The Standard Models:
Coupled-cluster theory

Zahra Jamshidi
Sharif University of Technology

4th Winter School
 February 2024

Excitation operators

- The lack of size-extensivity of truncated CI wave function arises from the linear parametrization $|\mathbf{C}\rangle = \sum_i C_i |i\rangle$.

- Instead of a linear expansion of the full n-electron wavefunction in terms of n-electron configurations, we will make a linear parameterization of the change in a **m-orbital multiplet** due to **m-body correlation**.

m-body excitation operators:

$$\hat{\tau}_I^A |HF\rangle = C_I^A a_A^+ a_I |HF\rangle \qquad\qquad \hat{\tau}_{IJ}^{AB} |HF\rangle = C_{IJ}^{AB} a_A^+ a_B^+ a_I a_J |HF\rangle$$

$\hat{\tau}_{IJK}^{ABC}$: performs the m orbital replacement from IJK to ABC, and the general form of this operator is $\hat{\tau}_\mu$

$$|\mathbf{FCI}\rangle = \left(1 + \sum_{AI} \hat{\tau}_I^A + \sum_{A>B, I>J} \hat{\tau}_{IJ}^{AB} + \cdots \right) |HF\rangle$$

Excitation operators

Exercise: Show

$$\hat{\tau}_i^a |0\rangle = |{}_i^a\rangle, \qquad \hat{\tau}_i^a |{}_j^b\rangle = |{}_{ij}^{ab}\rangle, \qquad \hat{\tau}_i^b |{}_i^a\rangle = 0, \qquad \hat{\tau}_j^a |{}_i^a\rangle = 0$$

$$[\hat{\tau}_\mu, \hat{\tau}_\nu] = 0$$

$$\hat{\tau}_\mu^2 = 0.$$

Coupled-cluster wavefunction

- Try to overcome the main problem of configuration interaction by **non-linear** and separable parametrization of the correlated electronic state.

- For coupled-cluster wavefunction, all **m-body correlation** processes can happen **simultaneously** rather than one by one.

$$|\mathbf{CC}\rangle = \left[\prod_{AI} (1 + \hat{\tau}_I^A) \right] \left[\prod_{A>B,I>J} (1 + \hat{\tau}_{IJ}^{AB}) \right] \cdots |HF\rangle$$

These two wave functions are **entirely equivalent** if all excitations are included, differing only in their **parametrization.**

$$(1 + \hat{X}_{IJ}^{AB})|0\rangle = |0\rangle + C_{IJ}^{AB} a_A^\dagger a_B^\dagger a_I a_J |0\rangle$$

Each operator produces the superposition of the original state and the **correction** term represents the **excitation from the original state.**

Quadruply excited relative to HF state**:**
$$\left| \begin{matrix} ABCD \\ IJKL \end{matrix} \right\rangle = a_A^\dagger a_B^\dagger a_C^\dagger a_D^\dagger a_I a_J a_K a_L |\text{HF}\rangle$$

Apply single quadruple operator:
$$(1 + \hat{X}_{IJKL}^{ABCD})|\text{HF}\rangle = |\text{HF}\rangle + C_{IJKL}^{ABCD} \left| \begin{matrix} ABCD \\ IJKL \end{matrix} \right\rangle$$

The results of two independent interaction:
$$(1 + \hat{X}_{IJ}^{AB})(1 + \hat{X}_{KL}^{CD})|\text{HF}\rangle = |\text{HF}\rangle + C_{IJ}^{AB} \left| \begin{matrix} AB \\ IJ \end{matrix} \right\rangle + C_{KL}^{CD} \left| \begin{matrix} CD \\ KL \end{matrix} \right\rangle + C_{IJ}^{AB} C_{KL}^{CD} \left| \begin{matrix} ABCD \\ IJKL \end{matrix} \right\rangle$$

Coupled-cluster Theory

Since $\quad \hat{\tau}_{IJ}^{AB} \hat{\tau}_{IJ}^{AB} = 0$

$$1 + \hat{\tau}_{IJ}^{AB} = 1 + \hat{\tau}_{IJ}^{AB} + \frac{1}{2}\hat{\tau}_{IJ}^{AB}\hat{\tau}_{IJ}^{AB} + \cdots = exp(\hat{\tau}_{IJ}^{AB})$$

The **exponential ansatz** of coupled-cluster theory is opportune and guarantee the **size-extensivity** of the solution.

$$|\mathbf{CC}\rangle = exp\left(\sum_{AI} t_I^A a_A^+ a_I + \sum_{A>B,I>J} t_{IJ}^{AB} a_A^+ a_B^+ a_I a_J + \cdots\right)|\mathbf{HF}\rangle$$

$$|\mathbf{CC}\rangle = exp(\hat{T})|\mathbf{HF}\rangle$$

where the **cluster operator** $\quad \hat{T} = \sum_{\mu} t_\mu \hat{\tau}_\mu$

Cluster Operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \cdots$$

If all excitations are included in $\hat{T}$, the CC wavefunction is identical to the CI wavefunction.

$$\hat{T}_1 = \sum_{AI} t_I^A a_A^+ a_I = \sum_{AI} t_I^A \hat{\tau}_I^A$$
Parameterises the correlation induced orbital relaxation.

$$\hat{T}_2 = \sum_{A>B,I>J} t_{IJ}^{AB} a_A^+ a_B^+ a_I a_J = \frac{1}{4} \sum_{A,B,I,J} t_{IJ}^{AB} a_A^+ a_B^+ a_I a_J = \frac{1}{4} \sum_{A,B,I,J} t_{IJ}^{AB} \hat{\tau}_{IJ}^{AB}$$
Parameterises two-body correlation

$$t_I^A, t_{IJ}^{AB}, \cdots$$
Cluster amplitudes

The correspondence between the CC operators $\hat{T}_i$ and the CI operators $\widehat{C}_i$:

$$|\mathbf{FCI}\rangle = \left(1 + \sum_{AI} \hat{\tau}_I^A + \sum_{A>B,I>J} \hat{\tau}_{IJ}^{AB} + \cdots \right) |HF\rangle$$

$$exp(\hat{T})\,|\mathbf{HF}\rangle = \sum_{i=0}^{N} \widehat{C}_i\,|\mathbf{HF}\rangle$$

$\hat{C}_0 = 1$

$\hat{C}_1 = \hat{T}_1$

$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2$

$\hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3$

$\hat{C}_4 = \hat{T}_4 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4$

$\hat{T}_2^2$ = **independent interactions** within two distinct pairs

$\hat{T}_4$ = **simultaneous interaction** of four electrons

The **CC amplitudes** decay much more quickly with excitation rank than the **CI coefficients**.

Coupled-cluster Hierarchy of Excitation Levels

The coupled-cluster wave function as a product of correlating operators working on HF state:

$$|\mathbf{CC}\rangle = exp(\hat{T})\,|\mathbf{HF}\rangle$$

$$|\mathbf{CC}\rangle = (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \cdots)\,|\mathbf{HF}\rangle \qquad \hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots$$

CCSD **wave function**, for instance, contains contributions from **triple and higher excitations** as products of lower-order excitations:

$$|\mathbf{CCSD}\rangle = |\mathbf{HF}\rangle + \hat{T}_1\,|\mathbf{HF}\rangle + (\frac{1}{2}\hat{T}_1^2 + \hat{T}_2)\,|\mathbf{HF}\rangle + (\frac{1}{6}\hat{T}_1^3 + \hat{T}_1\hat{T}_2)\,|\mathbf{HF}\rangle + \cdots$$

$$+ (\frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{24}\hat{T}_1^4)\,|\mathbf{HF}\rangle + \cdots$$

Truncated coupled-cluster

- The advantages of the cluster parametrization become apparent only upon truncation.
- At the truncated level, the coupled-cluster state contains contributions from all determinants in the FCI wave function.

Water molecule in the cc-pVDZ basis.

Excitation level	R_{ref}		$2R_{ref}$	
	CCSD	FCI	CCSD	FCI
0	0.94410	0.94100	0.65114	0.58966
1	0.00056	0.00053	0.02494	0.02680
2	0.05413	0.05650	0.28762	0.33300
3	0.00002	0.00055	0.00371	0.01040
4	0.00115	0.00137	0.03225	0.03970
5	0.00000	0.00002	0.00006	0.00080
6	0.00001	0.00002	0.00028	0.00044

- CCSD recovers **95%** of the FCI singles and doubles weight.
- CCSD recovers **84%** of the FCI quadruple weight.
- CCSD recovers **4%** of the triple excitations weight.
- At 2R , the single-determinant state is not a good approximation.
- At 2R, CCSD recovers **14%** of the FCI doubles weight.
- For high accuracy, connected triple excitations should consider.

Coupled-cluster Schrödinger equation

Given the product ansatz for coupled cluster and consider the optimization of CC wavefunction:

CI wavefunction minimize with respect to **linear expectation coefficients**:

$$E_{CI} = \min_{C_\mu \to 0} \frac{\left\langle CI \left| \widehat{H} \right| CI \right\rangle}{\langle CI | CI \rangle}$$

CC wavefunction minimize with respect to **amplitudes**:

$$E_{min} = \min_{t_\mu \to 0} \frac{\left\langle CC \left| \widehat{H} \right| CC \right\rangle}{\langle CC | CC \rangle}$$

Coupled-cluster Schrödinger equation

Derivative of **CI** wavefunction with respect to variational parameters:

$$\frac{\partial}{\partial C_\mu} | \mathbf{CI} \rangle = | \mu \rangle$$

Give rise to a standard eigenvalue problem for **CI** coefficients:

$$\left\langle \mu \left| \widehat{H} \right| CI \right\rangle = E_{CI} \langle \mu | CI \rangle$$

Nonlinear parametrization of **CC** wavefunction, and complicated derivative of CC state:

$$\frac{\partial}{\partial C_\mu} | \mathbf{CC} \rangle = \left[\prod_\nu (1 + t_\nu \hat{\tau}_\nu) \right] | \mu \rangle$$

Give rise to intractable set of nonlinear equation for **CC** amplitude :

Involves full set of FCI determinants and higher order products of amplitudes.

$$\langle \mu | \left[\prod_\nu (1 + t_\nu \hat{\tau}_\nu^\dagger) \right] \hat{H} | \mathbf{CC} \rangle = E_{\min} \langle \mu | \left[\prod_\nu (1 + t_\nu \hat{\tau}_\nu^\dagger) \right] | \mathbf{CC} \rangle$$

12

Projected coupled-cluster equation

- For the **linear CI** wave function, the variational minimization of the energy is entirely equivalent to the solution of the projected Schrodinger equation

- For **nonlinearly parametrized CC** wave functions, the solution of the projected Schrodinger equation is, in general, not equivalent to the minimization of the energy.

- For CC wave function solution of the projected Schrodinger equation as an alternative to the minimization of the energy.

- In particular, applied to the coupled-cluster model, projection of the Schrodinger equation against those determinants that enter the coupled-cluster state with connected amplitudes.

$$\langle \mu | = \langle \mathbf{HF} | \, \hat{\tau}_{\mu}^{+}$$

The projected CC equations:

$$\left\langle \mu \left| \widehat{H} \right| \mathbf{CC} \right\rangle = E\langle \mu | \mathbf{CC}\rangle \qquad \langle \mu | = \langle \mathbf{HF} | \, \widehat{\tau}_{\mu}^{+}$$

The coupled-cluster energy is obtained by projection against the HF state

$$\left\langle \mathbf{HF} \left| \widehat{H} \right| \mathbf{CC} \right\rangle = E\langle \mathbf{HF} | \mathbf{CC}\rangle \qquad \langle \mathbf{HF} | \mathbf{CC}\rangle = 1$$

$$\left\langle \mathbf{HF} \left| \widehat{H} \right| \mathbf{CC} \right\rangle = E$$

Unlike the variational conditions, the expansion of the wave function terminates after a few terms, **higher than double** excitations.
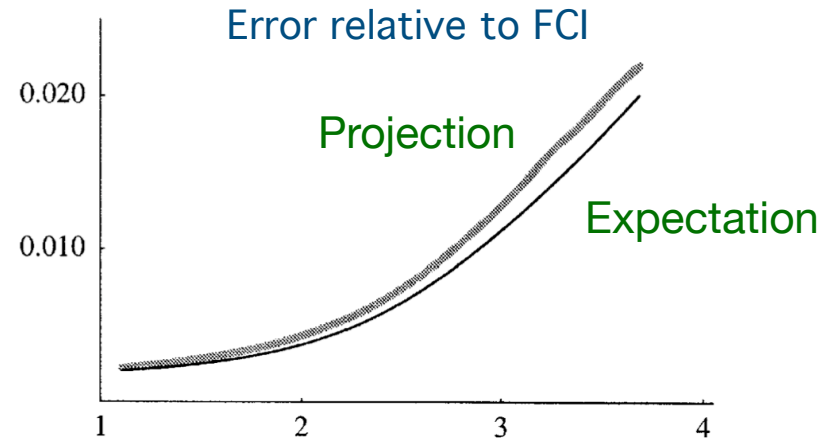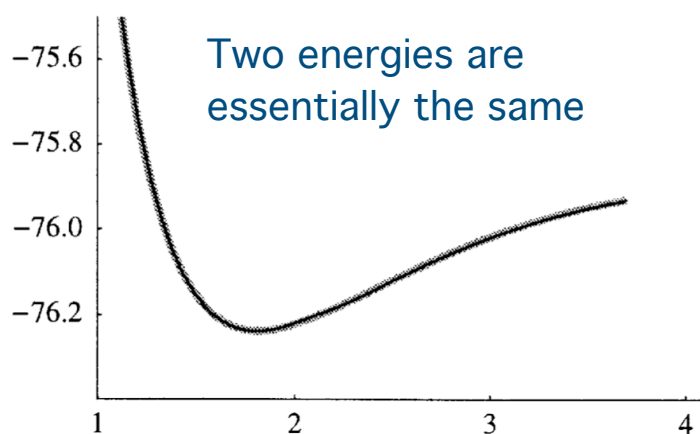
CCSD dissociation energy of water for fix angle:

Projection:

$$\left\langle \mathbf{HF} \left| \widehat{H} \right| \mathbf{CCSD} \right\rangle = E$$

Expectation:

$$E_{ave} = \frac{\left\langle CCSD \left| \widehat{H} \right| CCSD \right\rangle}{\langle CCSD | CCSD \rangle}$$

Small difference between the energy calculated as an **expectation** value and by **projection.**

Two energies are essentially the same

Error relative to FCI

Projection

Expectation

More complicated variational expression for the expectation formula **does not improve energy.**

Projected coupled-cluster equation

Full coupled-cluster wavefunction satisfies Schrödinger equation:

$$\widehat{H}\, e^{\hat{T}}\, |\mathbf{HF}\rangle = E e^{\hat{T}}\, |\mathbf{HF}\rangle \qquad\qquad |\mathbf{CC}\rangle = e^{\hat{T}}\, |\mathbf{HF}\rangle$$

Truncated coupled-cluster wavefunction **cannot satisfy** this equation **exactly.**

Projected coupled equation:

$$\left\langle \mathbf{HF}\, |\, \widehat{H}\, e^{\hat{T}}\, |\mathbf{HF} \right\rangle = E$$

$$\left\langle \mu \,\left|\, \widehat{H}\, e^{\hat{T}} \,\right|\, \mathbf{HF} \right\rangle = E \left\langle \mu \,\left|\, e^{\hat{T}} \,\right|\, \mathbf{HF} \right\rangle$$

Projected coupled-cluster equation

$$\widehat{H} e^{\hat{T}} | \mathbf{HF} \rangle = E e^{\hat{T}} | \mathbf{HF} \rangle \qquad \text{multiply from left} \quad e^{-\hat{T}}$$

$$e^{-\hat{T}} \widehat{H} e^{\hat{T}} | \mathbf{HF} \rangle = E | \mathbf{HF} \rangle \qquad \left\langle \mathbf{HF} | e^{-\hat{T}} \widehat{H} e^{\hat{T}} | \mathbf{HF} \right\rangle = E$$

$$\left\langle \mathbf{HF} | e^{-\hat{T}} \widehat{H} e^{\hat{T}} | \mathbf{HF} \right\rangle = E \langle \mathbf{HF} | \mathbf{HF} \rangle \qquad \langle \mathbf{HF} | e^{-\hat{T}} = \langle \mathbf{HF} |$$

$$\left\langle \mu \left| \widehat{H} e^{\hat{T}} \right| \mathbf{HF} \right\rangle = E \left\langle \mu \left| e^{\hat{T}} \right| \mathbf{HF} \right\rangle \qquad \text{multiply from left} \quad e^{-\hat{T}}$$

$$\left\langle \mu | e^{-\hat{T}} \widehat{H} e^{\hat{T}} | \mathbf{HF} \right\rangle = E \left\langle \mu | e^{-\hat{T}} e^{\hat{T}} | \mathbf{HF} \right\rangle = E \langle \mu | \mathbf{HF} \rangle = 0 \qquad \left\langle \mu | e^{-\hat{T}} \widehat{H} e^{\hat{T}} | \mathbf{HF} \right\rangle = 0$$

Project onto the **Hartree-Fock reference** to obtain the **energy**:

$$\left\langle \mathbf{HF} \,|\, e^{-\hat{T}} \widehat{H} \, e^{\hat{T}} \,|\, \mathbf{HF} \right\rangle = E$$

Project onto **excited determinants** to obtain the equations for the **amplitudes**:

$$\left\langle \mu \,|\, e^{-\hat{T}} \widehat{H} \, e^{\hat{T}} \,|\, \mathbf{HF} \right\rangle = 0$$

Similarity transformation yields the Cambell-Baker-Hausdorff expansion:

$$\widetilde{H} = e^{-\hat{T}} \widehat{H} \, e^{\hat{T}}$$

$$\tilde{H} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{6}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{24}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}]$$

$\widehat{H}$ is a **two-body operator** and the amplitude equations are therefore coupled **fourth order polynomials.**

The coupled cluster energy

$$E = \left\langle \mathbf{HF} \,|\, e^{-\hat{T}} \widehat{H} \, e^{\hat{T}} \,|\, \mathbf{HF} \right\rangle = \left\langle \mathbf{HF} \,|\, \widehat{H} \, e^{\hat{T}} \,|\, \mathbf{HF} \right\rangle$$

Expanding the cluster amplitudes, we obtain:

$$E = \left\langle \mathbf{HF} \,|\, \widehat{H} \left(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \dots\right) |\, \mathbf{HF} \right\rangle = \left\langle \mathbf{HF} \,|\, \widehat{H} \left(1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right) |\, \mathbf{HF} \right\rangle$$

Cluster operators **higher than doubles** do **not contribute** to the energy since $\widehat{H}$ is a two-particle operator.

Because of the **Brillouin theorem**, the one-particle operators contribute only to **second-order**:

$$\left\langle \mathbf{HF} \,|\, \widehat{H}\, \hat{T}_1 \,|\, \mathbf{HF} \right\rangle = 0$$

Only singles and doubles amplitudes contribute **directly** to the coupled-cluster energy. The **higher-order** excitations contribute **indirectly** since all amplitudes are coupled by the **projected equations**.

The coupled cluster amplitude equations

$$\left\langle \mu \,|\, e^{-\hat{T}} \widehat{H} e^{\hat{T}} \,|\, \mathbf{HF} \right\rangle = 0$$

$$\tilde{H} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{6}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{24}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}]$$

The expressions for the CCSD amplitude equations:

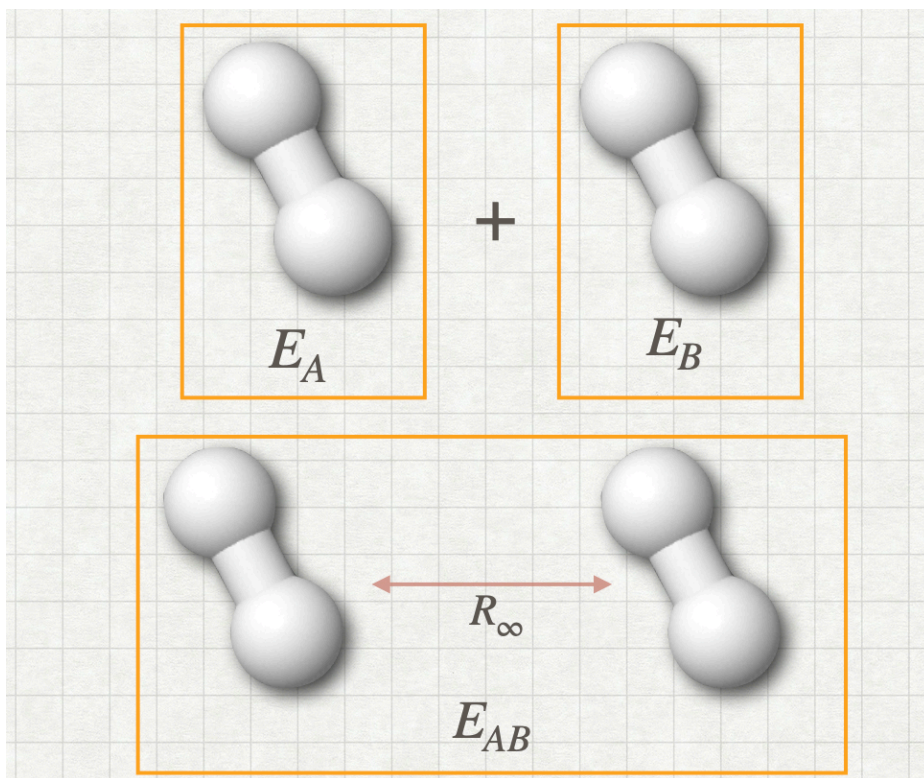$$\langle \mu_1 | \hat{H} | \mathrm{HF} \rangle + \langle \mu_1 | [\hat{H}, \hat{T}_1] | \mathrm{HF} \rangle + \langle \mu_1 | [\hat{H}, \hat{T}_2] | \mathrm{HF} \rangle + \tfrac{1}{2} \langle \mu_1 | [[\hat{H}, \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle$$
$$+ \langle \mu_1 | [[\hat{H}, \hat{T}_1], \hat{T}_2] | \mathrm{HF} \rangle + \tfrac{1}{6} \langle \mu_1 | [[[\hat{H}, \hat{T}_1], \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle = 0$$

$$\mu_1 = \Phi_i^a$$

$$\langle \mu_2 | \hat{H} | \mathrm{HF} \rangle + \langle \mu_2 | [\hat{H}, \hat{T}_1] | \mathrm{HF} \rangle + \langle \mu_2 | [\hat{H}, \hat{T}_2] | \mathrm{HF} \rangle + \tfrac{1}{2} \langle \mu_2 | [[\hat{H}, \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle$$
$$+ \langle \mu_2 | [[\hat{H}, \hat{T}_1], \hat{T}_2] | \mathrm{HF} \rangle + \tfrac{1}{2} \langle \mu_2 | [[\hat{H}, \hat{T}_2], \hat{T}_2] | \mathrm{HF} \rangle$$
$$+ \tfrac{1}{6} \langle \mu_2 | [[[\hat{H}, \hat{T}_1], \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle + \tfrac{1}{2} \langle \mu_2 | [[[\hat{H}, \hat{T}_1], \hat{T}_1], \hat{T}_2] | \mathrm{HF} \rangle$$
$$+ \tfrac{1}{24} \langle \mu_2 | [[[[\hat{H}, \hat{T}_1], \hat{T}_1], \hat{T}_1], \hat{T}_1] | \mathrm{HF} \rangle = 0$$

$$\mu_2 = \Phi_{ij}^{ab}$$

Size-consistency

Sum of separate calculations on each fragment

A single calculation on both fragments: "supermolecule"

For this property to hold, the wave function must be **multiplicatively separable:**

$$|\Psi^{AB}\rangle = \mathcal{A}|\Psi^A\rangle|\Psi^B\rangle$$

Size-consistency

$$|\Psi\rangle_{\text{exact}} = |\Psi\rangle_{\text{CID}} = \left(1 + \hat{T}_2^A\right)|\Phi_0^A\rangle$$
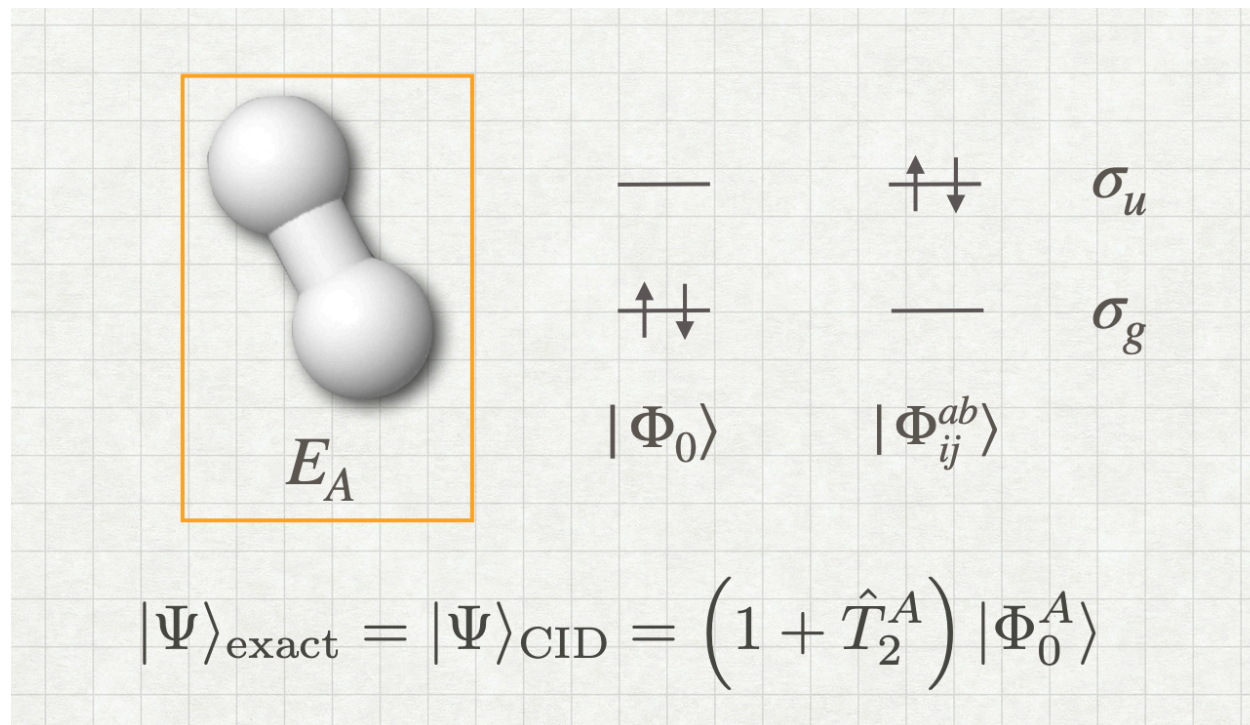
The "configuration interaction doubles" (CID) wave function, in which only linear terms in the cluster expansion are retained, is exact in this case.

Size-consistency

$$|\Psi\rangle^{AB}_{\text{exact}} = \mathcal{A}\left\{\left(1 + \hat{T}_2^A\right)|\Phi_0^A\rangle \times \left(1 + \hat{T}_2^B\right)|\Phi_0^B\rangle\right\}$$

$$= \left(1 + \hat{T}_2^A + \hat{T}_2^B + \hat{T}_2^A\hat{T}_2^B\right)|\Phi_0^{AB}\rangle$$

$$\neq \left(1 + \hat{T}_2^A + \hat{T}_2^B\right)|\Phi_0^{AB}\rangle$$

$$= |\Psi\rangle^{AB}_{\text{CID}}$$
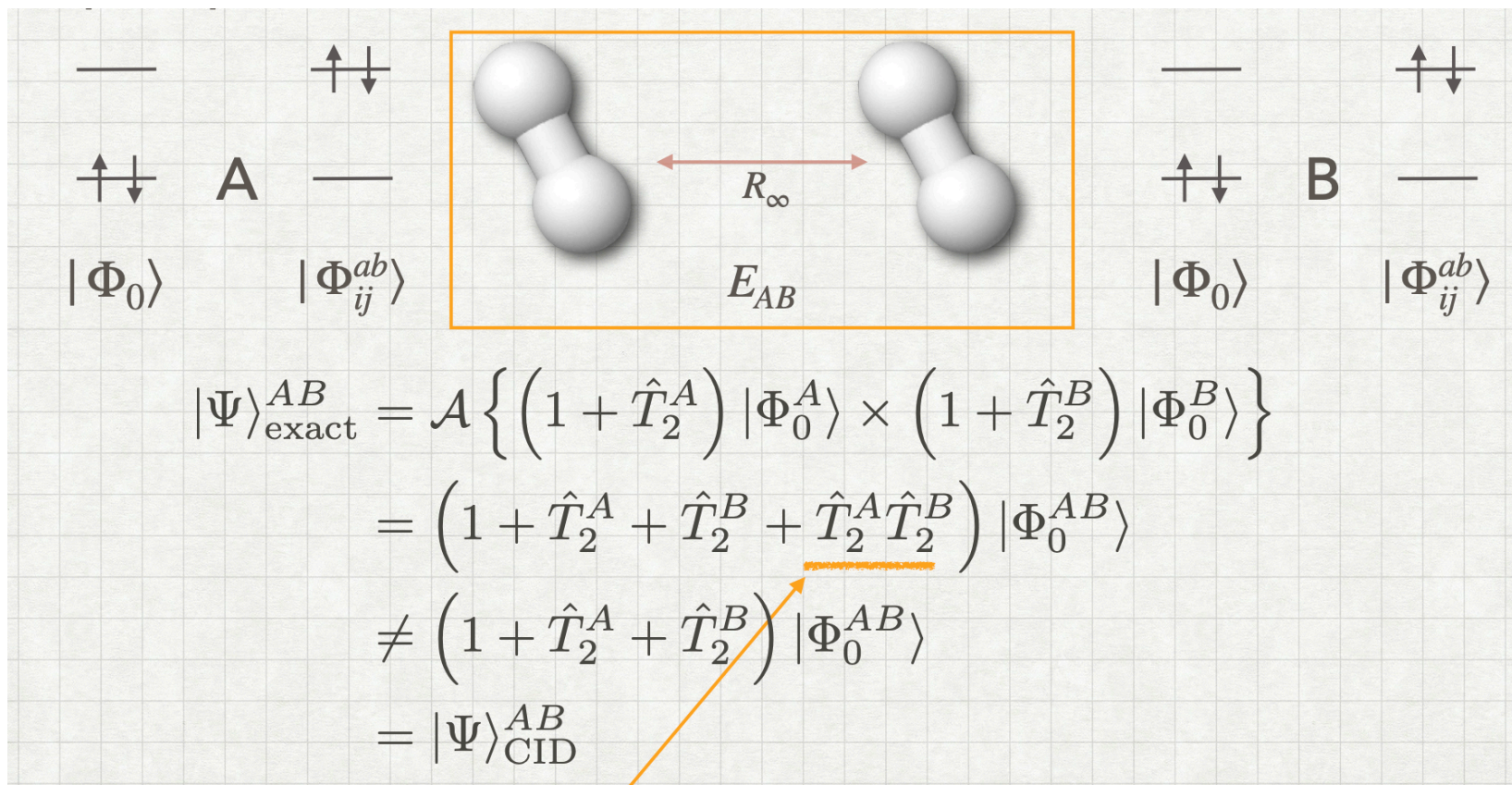
CID does not include this term and thus is **not size consistent.**

Size-consistency

$$|\Psi\rangle^{AB}_{CCD} = \mathcal{A}\left\{ e^{\hat{T}^A_2} |\Phi^A_0\rangle \times e^{\hat{T}^B_2} |\Phi^B_0\rangle \right\}$$

$$= e^{\hat{T}^A_2} e^{\hat{T}^B_2} |\Phi^{AB}_0\rangle$$

$$= e^{\hat{T}^A_2 + \hat{T}^B_2} |\Phi^{AB}_0\rangle$$

$$= |\Phi^{AB}_{CCD}\rangle$$
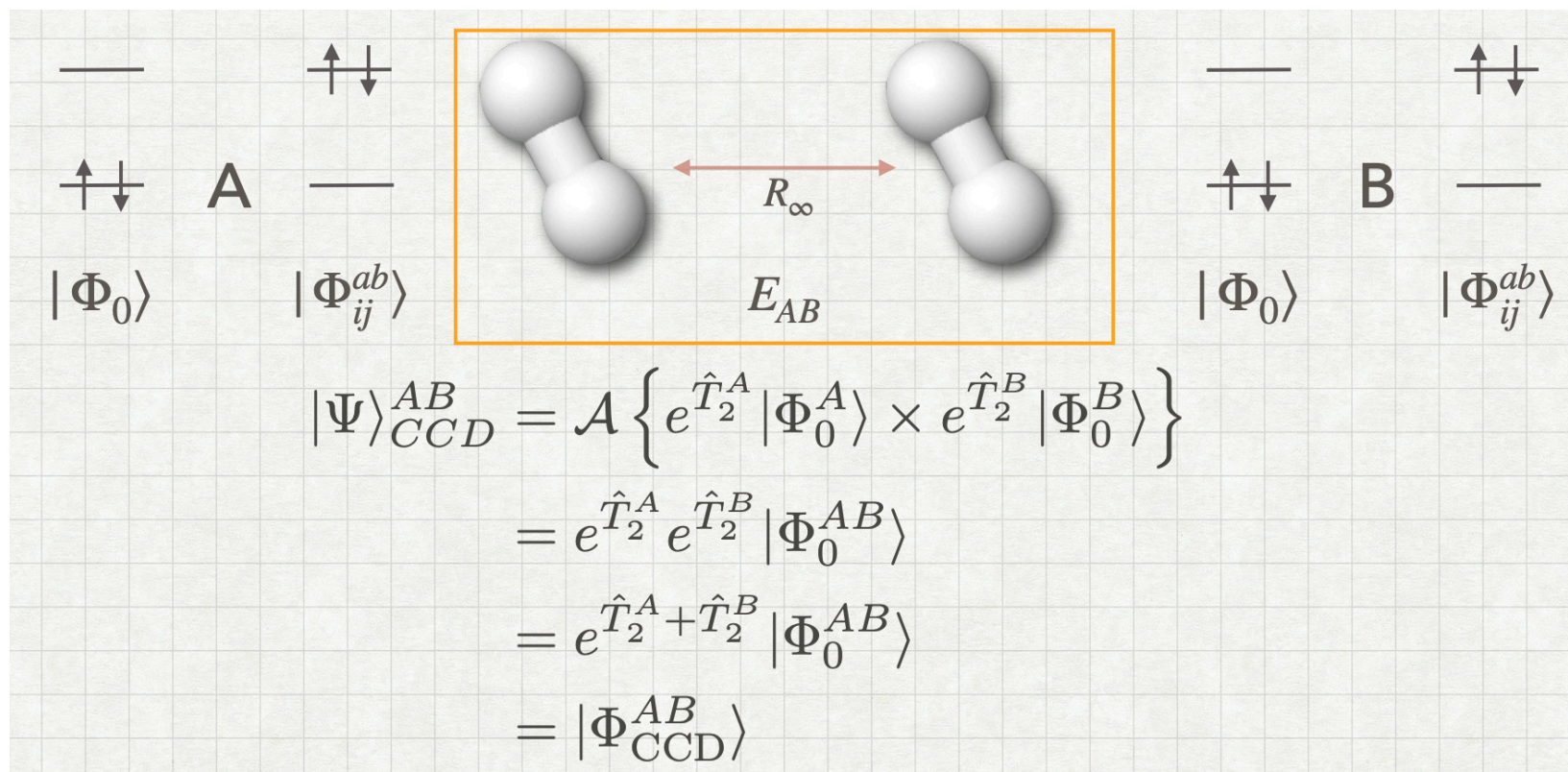
CCD gives a multiplicatively separable wave function and thus is **size consistent**.

Size-consistency

$$|\Psi\rangle_{\text{exact}}^{AB} = \mathcal{A}\left\{\left(1 + \hat{T}_2^A\right)|\Phi_0^A\rangle \times \left(1 + \hat{T}_2^B\right)|\Phi_0^B\rangle\right\}$$

$$= \left(1 + \hat{T}_2^A + \hat{T}_2^B + \hat{T}_2^A\hat{T}_2^B\right)|\Phi_0^{AB}\rangle$$

$$\neq \left(1 + \hat{T}_2^A + \hat{T}_2^B\right)|\Phi_0^{AB}\rangle$$

$$= |\Psi\rangle_{\text{CID}}^{AB}$$