# R12 methods: Approximations and performance assessment

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C$^4$ Tutorial, Zürich, 2–4 October 2006

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## The closed-shell CCSD-R12 Ansatz

- CCSD-R12 theory has been implemented in a spin-free closed-shell fashion as well as in a spin-orbital formalism.
- Here, we focus on the closed-shell CCSD-R12 method, where the cluster operator $\hat{T}$ is written as

$$\begin{aligned}\hat{T} &= \hat{T}_1 + \hat{T}_2 + \hat{T}_{2'} \\ \hat{T}_1 &= t_i^a E_{ai} \\ \hat{T}_2 &= t_{ij}^{ab} E_{ai} E_{bj} \\ \hat{T}_{2'} &= t_{ij}^{\alpha\beta} E_{\alpha i} E_{\beta j} = c_{ij}^{mn} r_{\alpha m \beta n} E_{\alpha i} E_{\beta j}\end{aligned}$$

- Summation over repeated indices is assumed (Einstein summation convention).
- The indices $\alpha$ and $\beta$ refer to a *complete basis* of virtuals.

## Correlation functions

- The two-electron integrals

$$r_{\alpha m \beta n} = \langle \alpha\beta | \hat{Q}_{12} f_{12} | mn \rangle$$

  contain the projection operator $\hat{Q}_{12}$ and the correlation function $f_{12}$, which is a function of the interelectronic distance $r_{12}$. Examples are:

$$\begin{aligned} f_{12} = f(r_{12}) &= r_{12} \\ f_{12} = f(r_{12}) &= \exp(-\gamma r_{12}) \\ f_{12} = f(r_{12}) &= c_k \exp(-\gamma_k r_{12}^2) \\ f_{12} = f(r_{12}) &= c_k r_{12} \exp(-\gamma_k r_{12}^2) \end{aligned}$$

- The form of the correlation function $f_{12}$ will only become important later.

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## Ansätze 1 and 2

- The projection operator $\hat{Q}_{12}$ can be chosen in two manners, which are referred to as Ansatz 1 and Ansatz 2,

$$\hat{Q}_{12} = \begin{cases} \hat{Q}_{12}^{(1)} = (1 - \hat{P}_1)(1 - \hat{P}_2) & \text{Ansatz 1} \\ \hat{Q}_{12}^{(2)} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2 & \text{Ansatz 2} \end{cases}$$

- The projectors are:

| | |
|---|---|
| $\hat{P} = \lvert\phi_p\rangle\langle\phi_p\rvert$ | is the projector onto the whole finite space |
| $\hat{V} = \lvert\phi_a\rangle\langle\phi_a\rvert$ | is the projector onto the virtual space |
| $\hat{O} = \lvert\phi_i\rangle\langle\phi_i\rvert$ | is the projector onto the occupied space |

# Ansätze 1 and 2 (continued)

- Within the complete basis $\{\phi_\alpha\}_{n_{\text{occ}}+1\ldots\infty}$ of virtual orbitals, there are virtual orbitals $\{\phi_a\}_{n_{\text{occ}}+1\ldots n_{\text{bas}}}$ inside the finite basis and virtual orbitals $\{\phi_{\alpha^\perp}\}_{n_{\text{bas}}+1\ldots\infty}$ outside the finite basis,

  $$\{\phi_\alpha\} = \{\phi_a\} \cup \{\phi_{\alpha^\perp}\}$$

  $$\begin{aligned}
  \hat{Q}_{12}^{(1)} \sum_{\alpha\beta} |\alpha\beta\rangle &= \sum_{\alpha^\perp\beta^\perp} |\alpha^\perp\beta^\perp\rangle \\
  \hat{Q}_{12}^{(2)} \sum_{\alpha\beta} |\alpha\beta\rangle &= \sum_{\alpha^\perp\beta^\perp} |\alpha^\perp\beta^\perp\rangle + \sum_{a\beta^\perp} |a\beta^\perp\rangle + \sum_{\alpha^\perp b} |\alpha^\perp b\rangle
  \end{aligned}$$

  Double excitations with one or two virtuals outside the finite space are generated in Ansatz 2, whereas Ansatz 1 is restricted to excitations with both virtuals in the orthogonal complement.

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# The CCSD-R12 energy

- The CCSD-R12 energy can be written as

  $$\begin{aligned}
  E_{\text{CCSD-R12}} &= E_{\text{HF}} + \tfrac{1}{2}\langle \text{HF}|[[\hat{H},\hat{T}_1],\hat{T}_1] + [\hat{H},\hat{T}_2] + [\hat{H},\hat{T}_{2'}]|\text{HF}\rangle \\
  &= E_{\text{CCSD}} + \Delta E_{\text{R12}}
  \end{aligned}$$

- Our task is to evaluate the R12 contribution

  $$\Delta E_{\text{R12}} = \tfrac{1}{2} c_{mn}^{ij} r_{\alpha m \beta n} \langle \text{HF}|[\hat{H}, E_{\alpha i} E_{\beta j}]|\text{HF}\rangle$$

  with the Hamiltonian

  $$\hat{H} = h_{\text{nuc}} + h_{\kappa\lambda} E_{\kappa\lambda} + \tfrac{1}{2} g_{\kappa\lambda\mu\nu}\, e_{\kappa\lambda\mu\nu}$$

  The Greek letters $\kappa, \lambda, \mu, \nu$ denote a complete basis.

- $\langle \text{HF}|[\hat{H}, E_{\alpha i} E_{\beta j}]|\text{HF}\rangle$ must be evaluated in the *complete Fock space*.

# The CCSD-R12 energy

- We know from standard CCSD theory that

$$\langle \mathrm{HF}|[\hat{H}, E_{ai}E_{bj}]|\mathrm{HF}\rangle = 2L_{iajb} = 4g_{iajb} - 2g_{ibja}$$

Hence, the R12 contribution is

$$\Delta E_{\mathrm{R12}} = c_{ij}^{mn} r_{\alpha m \beta n} L_{i\alpha j\beta}$$

- If we define the amplitudes $t_{ij}^{\alpha\beta} = c_{ij}^{mn} r_{\alpha m \beta n}$,
we can write the CCSD-R12 energy as

$$E_{\text{CCSD-R12}} = E_{\mathrm{HF}} + (t_{ij}^{ab} + t_i^a t_j^b)L_{iajb} + t_{ij}^{\alpha\beta} L_{i\alpha j\beta}$$

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# The CCSD-R12 singles projection

- In terms of the *T1-transformed Hamiltonian* $\tilde{\hat{H}}$, we find

$$\begin{aligned}
\Omega_{ai} &= \left\langle \begin{matrix}\bar{a}\\ i\end{matrix} \middle| \tilde{\hat{H}} + [\tilde{\hat{H}}, \hat{T}_2 + \hat{T}_{2'}] \middle| \mathrm{HF} \right\rangle = \Omega_{ai}^{\mathrm{CCSD}} + \Omega_{ai}^{\mathrm{R12}} \\
\Omega_{ai}^{\mathrm{R12}} &= \left\langle \begin{matrix}\bar{a}\\ i\end{matrix} \middle| [\tilde{\hat{H}}, \hat{T}_{2'}] \middle| \mathrm{HF} \right\rangle
\end{aligned}$$

| Term | CCSD part | Corresponding R12 contribution |
|---|---|---|
| $\Omega_{ai}^{\mathrm{A1}}$ | $u_{ki}^{cd}\tilde{g}_{adkc}$ | $u_{ki}^{\gamma\delta}\tilde{g}_{a\delta k\gamma} = (2c_{ki}^{mn} - c_{ik}^{mn})\, r_{\gamma m\delta n}\, \tilde{g}_{a\delta k\gamma}$ |
| $\Omega_{ai}^{\mathrm{B1}}$ | $-u_{kl}^{ac}\tilde{g}_{kilc}$ | $-u_{kl}^{a\gamma}\tilde{g}_{kil\gamma} = -(2c_{kl}^{mn} - c_{lk}^{mn})\, r_{am\gamma n}\, \tilde{g}_{kil\gamma}$ |
| $\Omega_{ai}^{\mathrm{C1}}$ | $u_{ik}^{ac}\, {}^{\mathrm{I}}\tilde{F}_{kc}$ | $u_{ik}^{a\gamma}\, {}^{\mathrm{I}}\tilde{F}_{k\gamma} = (2c_{ik}^{mn} - c_{ki}^{mn})\, r_{am\gamma n}\, {}^{\mathrm{I}}\tilde{F}_{k\gamma}$ |
| $\Omega_{ai}^{\mathrm{D1}}$ | ${}^{\mathrm{I}}\tilde{F}_{ai}$ | 0 |

# Recipe for deriving the CCSD-R12 equations

- Using a complete Fock space, the CCSD-R12 equations are easily derived by a *correspondence principle*. Virtual indices $ab$ in doubles amplitudes $t_{ij}^{ab}$ in the conventional formulation must be replaced by those of the complete basis $\alpha\beta$.
- Amplitudes $t_{ij}^{\alpha\beta}$, $t_{ij}^{a\beta}$, and $t_{ij}^{\alpha b}$ must be identified with $c_{ij}^{mn}\, r_{\alpha m\beta n}$, $c_{ij}^{mn}\, r_{am\beta n}$, and $c_{ij}^{mn}\, r_{\alpha mbn}$.
- In Ansatz 1, all integrals $r_{\alpha m\beta n}$ are zero except $r_{\alpha^{\perp} m\beta^{\perp} n}$.

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# Matrix elements $V_{pq}^{rs}$

- In the following, we shall use a compact notation for products of the two-electron integrals $r_{\alpha p\beta q}$ and $g_{r\alpha s\beta}$,

$$r_{\alpha p\beta q} g_{r\alpha s\beta} = V_{pq}^{rs}$$

- Hence,

$$\begin{aligned}
\Delta E_{\text{R12}} &= c_{ij}^{mn} r_{\alpha m\beta n}(2g_{i\alpha j\beta} - g_{i\beta j\alpha}) = (2c_{ij}^{mn} - c_{ji}^{mn})V_{mn}^{ij} \\
\Omega_{ai}^{\text{A1-R12}} &= (2c_{ki}^{mn} - c_{ik}^{mn})\, r_{\gamma m\delta n}\, \tilde{g}_{a\delta k\gamma} = (2c_{ki}^{mn} - c_{ik}^{mn})V_{nm}^{\tilde{a}k} \\
&= (2c_{ik}^{mn} - c_{ki}^{mn})V_{mn}^{\tilde{a}k}
\end{aligned}$$

- In first quantization,

$$V_{pq}^{rs} = \langle pq | f_{12} \hat{Q}_{12} r_{12}^{-1} | rs \rangle$$

# Complementary auxiliary basis set (CABS)

- The $\Omega_{ai}^{\text{B1-R12}}$ and $\Omega_{ai}^{\text{C1-R12}}$ terms of the singles vector function cannot be expressed in terms of the $V$ intermediate.
- Two-electron integrals with one index in the complementary virtual space are *approximated* by inserting an orthonormal, finite complementary auxiliary basis set (CABS),

$$\{\phi_{p'}\}_{1\ldots n_{\text{cabs}}}, \qquad \langle\phi_p|\phi_{q'}\rangle = 0, \qquad \langle\phi_{p'}|\phi_{q'}\rangle = \delta_{p'q'}$$

- For example,

$$\Omega_{ai}^{\text{B1-R12}} = \begin{cases} 0 & \text{in Ansatz 1} \\ -(2c_{kl}^{mn} - c_{lk}^{mn})r_{amp'n}\, g_{k\tilde{i}lp'} & \text{in Ansatz 2} \end{cases}$$

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# The C1 term of the singles vector function

- Using the CABS, the C1 term of the singles vector function becomes

$$\Omega_{ai}^{\text{C1-R12}} = \begin{cases} 0 & \text{in Ansatz 1} \\ (2c_{ik}^{mn} - c_{ki}^{mn})r_{amp'n}\,{}^{\mathrm{I}}\tilde{F}_{kp'} & \text{in Ansatz 2} \end{cases}$$

- The matrix ${}^{\mathrm{I}}\tilde{\mathbf{F}}$ is the standard inactive Fock matrix calculated from the T1-transformed one- and two-electron integrals,

$$\begin{aligned} {}^{\mathrm{I}}\tilde{F}_{kp'} &= h_{kp'} + 2g_{kp'i\tilde{i}} - g_{k\tilde{i}ip'} \\ &= {}^{\mathrm{I}}F_{kp'} + (2g_{kp'ic} - g_{kcip'})t_i^c \end{aligned}$$

# Three-electron integrals

- Thus far, we have introduced *only one approximation*, and only in the framework of Ansatz 2.
- This approximation concerns $\Omega_{ai}^{\text{B1-R12}}$ and $\Omega_{ai}^{\text{C1-R12}}$.
- For example, the exact evaluation of $\Omega_{ai}^{\text{B1-R12}}$ requires the computation of *three-electron integrals*,

$$\begin{aligned} r_{am\gamma n}\, g_{k\tilde{i}l\gamma} &= r_{am\gamma^\perp n}\, g_{k\tilde{i}l\gamma^\perp} \\ &= \langle mn\tilde{i}|f_{12}r_{23}^{-1}|alk\rangle - \langle mn|f_{12}|ap\rangle\langle p\tilde{i}|r_{12}^{-1}|lk\rangle \\ &= \langle mn\tilde{i}|f_{12}r_{23}^{-1}|alk\rangle - f_{ampn}\, g_{k\tilde{i}lp} \end{aligned}$$

- The key to the success of the R12 methods is the introduction of an approximation that avoids the evaluation of three-electron integrals.

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# The standard approximation (SA)

- In R12 theory, the three-electron integrals are computed by inserting a resolution-of-the-identity (RI) approximation, that is

$$1 \approx |p''\rangle\langle p''|$$

  where $\{p''\}_{1\ldots n_{\text{abs}}}$ is an orthonormal auxiliary basis set (ABS).
- Here and in the following, we choose this ABS as the union of the finite basis and the CABS,

$$\{\phi_{p''}\}_{1\ldots n_{\text{abs}}} = \{\phi_p\}_{1\ldots n_{\text{bas}}} \cup \{\phi_{p'}\}_{1\ldots n_{\text{cabs}}}$$

- Inserting the RI approximation into the three-electron integrals leads to

$$\langle mn\tilde{i}|f_{12}r_{23}^{-1}|alk\rangle \approx f_{amp''n}\, g_{k\tilde{i}lp''}$$

# Standard approximation for $V_{pq}^{rs}$

- The projection operators

$$\hat{Q}_{12} = \begin{cases} \hat{Q}_{12}^{(1)} = (1-\hat{P}_1)(1-\hat{P}_2) & \text{Ansatz 1} \\ \hat{Q}_{12}^{(2)} = (1-\hat{O}_1)(1-\hat{O}_2) - \hat{V}_1\hat{V}_2 & \text{Ansatz 2} \end{cases}$$

lead to three-electron integrals, which are computed using the standard approximation,

$$\begin{aligned} (1-\hat{P}_1)(1-\hat{P}_2) &\approx 1 - \hat{P}_1\hat{P}_2 - \hat{P}_1\hat{P}_2' - \hat{P}_1'\hat{P}_2 \\ (1-\hat{O}_1)(1-\hat{O}_2) - \hat{V}_1\hat{V}_2 &\approx 1 - \hat{P}_1\hat{P}_2 - \hat{O}_1\hat{P}_2' - \hat{P}_1'\hat{O}_2 \end{aligned}$$

- Clearly, there is no difference between $\hat{Q}_{12}^{(1)}$ and $\hat{Q}_{12}^{(2)}$ when CABS is not used.

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# Standard approximation for $V_{pq}^{rs}$

- SA for $V_{pq}^{rs}$ in Ansatz 1:

$$\begin{aligned} \langle pq|f_{12}\hat{Q}_{12}^{(1)}r_{12}^{-1}|rs\rangle &\approx \langle pq|f_{12}(1 - \hat{P}_1\hat{P}_2 - \hat{P}_1\hat{P}_2' - \hat{P}_1'\hat{P}_2)r_{12}^{-1}|rs\rangle \\ &= \langle pq|f_{12}r_{12}^{-1}|rs\rangle \\ &- f_{pvqw}\,g_{vrws} - f_{pv'qw}\,g_{v'rws} - f_{pvqw'}\,g_{vrw's} \end{aligned}$$

- SA for $V_{pq}^{rs}$ in Ansatz 2:

$$\begin{aligned} \langle pq|f_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}|rs\rangle &\approx \langle pq|f_{12}(1 - \hat{P}_1\hat{P}_2 - \hat{O}_1\hat{P}_2' - \hat{P}_1'\hat{O}_2)r_{12}^{-1}|rs\rangle \\ &= \langle pq|f_{12}r_{12}^{-1}|rs\rangle \\ &- f_{pvqw}\,g_{vrws} - f_{pv'qi}\,g_{v'ris} - f_{piqw'}\,g_{irw's} \end{aligned}$$

# Standard approximation for $r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}$

- For He in the cc-pVTZ basis, the three-electron integral $\langle 11|r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}|11\rangle$ can be evaluated analytically.
- It amounts to $\langle 11|r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}|11\rangle = -0.147\,806\,6$ a.u.
- Using an ABS, this integral is computed as follows:

| ABS | $\langle 11\|r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}\|11\rangle$ | Error |
|---|---|---|
| 4s (uncontracted cc-pVDZ) | $-0.148\,427\,4$ | $-0.42\%$ |
| 6s (uncontracted cc-pVTZ) | $-0.147\,858\,3$ | $-0.035\%$ |
| 7s (uncontracted cc-pVQZ) | $-0.147\,789\,8$ | $0.011\%$ |
| 8s (uncontracted cc-pV5Z) | $-0.147\,769\,7$ | $0.025\%$ |
| 10s (uncontracted cc-pV6Z) | $-0.147\,751\,9$ | $0.037\%$ |

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# SA w/CABS for $r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}$

- For He in the cc-pVTZ basis, the three-electron integral $\langle 11|r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}|11\rangle$ can be evaluated analytically.
- It amounts to $\langle 11|r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}|11\rangle = -0.147\,806\,6$ a.u.
- Using a CABS, this integral is computed as follows:

| CABS | $\langle 11\|r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}\|11\rangle$ | Error |
|---|---|---|
| 4s (uncontracted cc-pVDZ) | $-0.147\,828\,9$ | $0.015\%$ |
| 6s (uncontracted cc-pVTZ) | $-0.147\,858\,3$ | $0.035\%$ |
| 7s (uncontracted cc-pVQZ) | $-0.147\,812\,4$ | $0.004\%$ |
| 8s (uncontracted cc-pV5Z) | $-0.147\,808\,6$ | $0.001\%$ |
| 10s (uncontracted cc-pV6Z) | $-0.147\,808\,6$ | $0.001\%$ |

# Standard approximation for $r_{12}\hat{Q}_{12}^{(2)}r_{12}$

- For He in the cc-pVTZ basis, the three-electron integral $\langle 11|r_{12}\hat{Q}_{12}^{(2)}r_{12}|11\rangle$ can be evaluated analytically.
- It amounts to $\langle 11|r_{12}\hat{Q}_{12}^{(2)}r_{12}|11\rangle = 0.150\,750\,9$ a.u.
- Using an ABS, this integral is computed as follows:

| ABS | $\langle 11\|r_{12}\hat{Q}_{12}^{(2)}r_{12}^{-1}\|11\rangle$ | Error |
|---|---|---|
| 4s (uncontracted cc-pVDZ) | 0.199 670 2 | 32% |
| 6s (uncontracted cc-pVTZ) | 0.154 384 5 | 2.4% |
| 7s (uncontracted cc-pVQZ) | 0.151 357 9 | 0.40% |
| 8s (uncontracted cc-pV5Z) | 0.150 974 6 | 0.15% |
| 10s (uncontracted cc-pV6Z) | 0.151 606 1 | 0.57% |

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# SA w/CABS for $r_{12}\hat{Q}_{12}^{(2)}r_{12}$

- For He in the cc-pVTZ basis, the three-electron integral $\langle 11|r_{12}\hat{Q}_{12}^{(2)}r_{12}|11\rangle$ can be evaluated analytically.
- It amounts to $\langle 11|r_{12}\hat{Q}_{12}^{(2)}r_{12}|11\rangle = 0.150\,750\,9$ a.u.
- Using a CABS, this integral is computed as follows:

| CABS | $\langle 11\|r_{12}\hat{Q}_{12}^{(2)}r_{12}\|11\rangle$ | Error |
|---|---|---|
| 4s (uncontracted cc-pVDZ) | 0.150 872 1 | 0.080% |
| 6s (uncontracted cc-pVTZ) | 0.154 384 5 | 2.4% |
| 7s (uncontracted cc-pVQZ) | 0.150 771 1 | 0.013% |
| 8s (uncontracted cc-pV5Z) | 0.150 766 9 | 0.011% |
| 10s (uncontracted cc-pV6Z) | 0.150 760 4 | 0.006% |

# The vector function $\Omega_{aibj}$

- To illustrate the derivation of the CCSD-R12 equations, we focus in the following on Ansatz 1.
- The equations for Ansatz 2 are left as an excercise.
- All of the equations can be derived from the standard CCSD equations,

$$\Omega_{aibj} = \Omega^{\text{A2}}_{aibj} + \Omega^{\text{B2}}_{aibj} + P^{ab}_{ij}\left(\Omega^{\text{C2}}_{aibj} + \Omega^{\text{D2}}_{aibj} + \Omega^{\text{E2}}_{aibj}\right)$$

with

$$P^{ab}_{ij} A^{ab}_{ij} = A^{ab}_{ij} + A^{ba}_{ji}$$

- The R12 contributions to the conventional $\Omega_{aibj}$ vector function are obtained by virtue of the correspondence principle. Doubles amplitudes $t^{ab}_{ij}$ in the conventional formulation must be replaced by those of the complete basis $\alpha\beta$.

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# The conventional vector function $\Omega_{aibj}$

$$\begin{aligned}
\Omega^{\text{A2}}_{aibj} &= \tilde{g}_{aibj} + t^{cd}_{ij}\tilde{g}_{acbd} \\
\Omega^{\text{B2}}_{aibj} &= t^{ab}_{kl}\left(\tilde{g}_{kilj} + t^{cd}_{ij}\tilde{g}_{kcld}\right) \\
\Omega^{\text{C2}}_{aibj} &= -\tfrac{1}{2}t^{bc}_{kj}\left(\tilde{g}_{kiac} - \tfrac{1}{2}t^{ad}_{li}\tilde{g}_{kdlc}\right) - t^{bc}_{ki}\left(\tilde{g}_{kjac} - \tfrac{1}{2}t^{ad}_{lj}\tilde{g}_{kdlc}\right) \\
\Omega^{\text{D2}}_{aibj} &= \tfrac{1}{2}u^{bc}_{jk}\left(\tilde{L}_{aikc} + \tfrac{1}{2}u^{ad}_{il}\tilde{L}_{ldkc}\right) \\
\Omega^{\text{E2}}_{aibj} &= t^{ac}_{ij}\left({}^{\mathrm{I}}\tilde{F}_{bc} - u^{bd}_{kl}\tilde{g}_{ldkc}\right) - t^{ab}_{ik}\left({}^{\mathrm{I}}\tilde{F}_{kj} + u^{cd}_{lj}\tilde{g}_{kdlc}\right)
\end{aligned}$$

- The intermediates $L$ and $u$ are defined as before,

$$L_{pqrs} = 2g_{pqrs} - g_{psrq}, \qquad u^{ab}_{ij} = 2t^{ab}_{ij} - t^{ab}_{ji}$$

- In Ansatz 1, the R12 contributions to the conventional vector function $\Omega_{aibj}$ are obtained from the terms with $t^{cd}_{\cdots}$ or $u^{cd}_{\cdots}$.

# R12 contributions to $\Omega_{aibj}$ in Ansatz 1

$$\Omega_{aibj}^{\text{A2-R12}} = t_{ij}^{\gamma\delta}\tilde{g}_{a\gamma b\delta} = c_{ij}^{mn} r_{m\gamma n\delta}\tilde{g}_{a\gamma b\delta} = c_{ij}^{mn} V_{mn}^{\tilde{a}\tilde{b}}$$

$$\Omega_{aibj}^{\text{B2-R12}} = t_{kl}^{ab} t_{ij}^{\gamma\delta}\tilde{g}_{k\gamma l\delta} = t_{kl}^{ab} c_{ij}^{mn} r_{m\gamma n\delta}\tilde{g}_{k\gamma l\delta} = t_{kl}^{ab} c_{ij}^{mn} V_{mn}^{kl}$$

$$\begin{aligned}\Omega_{aibj}^{\text{E2-R12}} &= -t_{ik}^{ab}\left(2t_{lj}^{\gamma\delta} - t_{jl}^{\gamma\delta}\right)\tilde{g}_{k\delta l\gamma} \\ &= -t_{ik}^{ab}\left(2c_{lj}^{mn} - c_{jl}^{mn}\right) r_{m\gamma n\delta}\tilde{g}_{k\delta l\gamma} \\ &= -t_{ik}^{ab}\left(2c_{lj}^{mn} - c_{jl}^{mn}\right) V_{nm}^{kl} = -t_{ik}^{ab}\left(2c_{jl}^{mn} - c_{lj}^{mn}\right) V_{mn}^{kl}\end{aligned}$$

- Before we proceed, we shall investigate the CC2-R12 model.
- Moreover, it is worthwile to rewrite the above equations explicitly for a two-electron system, where $c_{11}^{11}V_{11}^{11}$ is the R12 contribution to the energy.

# CID-R12 eigenvalue equation for two electrons

- The explicitly-correlated configuration-interaction-with-doubles (CID-R12) eigenvalue equation for a two-electron system can be written in matrix form as follows:

$$\begin{pmatrix} 0 & V & \mathbf{g}^{\mathsf{T}} \\ V & H^{\text{R12}} - E_{\text{HF}} & \mathbf{V}^{\mathsf{T}} \\ \mathbf{g} & \mathbf{V} & \mathbf{H}^{\text{conv}} - E_{\text{HF}} \end{pmatrix} \begin{pmatrix} 1 \\ c \\ \mathbf{t} \end{pmatrix} = \Delta E \begin{pmatrix} 1 \\ c \\ \mathbf{t} \end{pmatrix}$$

- Thus, the conventional doubles equation reads

$$\mathbf{g} + \mathbf{V}c + \left(\mathbf{H}^{\text{conv}} - E_{\text{HF}}\right)\mathbf{t} - \Delta E\mathbf{t} = \mathbf{0}$$

- The R12 contributions to this equation are

$$\mathbf{V}c - \Delta E^{\text{R12}}\mathbf{t} = \Omega_{a1b1}^{\text{A2-R12}} + \Omega_{a1b1}^{\text{B2-R12}} + 2\Omega_{a1b1}^{\text{E2-R12}} = c_{11}^{11}V_{11}^{ab} - t_{11}^{ab}c_{11}^{11}V_{11}^{11}$$

# T1 transformation of the Fock operator

- The idea of the CC2 model is to partition the Hamiltionian in the Møller–Plesset manner into the Fock operator $\hat{f}$ and the fluctuation potential $\hat{\Phi} = \hat{H} - \hat{F} - h_{\mathsf{nuc}}$.
- Hence, we need to investigate the T1 transformations of $\hat{f}$ and $\hat{\Phi}$ separately.
- Concerning $\tilde{\hat{f}}$, we find

$$\tilde{\hat{f}} = \mathsf{exp}(-\hat{T}_1)\hat{f}\,\mathsf{exp}(\hat{T}_1) = \hat{f} + [\hat{f}, \hat{T}_1]$$

$$[\hat{f}, \hat{T}_1] = t_i^a\, {}^{\mathsf{I}}F_{\kappa\lambda}[E_{\kappa\lambda}, E_{ai}] = t_i^a \left({}^{\mathsf{I}}F_{\kappa a}E_{\kappa i} - {}^{\mathsf{I}}F_{i\lambda}E_{a\lambda}\right)$$

- Assuming *canonical orbitals*, working onto the Hartree–Fock state yields

$$[\hat{f}, \hat{T}_1]|\mathsf{HF}\rangle = t_i^a(\varepsilon_a - \varepsilon_i)E_{ai}|\mathsf{HF}\rangle + t_i^a\, {}^{\mathsf{I}}F_{\alpha^\perp a}E_{\alpha^\perp i}|\mathsf{HF}\rangle$$

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# The similarity-transformed Fock operator

- In the CCSD-R12 model, the similarity-transformed Fock operator is

$$e^{-\hat{T}_1 - \hat{T}_2 - \hat{T}_{2'}}\,\hat{f}\,e^{\hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}} = \hat{f} + [\hat{f}, \hat{T}_1] + [\hat{f}, \hat{T}_2] + [\hat{f}, \hat{T}_{2'}]$$

- The commutators with $\hat{T}_2$ and $\hat{T}_{2'}$ give rise to

$$\begin{aligned} [\hat{f}, \hat{T}_2]|\mathsf{HF}\rangle &= t_{ij}^{ab}(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)E_{ai}E_{bj}|\mathsf{HF}\rangle \\ &+ t_{ij}^{ab}\left({}^{\mathsf{I}}F_{\alpha^\perp a}E_{\alpha^\perp i}E_{bj} + {}^{\mathsf{I}}F_{\beta^\perp b}E_{ai}E_{\beta^\perp j}\right)|\mathsf{HF}\rangle \end{aligned}$$

$$\begin{aligned} [\hat{f}, \hat{T}_{2'}]|\mathsf{HF}\rangle &= t_{ij}^{\alpha\beta}\left({}^{\mathsf{I}}F_{\kappa\alpha}E_{\kappa i}E_{\beta j} + {}^{\mathsf{I}}F_{\kappa\beta}E_{\alpha i}E_{\kappa j}\right)|\mathsf{HF}\rangle \\ &- t_{ij}^{\alpha\beta}\left(\varepsilon_i + \varepsilon_j\right)E_{\alpha i}E_{\beta j}|\mathsf{HF}\rangle \end{aligned}$$

$$\left\langle \begin{matrix} \bar{a} \\ i \end{matrix} \right| e^{-\hat{T}_1 - \hat{T}_2 - \hat{T}_{2'}}\,\hat{f}\,e^{\hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}}|\mathsf{HF}\rangle = t_i^a(\varepsilon_a - \varepsilon_i)$$

# The conventional doubles projection

- Of special interest is the projection of $[\hat{f}, \hat{T}_{2'}]$ onto the conventional doubles.
- In Ansatz 1, this projection is exactly zero.
- In Ansatz 2, we obtain

$$\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| [\hat{f}, \hat{T}_{2'}] \middle| \text{HF} \right\rangle \begin{array}{l} = {}^{\text{I}}F_{a\alpha_\perp}\, t_{ij}^{\alpha_\perp b} + {}^{\text{I}}F_{b\beta_\perp}\, t_{ij}^{a\beta_\perp} \\ \approx \left({}^{\text{I}}F_{ap'}\, r_{p'mbn} + {}^{\text{I}}F_{bq'}\, r_{amq'n}\right) c_{ij}^{mn} \end{array}$$

  In Ansatz 2, the projection is nonzero but (usually) very small.
- In Ansatz 2, the projection is zero if we assume that ${}^{\text{I}}F_{a\alpha_\perp} = 0$ (extended Brillouin condition, EBC).

# GBC and EBC

- Besides the usual Brillouin condition (${}^{\text{I}}F_{ai} = 0$), we introduce two more conditions.
- The *generalized Brillouin condition* (GBC),

$$ {}^{\text{I}}F_{\alpha_\perp i} \approx 0 \qquad ({}^{\text{I}}F_{\alpha i} \approx 0)$$

  The occupied space is closed under the Fock operator.
- The *extended Brillouin condition* (EBC),

$$ {}^{\text{I}}F_{\alpha_\perp i} \approx 0 \qquad \text{and} \qquad {}^{\text{I}}F_{\alpha_\perp b} \approx 0$$

  The (finite) orbital space is closed under the Fock operator.
- Assuming canonical orbitals, we may write

$$ {}^{\text{I}}F_{\kappa i} = \delta_{\kappa i}\varepsilon_i \quad \text{(GBC)}, \qquad {}^{\text{I}}F_{\kappa p} = \delta_{\kappa p}\varepsilon_p \quad \text{(EBC)}$$

# The vector function $\Omega_{aibj}^{\text{CC2-R12}}$

- The CC2 model is an approximation to CCSD. In the doubles equation, the commutators with $\tilde{\tilde{H}}$ are replaced by commutators with the Fock operator $\hat{f}$,

$$\Omega_{aibj}^{\text{CC2}} = \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| \tilde{\tilde{H}} + [\hat{f}, \hat{T}_2] \middle| \text{HF} \right\rangle$$

- For CC2-R12, we find

$$\Omega_{aibj}^{\text{CC2-R12}} = \Omega_{aibj}^{\text{CC2}} + \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| [\hat{f}, \hat{T}_{2'}] \middle| \text{HF} \right\rangle$$

- In Ansatz 1, $\Omega_{aibj}^{\text{CC2-R12}} = \Omega_{aibj}^{\text{CC2}}$. In Ansatz 2,

$$\Omega_{aibj}^{\text{CC2-R12}} \approx \Omega_{aibj}^{\text{CC2}} + \left( {}^{\mathrm{I}}F_{ap'}\, r_{p'mbn} + {}^{\mathrm{I}}F_{bq'}\, r_{amq'n} \right) c_{ij}^{mn}$$

---

# Some observations concerning CCSD-R12

- The projection onto the singles is easily computed for both Ansätze 1 and 2. The main ingredient is the intermediate $V_{mn}^{\tilde{a}k}$.
  - All integrals can be evaluated using the standard approximation (CABS). GBS or EBC are not needed.
- The projection onto the doubles is easily obtained for both Ansätze 1 and 2 within the CC2-R12 model.
  - There is no R12 contribution in Ansatz 1. There is no R12 contribution in Ansatz 2 if the EBC holds.
- The CCSD-R12 projection onto the doubles is easily obtained for Ansatz 1 but its derivation is a bit tedious for Ansatz 2. The main ingredient is the intermediate $V_{mn}^{\tilde{a}\tilde{b}}$.
  - All integrals can be evaluated using the standard approximation (CABS). GBS and EBC are not needed.

# The projection onto the R12 doubles

- The projection onto the R12 doubles is a projection onto the manifold

$$r_{\alpha m\beta n}\left\langle \begin{matrix}\overline{\alpha\beta}\\ ij\end{matrix}\right|$$

  Note that the total number of such projections is $n_{\mathrm{occ}}^4$.

- Let us first consider the CC2-R12 model,

$$\begin{aligned}
r_{\alpha m\beta n}\left\langle \begin{matrix}\overline{\alpha\beta}\\ ij\end{matrix}\right|\hat{f}+[\hat{f},\hat{T}_1]+[\hat{f},\hat{T}_2]\left|\mathrm{HF}\right\rangle &= r_{\alpha m\beta n}\left\langle \begin{matrix}\overline{\alpha\beta}\\ ij\end{matrix}\right|[\hat{f},\hat{T}_2]\left|\mathrm{HF}\right\rangle \\
&= \left({}^{\mathrm{I}}F_{a\alpha_\perp}\, r_{\alpha_\perp mbn} + {}^{\mathrm{I}}F_{b\beta_\perp}\, r_{am\beta_\perp n}\right) t_{ij}^{ab} \\
&\approx \left({}^{\mathrm{I}}F_{ap'}\, r_{p'mbn} + {}^{\mathrm{I}}F_{bq'}\, r_{amq'n}\right) t_{ij}^{ab}
\end{aligned}$$

- In Ansatz 1, the above projection vanishes.

---

# The projection of $[\hat{f},\hat{T}_{2'}]$ onto the R12 doubles

- Recall that

$$\begin{aligned}
[\hat{f},\hat{T}_{2'}]|\mathrm{HF}\rangle &= t_{ij}^{\alpha\beta}\left({}^{\mathrm{I}}F_{\kappa\alpha}E_{\kappa i}E_{\beta j} + {}^{\mathrm{I}}F_{\kappa\beta}E_{\alpha i}E_{\kappa j}\right)|\mathrm{HF}\rangle \\
&- t_{ij}^{\alpha\beta}\left(\varepsilon_i+\varepsilon_j\right)E_{\alpha i}E_{\beta j}|\mathrm{HF}\rangle
\end{aligned}$$

- We hence obtain

$$\begin{aligned}
& r_{\alpha m\beta n}\left\langle \begin{matrix}\overline{\alpha\beta}\\ ij\end{matrix}\right|[\hat{f},\hat{T}_{2'}]\left|\mathrm{HF}\right\rangle \\
&= \left\{r_{\gamma m\beta n}{}^{\mathrm{I}}F_{\gamma\alpha} + r_{\alpha m\delta n}{}^{\mathrm{I}}F_{\delta\beta} - r_{\alpha m\beta n}\left(\varepsilon_i+\varepsilon_j\right)\right\} r_{\alpha k\beta l}\, c_{ij}^{kl} \\
&= \langle mn|f_{12}\hat{Q}_{12}\left(\hat{f}_1+\hat{f}_2-\varepsilon_i-\varepsilon_j\right)\hat{Q}_{12}f_{12}|kl\rangle c_{ij}^{kl} \\
&= B_{mnkl}^{(ij)}\, c_{ij}^{kl} = \left\{B_{mnkl}-(\varepsilon_i+\varepsilon_j)X_{mnkl}\right\} c_{ij}^{kl}
\end{aligned}$$

# The R12 doubles equation in CC2-R12

- The complete R12 doubles equation in the CC2-R12 model is

$$r_{\alpha m\beta n}\left\langle \overline{\begin{matrix}\alpha\beta\\ ij\end{matrix}}\right|[\hat{f},\hat{T}_{2'}]+\tilde{\hat{\Phi}}\left|\text{HF}\right\rangle = B^{(ij)}_{mnkl}\,c^{kl}_{ij}+\tilde{V}^{ij}_{mn}=0$$

with

$$\tilde{V}^{ij}_{mn}=r_{\alpha m\beta n}\tilde{g}_{\alpha i\beta j}$$

- For evaluating $\tilde{V}^{ij}_{mn}$, it is useful to note that

$$\begin{aligned}
|\alpha\rangle\langle\tilde{\alpha}| &= |\alpha_\perp\rangle\langle\alpha_\perp|+|a\rangle\langle\tilde{a}| \\
|a\rangle\langle\tilde{a}|+|\tilde{k}\rangle\langle k| &= |p\rangle\langle p| \\
|\alpha\rangle\langle\tilde{\alpha}|+|\tilde{k}\rangle\langle k| &= 1
\end{aligned}$$

---

# The intermediate $\tilde{V}^{ij}_{mn}$

- In Ansatz 1, we find

$$\begin{aligned}
\tilde{V}^{ij}_{mn} &= r_{\alpha_\perp m\beta_\perp n}\tilde{g}_{\alpha_\perp i\beta_\perp j}=V^{\tilde{i}\tilde{j}}_{mn} \\
&\approx \langle mn|f_{12}r_{12}^{-1}|\tilde{i}\tilde{j}\rangle - f_{mvnw}\,g_{v\tilde{i}w\tilde{j}} \\
&- f_{mv'nw}\,g_{v'\tilde{i}w\tilde{j}} - f_{mvnw'}\,g_{v\tilde{i}w'\tilde{j}}
\end{aligned}$$

- In Ansatz 2, we need the following relation:

$$\begin{aligned}
&|\alpha_\perp\beta_\perp\rangle\langle\alpha_\perp\beta_\perp| + |\alpha_\perp b\rangle\langle\alpha_\perp\tilde{b}| + |a\beta_\perp\rangle\langle\tilde{a}\beta_\perp| \\
&= 1 - |vw\rangle\langle vw| - |\alpha_\perp\tilde{k}\rangle\langle\alpha_\perp k| - |\tilde{k}\beta_\perp\rangle\langle k\beta_\perp|
\end{aligned}$$

- This yields for Ansatz 2,

$$\begin{aligned}
\tilde{V}^{ij}_{mn} &\approx \langle mn|f_{12}r_{12}^{-1}|\tilde{i}\tilde{j}\rangle - f_{mvnw}\,g_{v\tilde{i}w\tilde{j}} \\
&- f_{mv'n\tilde{k}}\,g_{v'\tilde{i}k\tilde{j}} - f_{m\tilde{k}nw'}\,g_{k\tilde{i}w'\tilde{j}}
\end{aligned}$$

# Summarizing the CC2-R12 model (Ansatz 1)

- The CC2-R12 equations for Ansatz 1 are:

$$\begin{aligned}
E_{\text{CC2-R12}} &= E_{\text{CC2}} + (2c_{ij}^{mn} - c_{ji}^{mn})V_{mn}^{ij} \\
0 &= \Omega_{ai}^{\text{CC2-R12}} = \Omega_{ai}^{\text{CC2}} + (2c_{ik}^{mn} - c_{ki}^{mn})V_{mn}^{\tilde{a}k} \\
0 &= \Omega_{aibj}^{\text{CC2-R12}} = \Omega_{aibj}^{\text{CC2}} \\
0 &= \Omega_{minj}^{\text{CC2-R12}} = B_{mnkl}^{(ij)}\, c_{ij}^{kl} + \tilde{V}_{mn}^{ij}
\end{aligned}$$

- At this point, we note that the range of orbitals $\phi_i, \phi_j$ is restricted to the set of occupied Hartree–Fock orbitals (canonical or localized). The orbitals $\phi_k, \phi_l, \phi_m, \phi_n$, however, may comprise (seminatural) virtual orbitals as well as occupied orbitals.
- The MP2-R12 model (Ansatz 1) is obtained by omitting the singles projection and replacing $\tilde{V}_{mn}^{ij}$ by $V_{mn}^{ij}$.

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# Summarizing the CC2-R12 model (Ansatz 2)

- Ansatz 2 involves more terms than Ansatz 1,

$$\begin{aligned}
E_{\text{CC2-R12}} &= E_{\text{CC2}} + (2c_{ij}^{mn} - c_{ji}^{mn})V_{mn}^{ij} \\
0 &= \Omega_{ai}^{\text{CC2-R12}} = \Omega_{ai}^{\text{CC2}} + (2c_{ik}^{mn} - c_{ki}^{mn})V_{mn}^{\tilde{a}k} \\
&- (2c_{kl}^{mn} - c_{lk}^{mn})r_{amp'n}\, g_{k\tilde{i}lp'} \\
&+ (2c_{ik}^{mn} - c_{ki}^{mn})r_{amp'n}\,{}^{\mathsf{I}}\tilde{F}_{kp'} \\
0 &= \Omega_{aibj}^{\text{CC2-R12}} = \Omega_{aibj}^{\text{CC2}} + C_{mnab}c_{ij}^{mn} \\
0 &= \Omega_{minj}^{\text{CC2-R12}} = B_{mnkl}^{(ij)}\, c_{ij}^{kl} + \tilde{V}_{mn}^{ij} + C_{mnab}t_{ij}^{ab}
\end{aligned}$$

with

$$C_{mnab} = {}^{\mathsf{I}}F_{ap'}\, r_{p'mbn} + {}^{\mathsf{I}}F_{bq'}\, r_{amq'n}$$

- Again, the MP2-R12 model is obtained by omitting the singles projection and replacing $\tilde{V}_{mn}^{ij}$ by $V_{mn}^{ij}$.

# CC2-R12 excitation energies

- CC2-R12 excitation energies are obtained from the generalized eigenvalue problem
$$\mathbf{A}\mathbf{r} = \omega \mathbf{S}\mathbf{r}$$
where $\mathbf{A}$ is the Jacobian, $\mathbf{r}$ its right eigenvector, $\omega$ the excitation energy, and $\mathbf{S}$ the metric,
$$\mathbf{S} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & S^{mni'j'}_{klij} \end{pmatrix}, \qquad S^{mni'j'}_{klij}\, r^{i'j'}_{mn} = X_{klmn}\, r^{ij}_{mn}$$
- The Jacobian $\mathbf{A}$ contains the first derivatives of the vector functions, for example,
$$A^{mni'j'}_{klij} = \frac{\partial \Omega^{\text{CC2-R12}}_{kilj}}{\partial c^{i'j'}_{mn}} = \delta_{ii'}\delta_{jj'} B^{(ij)}_{klmn}, \quad A^{mni'j'}_{klij}\, r^{i'j'}_{mn} = B^{(ij)}_{klmn}\, r^{ij}_{mn}$$

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# CC2-R12 performance on excitation energies

- Calculated $^1$P (2p←2s) excitation energy of Be in eV. A subset of the 20s17p14d11f8g5h set was used as orbital basis as well as ABS.

| Basis | CC2 | CC2-R12 | CC2-R12+ |
|---|---|---|---|
| sp | 5.54 | 5.70 | 5.30 |
| spd | 5.21 | 5.27 | 5.13 |
| spdf | 5.15 | 5.17 | 5.12 |
| spdfg | 5.13 | 5.14 | 5.11 |
| spdfgh | 5.12 | 5.13 | 5.11 |
| $\infty$ | | 5.11 | |

- The CC2-R12+ calculations include one additional set of seminatural p-type virtuals, providing R12 pair functions of $^1$P symmetry.

# The CCSD-R12 method in `DIRCCR12-OS`

- The CCSD-R12 method was developed and implemented into the `DIRCCR12` program in 1992–1995.
- An open-shell version (UCCSD based on ROHF or UHF references) was developed in 2000. The program has since then be denoted `DIRCCR12-OS`.
- Triples corrections are available in the CCSD[T]-R12 and CCSD(T)-R12 models. Note that CCSD[T] is sometimes denoted CCSD+T(CCSD).
- The `DIRCCR12` program uses neither ABS nor CABS. There is hence no distinction between Ansätze 1 and 2.
- The program is used for benchmark calculations on small closed- and open-shell systems using large basis sets.
- See http://www-laog.obs.ujf-grenoble.fr/˜valiron/ccr12.

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# CCSD-R12 performance of ground-state energies

- 2001: CCSD-R12 calculations w/`DIRCCR12` on Ne in a 19s14p8d6f4g3h (orbital) basis. Singlet valence-shell correlation energy: $\Delta E_{\mathrm{S}}^{\text{CCSD-R12}} = -210.61$ m$E_{\mathrm{h}}$.
- 2006: Feller *et al.* developed cc-pVXZ basis sets up to X=10.

| Basis | Computed | Extrapolated ($X^{-3}$) |
|---|---|---|
| cc-pVTZ | $-170.53$ | |
| cc-pVQZ | $-192.73$ | $-208.93$ |
| cc-pV5Z | $-201.63$ | $-210.96$ |
| cc-pV6Z | $-205.47$ | $-210.75$ |
| cc-pV7Z | $-207.46$ | $-210.84$ |
| cc-pV8Z | $-208.56$ | $-210.80$ |
| cc-pV9Z | $-209.17$ | $-210.61$ |
| cc-pV10Z | $-209.56$ | $-210.59$ |
| CCSD-R12 | $-210.61$ | |

# CCSD-R12 performance of ground-state energies

- 2001: CCSD-R12 calculations w/`DIRCCR12` on Ne in a 19s14p8d6f4g3h (orbital) basis. Triplet valence-shell correlation energy: $\Delta E_{\mathrm{T}}^{\text{CCSD-R12}} = -104.87$ m$E_{\mathrm{h}}$.
- 2006: Feller *et al.* developed cc-pVXZ basis sets up to X=10.

| Basis | Computed | Extrapolated ($\mathrm{X}^{-5}$) |
|---|---|---|
| cc-pVTZ | $-95.81$ | |
| cc-pVQZ | $-101.95$ | $-103.86$ |
| cc-pV5Z | $-103.86$ | $-104.79$ |
| cc-pV6Z | $-104.43$ | $-104.82$ |
| cc-pV7Z | $-104.65$ | $-104.84$ |
| cc-pV8Z | $-104.76$ | $-104.88$ |
| cc-pV9Z | $-104.81$ | $-104.86$ |
| cc-pV10Z | $-104.83$ | $-104.86$ |
| CCSD-R12 | $-104.87$ | |

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# CCSD(T)-R12 calculations on $\mathrm{C}_x\mathrm{H}_y$

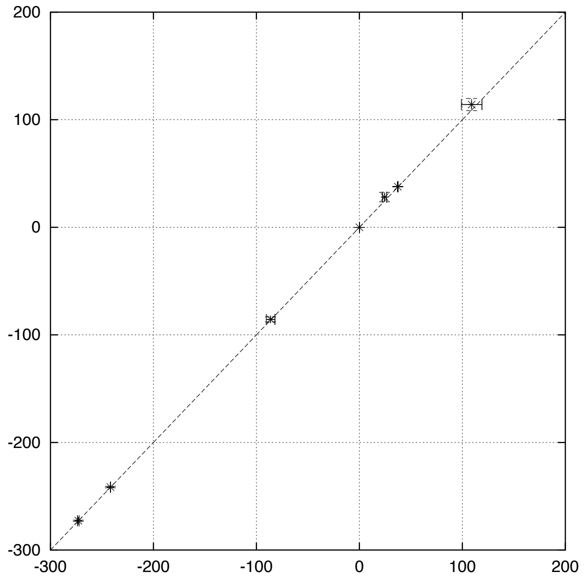
- CCSD(T)-R12 calculated atomization energies $D_0(0K)$ in kJ/mol. Basis set: 19s14p8d6f4g3h for C and 9s6p4d3f for H.

| Molecule | State | Calc.[a] | Exptl.[b] |
|---|---|---|---|
| Methylidyne, CH | ${}^2\Pi$ | 334.48 | 333.20 |
| Methylene, $CH_2$ | ${}^3B_1$ | 751.85 | 753.26 |
| Methyl, $CH_3$ | ${}^2A_2''$ | 1 209.64 | 1 209.61 |
| Methane, $CH_4$ | ${}^1A_1$ | 1 641.97 | 1 641.96 |
| Carbon dimer, $C_2$ | ${}^1\Sigma_g^+$ | 598.42 | 600.00 |
| Ethynyl, $C_2H$ | ${}^2\Sigma^+$ | 1 071.20 | 1 073.42 |
| Ethyne, $C_2H_2$ | ${}^1\Sigma_g^+$ | 1 624.27 | 1 626.50 |
| Vinyl, $C_2H_3$ | ${}^2A'$ | 1 766.81 | $1769 \pm 5$ |
| Ethene, $C_2H_4$ | ${}^1A_g$ | 2 225.11 | 2 225.54 |
| Allene, $CH_2CCH_2$ | ${}^1A_1$ | 2 798.71 | 2 799.3 |

[a] From CCSD(T)-R12 calculations including core-correlation effects, anharmonic zero-point vibrational energies, and scalar-relativistic and spin–orbit effects.

[b] Computational Chemistry Comparison and Benchmark DataBase, http://srdata.nist.gov.cccbdb/.

# CCSD(T)-R12 heats of formation



Calculated *vs* experimental enthalpy of formation, $\Delta H_f^0$ (298.15 K) in kJ/mol, for HF, $H_2O$, HOF, $H_2$, $F_2O$, OH, and FO (from left to right).

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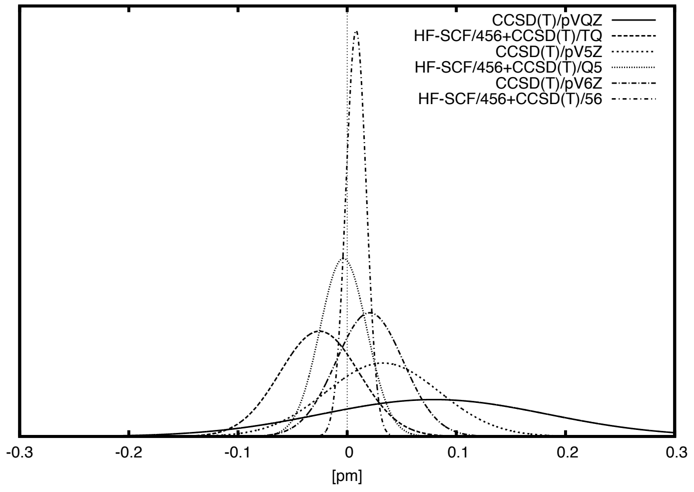
# CCSD(T)-R12 geometries

- Analytical gradients are *not* available in `DIRCCR12-OS`. The geometries of the molecules CO, $N_2$, $F_2$, HF, $H_2O$, $NH_3$, $CH_4$, $C_2H_2$, HCN, HNC, $CO_2$, CN, NO, OH, $NH_2$, and $CH_2$ were computed by calculating the PES.



Basis:
19s14p8d6f4g3h2i for C, N, F, O and 9s6p4d3f2g for H.

56-Extrapolated results agree to within 0.01 pm with the CCSD(T)-R12 geometries.

# CCSD(T)-R12 harmonic frequencies

- Harmonic vibrational frequencies have also been computed for the same molecules. For $H_2O$, for example, we find:

| $\omega_e$ / $cm^{-1}$ | cc-pV5Z[a] | cc-pV6Z[a] | CCSD(T)-R12[b] |
|---|---|---|---|
| Symm. stre. $\nu_1$ $(a_1)$ | 3840.1 | 3837.3 | 3835.9 |
| Bend $\nu_2$ $(a_1)$ | 1653.4 | 1651.3 | 1649.4 |
| Antisymm. stre. $\nu_3$ $(b_2)$ | 3949.3 | 3947.2 | 3946.7 |

[a] Computed analytically using `Aces II`. [b] Computed numerically using `DIRCCR12-OS`.

- Benchmark calculations of this type are possible but time-consuming for molecules such as $NH_3$, $CH_4$, $CO_2$, and $C_2H_2$, in the 19s14p8d6f4g3h2i/9s6p4d3f2g basis set.
- The frequencies were obtained using Richardson's extrapolation.

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# Recent developments in CCSD-R12 theory

- Development of the CCSD(R12) model.
- Use of an auxiliary basis set (ABS or CABS).
- Implementation of Ansätze 1 and 2.
- Implementation of new correlation factors $f_{12} \neq r_{12}$.
- Implementation of CC2-R12 and CCSD(R12) response theory.
- Implementation of MP2-R12 nuclear gradients.
- All recent work took place in the framework of the `Dalton` program, for *closed-shell* coupled-cluster theory (see http://www.kjemi.uio.no/software/dalton).

# The CCSD(R12) model: Theory

- Up to double excitations, the cluster operator is

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}$$

- The CC2 model can be interpreted as an approximation to CCSD. In the doubles equations, the fluctuation potential is only transformed with the singles cluster operator $\hat{T}_1$.
- In a similar manner, the CCSD(R12) model is an approximation to CCSD-R12. In the R12 doubles equations, the similarity transformation of the fluctuation potential is restricted to the *conventional singles and doubles* operators $\hat{T}_1$ and $\hat{T}_2$,

$$\begin{aligned} \text{CCSD-R12} \quad &: \quad \langle \mu_{2'} | [\hat{f}, \hat{T}] + e^{-\hat{T}} \hat{\Phi} e^{T} | \text{HF} \rangle = \Omega_{\mu_{2'}} = 0 \\ \text{CCSD(R12)} \quad &: \quad \langle \mu_{2'} | [\hat{f}, \hat{T}] + e^{-\hat{T}_1 - \hat{T}_2} \hat{\Phi} e^{\hat{T}_1 + \hat{T}_2} | \text{HF} \rangle = \Omega_{\mu_{2'}} = 0 \end{aligned}$$

---

# The CCSD(R12) model: Further approximations

- In addition to the restricted similarity transformation in the R12 doubles equations, we omit terms in the conventional doubles equations that are quadratic in $\hat{T}_{2'}$,

$$\tfrac{1}{2} \langle \mu_2 | [[\tilde{\hat{H}}, \hat{T}_{2'}], \hat{T}_{2'}] | \text{HF} \rangle \approx 0$$

- Concerning triples corrections within the CCSD(T)(R12) model,

$$\langle \mu_3 | [\hat{f}, \hat{T}_3] + [\hat{\Phi}, \hat{T}_2] + [\hat{\Phi}, \hat{T}_{2'}] | \text{HF} \rangle = 0$$

  the contribution from $\hat{T}_{2'}$ is neglected.
- These further approximations are motivated by the fact that the contributions are small. In Ansatz 1, the contributions vanish exactly. In Ansatz 2, they are nonzero but very small.
- Neglecting commutators does not violate the size-extensivity of the methods.

# The CCSD(R12) model: Performance

- Comparison between CCSD-R12 and CCSD(R12) valence-shell correlation energies of Ne in m$E_\mathrm{h}$.

| Basis | CCSD-R12<br>`DIRCCR12-OS` | CCSD(R12)<br>`Dalton` | Difference |
|---|---|---|---|
| aug-cc-pVDZ | $-320.40$ | $-295.13$ | 25.27 |
| aug-cc-pVTZ | $-307.84$ | $-301.24$ | 6.60 |
| aug-cc-pVQZ | $-310.43$ | $-309.32$ | 1.11 |
| aug-cc-pV5Z | $-313.22$ | $-312.99$ | 0.23 |
| aug-cc-pV6Z | $-314.49$ | $-314.52$ | $-0.03$ |

- Also for various small molecules, the differences between the CCSD-R12 and CCSD(R12) energies become negligible in the aug-cc-pVQZ basis.
- In a very small basis (aug-cc-pVDZ), the CCSD-R12 terms that are neglected in CCSD(R12) cannot be computed accurately.

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# Correlation functions other than $r_{12}$

- The two-electron integrals

$$r_{\alpha m \beta n} = \langle \alpha\beta | \hat{Q}_{12} f_{12} | mn \rangle$$

contain the correlation function $f_{12} = f(r_{12})$. In `Dalton`, various functions can be chosen.

- The only complication in the theory is that the product $f_{12} r_{12}^{-1}$ and the double commutator $\frac{1}{2}[f_{12}, [\hat{t}_1 + \hat{t}_2, f_{12}]]$ are more involved with a general $f_{12}$, because

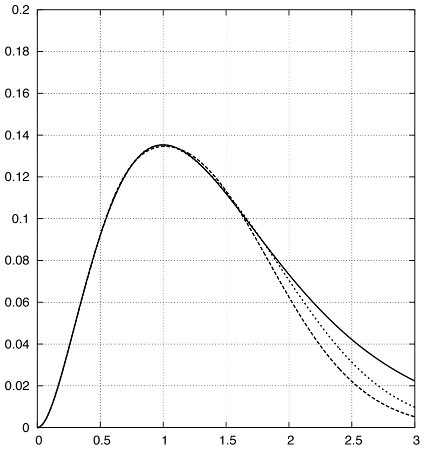
$$\begin{aligned} r_{12}\, r_{12}^{-1} &= 1 \\ \tfrac{1}{2}[r_{12}, [\hat{t}_1 + \hat{t}_2, r_{12}]] &= 1 \end{aligned}$$

- Since a few years, it has turned out that Slater-type geminals of the form $\exp(-\zeta r_{12})$ are very effective in explicitly-correlated methods.

# $\exp(-r_{12})$ expanded in $n$ Gaussians

- Similar to STO-$n$G basis sets, the Slater-type geminal $\exp(-r_{12})$ can be expanded in $n$ Gaussians by minimizing

$$T = \int_0^\infty \left\{ e^{-r_{12}} - \sum_{k=1}^{n} c_k \, e^{-\zeta_k r_{12}^2} \right\}^2 e^{-2r_{12}} \, r_{12}^2 \, \mathrm{d}r_{12}$$



The figure shows the function $r_{12}^2 \exp(-2\, r_{12})$ (solid line) and the corresponding expansions with $n$=3 and $n$=4 Gaussians (dashed lines).

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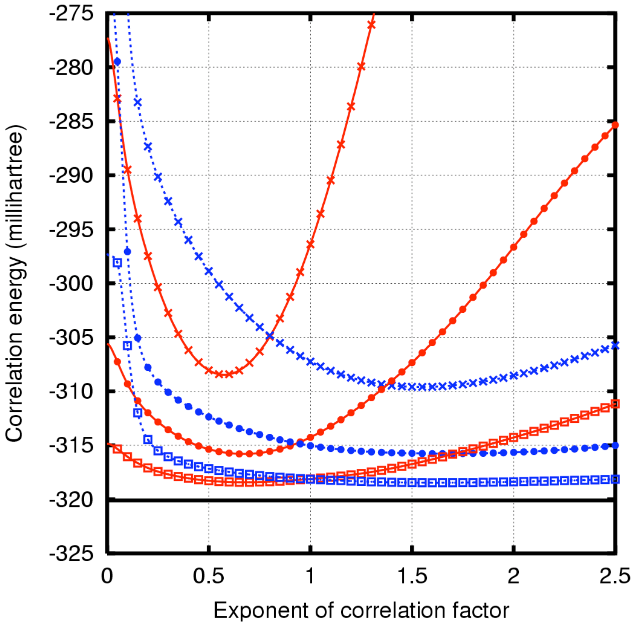
# Performance of the Slater-type geminals



The figure shows the valence-shell MP2 correlation energy of the Ne atom.

Blue : $\exp(-\zeta r_{12})$

Red : $r_{12} \exp(-\zeta r_{12})$

× : aug-cc-VDZ

● : aug-cc-VTZ

☐ : aug-cc-VQZ

# Comparison of correlation functions

- The correlation functions $\exp(-\zeta r_{12})$ and $r_{12}\exp(-\zeta r_{12})$ yield very similar results when the exponents differ by a factor of two.
- The Taylor expansions of both correlation functions have the same quadratic term when the exponents differ by a factor of two.
- The following valence-shell MP2 correlation energies (m$E_\mathrm{h}$) are obtained in the aug-cc-pVQZ basis:

| Molecule | $r_{12}$ | $\exp(-r_{12})$ | $r_{12}\exp(-\frac{1}{2}r_{12})$ | Limit |
|---|---|---|---|---|
| $CH_2$ | $-154.3$ | $-155.5$ | $-155.5$ | $-156$ |
| $H_2O$ | $-297.1$ | $-299.5$ | $-299.5$ | $-300$ |
| $NH_3$ | $-262.1$ | $-263.9$ | $-263.9$ | $-264$ |
| $N_2$ | $-416.0$ | $-419.5$ | $-419.5$ | $-421$ |
| $F_2$ | $-603.0$ | $-608.7$ | $-608.8$ | $-612$ |

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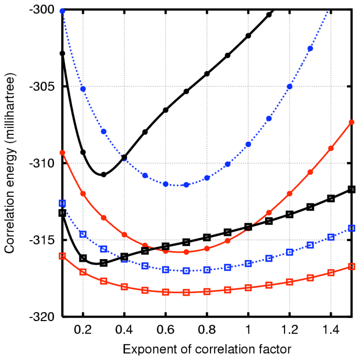
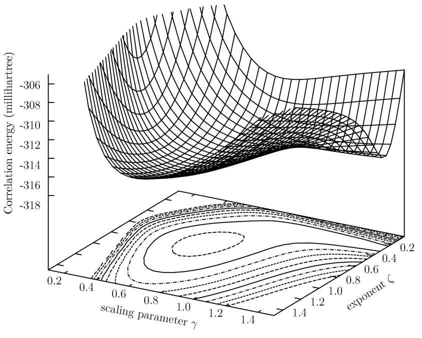
# Room for improvement: Basis sets

- Consider calculations on Ne with the correlation factor $r_{12}\exp -\zeta r_{12}$. Scaling of the exponents of the polarization functions of a cc-pVXZ basis yields improved performance.
- Special basis sets for R12 calculations are needed.



Aug-cc-pVXZ (red), cc-pVXZ (black), and

scaled cc-pVXZ (blue) results for X = 3, 4.



Dependence on exponent and scaling

of the cc-pVQZ results.

# Performance of CCSD(T)(R12) w/STG

- CCSD(T)(R12) calculations were performed with an STG (exponent 1.3) in the aug-cc-pV(T+d)Z basis using Ansatz 2 and a 21s13p6d4f3g2h(S), 15s9p5d4f3g2h(N,O), 9s5p4d3f2g(H) CABS. The table reports valence-shell corr. energies in m$E_\mathrm{h}$.
- This calculation performs as well as a conventional calculation in the aug-cc-pV(5+d)Z basis.
- Basis sets (orbital and CABS) have not yet been optimized!

| Basis | $SO_3$ | | $HNO_3$ | |
|---|---|---|---|---|
| | Conv. | (R12) | Conv. | (R12) |
| aug-cc-pV(T+d)Z | −945.27 | −1 023.82 | −983.93 | −1 057.88 |
| aug-cc-pV(Q+d)Z | −1 003.78 | | −1 038.49 | |
| aug-cc-pV(5+d)Z | −1 024.97 | | −1 057.58 | |
| TQ-Extrapolation | −1 046.48 | | −1 078.30 | |
| Q5-Extrapolation | −1 047.20 | | −1 077.61 | |

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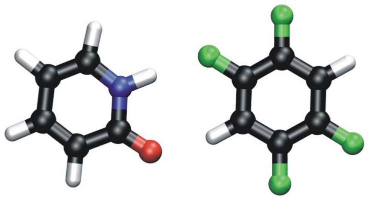
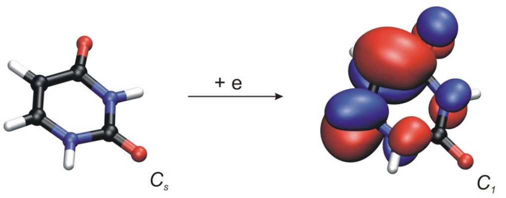
# Outlook: RI-MP2-R12

- The RI approximation of the RI-MP2 method (as implemented in `Turbomole`) can also be applied to the MP2-R12 approach. Highly accurate calculations on larger systems are becoming possible.

Binding energies of $\pi$-stacked and H-bonded dimers of 2-pyridone and 1,2,4,5-tetrafluorobenzene, computed in the aug-cc-pVQZ basis.



Adiabatic electron affinity of uracil, computed in the aug-cc-pVQZ basis.



# Outlook: To do's in `Turbomole`

- RI-MP2-R12 approach with "approximation C", which avoids the two-electron integrals over $[\hat{t}_1 + \hat{t}_2, f_{12}]$.
- RI-MP2-R12 approach with effective core potentials (ECPs), possibly within a two-component framework to account for spin–orbit effects.
- RI-MP2-R12 approach with a Slater-type geminal.
- RI-MP2-R12 approach with CABS in the framework of Ansatz 2.
- RI-CC2-R12 and CCSD(R12) ground-state energies (Ansatz 2).
- RI-CC2-R12 and CCSD(R12) excitation energies and response properties (Ansatz 2).
- Molecular gradients.

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# An unsolved problem: The $B^{(ij)}_{mnkl}$ matrix

- The matrix $\mathbf{B}^{(ij)}$ is defined as

$$B^{(ij)}_{mnkl} = \left\{ r_{\gamma m \beta n}\,{}^{\mathrm{I}}F_{\gamma\alpha} + r_{\alpha m \delta n}\,{}^{\mathrm{I}}F_{\delta\beta} - r_{\alpha m \beta n}\left(\varepsilon_i + \varepsilon_j\right) \right\} r_{\alpha k \beta l}$$

- $\mathbf{B}^{(ij)}$ is a positive definite matrix. This is most easily seen by assuming that ${}^{\mathrm{I}}F_{\alpha\beta}$ is diagonal with ${}^{\mathrm{I}}F_{\alpha\beta} = \delta_{\alpha\beta}\varepsilon_\alpha$. Then,

$$B^{(ij)}_{mnkl} = r_{\alpha m \beta n}\left(\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_i - \varepsilon_j\right) r_{\alpha k \beta l}$$

- It may happen that, due to the approximations in the theory, the actually computed matrix $\mathbf{B}^{(ij)}$ is not positive definite. This may give rise to numerical instabilities and unphysical excitation energies and/or response properties.
- We should invoke only those approximations that do not violate the positive definiteness of the exact matrix $\mathbf{B}^{(ij)}$.

## The simplest approach to the $B^{(ij)}_{mnkl}$ matrix

- We rewrite $\mathbf{B}^{(ij)}$ as

$$\begin{aligned} B^{(ij)}_{mnkl} &= \left\{ r_{\gamma m \beta n}{}'F_{\gamma\alpha} + r_{\alpha m \delta n}{}'F_{\delta\beta} \right\} r_{\alpha k \beta l} - (\varepsilon_i + \varepsilon_j)\, X_{mnkl} \\ &= B_{mnkl} - (\varepsilon_i + \varepsilon_j)\, X_{mnkl} \end{aligned}$$

- The term $-(\varepsilon_i + \varepsilon_j)\, X_{mnkl}$ is easy to compute and positive definite. We hence focus on $B_{mnkl}$. For example,

$$\begin{aligned} r_{\gamma m \beta n}{}'F_{\gamma\alpha} r_{\alpha k \beta l} &= r_{\gamma_\perp m \beta_\perp n}{}'F_{\gamma_\perp \alpha_\perp} r_{\alpha_\perp k \beta_\perp l} + r_{\gamma_\perp m \beta_\perp n}{}'F_{\gamma_\perp a} r_{a k \beta_\perp l} \\ &+ r_{c m \beta_\perp n}{}'F_{c a} r_{a k \beta_\perp l} + r_{c m \beta_\perp n}{}'F_{c \alpha_\perp} r_{\alpha_\perp k \beta_\perp l} \\ &+ r_{\gamma_\perp m b n}{}'F_{\gamma_\perp \alpha_\perp} r_{\alpha_\perp k b l} \end{aligned}$$

- A CABS is required to evaluate the above expression. The numerical results are poor if we use

$$B_{mnkl} \approx 0 \quad \text{and} \quad B^{(ij)}_{mnkl} \approx -(\varepsilon_i + \varepsilon_j)\, X_{mnkl}$$

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## The commutator integrals

- We write $B^{(ij)}_{mnkl}$ in first quantization,

$$B^{(ij)}_{mnkl} = \langle mn | f_{12} \hat{Q}_{12} \left( \hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j \right) \hat{Q}_{12} f_{12} | kl \rangle$$

  Assuming the GBC, we may write

$$\begin{aligned} B^{(ij)}_{mnkl} &\approx \tfrac{1}{2} \langle mn | f_{12} \hat{Q}_{12} [\hat{f}_1 + \hat{f}_2, \hat{Q}_{12} f_{12}] | kl \rangle \\ &+ \tfrac{1}{2} \langle mn | [f_{12} \hat{Q}_{12}, \hat{f}_1 + \hat{f}_2] \hat{Q}_{12} f_{12} | kl \rangle \\ &+ \tfrac{1}{2} \left( \varepsilon_k + \varepsilon_l + \varepsilon_m + \varepsilon_n - 2\varepsilon_i - 2\varepsilon_j \right) X_{mnkl} \end{aligned}$$

- This reformulation leads to the commutator $[f_{12}\hat{Q}_{12}, \hat{f}_1 + \hat{f}_2]$ and thus to $[f_{12}, \hat{f}_1]$. Since only the kinetic energy and the exchange operator do not commute with $f_{12}$, we obtain

$$[f_{12}, \hat{f}_1] = [f_{12}, \hat{t}_1] - [f_{12}, \hat{k}_1]$$

# Standard approximations A, B, C, . . .

- Considering $[f_{12}, \hat{f}_1] = [f_{12}, \hat{t}_1] - [f_{12}, \hat{k}_1]$, one can assume that the contributions from the commutator $[f_{12}, \hat{k}_1]$ are small and negligible.
- The integrals over $[f_{12}, \hat{t}_1]$ can be computed analytically while the integrals over $[f_{12}, \hat{k}_1]$ require completeness insertions in terms of the (C)ABS.
- The complete neglect of $[f_{12}, \hat{k}_1]$ is denoted as “approximation A”. The first implementation of the MP2-R12 method (in 1987) was based on this approximation.
- Approximation A is only used in MP2-R12 theory. The MP2-R12/A model tends to overestimate (slightly) the magnitude of the MP2 correlation energy.
- The integrals over $[f_{12}, \hat{k}_1]$ are considered in the MP2-R12/B model. Approximation B is usually used beyond MP2.