Hartree-Fock approximation and short-range electron correlation in quantum chemistry

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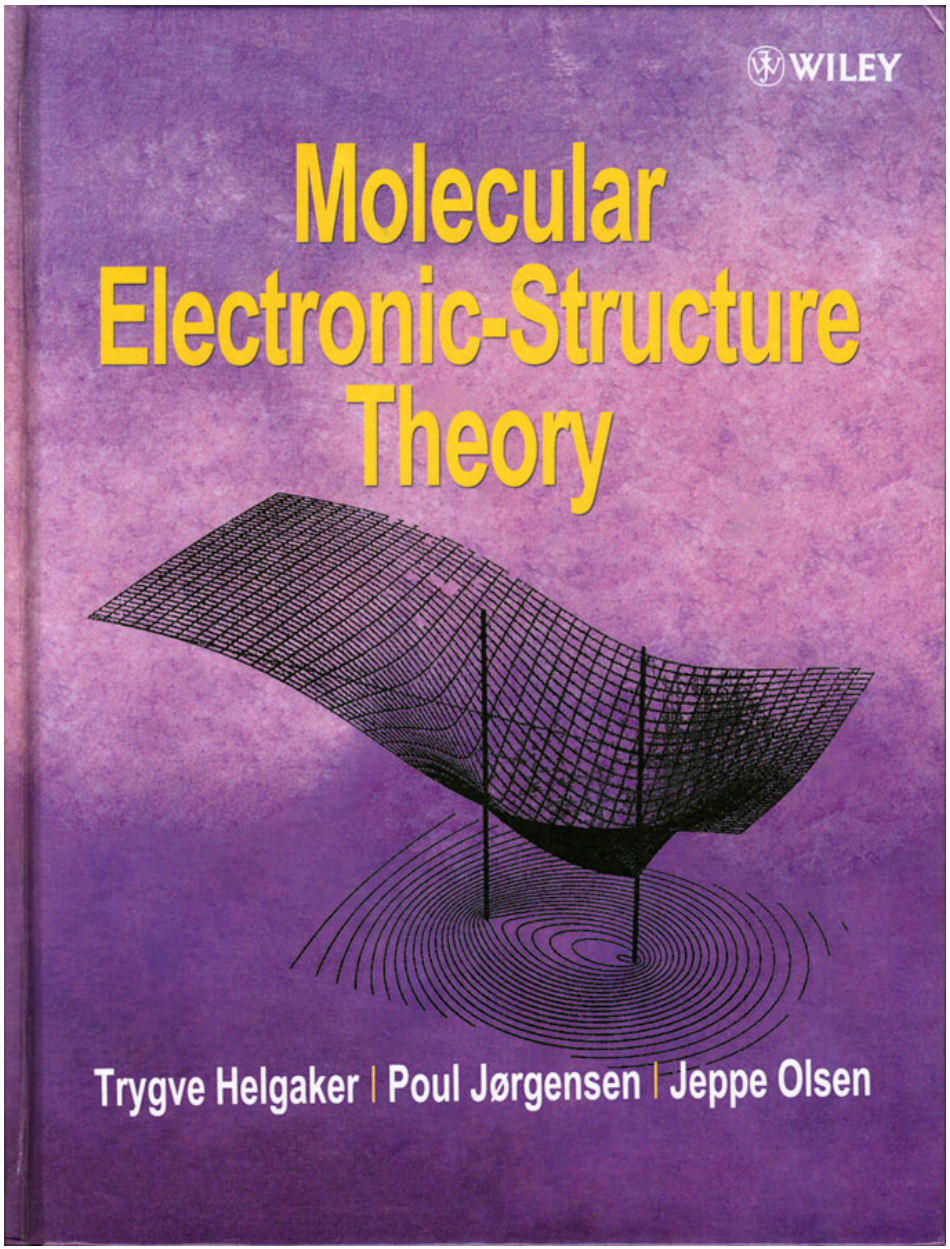
WILEY
Molecular Electronic-Structure Theory
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Notations

N-electron Hamiltonian within the Born-Oppenheimer approximation:

$$\hat{H} = \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}}$$

$$\hat{T} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 \qquad \rightarrow \quad \text{kinetic energy}$$

$$\hat{W}_{\mathrm{ee}} = \frac{1}{2}\sum_{i\neq j}^{N} \hat{w}_{\mathrm{ee}}(r_{ij}) \qquad \text{with } w_{\mathrm{ee}}(r_{12}) = \frac{1}{r_{12}} \qquad \rightarrow \quad \text{electron-electron repulsion}$$

$$\hat{V}_{\mathrm{ne}} = \sum_{i=1}^{N} \hat{v}_{\mathrm{ne}}(\mathbf{r_i}) \qquad \text{with } v_{\mathrm{ne}}(\mathbf{r}) = -\sum_{A}^{\text{nuclei}} \frac{Z_A}{|\mathbf{r}-\mathbf{r}_A|} \qquad \rightarrow \quad \text{electron-nuclei attraction}$$

Notations

- Molecular orbitals: $\phi_p(\mathbf{r}) = \sum_\mu C_{\mu p}\ \chi_\mu(\mathbf{r})$ $\qquad\qquad$ $\langle\phi_p|\phi_q\rangle = \delta_{pq}$
- Non-orthogonal set of atomic orbitals (Gaussian functions): $\qquad$ $\langle\chi_\mu|\chi_\nu\rangle = S_{\mu\nu}$
- one-electron states based on spin-orbitals: $\qquad$ $|P\rangle = |\phi_p, \sigma\rangle = \hat{a}^\dagger_{p,\sigma}|\mathrm{vac}\rangle, \qquad \sigma = \alpha, \beta$
- Second-quantized expression for the (non-relativistic) Hamiltonian:

$$\boxed{\hat{T} + \hat{V}_{\mathrm{ne}} = \sum_{P,Q} \langle P|\hat{h}|Q\rangle\ \hat{a}^\dagger_P \hat{a}_Q} \qquad \text{where} \qquad \hat{h} = \hat{t} + \hat{v}_{\mathrm{ne}},$$

$$= \sum_{p,q,\sigma,\sigma'} \underbrace{\langle\phi_p, \sigma|\hat{h}|\phi_q, \sigma'\rangle}_{\delta_{\sigma,\sigma'}\langle\phi_p|\hat{h}|\phi_q\rangle} \hat{a}^\dagger_{p,\sigma}\hat{a}_{q,\sigma'} = \sum_{p,q} \underbrace{\langle\phi_p|\hat{h}|\phi_q\rangle}_{h_{pq}} \underbrace{\left(\sum_\sigma \hat{a}^\dagger_{p,\sigma}\hat{a}_{q,\sigma}\right)}_{\hat{E}_{pq}} = \sum_{p,q} h_{pq}\hat{E}_{pq}$$

Notations

Similarly $\boxed{\hat{W}_{\text{ee}} = \frac{1}{2} \sum_{P,Q,R,S} \langle PR|QS\rangle a_P^\dagger \hat{a}_R^\dagger \hat{a}_S \hat{a}_Q}$

$$= \frac{1}{2} \sum_{p,q,r,s} \sum_{\sigma,\tau,\sigma',\tau'} \underbrace{\langle \phi_p, \sigma\, \phi_r, \sigma' | \phi_q, \tau\, \phi_s, \tau' \rangle}\, \underbrace{\hat{a}^\dagger_{p,\sigma} \hat{a}^\dagger_{r,\sigma'} \hat{a}_{s,\tau'} \hat{a}_{q,\tau}}$$

$$\delta_{\sigma\tau}\delta_{\sigma'\tau'} \langle \phi_p \phi_r | \phi_q \phi_s \rangle \quad - \hat{a}^\dagger_{p,\sigma} \hat{a}^\dagger_{r,\sigma'} \hat{a}_{q,\tau} \hat{a}_{s,\tau'} = -\delta_{qr}\delta_{\sigma'\tau} \hat{a}^\dagger_{p,\sigma} \hat{a}_{s,\tau'} + \hat{a}^\dagger_{p,\sigma} \hat{a}_{q,\tau} \hat{a}^\dagger_{r,\sigma'} \hat{a}_{s,\tau'}$$

where $\langle \phi_p \phi_r | \phi_q \phi_s \rangle = \int d\mathbf{r_1} d\mathbf{r_2}\ \phi_p(\mathbf{r_1}) \phi_r(\mathbf{r_2})\, r_{12}^{-1}\, \phi_q(\mathbf{r_1}) \phi_s(\mathbf{r_2}) = \langle pr|qs\rangle$

$$\hat{W}_{\text{ee}} = \frac{1}{2} \sum_{p,q,r,s} \langle pr|qs\rangle \left(- \delta_{qr} \underbrace{\sum_\sigma \hat{a}^\dagger_{p,\sigma} \hat{a}_{s,\sigma}}_{\hat{E}_{ps}} + \Big(\underbrace{\sum_\sigma \hat{a}^\dagger_{p,\sigma} \hat{a}_{q,\sigma}}_{\hat{E}_{pq}} \Big) \Big(\underbrace{\sum_{\sigma'} \hat{a}^\dagger_{r,\sigma'} \hat{a}_{s,\sigma'}}_{\hat{E}_{rs}} \Big) \right)$$

In summary: $\boxed{\hat{H} = \sum_{p,q} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{p,q,r,s} \langle pr|qs\rangle \left(\hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} \right)}$

Variational and non-variational approximations

- The exact electronic ground state Ψ_0 and its energy E_0 can be obtained in two ways:

$$E_0 = \min_{\Psi} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \qquad \hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$$

- Approximate parametrized ground-state wave function: $\Psi(\boldsymbol{\lambda}_0)$

  where $\boldsymbol{\lambda}_0$ denotes the complete set of optimized parameters.

Variational calculation

$$\frac{\partial}{\partial \boldsymbol{\lambda}} \frac{\langle \Psi(\boldsymbol{\lambda}) | \hat{H} | \Psi(\boldsymbol{\lambda}) \rangle}{\langle \Psi(\boldsymbol{\lambda}) | \Psi(\boldsymbol{\lambda}) \rangle} \bigg|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}_0} = 0$$

$\downarrow$

Hartree-Fock (HF)
Configuration Interaction (CI)
Multi-Configurational Self-Consistent Field (MCSCF)

Non-variational calculation

$$\hat{H}|\Psi(\boldsymbol{\lambda})\rangle - E(\boldsymbol{\lambda})|\Psi(\boldsymbol{\lambda})\rangle = 0 \qquad \text{for } \boldsymbol{\lambda} = \boldsymbol{\lambda}_0$$

$\downarrow$

Many-Body Perturbation Theory (MBPT)
Coupled Cluster (CC)

Spin-orbital rotations

- Let $\{|P\rangle\}$ denote an orthonormal basis of spin-orbitals and $\{|\tilde{P}\rangle\}$ another orthonormal basis obtained by unitary transformation:

$$|\tilde{P}\rangle = \sum_Q U_{QP}|Q\rangle$$

- **U** can be written as $\boxed{\mathbf{U} = e^{-\boldsymbol{\kappa}} \text{ with } \boldsymbol{\kappa}^\dagger = -\boldsymbol{\kappa}}$ $\leftarrow$ $\boldsymbol{U}^\dagger = \left(e^{-\boldsymbol{\kappa}}\right)^\dagger = e^{-\boldsymbol{\kappa}^\dagger} = e^{\boldsymbol{\kappa}} = \boldsymbol{U}^{-1}$

- κ_{PQ} can be used instead of U_{PQ} to parametrize the spin-orbital rotations

EX1: Using **EX2**, show that in second quantization the unitary transformation can be simply written as

$$\hat{a}^\dagger_{\tilde{P}} = \sum_Q \left(e^{-\boldsymbol{\kappa}}\right)_{QP} \hat{a}^\dagger_Q = \boxed{e^{-\hat{\kappa}}\ \hat{a}^\dagger_P\ e^{\hat{\kappa}} = \hat{a}^\dagger_{\tilde{P}}} \qquad \text{where} \qquad \hat{\kappa} = \sum_{PQ} \kappa_{PQ}\ \hat{a}^\dagger_P \hat{a}_Q$$

Spin-orbital rotations

- Note that the rotation operator $\hat{\kappa}$ is anti-Hermitian:

$$\hat{\kappa}^\dagger = \sum_{PQ} \kappa^*_{PQ}\ \hat{a}^\dagger_Q \hat{a}_P = \sum_{PQ} \kappa^\dagger_{QP}\ \hat{a}^\dagger_Q \hat{a}_P = -\sum_{PQ} \kappa_{QP}\ \hat{a}^\dagger_Q \hat{a}_P = -\hat{\kappa}$$

- Unitary transformation for a N-electron Slater determinant:

$$|\tilde{P}_1 \tilde{P}_2 \dots \tilde{P}_N\rangle = \hat{a}^\dagger_{\tilde{P}_1} \hat{a}^\dagger_{\tilde{P}_2} \dots \hat{a}^\dagger_{\tilde{P}_N} |\text{vac}\rangle = e^{-\hat{\kappa}} \hat{a}^\dagger_{P_1}\ e^{\hat{\kappa}} e^{-\hat{\kappa}} \hat{a}^\dagger_{P_2}\ e^{\hat{\kappa}} \dots e^{-\hat{\kappa}} \hat{a}^\dagger_{P_N}\ e^{\hat{\kappa}} |\text{vac}\rangle$$

$$= e^{-\hat{\kappa}} \hat{a}^\dagger_{P_1} \hat{a}^\dagger_{P_2} \dots \hat{a}^\dagger_{P_N}\ \underbrace{e^{\hat{\kappa}}|\text{vac}\rangle}_{|\text{vac}\rangle}$$

$$\boxed{|\tilde{P}_1 \tilde{P}_2 \dots \tilde{P}_N\rangle = e^{-\hat{\kappa}}\ |P_1 P_2 \dots P_N\rangle}$$

Spin-restricted orbital rotations

- In a restricted formalism the same set of orbitals is used for α and β spin:

$$\hat{\kappa} = \sum_{PQ} \kappa_{PQ}\, \hat{a}^\dagger_P \hat{a}_Q = \sum_{pq} \sum_{\sigma\sigma'} \underbrace{\kappa_{p,\sigma q,\sigma'}}_{\kappa_{pq}\delta_{\sigma\sigma'}} \hat{a}^\dagger_{p,\sigma} \hat{a}_{q,\sigma'} = \sum_{pq} \kappa_{pq} \hat{E}_{pq}$$

- Since $\kappa_{pq} = -\kappa_{qp}$ (real algebra)

$$\hat{\kappa} = \sum_{p>q} \kappa_{pq} \hat{E}_{pq} - \sum_{p<q} \kappa_{qp} \hat{E}_{pq}$$

$$\boxed{\hat{\kappa} = \sum_{p>q} \kappa_{pq} \left(\hat{E}_{pq} - \hat{E}_{qp} \right)}$$

Hartree-Fock approximation

- For simplicity we consider here the particular case of a non-degenerate singlet closed-shell ground state

- The HF method consists then in approximating the exact wave function Ψ_0 by a single Slater determinant Φ_0. The orbital space is thus divided in two:

  doubly occupied molecular orbitals $\phi_i, \phi_j, \ldots$ **unoccupied molecular orbitals** $\phi_a, \phi_b, \ldots$

$$|\Phi_0\rangle = \prod_{i}^{\text{occ.}} \prod_{\sigma=\alpha,\beta} \hat{a}^{\dagger}_{i,\sigma} |\text{vac}\rangle$$

- The initial set of molecular orbitals is usually not optimized $\rightarrow$ the optimized HF molecular orbitals will be obtained by means of unitary transformations (orbital rotations)

Hartree-Fock approximation

- Exponential parametrization: $|\Phi(\boldsymbol{\kappa})\rangle = e^{-\hat{\kappa}} |\Phi_0\rangle$ with $\hat{\kappa} = \sum_{p>q} \kappa_{pq} \left(\hat{E}_{pq} - \hat{E}_{qp} \right)$

$$\boldsymbol{\kappa} = \begin{bmatrix} \vdots \\ \kappa_{pq} \\ \vdots \end{bmatrix}_{p>q}$$ denotes the column vector containing all the parameters to be optimized

- occupied-occupied and unoccupied-unoccupied rotations:

$$\hat{\kappa} = \underbrace{\sum_{i>j} \kappa_{ij} \left(\hat{E}_{ij} - \hat{E}_{ji} \right)}_{\hat{\kappa}^{\text{occ.}}} + \sum_{i,a} \kappa_{ai} \left(\hat{E}_{ai} - \hat{E}_{ia} \right) + \underbrace{\sum_{a>b} \kappa_{ab} \left(\hat{E}_{ab} - \hat{E}_{ba} \right)}_{\hat{\kappa}^{\text{unocc.}}}$$

$\hat{\kappa}^{\text{occ.}}|\Phi_0\rangle = \hat{\kappa}^{\text{unocc.}}|\Phi_0\rangle = 0 \rightarrow$ only occupied-unoccupied rotations have to be optimized $\rightarrow \boldsymbol{\kappa} = \begin{bmatrix} \vdots \\ \kappa_{ai} \\ \vdots \end{bmatrix}$

Hartree-Fock approximation

- Hartree-Fock energy expression:

$$E(\boldsymbol{\kappa}) = \frac{\langle \Phi(\boldsymbol{\kappa})|\hat{H}|\Phi(\boldsymbol{\kappa})\rangle}{\langle \Phi(\boldsymbol{\kappa})|\Phi(\boldsymbol{\kappa})\rangle} = \frac{\langle \Phi_0|e^{-\hat{\kappa}^\dagger}\ \hat{H}\ e^{-\hat{\kappa}}|\Phi_0\rangle}{\langle \Phi_0|e^{-\hat{\kappa}^\dagger}\ e^{-\hat{\kappa}}|\Phi_0\rangle} = \boxed{\langle \Phi_0|e^{\hat{\kappa}}\hat{H}e^{-\hat{\kappa}}|\Phi_0\rangle = E(\boldsymbol{\kappa})}$$

- Variational optimization of $\boldsymbol{\kappa}$: $\quad E^{[1]}_{\boldsymbol{\kappa}_+} = \left.\frac{\partial E(\boldsymbol{\kappa})}{\partial \boldsymbol{\kappa}}\right|_{\boldsymbol{\kappa}_+} = 0$

- Iterative procedure (Newton method):

$$E(\boldsymbol{\kappa}) \approx E(0) + \boldsymbol{\kappa}^T E^{[1]}_0 + \frac{1}{2}\boldsymbol{\kappa}^T E^{[2]}_0 \boldsymbol{\kappa} \quad \rightarrow \quad E^{[1]}_{\boldsymbol{\kappa}_+} \approx E^{[1]}_0 + E^{[2]}_0 \boldsymbol{\kappa}_+ = 0 \quad \rightarrow \quad E^{[2]}_0 \underbrace{\boldsymbol{\kappa}_+}_{\textbf{Newton step}} = -E^{[1]}_0$$

- Update the HF determinant: $\quad \Phi_0 \leftarrow \Phi(\boldsymbol{\kappa}_+)$

- HF calculation converged when $\quad \boxed{E^{[1]}_0 = 0}$

Hartree-Fock approximation

Note: The exponential parametrization can also be used in Kohn-Sham DFT

$$\langle\Phi(\boldsymbol{\kappa})|\hat{H}|\Phi(\boldsymbol{\kappa})\rangle \quad \longrightarrow \quad \langle\Phi(\boldsymbol{\kappa})|\hat{T}+\hat{V}_{\mathrm{ne}}|\Phi(\boldsymbol{\kappa})\rangle + E_{\mathrm{Hxc}}[n(\boldsymbol{\kappa})]$$

where $|\Phi(\boldsymbol{\kappa})\rangle = e^{-\hat{\kappa}}|\Phi^{\mathrm{KS}}\rangle, \qquad n(\boldsymbol{\kappa},\mathbf{r}) = \langle\Phi(\boldsymbol{\kappa})|\hat{n}(\mathbf{r})|\Phi(\boldsymbol{\kappa})\rangle,$

$$\hat{n}(\mathbf{r}) = \hat{E}_{\mathbf{rr}} = \sum_{\sigma}\hat{\Psi}^{\dagger}_{\sigma}(\mathbf{r})\hat{\Psi}_{\sigma}(\mathbf{r}) = \sum_{p,q}\phi_p(\mathbf{r})\phi_q(\mathbf{r})\hat{E}_{pq} \qquad \longleftarrow \text{density operator}$$

Hartree-Fock approximation

EX2: Using the Taylor expansion of $\hat{f}(x) = e^{-x\hat{A}}\,\hat{B}\,e^{x\hat{A}}$ about $x = 0$, prove the *Baker-Campbell-Hausdorff* (BCH) expansion:

$$e^{-\hat{A}}\,\hat{B}\,e^{\hat{A}} = \hat{B} + \sum_{n=1}^{+\infty} \frac{1}{n!}\,[\![\hat{B},\hat{A}]\!]_n \qquad [\![\hat{B},\hat{A}]\!]_{n+1} = [[\hat{B},\hat{A}]\!]_n,\hat{A}], \qquad [\![\hat{B},\hat{A}]\!]_1 = [\hat{B},\hat{A}]$$

$$= \hat{B} + [\hat{B},\hat{A}] + \frac{1}{2}[[\hat{B},\hat{A}],\hat{A}] + \ldots$$

- Analytical formulas for the gradient and the hessian:

$$E(\boldsymbol{\kappa}) = E(0) + \underbrace{\langle\Phi_0|[\hat{\kappa},\hat{H}]|\Phi_0\rangle} + \frac{1}{2}\langle\Phi_0|[\hat{\kappa},[\hat{\kappa},\hat{H}]]|\Phi_0\rangle + \ldots$$

$$\sum_{ai} \kappa_{ai}\langle\Phi_0|[\hat{E}_{ai} - \hat{E}_{ia},\hat{H}]|\Phi_0\rangle \quad \rightarrow \quad E^{[1]}_{0,ai} = \langle\Phi_0|[\hat{E}_{ai} - \hat{E}_{ia},\hat{H}]|\Phi_0\rangle$$

$$= -2\langle\Phi_0|\hat{H}\hat{E}_{ai}|\Phi_0\rangle = 0 \text{ (**Brillouin theorem**)}$$

Fock matrix and canonical orbitals

EX3: Using the simplified commutator expression $[\hat{E}_{pq}, \hat{E}_{rs}] = \delta_{qr}\hat{E}_{ps} - \delta_{ps}\hat{E}_{rq}$, show that

$$E^{[1]}_{0,ai} = 2\langle\Phi_0|[\hat{E}_{ai}, \hat{H}]|\Phi_0\rangle = \boxed{-4f_{ia} = E^{[1]}_{0,ai}}$$

where the Fock matrix elements are defined as $f_{pq} = h_{pq} + \sum_{rs}\left(\langle pr|qs\rangle - \frac{1}{2}\langle pr|sq\rangle\right)D_{rs}$,

$D_{rs} = \langle\Phi_0|\hat{E}_{rs}|\Phi_0\rangle$ ← one-electron density matrix

- Canonical HF orbitals:

$$\mathbf{D} = \begin{bmatrix} \mathbf{D}^{\text{occ.}} & 0 \\ 0 & 0 \end{bmatrix} \quad \mathbf{f} = \begin{bmatrix} \mathbf{f}^{\text{occ.}} & 0 \\ 0 & \mathbf{f}^{\text{unocc.}} \end{bmatrix} \longrightarrow \mathbf{D}' = \mathbf{D}, \quad \mathbf{f}' = \begin{bmatrix} \mathbf{f}'^{\text{occ.}} & 0 \\ 0 & \mathbf{f}'^{\text{unocc.}} \end{bmatrix}$$

$$\mathbf{D}^{\text{occ.}}_{ij} = 2\delta_{ij} \qquad \mathbf{f}^{\text{occ.}}_{ij} = f_{ij}, \quad \mathbf{f}^{\text{unocc.}}_{ab} = f_{ab} \qquad \mathbf{f}'^{\text{occ.}}_{ij} = \delta_{ij}\varepsilon_i, \quad \mathbf{f}'^{\text{unocc.}}_{ab} = \delta_{ab}\varepsilon_a$$

- Fock operator in second-quantized form using canonical orbitals:

$$\hat{F} = \sum_{p,q} f_{pq} \hat{E}_{pq} = \sum_{i} \varepsilon_i \hat{E}_{ii} + \sum_{a} \varepsilon_a \hat{E}_{aa}$$

- Møller-Plesset partitioning of the Hamiltonian: $\hat{H} = \underbrace{\hat{F}}_{\hat{H}_0} + \underbrace{(\hat{H} - \hat{F})}_{\hat{V}}$ with $\hat{F}|\Phi_0\rangle = \underbrace{2\sum_i \varepsilon_i}_{E^{(0)}} |\Phi_0\rangle$

- Using perturbation theory, the HF energy is recovered through first order:

$$E^{(0)} + E^{(1)} = E^{(0)} + \langle \Phi_0 | \hat{V} | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = E_{\mathrm{HF}}$$

- The correlation energy is defined as the difference between the exact and HF energies: it is a second- and higher-order energy correction

$$E_c = E_0 - E_{\mathrm{HF}} = E^{(2)} + E^{(3)} + \ldots$$

- Indeed, the HF determinant is an approximation to the exact ground-state wave function:

$$\hat{H}|\Phi_0\rangle = E^{(0)}|\Phi_0\rangle + \hat{V}|\Phi_0\rangle \neq E_0|\Phi_0\rangle$$

Møller-Plesset perturbation theory

$\langle \Phi_i^a | \hat{H} | \Phi_0 \rangle$=0 $\rightarrow$ no projection on the singly-excited configurations $|\Phi_i^a\rangle = \frac{1}{\sqrt{2}} \hat{E}_{ai} |\Phi_0\rangle$ ...

... but doubly-excited determinants appear when applying $\hat{V}$ to $|\Phi_0\rangle$:

$$\sum_D |D\rangle\langle D|\hat{V}|\Phi_0\rangle = \frac{1}{2} \sum_{a,b,i,j} \langle ab|ij\rangle \hat{E}_{ai}\hat{E}_{bj}|\Phi_0\rangle =$$

$$\sum_{b>a}\sum_{j>i}\sum_{\sigma} \Big(\Big(\langle ab|ij\rangle - \langle ab|ji\rangle \Big) \hat{a}^\dagger_{a,\sigma}\hat{a}_{i,\sigma}\hat{a}^\dagger_{b,\sigma}\hat{a}_{j,\sigma}|\Phi_0\rangle + \langle ab|ij\rangle \hat{a}^\dagger_{a,\sigma}\hat{a}_{i,\sigma}\hat{a}^\dagger_{b,-\sigma}\hat{a}_{j,-\sigma}|\Phi_0\rangle$$

$$- \langle ab|ji\rangle \hat{a}^\dagger_{a,\sigma}\hat{a}_{i,-\sigma}\hat{a}^\dagger_{b,-\sigma}\hat{a}_{j,\sigma}|\Phi_0\rangle \Big) + \sum_{a}\sum_{j>i}\sum_{\sigma} \langle aa|ij\rangle \hat{a}^\dagger_{a,\sigma}\hat{a}_{i,\sigma}\hat{a}^\dagger_{a,-\sigma}\hat{a}_{j,-\sigma}|\Phi_0\rangle$$

$$+ \sum_{i}\sum_{b>a}\sum_{\sigma} \langle ab|ii\rangle \hat{a}^\dagger_{a,\sigma}\hat{a}_{i,\sigma}\hat{a}^\dagger_{b,-\sigma}\hat{a}_{i,-\sigma}|\Phi_0\rangle + \sum_{a,i} \langle aa|ii\rangle \hat{a}^\dagger_{a,\alpha}\hat{a}_{i,\alpha}\hat{a}^\dagger_{a,\beta}\hat{a}_{i,\beta}|\Phi_0\rangle$$

$$\boxed{\langle \hat{a}^\dagger_{a,\sigma}\hat{a}_{i,\sigma}\hat{a}^\dagger_{b,\sigma}\hat{a}_{j,\sigma}|\Phi_0|\hat{V}|\Phi_0\rangle = \langle ab|ij\rangle - \langle ab|ji\rangle \neq 0}$$

- Wave function through first order: $|\Psi_0\rangle = |\Phi_0\rangle + \sum_D \frac{|D\rangle\langle D|\hat{V}|\Phi_0\rangle}{E^{(0)} - E_D^{(0)}} + \ldots$

- Energy through second order (MP2): $E_0 = E_{\mathrm{HF}} + \sum_D \frac{\langle D|\hat{V}|\Phi_0\rangle^2}{E^{(0)} - E_D^{(0)}} + \ldots$

$$E_0 = E_{\mathrm{HF}} + 4\sum_{b>a}\sum_{j>i} \frac{\langle ab|ij\rangle^2 + \langle ab|ji\rangle^2 - \langle ab|ij\rangle\langle ab|ji\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + 2\sum_a \sum_{j>i} \frac{\langle aa|ij\rangle^2}{\varepsilon_i + \varepsilon_j - 2\varepsilon_a}$$
$$+2\sum_{b>a}\sum_i \frac{\langle ab|ii\rangle^2}{2\varepsilon_i - \varepsilon_a - \varepsilon_b} + \sum_{a,i} \frac{\langle aa|ii\rangle^2}{2\varepsilon_i - 2\varepsilon_a} + \ldots$$

$$\boxed{E_0 = E_{\mathrm{HF}} + \sum_{a,b,i,j} \frac{\langle ab|ij\rangle\Big(2\langle ab|ij\rangle - \langle ab|ji\rangle\Big)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + \ldots}$$

- Note that a correlated wave function cannot be packed into a single determinant. This is due to the double excitations.

- When single excitations contribute at first order to the wave function, they are not associated to correlation but to orbital relaxation instead: $|\Phi(\boldsymbol{\kappa})\rangle = e^{-\hat{\kappa}}\,|\Phi_0\rangle = |\Phi_0\rangle - \sum_{a,i} \kappa_{ai}\,\hat{E}_{ai}|\Phi_0\rangle + \ldots$

Görling-Levy perturbation theory

- Correlation is defined differently in DFT

- Görling-Levy partitioning of the Hamiltonian:

$$\hat{H} = \hat{F}^{\mathrm{KS}} + (\hat{H} - \hat{F}^{\mathrm{KS}}) = \hat{F}^{\mathrm{KS}} + \underbrace{(\hat{H} - \hat{F}[\Phi^{\mathrm{KS}}])}_{\text{Møller-Plesset}} + \underbrace{(\hat{F}[\Phi^{\mathrm{KS}}] - \hat{F}^{\mathrm{KS}})}_{\text{orbital relaxation}}$$

where $\hat{F}^{\mathrm{KS}} = \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{Hxc}}$ is the KS operator and $\hat{F}[\Phi^{\mathrm{KS}}]$ is the Fock operator built from the KS orbitals,

$$\hat{F}[\Phi^{\mathrm{KS}}] - \hat{F}^{\mathrm{KS}} = \sum_{p,q} \Delta f_{pq} \hat{E}_{pq} \qquad \text{and} \qquad \Delta f_{pq} = -\sum_{i} \langle pi|iq\rangle - \langle \phi_p|\hat{v}_{\mathrm{xc}}|\phi_q\rangle$$

- The Brillouin theorem is (of course) not fulfilled anymore: $\langle \hat{E}_{ai}\Phi^{\mathrm{KS}}|\hat{H}|\Phi^{\mathrm{KS}}\rangle = 2\Delta f_{ai} \neq 0$

- The exact exchange energy is recovered through first order:

$$E^{(0)} + E^{(1)} = \langle \Phi^{\mathrm{KS}} | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi^{\mathrm{KS}} \rangle + \langle \Phi^{\mathrm{KS}} | \hat{W}_{\mathrm{ee}} | \Phi^{\mathrm{KS}} \rangle$$

- Correlation energy is a second- and higher-order energy contribution:

$$E_c^{(2)} = \underbrace{2 \sum_{i,a} \frac{(\Delta f_{ai})^2}{\varepsilon_i - \varepsilon_a}}_{\downarrow} + \sum_{a,b,i,j} \frac{\langle ab|ij\rangle \Big(2\langle ab|ij\rangle - \langle ab|ji\rangle \Big)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

relaxation of the KS orbitals (single excitations)

- Note also that, for open-shell atoms, the HF calculation is based on the atomic terms (^{2S+1}L) which consist in linear combinations of Slater determinants which all correspond to the same configuration (for example $1s^2 2s^2 2p^3$ for nitrogen). The HF wave function is then multideterminantal but describes one single configuration (no correlation effects).

- ^1S ground state of the helium atom:

$$\Psi_0(\mathbf{r_1}, \sigma_1, \mathbf{r_2}, \sigma_2) = \Psi_0(r_1, r_2, r_{12}) \frac{1}{\sqrt{2}} \Big(\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1) \Big)$$

- Hamiltonian expressed in terms of r_1, r_2 and $r_{12} = |\mathbf{r_1} - \mathbf{r_2}|$:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{2} \left(\frac{\partial^2}{\partial r i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} + \frac{2Z}{r_i} \right) - \left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} - \frac{1}{r_{12}} \right)$$

$$- \left(\frac{\mathbf{r_1}}{r_1} \cdot \frac{\mathbf{r_{12}}}{r_{12}} \frac{\partial}{\partial r_1} + \frac{\mathbf{r_2}}{r_2} \cdot \frac{\mathbf{r_{21}}}{r_{21}} \frac{\partial}{\partial r_2} \right) \frac{\partial}{r_{12}}$$

- $E_0 = \dfrac{\hat{H}\Psi_0(r_1, r_2, r_{12})}{\Psi_0(r_1, r_2, r_{12})} =$ constant, especially when $r_i = 0$ or $r_{12} = 0$

- Nuclear cusp conditions: $\dfrac{\partial \Psi_0}{\partial r_1}(0, r_2, r_{12}) = -Z\Psi_0(0, r_2, r_{12})$, $\dfrac{\partial \Psi_0}{\partial r_2}(r_1, 0, r_{12}) = -Z\Psi_0(r_1, 0, r_{12})$

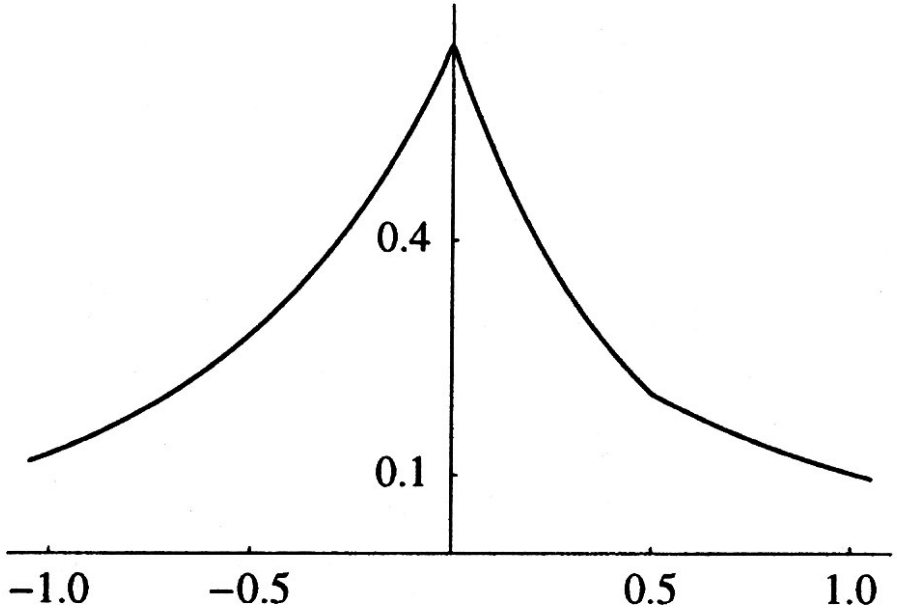
- Coulomb cusp condition: $\boxed{\dfrac{\partial \Psi_0}{\partial r_{12}}(r_1, r_2, 0) = \dfrac{1}{2}\Psi_0(r_1, r_2, 0)}$

- Expansion of the wave function around $r_2 = r_1 = 0.5$ a.u. and $r_{12} = 0$ for a collinear arrangement of the nucleus and the two electrons :

$$\Psi_0(r_1, r_2, r_{12}) = \Psi_0(r_1, r_2, |r_1 - r_2|)$$

$$= \Psi_0(r_1, r_1, 0) + (r_2 - r_1)\frac{\partial \Psi_0}{\partial r_2}(r_1, r_1, 0) + |r_1 - r_2|\frac{\partial \Psi_0}{\partial r_{12}}(r_1, r_1, 0) + \ldots$$

$$= \Psi_0(r_1, r_1, 0) + (r_2 - r_1)\frac{\partial \Psi_0}{\partial r_2}(r_1, r_1, 0) + \frac{1}{2}|r_1 - r_2|\Psi_0(r_1, r_1, 0) + \ldots$$



Short-range dynamical correlation

- The HF determinant does not fulfill the Coulomb cusp condition:

$$\Phi_0(r_1, r_2, r_{12}) = \phi_{1s}(r_1)\phi_{1s}(r_2) = e^{-\zeta(r_1+r_2)} = \Phi_0(r_1, r_2) \quad \longrightarrow \quad \frac{\partial \Phi_0}{\partial r_{12}} = 0 \quad \longrightarrow \quad \text{no cusp !}$$

- Describing short-range dynamical correlation is about recovering the Coulomb cusp

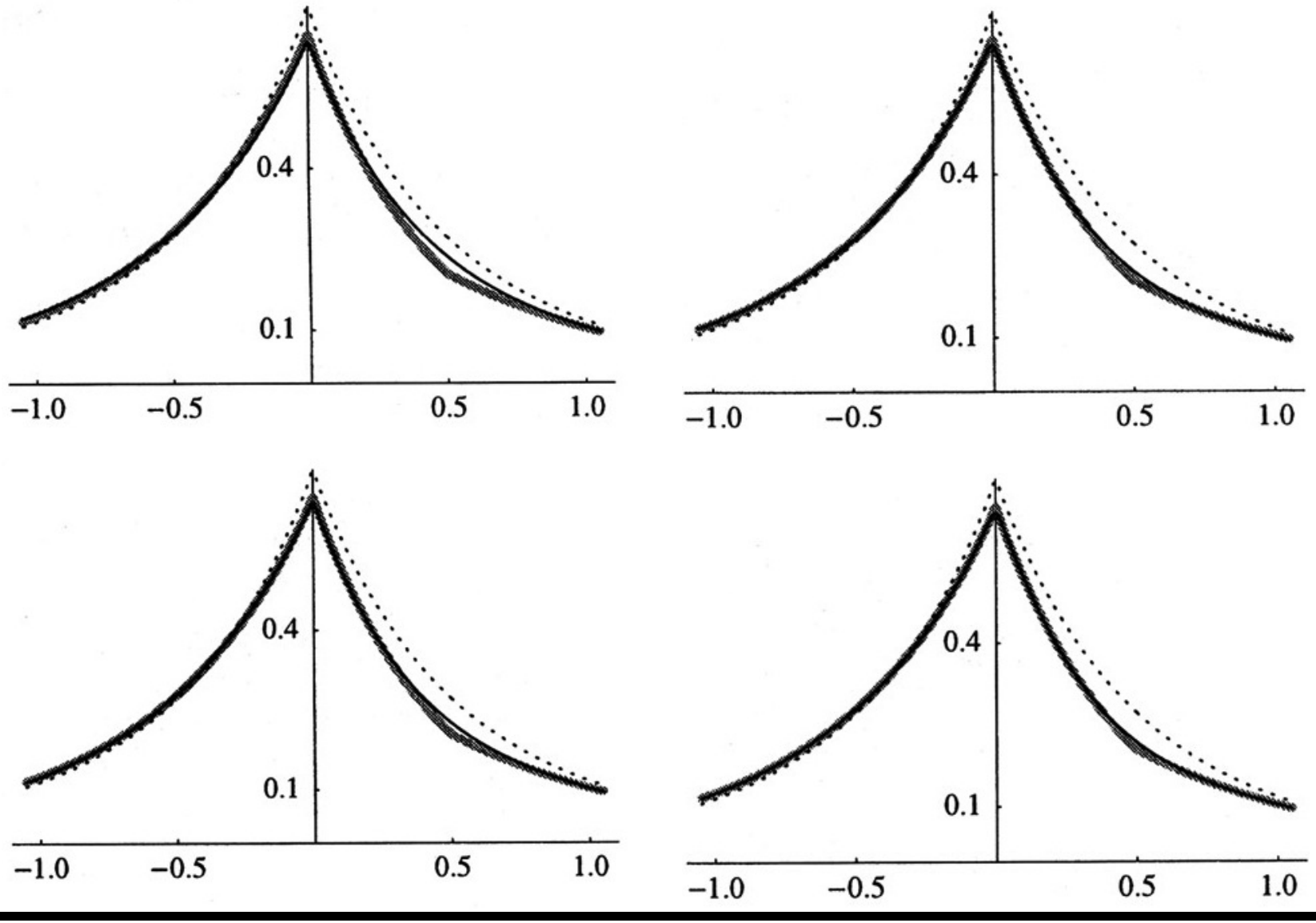
- **First approach:** expand the wave function in the basis of Slater determinants built from atomic orbitals $\phi_p(\mathbf{r})$ expressed as $r^{n-1}e^{-\zeta r}Y_l^m(\theta, \varphi)$. This is known as Configuration Interaction (CI)

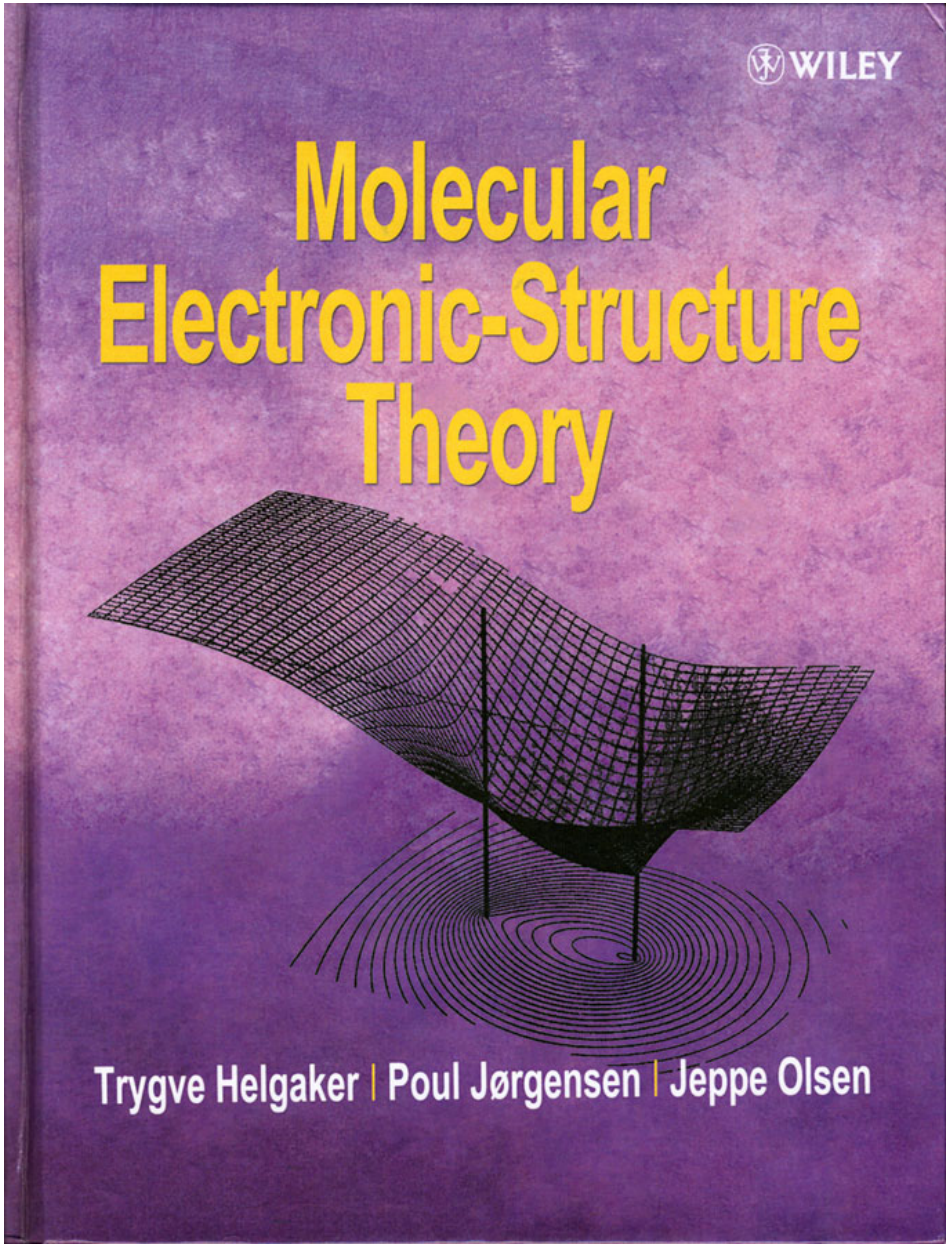
$$\Psi_0^{\mathrm{CI}}(r_1, r_2, r_{12}) = C_0\Phi_0(r_1, r_2)$$

$$+ \sum_a C_a \Big(\phi_a(\mathbf{r_1})\phi_{1s}(\mathbf{r_2}) + \phi_a(\mathbf{r_2})\phi_{1s}(\mathbf{r_1})\Big) \qquad \longleftarrow \text{ single excitations}$$

$$+ \sum_{a \leq b} C_{ab} \Big(\phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2}) + \phi_a(\mathbf{r_2})\phi_b(\mathbf{r_1})\Big) \qquad \longleftarrow \text{ double excitations}$$

Short-range dynamical correlation

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Short-range dynamical correlation

Slow convergence with respect to the number of Slater determinants ...

$$\frac{4\pi}{2l+1}\left(\sum_{m=-l}^{l}(-1)^m Y_l^m(\theta_1,\varphi_1)Y_l^{-m}(\theta_2,\varphi_2)\right) = P_l(\cos\theta_{12}) = a_l\,(\cos\theta_{12})^l + a_{l-1}\,(\cos\theta_{12})^{l-1} + \ldots$$

where $\quad r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}$

$$\frac{\partial \Psi_0^{\mathrm{CI}}}{\partial r_{12}}(r_1,r_2,0) \sim \frac{\partial r_{12}^2}{\partial r_{12}}(r_1,r_2,0) = 0 \quad \longrightarrow \quad \text{no cusp strictly speaking !}$$

Short-range dynamical correlation

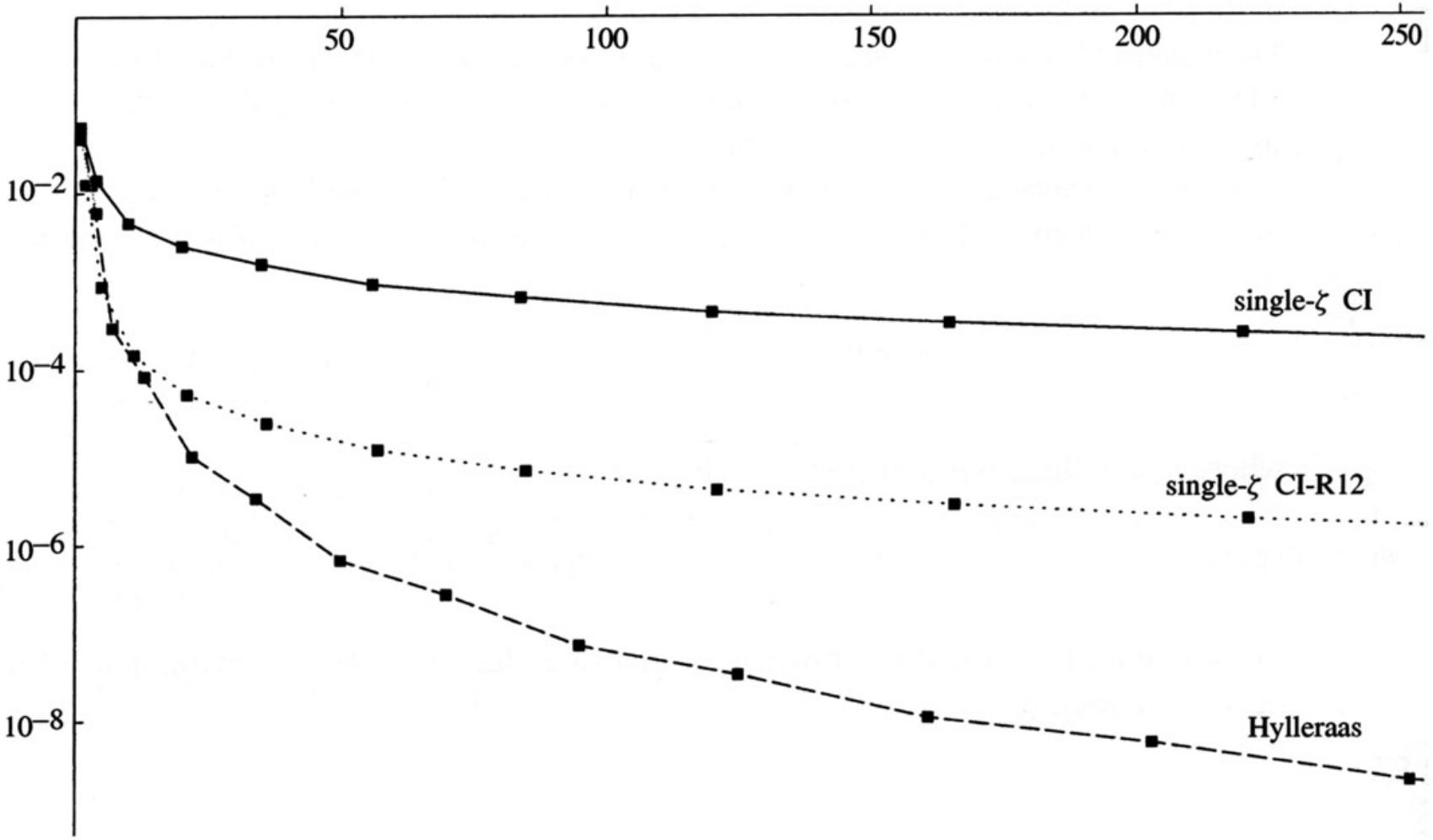
- **Second approach:** introduce r_{12} explicitly in the wave function.
  This is known as explicitly correlated method. For example:

$$\tilde{\Phi}_0(r_1, r_2, r_{12}) = \left(1 + \frac{1}{2} r_{12}\right) \Phi_0(r_1, r_2) \quad \text{or} \quad \tilde{\Phi}_0(r_1, r_2, r_{12}) = e^{\frac{1}{2} r_{12}} \Phi_0(r_1, r_2)$$

$$\frac{\partial \tilde{\Phi}_0}{\partial r_{12}}(r_1, r_2, 0) = \frac{1}{2} \Phi_0(r_1, r_2) = \frac{1}{2} \tilde{\Phi}_0(r_1, r_2, 0) \quad \longrightarrow \quad \text{cusp !}$$

- **Third approach:** combine the two first approaches

$$\tilde{\Psi}_0^{\mathrm{CI}}(r_1, r_2, r_{12}) = \Psi_0^{\mathrm{CI}}(r_1, r_2, r_{12}) + c_{12}\, r_{12}\, \Phi_0(r_1, r_2)$$



The error in the electronic energy of the ground-state helium atom (E_h). The error is plotted on a logarithmic scale as a function of the number of terms in the expansions.

Configuration Interaction method (CI)

- Expansion of the wave function in the basis of determinants based on the canonical doubly-occupied and unoccupied (virtual) HF orbitals.

- Those determinants are obtained when applying single, double, triple, quadruple, ... excitations to the HF determinant Φ_0.

$$|\Psi(\mathbf{C})\rangle = C_0|\Phi_0\rangle + \sum_S C_S|S\rangle + \sum_D C_D|D\rangle + \sum_T C_T|T\rangle + \sum_Q C_Q|Q\rangle + \ldots = \sum_i C_i|i\rangle$$

- If no truncation in the CI expansion (all excitations included) $\longrightarrow$ Full CI (FCI) $\longrightarrow$ exact for a given one-electron basis set

- Truncated CI models: CIS, CISD, CISDT, CISDTQ, ...

Configuration Interaction method (CI)

- Iterative optimization of the CI coefficients C_i:

$$|\Psi(\mathbf{C}^{(0)})\rangle = |\Psi^{(0)}\rangle = \sum_i C_i^{(0)} |i\rangle \quad \longleftarrow \quad \text{normalized starting CI wave function}$$

$$|\Psi(\boldsymbol{\delta})\rangle = \frac{|\Psi^{(0)}\rangle + \hat{Q}|\boldsymbol{\delta}\rangle}{\sqrt{1 + \langle\boldsymbol{\delta}|\hat{Q}|\boldsymbol{\delta}\rangle}} \quad \longleftarrow \quad \text{convenient parametrization} \quad \boldsymbol{\delta} = \begin{bmatrix} \vdots \\ \delta_i \\ \vdots \end{bmatrix}$$

$$\hat{Q} = 1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|, \qquad |\boldsymbol{\delta}\rangle = \sum_i \delta_i |i\rangle, \qquad \langle\Psi^{(0)}|\hat{Q}|\boldsymbol{\delta}\rangle = 0, \qquad \langle\Psi(\boldsymbol{\delta})|\Psi(\boldsymbol{\delta})\rangle = 1$$

- CI energy expression: $E(\boldsymbol{\delta}) = \langle\Psi(\boldsymbol{\delta})|\hat{H}|\Psi(\boldsymbol{\delta})\rangle$

$$= \frac{E(0) + 2\boldsymbol{\delta}^{\mathrm{T}}\mathbf{Q}\mathbf{H}\mathbf{C}^{(0)} + \boldsymbol{\delta}^{\mathrm{T}}\mathbf{Q}\mathbf{H}\mathbf{Q}\boldsymbol{\delta}}{1 + \boldsymbol{\delta}^{\mathrm{T}}\mathbf{Q}\boldsymbol{\delta}}$$

where $\mathbf{H}_{ij} = \langle i|\hat{H}|j\rangle$ and $\mathbf{Q} = 1 - \mathbf{C}^{(0)}\mathbf{C}^{(0)\mathrm{T}}$

Configuration Interaction method (CI)

- Variational condition: $E^{[1]}_{\boldsymbol{\delta}_+} = \left.\frac{\partial E(\boldsymbol{\delta})}{\partial \boldsymbol{\delta}}\right|_{\boldsymbol{\delta}_+} = 0$

- Newton method:

$$E(\boldsymbol{\delta}) \approx E(0) + \boldsymbol{\delta}^T E^{[1]}_0 + \frac{1}{2}\boldsymbol{\delta}^T E^{[2]}_0 \boldsymbol{\delta} \quad \rightarrow \quad E^{[1]}_{\boldsymbol{\delta}_+} \approx E^{[1]}_0 + E^{[2]}_0 \boldsymbol{\delta}_+ = 0 \quad \rightarrow \quad E^{[2]}_0 \underbrace{\boldsymbol{\delta}_+}_{\textbf{Newton step}} = -E^{[1]}_0$$

EX4: Show that the CI grandient and hessian can be expressed as

$$\boxed{E^{[1]}_0 = 2\Big(\mathbf{H} - E(0)\Big)\mathbf{C}^{(0)} \quad \text{and} \quad E^{[2]}_0 = 2\mathbf{Q}\Big(\mathbf{H} - E(0)\Big)\mathbf{Q}}$$

- Note that $E^{[2]}_0$ cannot be inverted since $E^{[2]}_0 \mathbf{C}^{(0)} = 0$

- We can choose $\boldsymbol{\delta}_+$ such that $\mathbf{C}^{(0)\mathrm{T}} \boldsymbol{\delta}_+ = 0 \quad \longrightarrow \quad \underbrace{\left(E^{[2]}_0 + 2\alpha \mathbf{C}^{(0)} \mathbf{C}^{(0)\mathrm{T}}\right)}_{G^{[2]}_0} \boldsymbol{\delta}_+ = -E^{[1]}_0$

  where $\alpha \neq 0$

Configuration Interaction method (CI)

After some algebra* ... $\boldsymbol{\delta}_+ = -\left(G_0^{[2]}\right)^{-1} E_0^{[1]} = -\mathbf{C}^{(0)} + \dfrac{\left(\mathbf{H} - E(0)\right)^{-1}\mathbf{C}^{(0)}}{\mathbf{C}^{(0)\mathrm{T}}\left(\mathbf{H} - E(0)\right)^{-1}\mathbf{C}^{(0)}}$

which does not depend on α since $\mathbf{C}^{(0)\mathrm{T}} E_0^{[1]} = 0$

- Update of the CI vector:

  $\mathbf{C}^{(0)} \longrightarrow \mathbf{C}^{(0)} + \mathbf{Q}\boldsymbol{\delta}_+ = \boxed{\mathbf{C}^{(0)} + \boldsymbol{\delta}_+ = \dfrac{\left(\mathbf{H} - E(0)\right)^{-1}\mathbf{C}^{(0)}}{\mathbf{C}^{(0)\mathrm{T}}\left(\mathbf{H} - E(0)\right)^{-1}\mathbf{C}^{(0)}}}$

  and then normalize.

- The CI calculation has converged when $E_0^{[1]} = 0 \longrightarrow \mathbf{H}\mathbf{C}^{(0)} = E(0)\mathbf{C}^{(0)}$
- This procedure is also known as Rayleigh method.

*T. Helgaker, P. Jørgensen, and J. Olsen, Molecular Electronic- Structure Theory (Wiley, Chichester, 2004), pp. 544-545.

Size-consistency problem in truncated CI calculations

- Size-consistency property of a method: multiplicatively separable wave function and additively separable energy that is $\boxed{E(1+2) = E(1) + E(2)}$

  where 1 and 2 denote two non-interacting monomers ($\hat{H} = \hat{H}_1 + \hat{H}_2$).

- Example: H_2 dimer in a minimal basis set

- For the monomer I ($I = 1, 2$), the $1\sigma_{gI}$ and $1\sigma_{uI}$ orbitals only are considered.

- Ground-state HF determinant for the monomer: $|\Phi_0(I)\rangle = \hat{a}^\dagger_{1\sigma_{gI},\alpha}\hat{a}^\dagger_{1\sigma_{gI},\beta}|\text{vac}\rangle$

- Ground-state HF determinant for the dimer: $|\Phi_0(1+2)\rangle = \left(\prod_{I=1}^{2} \hat{a}^\dagger_{1\sigma_{gI},\alpha}\hat{a}^\dagger_{1\sigma_{gI},\beta}\right)|\text{vac}\rangle$

$$E_{\text{HF}}(1+2) = \langle\Phi_0(1+2)|\hat{H}|\Phi_0(1+2)\rangle = \langle\Phi_0(1)|\hat{H}_1|\Phi_0(1)\rangle + \langle\Phi_0(2)|\hat{H}_2|\Phi_0(2)\rangle$$

$$= E_{\text{HF}}(1) + E_{\text{HF}}(2) \quad \longleftarrow \quad \text{size-consistent !}$$

Size-consistency problem in truncated CI calculations

- CID corresponds to FCI for the monomer:

$$|\Psi^{\mathrm{CID}}(I)\rangle = \left(1 + c\hat{D}_I\right)|\Phi_0(I)\rangle$$

where $\hat{D}_I = \hat{a}^\dagger_{1\sigma_{uI},\alpha}\hat{a}^\dagger_{1\sigma_{uI},\beta}\hat{a}_{1\sigma_{gI},\beta}\hat{a}_{1\sigma_{gI},\alpha}$ $\longleftarrow$ double excitation on monomer I

$$\mathbf{H}^{\mathrm{CID}}(I) - E_{\mathrm{HF}}(I) = \begin{bmatrix} 0 & K \\ K & 2\Delta \end{bmatrix} \longrightarrow \boxed{E^{\mathrm{CID}}(I) = E_{\mathrm{HF}}(I) + \Delta - \sqrt{\Delta^2 + K^2}}$$

- CID is not FCI for the dimer:

$$|\Psi^{\mathrm{CID}}(1+2)\rangle = \left(1 + c\hat{D}_1 + c\hat{D}_2\right)|\Phi_0(1+2)\rangle$$

$$|\Psi^{\mathrm{FCI}}(1+2)\rangle = \left(1 + c\hat{D}_1 + c\hat{D}_2 + c_{12}\hat{D}_1\hat{D}_2\right)|\Phi_0(1+2)\rangle$$

Size-consistency problem in truncated CI calculations

EX5: Show that, for the dimer,

(i) the CID Hamiltonian matrix equals $\mathbf{H}^{\mathrm{CID}}(1+2) - E_{\mathrm{HF}}(1+2) = \begin{bmatrix} 0 & K & K \\ K & 2\Delta & 0 \\ K & 0 & 2\Delta \end{bmatrix}$

(ii) the FCI Hamiltonian matrix equals $\mathbf{H}^{\mathrm{FCI}}(1+2) - E_{\mathrm{HF}}(1+2) = \begin{bmatrix} 0 & K & K & 0 \\ K & 2\Delta & 0 & K \\ K & 0 & 2\Delta & K \\ 0 & K & K & 4\Delta \end{bmatrix}$

(iii) CID is not size-consistent since

$$E^{\mathrm{CID}}(1+2) = E_{\mathrm{HF}}(1+2) + \Delta - \sqrt{\Delta^2 + 2K^2} \neq E^{\mathrm{CID}}(1) + E^{\mathrm{CID}}(2)$$

(iv) FCI is size-consistent and $c_{12} = c^2$

Size-consistency problem in truncated CI calculations

- $E^{\mathrm{FCI}}(1+2) - E^{\mathrm{CID}}(1+2) = \Delta\left(1 + \sqrt{1+2\left(\frac{K}{\Delta}\right)^2} - 2\sqrt{1+\left(\frac{K}{\Delta}\right)^2}\right)$

$$= \Delta\Big(-\frac{1}{4}\left(\frac{K}{\Delta}\right)^4 + \dots\Big)$$

- FCI wave function written as a Coupled-Cluster wave function (exponential ansatz):

$$|\Psi^{\mathrm{FCI}}(1+2)\rangle = \left(1 + c\hat{D}_1 + c\hat{D}_2 + c^2\hat{D}_1\hat{D}_2\right)|\Phi_0(1+2)\rangle$$

$$= \left(1 + c\hat{D}_1\right)\left(1 + c\hat{D}_2\right)|\Phi_0(1+2)\rangle = e^{c\hat{D}_1}\, e^{c\hat{D}_2}|\Phi_0(1+2)\rangle$$

$$\boxed{|\Psi^{\mathrm{FCI}}(1+2)\rangle = e^{c\hat{D}_1 + c\hat{D}_2}|\Phi_0(1+2)\rangle}$$

CCD generates quadruple excitations, by means of the exponential, as products of double excitations and thus ensures size-consistency !

Coupled-Cluster model (CC)

- Note that the exponential used in CC enables to describe not only orbital rotations (single excitations) but also electron correlation.
- Exponential ansatz in the general case: $\boxed{|\Psi(\mathbf{t})\rangle = e^{\hat{\mathcal{T}}}|\Phi_0\rangle}$ where

$$\hat{\mathcal{T}} = \sum_S t_S \hat{S} + \sum_D t_D \hat{D} + \sum_T t_T \hat{T} + \sum_Q t_Q \hat{Q} + \ldots = \sum_\mu t_\mu \hat{\tau}_\mu$$

$\hat{\tau}_\mu|\Phi_0\rangle = |\mu\rangle$ $\longleftarrow$ excited determinant

$$\mathbf{t} = \begin{bmatrix} \vdots \\ t_\mu \\ \vdots \end{bmatrix}$$

$\longleftarrow$ CC amplitudes to be optimized

- Truncated and approximate CC models: CCSD, CCSDT, CCSDTQ, CCSD(T), CC2, ...

Coupled-Cluster model (CC)

- Variational optimization of the CC amplitudes not convenient

$$\frac{\langle\Psi(\mathbf{t})|\hat{H}|\Psi(\mathbf{t})\rangle}{\langle\Psi(\mathbf{t})|\Psi(\mathbf{t})\rangle} = \frac{\langle\Phi_0|e^{\hat{T}^\dagger}\hat{H}e^{\hat{T}}|\Phi_0\rangle}{\langle\Phi_0|e^{\hat{T}^\dagger}e^{\hat{T}}|\Phi_0\rangle} \quad \longleftarrow \text{ the BCH expansion cannot be used } (\hat{T}^\dagger \neq -\hat{T})$$

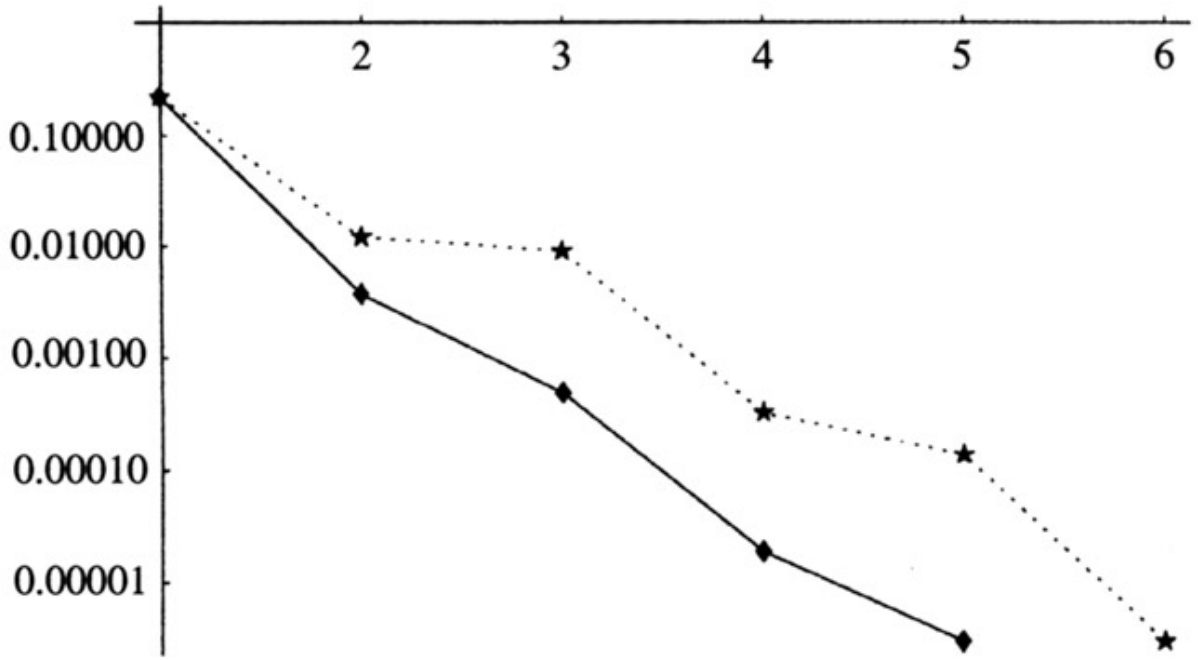
- Non-variational optimization: $\hat{H}|\Psi(\mathbf{t})\rangle = E(\mathbf{t})|\Psi(\mathbf{t})\rangle \longrightarrow \hat{H}e^{\hat{T}}|\Phi_0\rangle = E(\mathbf{t})e^{\hat{T}}|\Phi_0\rangle$

- "Linked" formulation: $e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E(\mathbf{t})|\Phi_0\rangle$

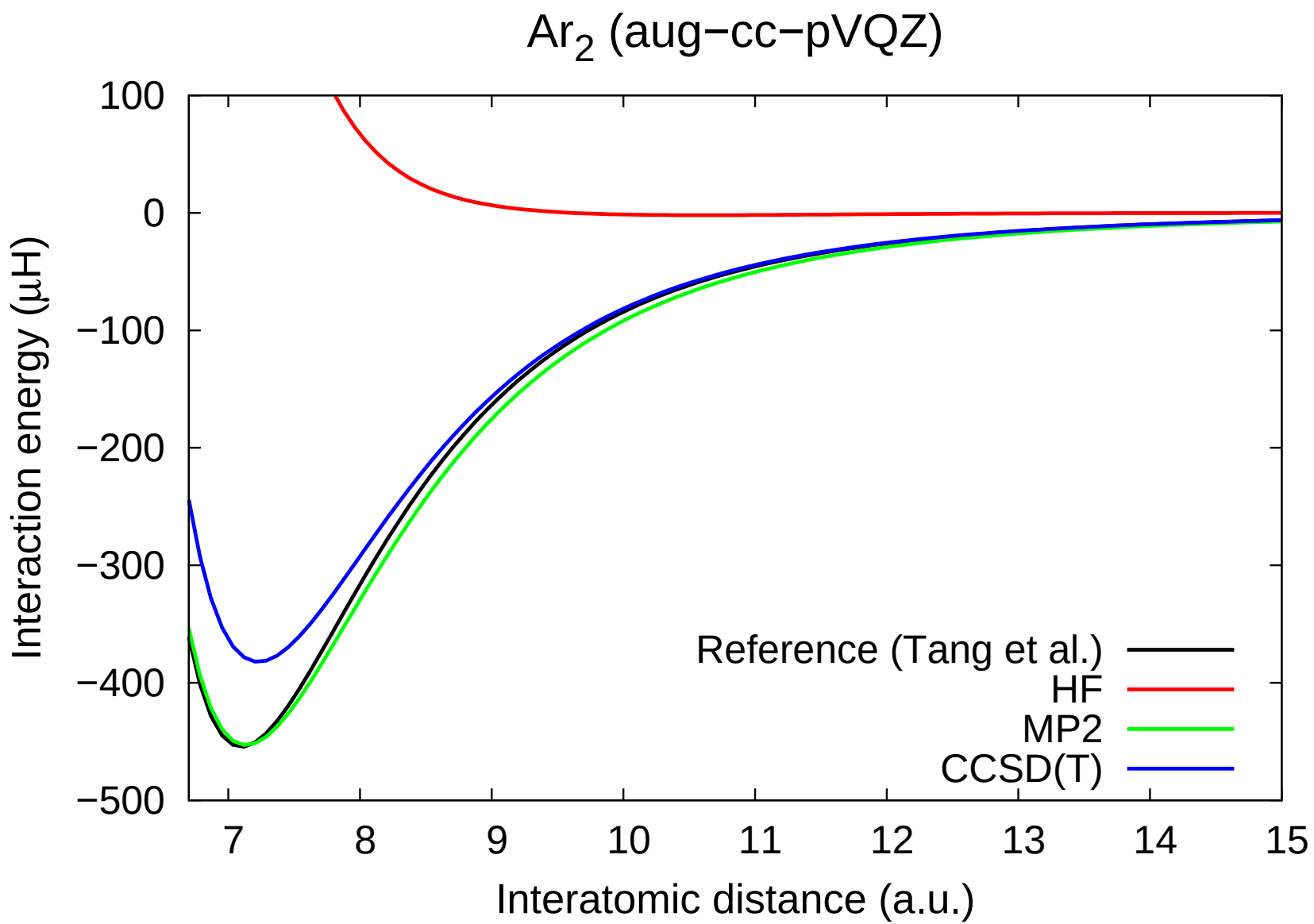
- CC energy: $E(\mathbf{t}) = \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = \langle\Phi_0|\hat{H}e^{\hat{T}}|\Phi_0\rangle$

$$\boxed{E(\mathbf{t}) = \langle\Phi_0|\hat{H}\left(1 + \sum_D t_D\hat{D} + \frac{1}{2}\Big(\sum_S t_S\hat{S}\Big)^2\right)|\Phi_0\rangle}$$

- CC amplitudes: $\langle\mu|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0 \quad \longleftarrow$ the BCH expansion can be used (no terms beyond fourth order !)



The error (with respect to FCI) in the total energy (E_h) of coupled-cluster wave functions (full line) and CI wave functions (dotted line) at different excitation levels for the water molecule at the equilibrium geometry in the cc-pVDZ basis.


Ar2 (aug−cc−pVQZ)
Interaction energy (μH)
100
0
−100
−200
−300
−400
−500
7
8
9
10
11
12
13
14
15
Interatomic distance (a.u.)
Reference (Tang et al.)
HF
MP2
CCSD(T)