Correlated electrons and complicated integrals

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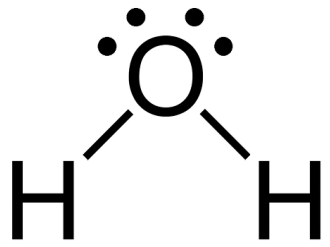
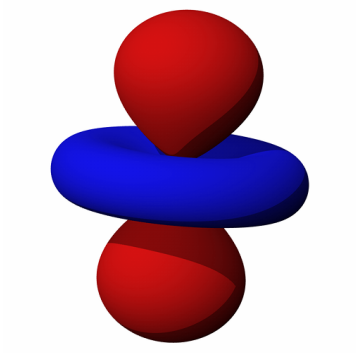
Tricky electrons

Chemistry is fundamentally about the behaviour of electrons

e.g. reaction, bonding, structure, catalysis





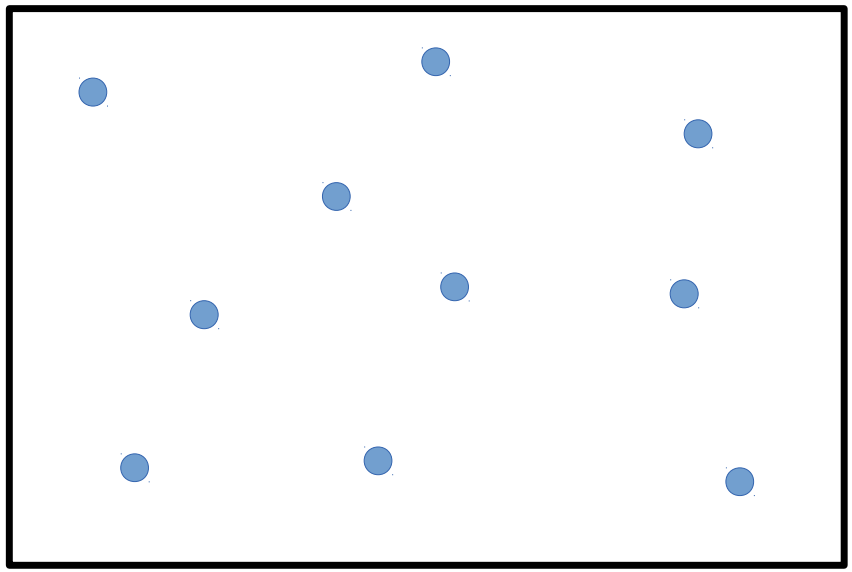
$$H\Psi = E\Psi$$

- 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"

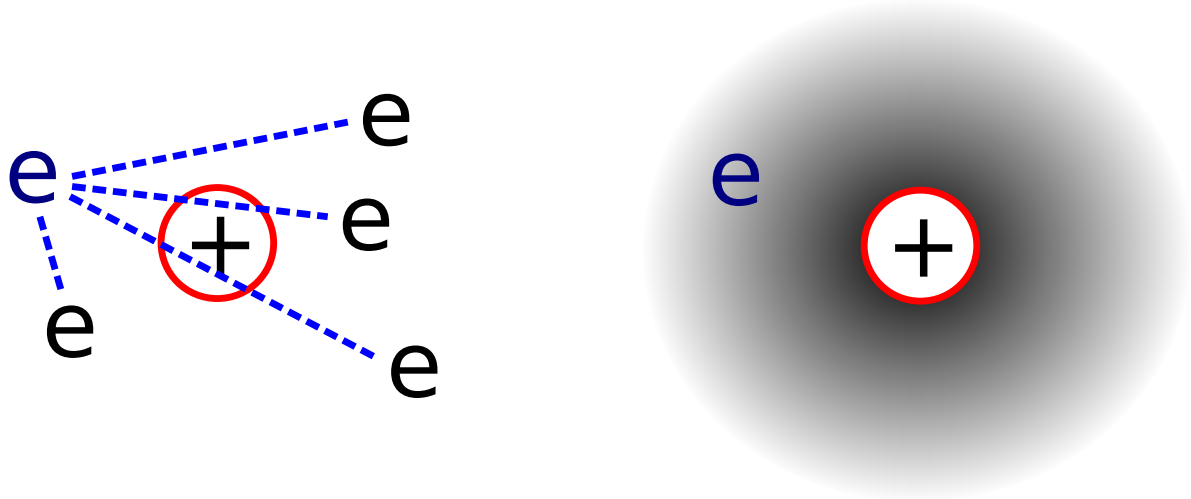


Many non-interacting particles $\rightarrow$ many 1-body problems.
BUT interactions are often important to describe properties.

Mattuck, R. D. A Guide to Feynman Diagrams in the Many-Body Problem. (Dover, 1992).

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_{exact}.



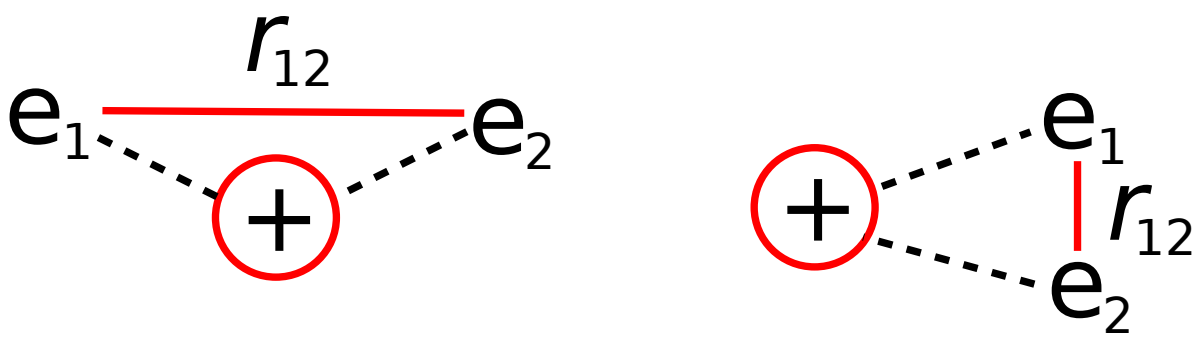
BUT some electron-electron interaction is neglected.

Jensen, F. Introduction to Computational Chemistry. (Wiley: 2007).

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

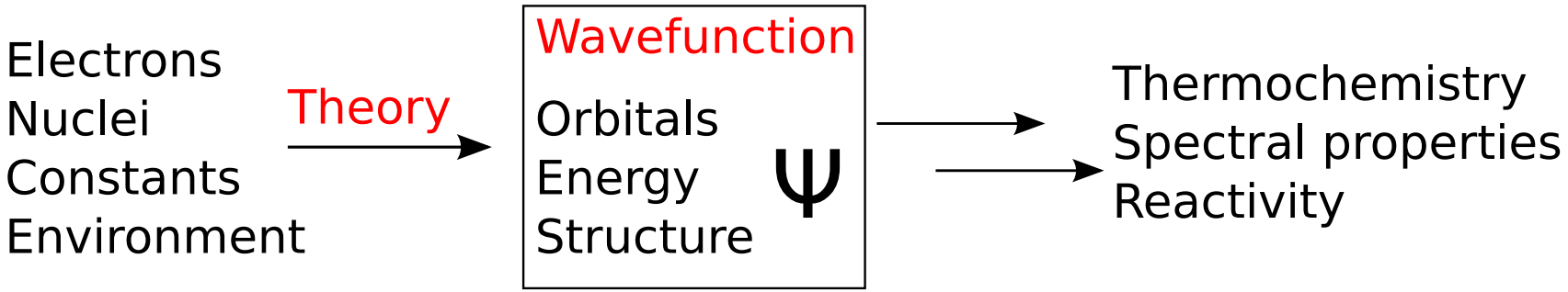
e.g. E_{corr} for H_2 is $\sim -100\,\text{kJ}\,\text{mol}^{-1}$.

Hättig, C., Klopper, W., Köhn, A. & Tew, D. P. Chem. Rev. 112, 4-74 (2011).

Approximate wavefunctions

Wavefunction

A mathematical object which fully describes the the state of a quantum mechanical system.



- We want to find Ψ, but this is hard!

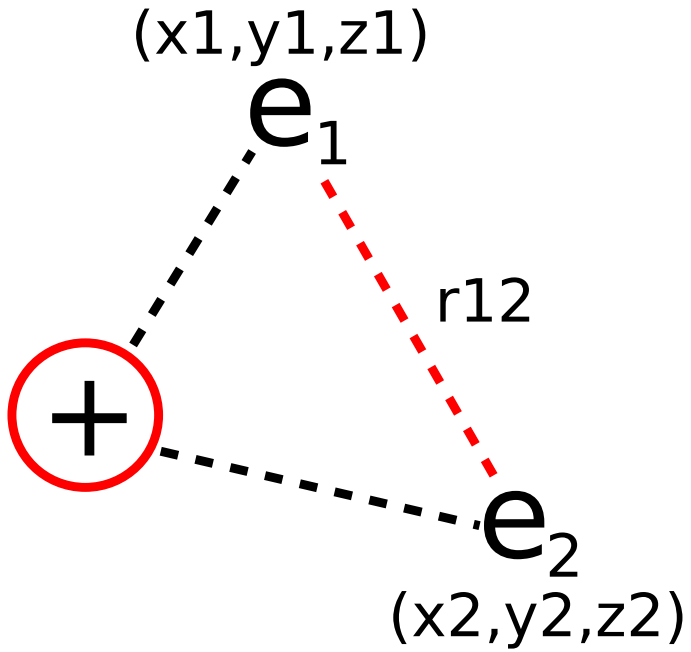
$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

- Build approximate Ψ from a **basis set** of simpler functions.

Atkins, P. Molecular Quantum Mechanics. (Oxford University Press, 1983), p.83.

Explicitly-correlated methods

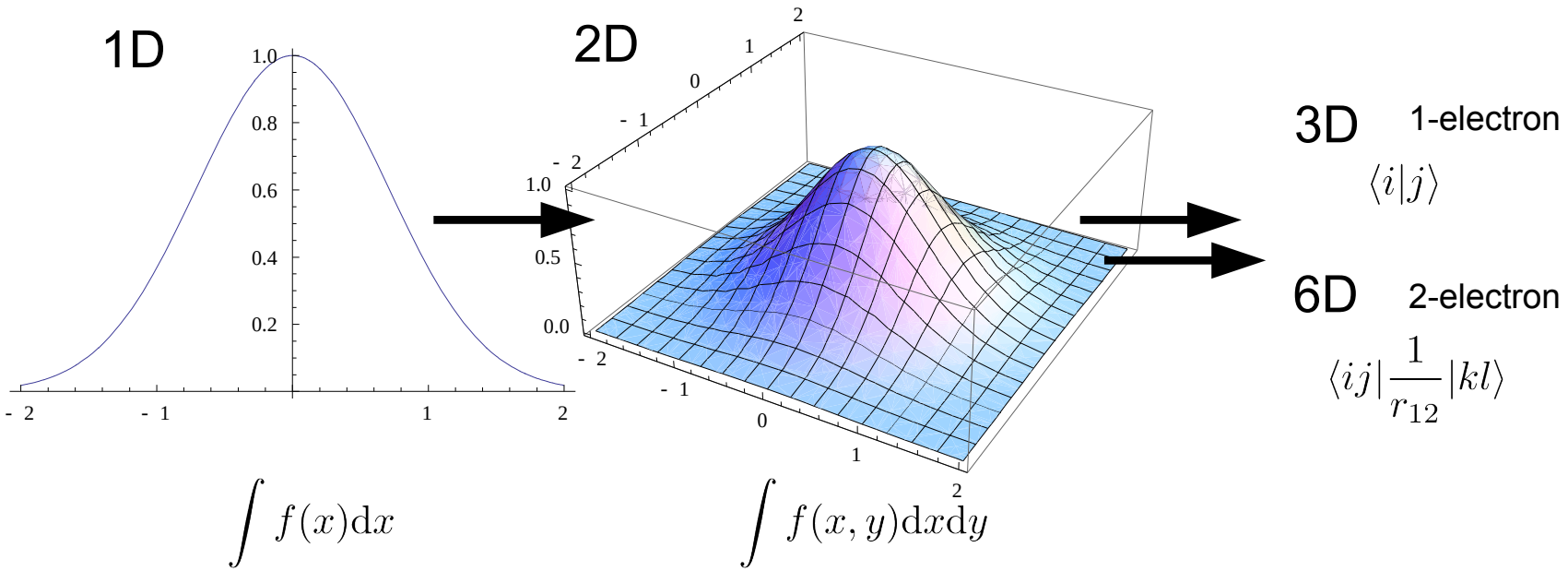
- Build upon Hartree-Fock theory.
- Efficiently describe electron correlation.
- Introduce functions with explicit dependence on r_{12}.
- More accurate E_{corr} with a smaller basis set.



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.

$$\langle ijm|r_{12}^{-1}F_{23}|mkl\rangle \approx \sum_{p}\langle ij|r_{12}^{-1}|mp\rangle\langle mp|F_{23}|kl\rangle$$

$1 \times$ 3-electron integral $\rightarrow$ sum over $2 \times$ 2-electron integral

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

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

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

Integral approximations

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.

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

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

Advantage: A good approximation with a smaller DF basis.

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

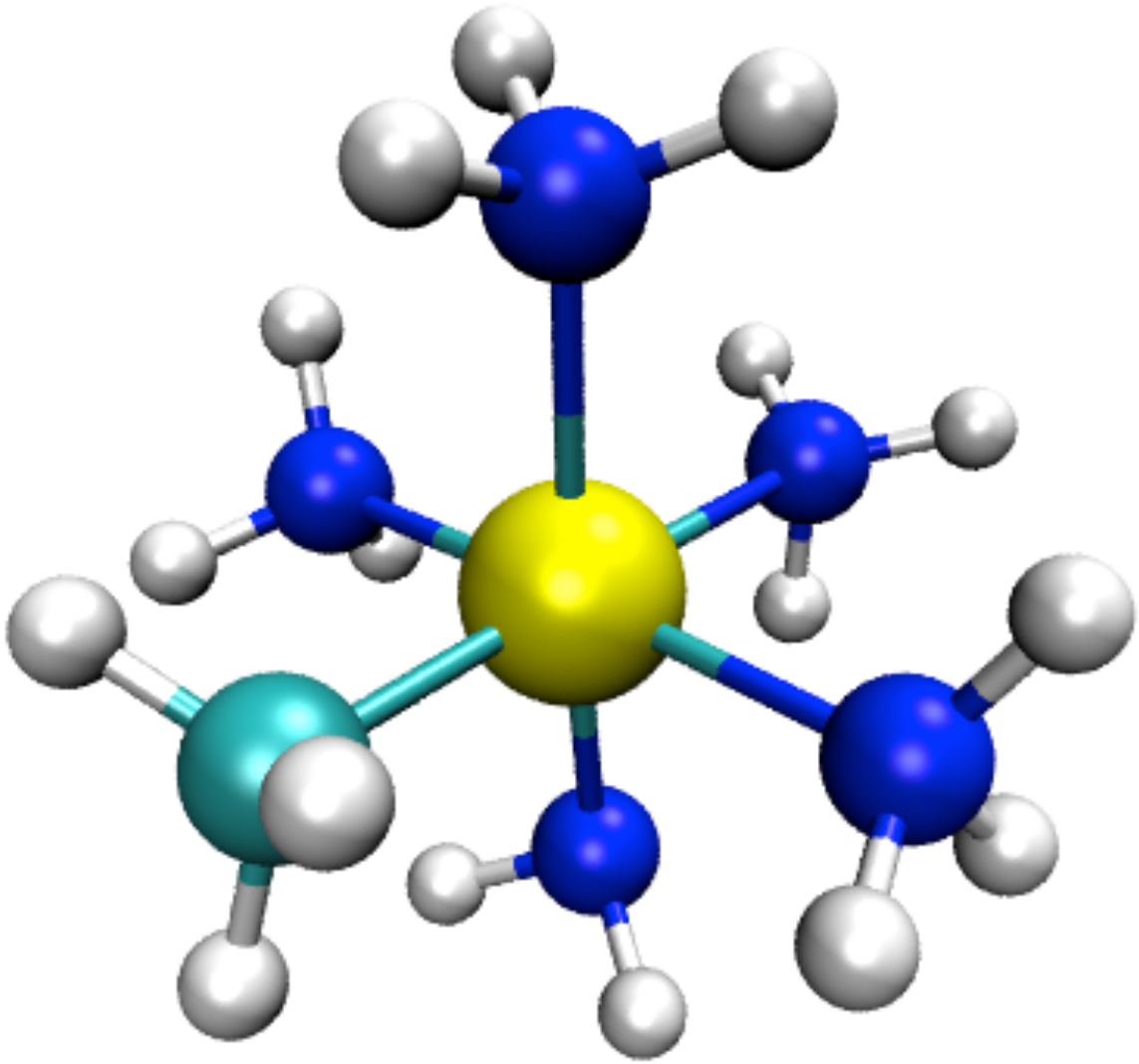
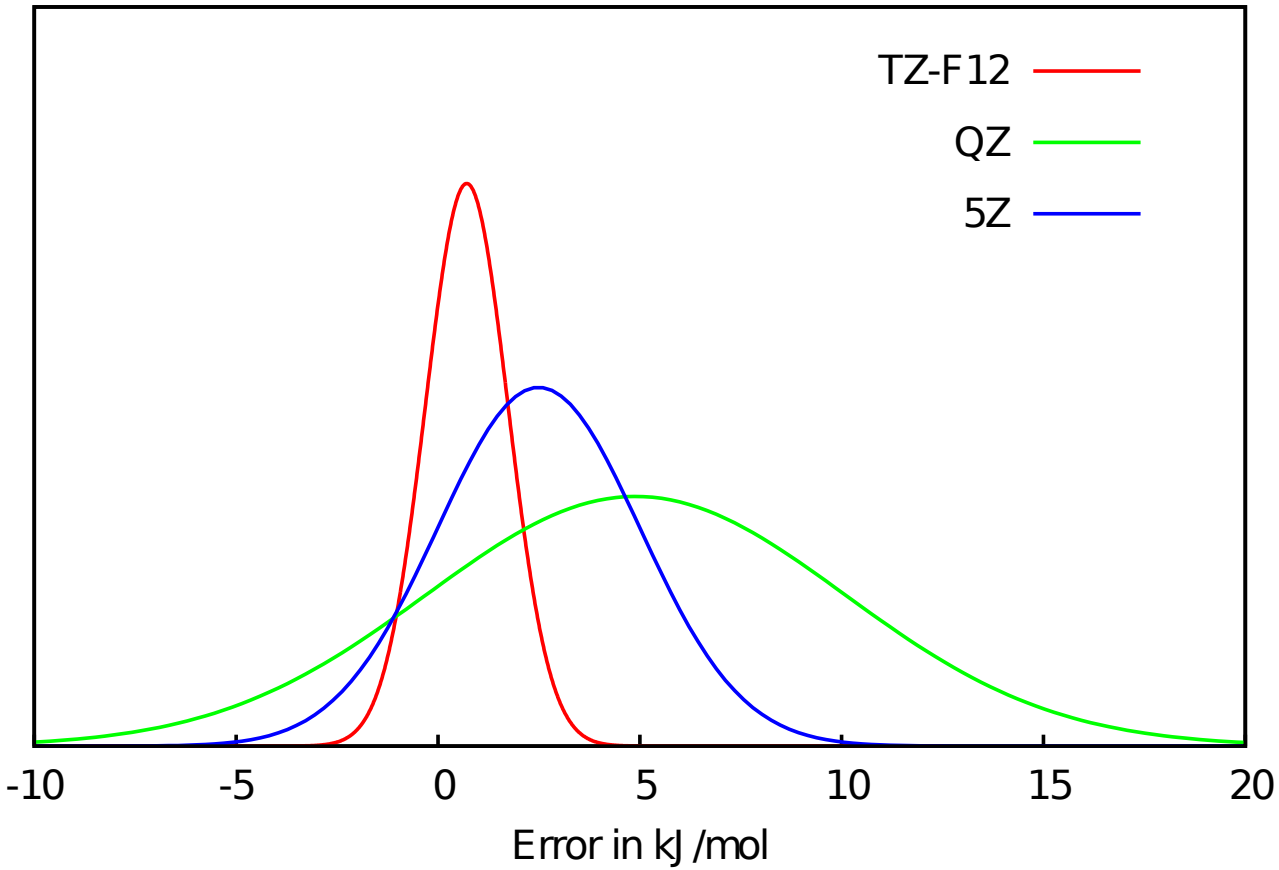


Image: Vitamin B12 model, $[Co(III)(NH_3)_4NH_2CH_3]^+$, Patrick von Glehn.

CCSD vs CCSD-F12 reaction energy errors for a set of 50 test reactions.



Plot: Dr. David Tew, University of Bristol

Implementation

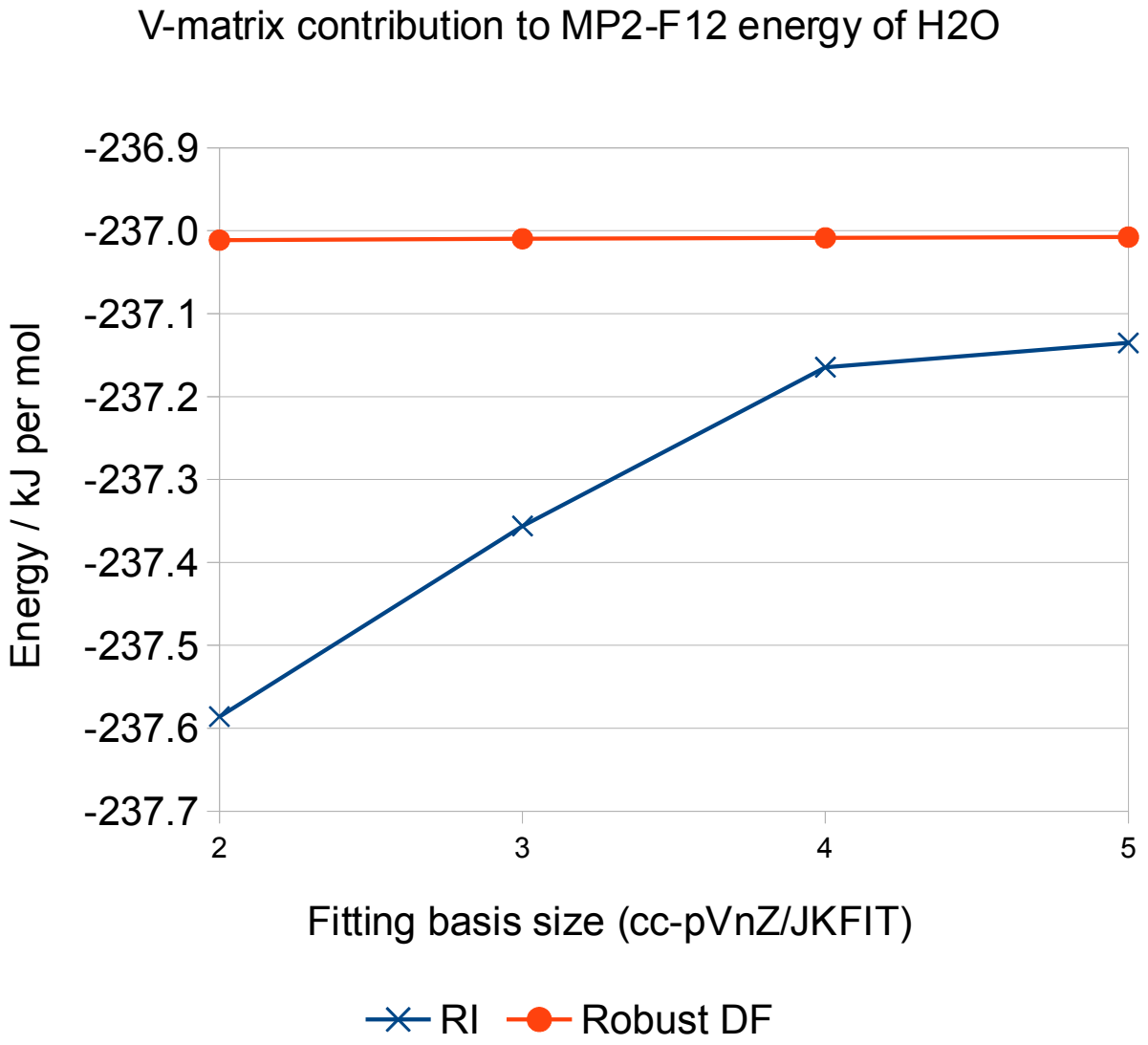
Aim

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.

Results



MP2-F12/3*A(DX,FIX) energies calculated in MOLPRO. The RI was performed with an ABS.

Summary + Further work

Summary

- DF may be competitive with RIs for approximating many-electron integrals in MP2-F12 theory.
- Promising intial 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.

Acknowledgements

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