

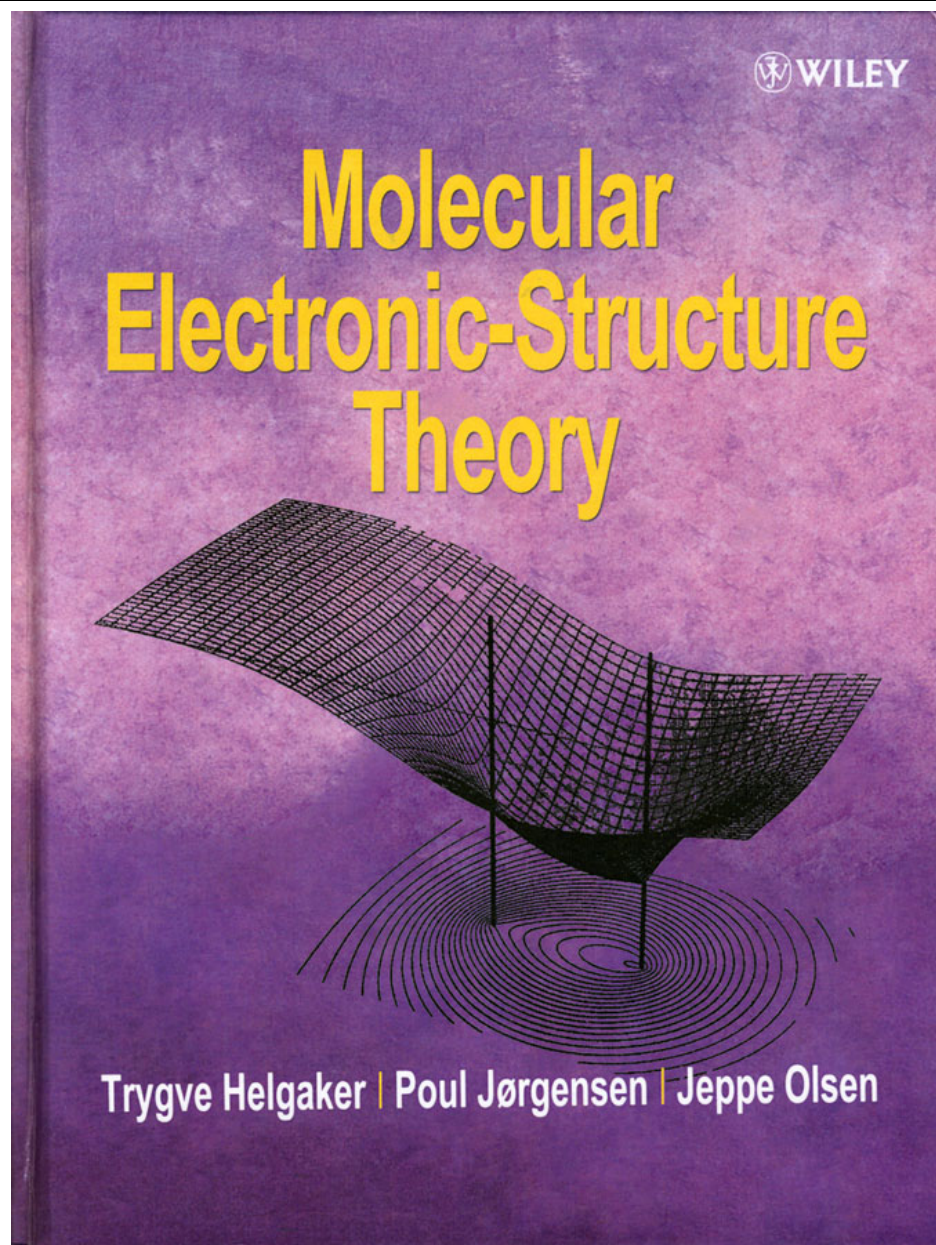
Introduction to Coupled-Cluster theory

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Variational and non-variational approximations

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

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

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

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

Variational calculation

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

↓

Hartree-Fock (HF)

Configuration Interaction (CI)

Multi-Configurational Self-Consistent Field (MCSCF)

Non-variational calculation

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

↓

Many-Body Perturbation Theory (MBPT)

Coupled Cluster (CC)

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

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

- If **no truncation** in the CI expansion (all excitations included) \rightarrow **Full CI** (FCI) \rightarrow exact for a given one-electron basis set.
- Truncated CI models: CIS, CISD, CISDT, CISDTQ, ...

H₂ in a minimal basis

- **Bonding** and **antibonding** orbitals in the minimal **1s orbital basis**:

$$\phi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}} \left(\phi_{1s_A}(\mathbf{r}) + \phi_{1s_B}(\mathbf{r}) \right) \quad \text{and} \quad \phi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}} \left(\phi_{1s_A}(\mathbf{r}) - \phi_{1s_B}(\mathbf{r}) \right)$$

- The Hamiltonian matrix for H₂ can be written in the basis of the two single-determinantal states $|1\sigma_g^\alpha 1\sigma_g^\beta\rangle$ and $|1\sigma_u^\alpha 1\sigma_u^\beta\rangle$ as follows,

$$[\hat{H}] = \begin{bmatrix} E_g & K \\ K & E_u \end{bmatrix}, \quad \text{where}$$

$$\text{for } i = g, u, \quad E_i = 2h_{ii} + \langle 1\sigma_i 1\sigma_i | 1\sigma_i 1\sigma_i \rangle, \quad h_{ii} = \langle 1\sigma_i | \hat{h} | 1\sigma_i \rangle, \quad K = \langle 1\sigma_u 1\sigma_u | 1\sigma_g 1\sigma_g \rangle.$$

- E_g corresponds to the HF energy in the minimal basis.
- Let $\Delta = \frac{1}{2} (E_u - E_g)$. The ratio $\frac{K}{\Delta}$ gives the strength of the **electron correlation**.
- The **symmetric Hubbard dimer** model is recovered when $\Delta = 2t$ and $K = \frac{U}{2} \rightarrow \frac{K}{\Delta} = \frac{U}{4t}$.

Size-consistency problem in truncated CI calculations

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

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

- Example: H₂ 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**: $|\Phi_0(I)\rangle = \hat{a}_{1\sigma_{gI},\alpha}^\dagger \hat{a}_{1\sigma_{gI},\beta}^\dagger |\text{vac}\rangle$

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

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

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

Size-consistency problem in truncated CI calculations

- CID corresponds to FCI for the **monomer**:

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

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

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

- CID is **not** FCI for the **dimer**:

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

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

Size-consistency problem in truncated CI calculations

EX5: Show that, for the dimer,

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

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

(iii) CID is not size-consistent since

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

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

Size-consistency problem in truncated CI calculations

- $$E^{\text{FCI}}(1+2) - E^{\text{CID}}(1+2) = \Delta \left(1 + \sqrt{1 + 2 \left(\frac{K}{\Delta} \right)^2} - 2 \sqrt{1 + \left(\frac{K}{\Delta} \right)^2} \right)$$
$$= \Delta \left(-\frac{1}{4} \left(\frac{K}{\Delta} \right)^4 + \dots \right)$$

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

$$\begin{aligned} |\Psi^{\text{FCI}}(1+2)\rangle &= \left(1 + c\hat{D}_1 + c\hat{D}_2 + c^2\hat{D}_1\hat{D}_2 \right) |\Phi_0(1+2)\rangle \\ &= \left(1 + c\hat{D}_1 \right) \left(1 + c\hat{D}_2 \right) |\Phi_0(1+2)\rangle = e^{c\hat{D}_1} e^{c\hat{D}_2} |\Phi_0(1+2)\rangle \end{aligned}$$

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

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

Coupled-Cluster theory (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: $|\Psi(\mathbf{t})\rangle = e^{\hat{T}} |\Phi_0\rangle$ where

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

$$\hat{\tau}_{\mu} |\Phi_0\rangle = |\mu\rangle \quad \leftarrow \text{excited determinant}$$

$$\mathbf{t} = \begin{bmatrix} \vdots \\ t_{\mu} \\ \vdots \end{bmatrix} \quad \leftarrow \text{CC amplitudes to be optimized}$$

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

Coupled-Cluster theory (CC)

- **Variational optimization** of the CC amplitudes **not convenient**

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

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

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

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

Example of approximate CC theory: the closed-shell CCSD model

- Let i, j, k, \dots and a, b, c, \dots denote **doubly occupied** and **virtual** (unoccupied) orbitals in the HF determinant, respectively.
- The **CCSD model** is an approximate version of CC theory where **single and double excitations only** are taken into account in the excitation operator \hat{T} :

$$\hat{T} \rightarrow \hat{T}_{\text{CCSD}} = \hat{T}_1 + \hat{T}_2,$$

where

$$\hat{T}_1 = \sum_S t_S \hat{S} = \sum_{ai} t_i^a \hat{E}_{ai} \quad \leftarrow \text{single excitations}$$

$$\hat{T}_2 = \sum_D t_D \hat{D} = \frac{1}{2} \sum_{abij} t_{ij}^{ab} \hat{E}_{ai} \hat{E}_{bj} \quad \leftarrow \text{double excitations}$$

and $t_{ij}^{ab} = t_{ji}^{ba}$, since $[\hat{E}_{ai}, \hat{E}_{bj}] = 0$.

CC energy expression

- As shown previously, the CC energy can be written as follows,

$$E_{\text{CC}} = E_{\text{HF}} + \frac{1}{2} \sum_{abij} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \langle \Phi_0 | \hat{H} \hat{E}_{ai} \hat{E}_{bj} | \Phi_0 \rangle,$$

where $\langle \Phi_0 | \hat{H} \hat{E}_{ai} \hat{E}_{bj} | \Phi_0 \rangle = \langle \Phi_0 | [\hat{H}, \hat{E}_{ai}] \hat{E}_{bj} | \Phi_0 \rangle = \langle \Phi_0 | [[\hat{H}, \hat{E}_{ai}], \hat{E}_{bj}] | \Phi_0 \rangle,$

since $\langle \Phi_0 | \hat{E}_{ai} = \langle \hat{E}_{ia} \Phi_0 | = 0 = \langle \Phi_0 | \hat{E}_{bj}.$

- From the second-quantized expression of the Hamiltonian,

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

it can be shown (see exercise page 19) that

$$\langle \Phi_0 | [[\hat{H}, \hat{E}_{ai}], \hat{E}_{bj}] | \Phi_0 \rangle = 2 \left(2 \langle ij | ab \rangle - \langle ij | ba \rangle \right).$$

CC energy expression

- Therefore, the final expression for the CC energy in terms of the singles and doubles CC amplitudes is

$$E_{CC} = E_{\text{HF}} + \sum_{abij} \left(t_{ij}^{ab} + t_i^a t_j^b \right) \left(2\langle ij|ab\rangle - \langle ij|ba\rangle \right).$$

- Note that this expression is "**exact**" (*i.e.*, corresponds to the Full CI energy) if exact amplitudes are used.
- The **CCSD energy** will be **approximate** because the amplitudes will be approximate. Indeed, they will be determined in the absence of higher-order excitation amplitudes.
- The energy is **linear** in the doubles amplitudes t_{ij}^{ab} and **quadratic** in the singles amplitudes t_i^a .
- As long as electron correlation is not too strong, we can expect the doubles to contribute the most to the CC energy (in agreement with MP2).
- Large singles amplitudes indicate a need for orbital reoptimization (**T_1 diagnostic**). This can happen when **electron correlation is strong**.
- Returning to the weakly correlated regime, let us ignore (as it could be the case in the first iteration of a CC calculation) the singles amplitudes, thus leading to the **CCD model**.

CCD amplitudes

- The CCD energy reads

$$E_{\text{CCD}} = E_{\text{HF}} + \sum_{abij} t_{ij}^{ab} \left(2\langle ij|ab\rangle - \langle ij|ba\rangle \right).$$

- The doubles amplitudes t_{ij}^{ab} will be determined by **projecting** the CC equation in the **linked formulation** onto the doubly-excited states $|\Phi_{ij}^{ab}\rangle = \hat{E}_{ai}\hat{E}_{bj}|\Phi_0\rangle$:

$$\langle \Phi_{ij}^{ab} | e^{-\hat{\mathcal{T}}_2} \hat{H} e^{\hat{\mathcal{T}}_2} | \Phi_0 \rangle = 0,$$

where $e^{-\hat{\mathcal{T}}_2} \hat{H} e^{\hat{\mathcal{T}}_2} = \hat{H} + [\hat{H}, \hat{\mathcal{T}}_2] + \frac{1}{2} [[\hat{H}, \hat{\mathcal{T}}_2], \hat{\mathcal{T}}_2] + \underbrace{\frac{1}{6} [[[\hat{H}, \hat{\mathcal{T}}_2], \hat{\mathcal{T}}_2], \hat{\mathcal{T}}_2]} + \dots$

creates sextuple and higher-order excitations than can be reduced to quadruple and higher-order excitations thanks to $\hat{H} \rightarrow$ does not contribute to the CCD amplitudes equations !

- Consequently, the CCD amplitudes equations can be simplified as follows,

$$\left\langle \Phi_{ij}^{ab} \left| \hat{H} + [\hat{H}, \hat{\mathcal{T}}_2] + \frac{1}{2} [[\hat{H}, \hat{\mathcal{T}}_2], \hat{\mathcal{T}}_2] \right| \Phi_0 \right\rangle = 0.$$

- In a weakly correlated regime, one may only keep the **linear term in $\hat{\mathcal{T}}_2$** , thus leading to

$$\left\langle \Phi_{ij}^{ab} \left| \hat{H} + [\hat{H}, \hat{\mathcal{T}}_2] \right| \Phi_0 \right\rangle \approx 0.$$

- From the Møller-Plesset (MP) partitioning $\hat{H} = \hat{f} + \hat{\mathcal{W}}$, where $\hat{f} = \sum_i \varepsilon_i \hat{E}_{ii} + \sum_a \varepsilon_a \hat{E}_{aa}$ is the **Fock operator** (written here in the canonical HF orbital basis), it comes

$$\left\langle \Phi_{ij}^{ab} \left| \hat{\mathcal{W}} + [\hat{f}, \hat{\mathcal{T}}_2] + [\hat{\mathcal{W}}, \hat{\mathcal{T}}_2] \right| \Phi_0 \right\rangle \approx 0.$$

where we used $\hat{f}|\Phi_0\rangle = 2\left(\sum_i \varepsilon_i\right)|\Phi_0\rangle$.

- $\hat{\mathcal{T}}_2$ is at least a first-order (linear) contribution in $\hat{\mathcal{W}}$. If we keep linear terms in $\hat{\mathcal{W}}$ only we obtain

$$\left\langle \Phi_{ij}^{ab} \left| \hat{\mathcal{W}} + [\hat{f}, \hat{\mathcal{T}}_2] \right| \Phi_0 \right\rangle \approx 0.$$

- Note that (see page 13)

$$\langle \Phi_{ij}^{ab} | \hat{\mathcal{W}} | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle = \langle \Phi_0 | \hat{H} \hat{E}_{ai} \hat{E}_{bj} | \Phi_0 \rangle = 2(2\langle ij|ab \rangle - \langle ij|ba \rangle),$$

so that the simplified CCD amplitudes equations read

$$\langle \Phi_{ij}^{ab} | [\hat{f}, \hat{\mathcal{T}}_2] | \Phi_0 \rangle \approx -2(2\langle ij|ab \rangle - \langle ij|ba \rangle).$$

- The term on the left-hand side can be rewritten in terms of nested commutators as follows,

$$\begin{aligned} \langle \Phi_{ij}^{ab} | [\hat{f}, \hat{\mathcal{T}}_2] | \Phi_0 \rangle &= \langle \Phi_0 | \hat{E}_{jb} \hat{E}_{ia} [\hat{f}, \hat{\mathcal{T}}_2] | \Phi_0 \rangle \\ &= -\langle \Phi_0 | \hat{E}_{jb} [[\hat{f}, \hat{\mathcal{T}}_2], \hat{E}_{ia}] | \Phi_0 \rangle \\ &= \langle \Phi_0 | [[[\hat{f}, \hat{\mathcal{T}}_2], \hat{E}_{ia}] \hat{E}_{jb},] | \Phi_0 \rangle \end{aligned}$$

- By using the exercise page 19, it can finally be shown that

$$\langle \Phi_{ij}^{ab} | [\hat{f}, \hat{\mathcal{T}}_2] | \Phi_0 \rangle = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j) (4t_{ij}^{ab} - 2t_{ji}^{ab}).$$

- Therefore, for any i, j, a, b we have (through first order in the fluctuation potential)

$$4t_{ij}^{ab} - 2t_{ji}^{ab} \approx \frac{2(2\langle ij|ab\rangle - \langle ij|ba\rangle)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b},$$

and, by **interchanging i and j** ,

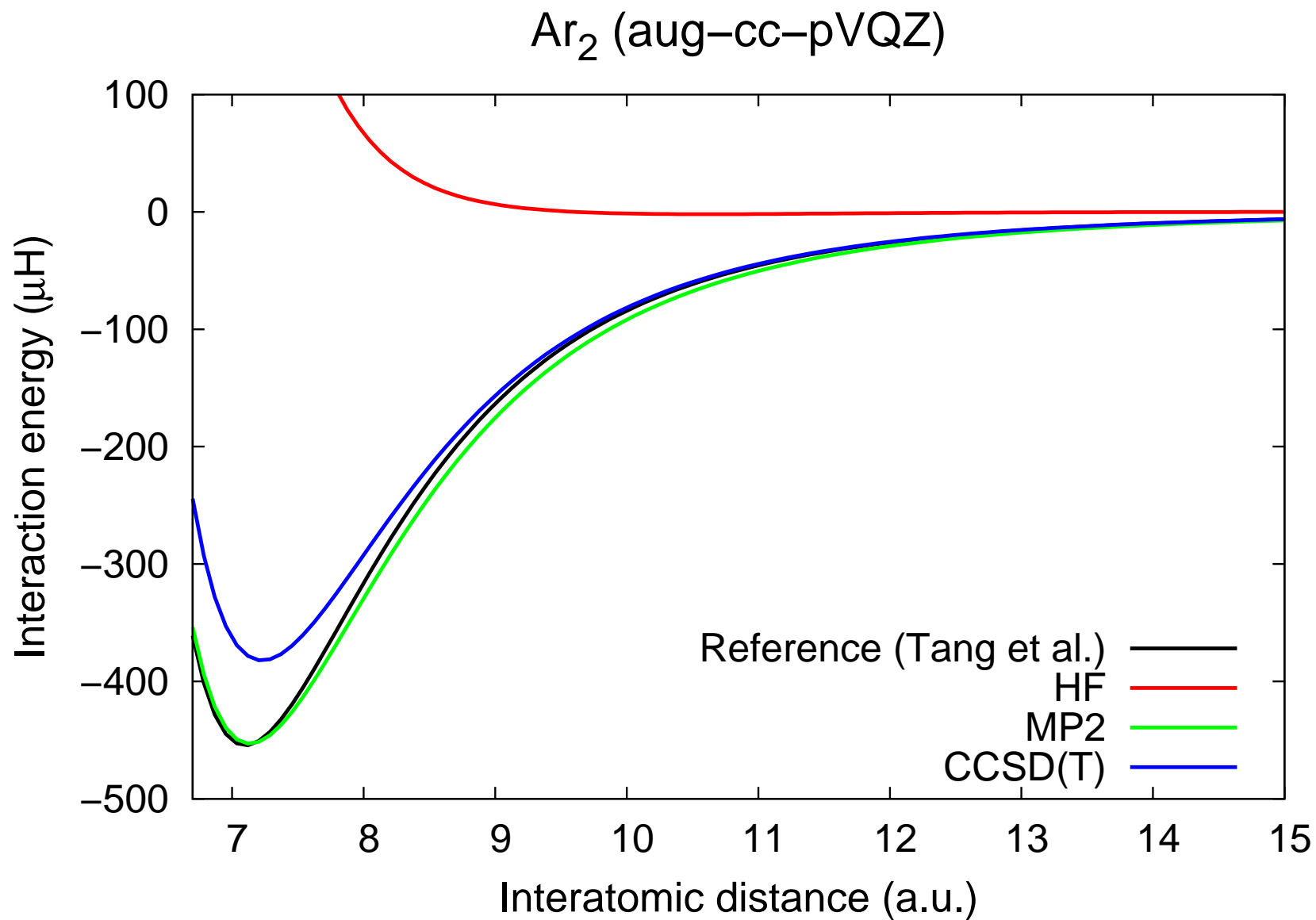
$$4t_{ji}^{ab} - 2t_{ij}^{ab} \approx \frac{2(2\langle ij|ba\rangle - \langle ij|ab\rangle)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}.$$

- Conclusion:

$$\frac{1}{3}(4t_{ij}^{ab} - 2t_{ji}^{ab}) + \frac{1}{6}(4t_{ji}^{ab} - 2t_{ij}^{ab}) = \boxed{t_{ij}^{ab} \approx \frac{\langle ij|ab\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}},$$

and

$$E_{\text{CCD}} \approx E_{\text{HF}} + \sum_{abij} \frac{\langle ij|ab\rangle (2\langle ij|ab\rangle - \langle ij|ba\rangle)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = E_{\text{MP2}} !$$



EXERCISE: (1) Show that $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] = [\hat{A}, \hat{B}]_+ \hat{C} - \hat{B}[\hat{A}, \hat{C}]_+$.

(2) Deduce from (1) that $[\hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma'}, \hat{a}_{r,\tau}^\dagger \hat{a}_{s,\tau'}] = \delta_{rq} \delta_{\tau\sigma'} \hat{a}_{p,\sigma}^\dagger \hat{a}_{s,\tau'} - \delta_{sp} \delta_{\tau'\sigma} \hat{a}_{r,\tau}^\dagger \hat{a}_{q,\sigma'}$ and conclude that

$$[\hat{E}_{pq}, \hat{E}_{rs}] = \delta_{rq} \hat{E}_{ps} - \delta_{sp} \hat{E}_{rq}.$$

(3) Let $\hat{e}_{pqrs} = \sum_{\sigma\tau} \hat{a}_{p,\sigma}^\dagger \hat{a}_{r,\tau}^\dagger \hat{a}_{s,\tau} \hat{a}_{q,\sigma} = \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps}$. Show from (2) that

$$[\hat{E}_{mn}, \hat{e}_{pqrs}] = \delta_{pn} \hat{e}_{mQRS} - \delta_{mq} \hat{e}_{pnrs} + \delta_{rn} \hat{e}_{pqms} - \delta_{ms} \hat{e}_{pqrn}.$$

(4) Let $D_{pq}^{\text{HF}} = \langle \Phi_0 | \hat{E}_{pq} | \Phi_0 \rangle$ and $D_{pqrs}^{\text{HF}} = \langle \Phi_0 | \hat{e}_{pqrs} | \Phi_0 \rangle$.

Explain why both matrix elements are **equal to zero** if one of the orbitals p, q, r or s is a **virtual one**.

(5) Show that, in the occupied orbital space, $D_{ij}^{\text{HF}} = 2\delta_{ij}$ and $D_{ijkl}^{\text{HF}} = 4\delta_{ij}\delta_{kl} - 2\delta_{jk}\delta_{il}$.

(6) Prove the equalities in boxes on pages 13 and 17.