculations using density-fitting in the places of resolutions of the identity.

- Derivation of relevant integral forms.
- Development of computer software to generate integrals.
- Interface with existing MP2-F12 software in MOLPRO.
- Run test calculations to compare approximation methods.

MOLPRO, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others, see http://www.molpro.net.
MP2-F12/3*A(DX,FIX) energies calculated in MOLPRO. The RI was performed with an ABS.
Summary

- DF may be competitive with RIs for approximating many-electron integrals in MP2-F12 theory.
- Promising initial results:
  - Accurate integrals.
  - Fast convergence with basis set size.
- Proof-of-concept implementation in MOLPRO.

Further work

- A completely RI-free MP2-F12 calculation.
- Improve performance of software.
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