

Configuration interaction and coupled-cluster theory

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Part 1: Mathematics

The purpose of these exercises is to get familiar with the formalism of second quantization and the evaluation of terms appearing in the CC equations.

1 Anticommutation rules

Consider the three determinants $|\mathbf{n}_1\rangle = |\varphi_1\varphi_2\varphi_3\rangle$, $|\mathbf{n}_2\rangle = |\varphi_1\varphi_4\varphi_5\rangle$, $|\mathbf{n}_3\rangle = |\varphi_2\varphi_3\varphi_4\rangle$ and the operator $X = \sum_{pq} x_p^q a_p^\dagger a_q$. Evaluate all 6 non-equivalent matrix elements using the anticommutation relations (see p.20 in the lecture) for creators and annihilators.

$$\text{Example: } \langle \mathbf{n}_1 | X | \mathbf{n}_1 \rangle = \langle \varphi_1\varphi_2\varphi_3 | X | \varphi_1\varphi_2\varphi_3 \rangle = \sum_{pq} x_p^q \langle \varphi_1\varphi_2\varphi_3 | a_p^\dagger a_q | \varphi_1\varphi_2\varphi_3 \rangle$$

$$= x_1^1 \langle \varphi_2\varphi_3 | \varphi_2\varphi_3 \rangle \quad (\text{case 1: } p = 1, q = 1, \text{ no permutation required, thus no sign change})$$

$$+ x_2^2 \langle \varphi_1\varphi_3 | \varphi_1\varphi_3 \rangle \quad (\text{case 2: } p = 2, q = 2, 1 \text{ permutation on the left, 1 on the right, thus no sign})$$

$$+ x_3^3 \langle \varphi_1\varphi_2 | \varphi_1\varphi_2 \rangle \quad (\text{case 3: } p = 3, q = 3, 2 \text{ permutations on the left, 2 on the right, thus no sign})$$

$$= x_1^1 + x_2^2 + x_3^3 \quad (\text{index combinations with } p \neq q \text{ vanish, convince yourself if it is not obvious to you})$$

The one-body operator X and the three Slater determinant states in terms of creation operators acting on the vacuum $|0\rangle$:

$$\begin{aligned} X &= \sum_{p,q} x_p^q a_p^\dagger a_q \\ |\mathbf{n}_1\rangle &= |123\rangle = a_1^\dagger a_2^\dagger a_3^\dagger |0\rangle \\ |\mathbf{n}_2\rangle &= |145\rangle = a_1^\dagger a_4^\dagger a_5^\dagger |0\rangle \\ |\mathbf{n}_3\rangle &= |234\rangle = a_2^\dagger a_3^\dagger a_4^\dagger |0\rangle \end{aligned}$$

We aim to evaluate the 6 unique matrix elements $\langle \mathbf{n}_i | X | \mathbf{n}_j \rangle$ using the fundamental anticommutation relations:

$$\{a_i, a_j^\dagger\} = \delta_{ij}, \quad \{a_i, a_j\} = 0, \quad \{a_i^\dagger, a_j^\dagger\} = 0 \quad (1)$$

Diagonal Elements $\langle \mathbf{n}_i | X | \mathbf{n}_i \rangle$

For diagonal elements, the operator must annihilate and create in the same orbital ($p = q$) to recover the same state

Case 1: $\langle \mathbf{n}_1 | X | \mathbf{n}_1 \rangle$

Occupied orbitals: $\{1, 2, 3\}$.

$$\langle \mathbf{n}_1 | X | \mathbf{n}_1 \rangle = x_1^1 + x_2^2 + x_3^3 \quad (2)$$

Case 2: $\langle \mathbf{n}_2 | X | \mathbf{n}_2 \rangle$

Occupied orbitals: $\{1, 4, 5\}$.

$$\langle \mathbf{n}_2 | X | \mathbf{n}_2 \rangle = x_1^1 + x_4^4 + x_5^5 \quad (3)$$

Case 3: $\langle \mathbf{n}_3 | X | \mathbf{n}_3 \rangle$

Occupied orbitals: $\{2, 3, 4\}$.

$$\langle \mathbf{n}_3 | X | \mathbf{n}_3 \rangle = x_2^2 + x_3^3 + x_4^4 \quad (4)$$

Off-Diagonal Elements $\langle \mathbf{n}_i | X | \mathbf{n}_j \rangle$ where $i \neq j$

According to the Slater-Condon rules for one-body operators, if two determinants differ by more than 1 orbital, the matrix element is zero.

Case 4: $\langle \mathbf{n}_1 | X | \mathbf{n}_2 \rangle$

- $|\mathbf{n}_1\rangle = |123\rangle$
- $|\mathbf{n}_2\rangle = |145\rangle$

They differ by 2 orbitals ($\{2, 3\}$ vs $\{4, 5\}$). The operator X involves only one creation and one annihilation ($a_p^\dagger a_q$), so it cannot transform $|\mathbf{n}_2\rangle$ into $|\mathbf{n}_1\rangle$.

$$\langle \mathbf{n}_1 | X | \mathbf{n}_2 \rangle = 0 \quad (5)$$

Case 5: $\langle \mathbf{n}_2 | X | \mathbf{n}_3 \rangle$

- $|\mathbf{n}_2\rangle = |145\rangle$
- $|\mathbf{n}_3\rangle = |234\rangle$

They differ by 2 orbitals ($\{1, 5\}$ vs $\{2, 3\}$).

$$\langle \mathbf{n}_2 | X | \mathbf{n}_3 \rangle = 0 \quad (6)$$

Case 6: $\langle \mathbf{n}_1 | X | \mathbf{n}_3 \rangle$

- $|\mathbf{n}_1\rangle = |123\rangle$
- $|\mathbf{n}_3\rangle = |234\rangle$

They differ by exactly 1 orbital: $|\mathbf{n}_1\rangle$ has orbital 1, while $|\mathbf{n}_3\rangle$ has orbital 4. The common orbitals are $\{2, 3\}$.

The only surviving term in the sum $X = \sum_{pq} x_p^q a_p^\dagger a_q$ is the one that annihilates the unique orbital of the ket ($q = 4$) and creates the unique orbital of the bra ($p = 1$).

$$x_1^4 a_1^\dagger a_4$$

We evaluate the matrix element step-by-step to determine the sign:

$$\langle \mathbf{n}_1 | X | \mathbf{n}_3 \rangle = x_1^4 \langle 123 | a_1^\dagger a_4 | 234 \rangle$$

We calculate $a_4 | 234 \rangle$. We use anticommutation to move a_4 to the right until it meets a_4^\dagger :

$$\begin{aligned} a_4 | 234 \rangle &= a_4 (a_2^\dagger a_3^\dagger a_4^\dagger | 0 \rangle) \\ &= (-1)^2 a_2^\dagger a_3^\dagger (a_4 a_4^\dagger) | 0 \rangle \quad (2 \text{ permutations over 2 and 3}) \\ &= +1 \cdot a_2^\dagger a_3^\dagger (\mathbf{1} - a_4^\dagger a_4) | 0 \rangle \\ &= | 23 \rangle \quad (\text{since } a_4 | 0 \rangle = 0) \end{aligned}$$

Now we apply a_1^\dagger to $| 23 \rangle$. The operator must be placed in canonical order (increasing index order).

$$\begin{aligned} a_1^\dagger | 23 \rangle &= a_1^\dagger (a_2^\dagger a_3^\dagger | 0 \rangle) \\ &= a_1^\dagger a_2^\dagger a_3^\dagger | 0 \rangle \quad (0 \text{ permutations needed, as } 1 \nlessdot 2) \\ &= | 123 \rangle \end{aligned}$$

Final Result:

$$\langle \mathbf{n}_1 | X | \mathbf{n}_3 \rangle = x_1^4 \langle 123 | 123 \rangle = x_1^4 \tag{7}$$

Summary of Results

Element	Value	Justification
$\langle \mathbf{n}_1 X \mathbf{n}_1 \rangle$	$x_1^1 + x_2^2 + x_3^3$	Diagonal
$\langle \mathbf{n}_2 X \mathbf{n}_2 \rangle$	$x_1^1 + x_4^4 + x_5^5$	Diagonal
$\langle \mathbf{n}_3 X \mathbf{n}_3 \rangle$	$x_2^2 + x_3^3 + x_4^4$	Diagonal
$\langle \mathbf{n}_1 X \mathbf{n}_2 \rangle$	0	Differs by 2 orbitals
$\langle \mathbf{n}_2 X \mathbf{n}_3 \rangle$	0	Differs by 2 orbitals
$\langle \mathbf{n}_1 X \mathbf{n}_3 \rangle$	$+x_1^4$	Differs by 1 orbital ($1 \leftrightarrow 4$)

2 Normal-ordered Hamiltonian

- a) The following expression for the Hamiltonian is normal-ordered with respect to the physical vacuum (= zero electrons):

$$H = \sum_{pq} h_p^q a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r.$$

This can be shown using Wick's theorem and the definition of contractions (see pp.23/24 in the lecture). For the one-electron part:

$$a_p^\dagger a_q = \{a_p^\dagger a_q\} + \overbrace{\{a_p^\dagger a_q\}} = \{a_p^\dagger a_q\} + \{a_p^\dagger a_q - \{a_p^\dagger a_q\}\} = \{a_p^\dagger a_q\} + \{a_p^\dagger a_q - a_p^\dagger a_q\} = \{a_p^\dagger a_q\}.$$

Work out the two-electron part in a similar fashion!

Wick's theorem:

$$A_1 A_2 A_3 A_4 = \{A_1 A_2 A_3 A_4\} + \sum_{1 \text{ contr.}} \{\cdots\} + \sum_{2 \text{ contr.}} \{\cdots\}. \quad (8)$$

$$\{\overline{a_p^\dagger a_q^\dagger}\} = \{a_p^\dagger a_q^\dagger - \{a_p^\dagger a_q^\dagger\}\} = \{a_p^\dagger a_q^\dagger - a_p^\dagger a_q^\dagger\} = 0 \quad (9)$$

$$\{\overline{a_p^\dagger a_q}\} = \{a_p^\dagger a_q - \{a_p^\dagger a_q\}\} = \{a_p^\dagger a_q - a_p^\dagger a_q\} = 0 \quad (10)$$

$$\{\overline{a_p a_q^\dagger}\} = \{a_p a_q^\dagger - \{a_p a_q^\dagger\}\} = \{a_p a_q^\dagger - (-a_q^\dagger a_p)\} = \{a_p a_q^\dagger + a_q^\dagger a_p\} = \delta_{pq} \quad (11)$$

$$\{\overline{a_p a_q}\} = \{a_p a_q - \{a_p a_q\}\} = \{a_p a_q - a_p a_q\} = 0 \quad (12)$$

The two electron part is:

$$\begin{aligned} a_p^\dagger a_q^\dagger a_s a_r &= \{a_p^\dagger a_q^\dagger a_s a_r\} \\ &+ \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} + \{a_p^\dagger \overline{a_q^\dagger a_s} a_r\} + \{a_p^\dagger a_q^\dagger \overline{a_s a_r}\} \\ &+ \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} + \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} + \{a_p^\dagger a_q^\dagger \overline{a_s a_r}\} \\ &+ \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} + \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} + \{a_p^\dagger a_q^\dagger \overline{a_s a_r}\}. \end{aligned} \quad (13)$$

$$\{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} = \{(a_p^\dagger a_q^\dagger - \{a_p^\dagger a_q^\dagger\}) a_s a_r\} = \{(a_p^\dagger a_q^\dagger - a_p^\dagger a_q^\dagger) a_s a_r\} = \{0 \cdot a_s a_r\} = 0 \quad (14)$$

$$\{a_p^\dagger \overline{a_q^\dagger a_s} a_r\} = \{a_p^\dagger (a_q^\dagger a_s - \{a_q^\dagger a_s\}) a_r\} = \{a_p^\dagger (a_q^\dagger a_s - a_q^\dagger a_s) a_r\} = \{0 \cdot a_p^\dagger a_r\} = 0 \quad (15)$$

$$\{a_p^\dagger a_q^\dagger \overline{a_s a_r}\} = \{(a_p^\dagger a_q^\dagger - \{a_p^\dagger a_q^\dagger\}) a_s a_r\} = \{(a_p^\dagger a_q^\dagger - a_p^\dagger a_q^\dagger) a_s a_r\} = \{0 \cdot a_s a_r\} = 0 \quad (16)$$

$$\{a_p^\dagger \overline{a_q^\dagger a_s a_r}\} = \{a_p^\dagger (a_q^\dagger a_s - \{a_q^\dagger a_s\}) a_r\} = \{a_p^\dagger (a_q^\dagger a_s - a_q^\dagger a_s) a_r\} = \{0 \cdot a_p^\dagger a_r\} = 0 \quad (17)$$

$$\{a_p^\dagger \overline{a_q^\dagger a_r a_s}\} = \{a_p^\dagger (a_q^\dagger a_r - \{a_q^\dagger a_r\}) a_s\} = \{a_p^\dagger (a_q^\dagger a_r - a_q^\dagger a_r) a_s\} = \{0 \cdot a_p^\dagger a_s\} = 0 \quad (18)$$

$$\{a_p^\dagger \overline{a_q^\dagger a_s a_r}\} = \{a_q^\dagger (a_p^\dagger a_s - \{a_p^\dagger a_s\}) a_r\} = \{a_q^\dagger (a_p^\dagger a_s - a_p^\dagger a_s) a_r\} = \{0 \cdot a_q^\dagger a_r\} = 0 \quad (19)$$

$$\{a_p^\dagger \overline{a_q^\dagger a_r a_s}\} = \{a_q^\dagger (a_p^\dagger a_r - \{a_p^\dagger a_r\}) a_s\} = \{a_q^\dagger (a_p^\dagger a_r - a_p^\dagger a_r) a_s\} = \{0 \cdot a_q^\dagger a_s\} = 0 \quad (20)$$

$$\{a_p^\dagger a_q^\dagger \overline{a_s a_r}\} = \{a_p^\dagger a_q^\dagger (a_s a_r - \{a_s a_r\})\} = \{a_p^\dagger a_q^\dagger (a_s a_r - a_s a_r)\} = \{0 \cdot a_p^\dagger a_q^\dagger\} = 0 \quad (21)$$

Since all single contractions with respect to the physical vacuum are 0, every double contraction will also be 0 because it is a product of two single contractions. Therefore the two-electron part of the Hamiltonian is normal-ordered with respect to the physical vacuum:

$$a_p^\dagger a_q^\dagger a_s a_r = \{a_p^\dagger a_q^\dagger a_s a_r\}.$$

- b) Starting from the expression in part a), show that the following expression is normal-ordered with respect to the Fermi vacuum:

$$H = E_{HF} + \sum_{pq} F_p^q \{a_p^\dagger a_q\}_0 + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\}_0$$

Hints:

1. Consider the different index combinations separately. There are 4 distinct contributions to the one-electron part: $\sum_{pq} h_p^q a_p^\dagger a_q = \sum_{ab} h_a^b a_a^\dagger a_b + \sum_{ai} h_a^i a_a^\dagger a_i + \sum_{ia} h_i^a a_i^\dagger a_a + \sum_{ij} h_i^j a_i^\dagger a_j$ and 9 distinct contributions to the two-electron part (see p.26 in the lecture).
2. Use contractions and Wick's theorem to achieve normal order (All creators to the left of all annihilators). Note that the definition of normal order only changes for the indices referring to occupied orbitals (i, j, \dots) when going from the physical vacuum to the Fermi vacuum (see p.25 in the lecture).

We start from

$$H = \sum_{pq} h_p^q a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r. \quad (22)$$

We normal-order with respect to the Fermi vacuum $|0\rangle$. Occupied indices are i, j, k, l, \dots and virtual indices are a, b, c, d, \dots

Basic contractions with respect to $|0\rangle$:

$$a_p^\dagger a_q = \{a_p^\dagger a_q\}_0 + \{a_p^\dagger \overline{a_q}\}_0 \quad (23)$$

with

$$\{\overline{a_p^\dagger a_q}\}_0 = \sum_i \delta_{pi} \delta_{qi} \quad (24)$$

therefore:

$$a_p^\dagger a_q = \{a_p^\dagger a_q\}_0 + \sum_i \delta_{pi} \delta_{qi} \quad (25)$$

We split the one-electron term into occupied/virtual blocks:

$$\sum_{pq} h_p^q a_p^\dagger a_q = \sum_{ab} h_a^b a_a^\dagger a_b + \sum_{ai} h_a^i a_a^\dagger a_i + \sum_{ia} h_i^a a_i^\dagger a_a + \sum_{ij} h_i^j a_i^\dagger a_j. \quad (26)$$

$$a_a^\dagger a_b = \{a_a^\dagger a_b\}_0, \quad a_a^\dagger a_i = \{a_a^\dagger a_i\}_0, \quad a_i^\dagger a_a = \{a_i^\dagger a_a\}_0 \quad (27)$$

$$a_i^\dagger a_j = \{a_i^\dagger a_j\}_0 + \{\overline{a_i^\dagger a_j}\}_0 = \{a_i^\dagger a_j\}_0 + \delta_{ij} \quad (28)$$

$$\sum_{pq} h_p^q a_p^\dagger a_q = \sum_{pq} h_p^q \{a_p^\dagger a_q\}_0 + \sum_i h_i^i. \quad (29)$$

The two-electron part is:

$$H^{(2)} = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r. \quad (30)$$

Expanding $a_p^\dagger a_q^\dagger a_s a_r$ using Wick's theorem with respect to the Fermi vacuum $|0\rangle$.

$$\begin{aligned} a_p^\dagger a_q^\dagger a_s a_r &= \{a_p^\dagger a_q^\dagger a_s a_r\}_0 + \{\overline{a_p^\dagger a_q^\dagger a_s a_r}\}_0 - \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\}_0 \\ &\quad - \{a_p^\dagger a_q^\dagger \overline{a_s a_r}\}_0 + \{a_p^\dagger a_q^\dagger \overline{a_s} a_r\}_0 \\ &\quad + \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\}_0 - \{\overline{a_p^\dagger a_q^\dagger} a_s\} a_r. \end{aligned} \quad (31)$$

With zero contractions:

$$H_{0 \text{ cont}}^{(2)} = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\}_0. \quad (32)$$

Single contractions:

From (31) the four single contractions give:

$$\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\}_0 = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \delta_{pr} \{a_q^\dagger a_s\}_0 = \frac{1}{4} \sum_{iqs} \langle iq || is \rangle \{a_q^\dagger a_s\}_0. \quad (33)$$

$$-\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{\overline{a_p^\dagger a_q^\dagger} a_s\} a_r = -\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \delta_{ps} \{a_q^\dagger a_r\}_0 = -\frac{1}{4} \sum_{iqr} \langle iq || ri \rangle \{a_q^\dagger a_r\}_0. \quad (34)$$

$$-\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \{a_p^\dagger \overline{a_q^\dagger} a_s a_r\}_0 = -\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \delta_{qr} \{a_p^\dagger a_s\}_0 = -\frac{1}{4} \sum_{pis} \langle pi||is \rangle \{a_p^\dagger a_s\}_0. \quad (35)$$

$$+\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \{a_p^\dagger \overline{a_q^\dagger} a_s a_r\}_0 = +\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \delta_{qs} \{a_p^\dagger a_r\}_0 = +\frac{1}{4} \sum_{pir} \langle pi||ri \rangle \{a_p^\dagger a_r\}_0. \quad (36)$$

Now bring all four sums to the same (p, q) -form by changing the repeated labels and applying antisymmetry for the sign $\langle pq||rs \rangle = -\langle pq||sr \rangle$:

$$-\frac{1}{4} \sum_{iqr} \langle iq||ri \rangle \{a_q^\dagger a_r\}_0 = -\frac{1}{4} \sum_{iqs} \langle iq||si \rangle \{a_q^\dagger a_s\}_0 = +\frac{1}{4} \sum_{iqs} \langle iq||is \rangle \{a_q^\dagger a_s\}_0, \quad (37)$$

$$-\frac{1}{4} \sum_{pis} \langle pi||is \rangle \{a_p^\dagger a_s\}_0 = +\frac{1}{4} \sum_{pis} \langle pi||si \rangle \{a_p^\dagger a_s\}_0, \quad (38)$$

so the four single-contraction contributions are identical after changing the repeated labels and they add up to:

$$H_{1\text{ cont}}^{(2)} = 4 \times \frac{1}{4} \sum_{iqs} \langle iq||is \rangle \{a_q^\dagger a_s\}_0 = \sum_{iqs} \langle iq||is \rangle \{a_q^\dagger a_s\}_0. \quad (39)$$

Finally renaming the indices ($q \rightarrow p$, $s \rightarrow q$) and use $\langle ip||iq \rangle = \langle pi||qi \rangle$ to obtain

$$H_{1\text{ cont}}^{(2)} = \sum_{ipq} \langle pi||qi \rangle \{a_p^\dagger a_q\}_0. \quad (40)$$

Double contractions:

The two double contractions from (31) give:

$$-\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \{a_p^\dagger \overline{a_q^\dagger} a_s a_r\}_0 = -\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \delta_{ps} \delta_{qr} = -\frac{1}{4} \sum_{ij} \langle ij||ji \rangle = +\frac{1}{4} \sum_{ij} \langle ij||ij \rangle, \quad (41)$$

$$+\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \{a_p^\dagger \overline{a_q^\dagger} a_s a_r\}_0 = +\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \delta_{pr} \delta_{qs} = +\frac{1}{4} \sum_{ij} \langle ij||ij \rangle. \quad (42)$$

Therefore,

$$E_{\text{HF}}^{(2)} = \frac{1}{2} \sum_{ij} \langle ij||ij \rangle. \quad (43)$$

Joining the three factors:

$$H^{(2)} = \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\}_0 + \sum_{ipq} \langle pi||qi \rangle \{a_p^\dagger a_q\}_0 + \frac{1}{2} \sum_{ij} \langle ij||ij \rangle. \quad (44)$$

Final result

Collecting one-electron and two-electron parts:

$$H = \sum_i h_i^i + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle + \sum_{pq} h_p^q \{a_p^\dagger a_q\}_0 + \sum_{pqi} \langle pi || qi \rangle \{a_p^\dagger a_q\}_0 + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\}_0. \quad (45)$$

The E_{HF} energy is:

$$E_{HF} = \sum_i h_i^i + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle. \quad (46)$$

Also the one electron term is:

$$\sum_{pq} F_p^q \{a_p^\dagger a_q\}_0 = \sum_{pq} h_p^q \{a_p^\dagger a_q\}_0 + \sum_{pqi} \langle pi || qi \rangle \{a_p^\dagger a_q\}_0, \quad (47)$$

Therefore,

$$H = E_{HF} + \sum_{pq} F_p^q \{a_p^\dagger a_q\}_0 + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\}_0, \quad (48)$$

which shows that the Hamiltonian is normal-ordered with respect to the Fermi vacuum $|0\rangle$.

3 Contractions

Evaluate the following terms, which appear in the amplitude equations of CC theory or similar approaches. Hints: Use Wick's theorem and normal order defined with respect to the Fermi vacuum $|0\rangle$. Note that only fully contracted terms contribute a non-zero value to an expectation value. The expectation value of a normal-ordered operator is zero!

$$a) \sum_{bc} \sum_{jd} \langle \Phi_i^a | F_b^c a_b^\dagger a_c t_j^d a_d^\dagger a_j | 0 \rangle = \sum_{bc} \sum_{jd} F_b^c t_j^d \langle 0 | a_i^\dagger a_a a_b^\dagger a_c a_d^\dagger a_j | 0 \rangle.$$

Wick: only fully contracted terms contribute, since $\langle 0 | \{\dots\} | 0 \rangle = 0$.

$$\langle 0 | a_i^\dagger a_a a_b^\dagger a_c a_d^\dagger a_j | 0 \rangle = \langle 0 | \overbrace{a_i^\dagger a_a a_b^\dagger a_c a_d^\dagger a_j}^{\text{full contraction}} | 0 \rangle + (\text{all other full contractions}).$$

With i, j occupied and a, b, c, d virtual, the only non-zero contractions are

$$\begin{aligned} \langle 0 | a_i^\dagger a_j | 0 \rangle &= \delta_{ij}, & \langle 0 | a_a a_b^\dagger | 0 \rangle &= \delta_{ab}, & \langle 0 | a_c a_d^\dagger | 0 \rangle &= \delta_{cd}, \\ \langle 0 | a_b^\dagger a_j | 0 \rangle &= 0, & \langle 0 | a_i^\dagger a_c | 0 \rangle &= 0, \end{aligned}$$

$$\Rightarrow \quad \langle 0 | a_i^\dagger a_a a_b^\dagger a_c a_d^\dagger a_j | 0 \rangle = \delta_{ij} \delta_{ab} \delta_{cd}.$$

$$\begin{aligned} \sum_{bc} \sum_{jd} F_b^c t_j^d \langle 0 | a_i^\dagger a_a a_b^\dagger a_c a_d^\dagger a_j | 0 \rangle &= \sum_{bc} \sum_{jd} F_b^c t_j^d \delta_{ij} \delta_{ab} \delta_{cd} \\ &= \sum_c F_a^c t_i^c. \end{aligned}$$

$$b) \sum_{ck} \sum_{\ell d} \langle \Phi_{ij}^{ab} | F_c^k a_c^\dagger a_k t_\ell^d a_d^\dagger a_\ell | 0 \rangle = \sum_{ck} \sum_{\ell d} F_c^k t_\ell^d \langle 0 | a_i^\dagger a_a a_j^\dagger a_b a_c^\dagger a_k a_d^\dagger a_\ell | 0 \rangle.$$

Wick: only fully contracted terms contribute.

The only non-zero full contractions are:

$$\begin{aligned} \langle 0 | a_i^\dagger a_a a_j^\dagger a_b a_c^\dagger a_k a_d^\dagger a_\ell | 0 \rangle &= \langle 0 | a_i^\dagger a_a a_j^\dagger a_b a_c^\dagger a_k a_d^\dagger a_\ell | 0 \rangle \\ &\quad - \langle 0 | a_i^\dagger a_a a_j^\dagger a_b a_c^\dagger a_k a_d^\dagger a_\ell | 0 \rangle \\ &\quad - \langle 0 | a_i^\dagger a_a a_j^\dagger a_b a_c^\dagger a_k a_d^\dagger a_\ell | 0 \rangle \\ &\quad + \langle 0 | a_i^\dagger a_a a_j^\dagger a_b a_c^\dagger a_k a_d^\dagger a_\ell | 0 \rangle. \\ &= \delta_{ik} \delta_{j\ell} \delta_{ac} \delta_{bd} - \delta_{ik} \delta_{j\ell} \delta_{ad} \delta_{bc} - \delta_{i\ell} \delta_{jk} \delta_{ac} \delta_{bd} + \delta_{i\ell} \delta_{jk} \delta_{ad} \delta_{bc}. \\ \Rightarrow \quad \sum_{ck} \sum_{\ell d} F_c^k t_\ell^d \langle 0 | a_i^\dagger a_a a_j^\dagger a_b a_c^\dagger a_k a_d^\dagger a_\ell | 0 \rangle &= \sum_{ck} \sum_{\ell d} F_c^k t_\ell^d \left(\delta_{ik} \delta_{j\ell} \delta_{ac} \delta_{bd} - \delta_{ik} \delta_{j\ell} \delta_{ad} \delta_{bc} \right. \\ &\quad \left. - \delta_{i\ell} \delta_{jk} \delta_{ac} \delta_{bd} + \delta_{i\ell} \delta_{jk} \delta_{ad} \delta_{bc} \right) \\ &= F_a^i t_j^b - F_b^i t_j^a - F_a^j t_i^b + F_b^j t_i^a. \end{aligned}$$

Part 2: Computations

The purpose of these exercises is to illustrate the impact of electron correlation on molecular electronic structure and to investigate some numerical aspects of post-Hartree-Fock methods. You need access to a suitable quantum chemistry software (e.g. Gaussian, Turbomole, Molpro, Q-Chem, CFOUR, Dalton, ...). Which one you use does not matter.

- It is a good idea to compare results between programs, e.g. by using two programs. All programs must yield **identical results** (and not “similar results”).
- Please report all total energies in atomic units with 9 significant digits after the decimal point, i.e. accurate to 10^{-9} Hartree. Equilibrium structures should be accurate to 10^{-7} bohr. This means that you need to set appropriate (= tight) convergence thresholds. **The default convergence thresholds are unreasonably loose in many programs.** Reaction energies should be additionally reported in kcal/mol; excitation energies in eV, both with one digit after the decimal point.
- Please include all outputs of the calculations you carried out as attachment.

1 Total energies

Compute the total energy of the methane molecule at the HF, MP2, CCSD, and CCSD(T) levels of theory using the cc-pVXZ (X=D, T, Q) basis sets. Use a CH distance of 1.09Å. Do not include the carbon 1s-orbital in the correlation treatment. Collect the results in a table and discuss the observed trends regarding method and basis set.

File	E_{tot} (Hartree)	E_{corr} (Hartree)
HF_D.out	-40.1987102780	—
HF_T.out	-40.2133009586	—
HF_Q.out	-40.2161109439	—
MP2_D.out	-40.35993690	-0.16122662
MP2_T.out	-40.41161182	-0.19831086
MP2_Q.out	-40.42621851	-0.21010757
CCSD_D.out	-40.38343476	-0.18472449
CCSD_T.out	-40.43180841	-0.21850745
CCSD_Q.out	-40.44394416	-0.22783321
CCSD(T)_D.out	-40.38714181	-0.00370704
CCSD(T)_T.out	-40.43809678	-0.00628837
CCSD(T)_Q.out	-40.45087687	-0.00693271

Table 1: Total and correlation energies for HF, MP2, CCSD and CCSD(T) methods using cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets.

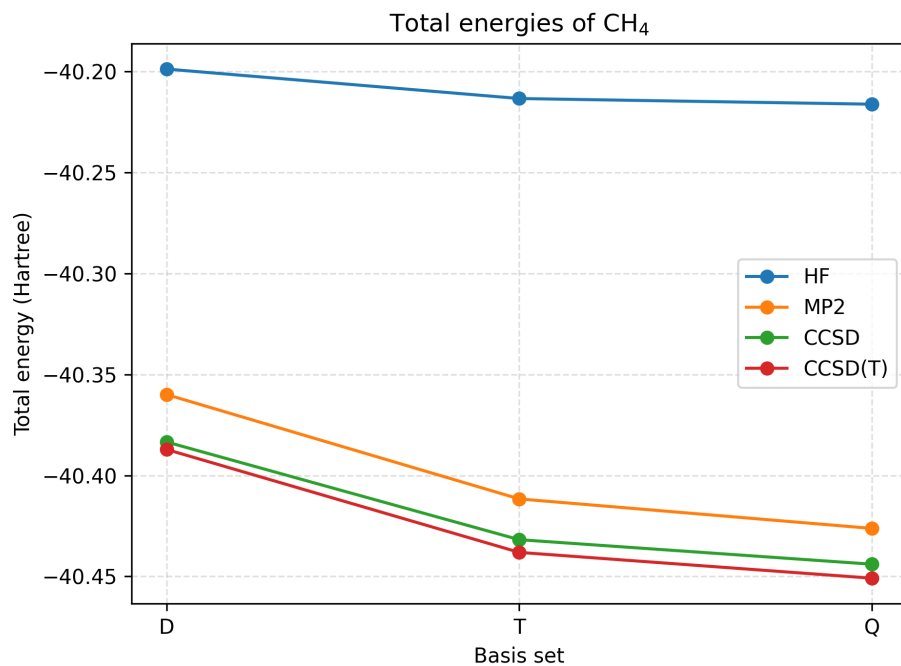


Figure 1: Total energies of methane computed with different electronic structure methods and basis sets.

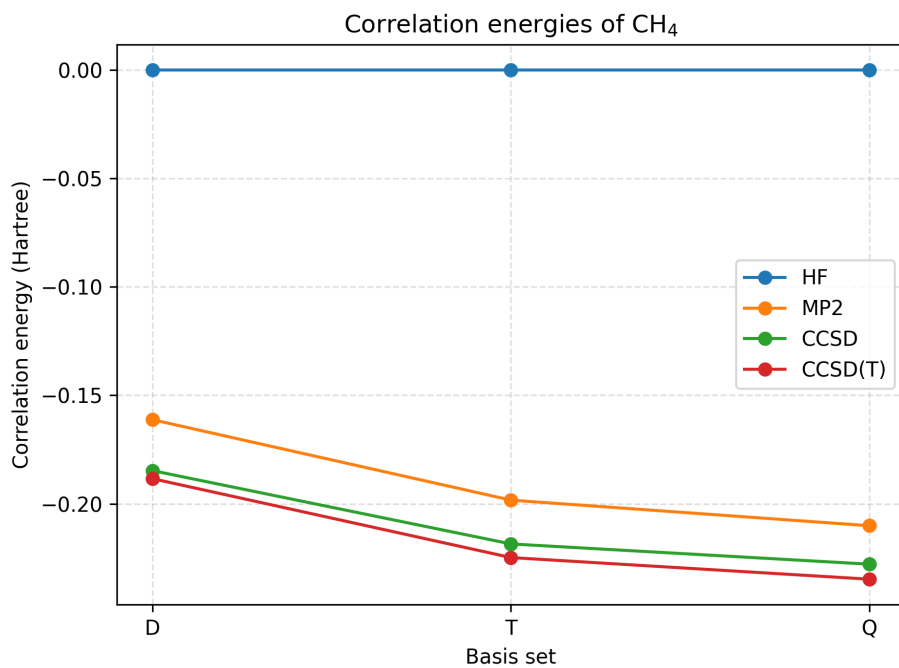


Figure 2: Correlation energies of methane for HF, MP2, CCSD and CCSD(T) methods as a function of the basis set.

Figures 1 and 2 show the total and correlation energies of methane obtained with different electronic structure methods and basis sets. For all methods, the total energy decreases when going from smaller to larger basis sets ($D \rightarrow T \rightarrow Q$), indicating an improved description of the electronic wavefunction as the basis set becomes more complete.

Hartree–Fock provides the highest energies, since electron correlation is not included. MP2 introduces a first correction to the HF reference by accounting for electron correlation at second order, which leads to a significant lowering of the energy. CCSD further improves the results by including higher-order correlation effects, resulting in an additional stabilization with respect to MP2. Finally, CCSD(T) applies a perturbative correction on top of CCSD, which produces a smaller but systematic decrease in the energy. This behavior is clearly reflected in the correlation energy plot and explains the observed trend of decreasing total energies as the level of theory increases. The computational cost increases with both the size of the basis set and the level of theory, with CCSD(T) being significantly more expensive than HF, MP2 and CCSD calculations.

2 Molecular equilibrium structures

Optimize the structure of the methane molecule at the HF, MP2, and CCSD levels of theory using the cc-pVXZ ($X=D, T, Q$) basis sets. Do not include the carbon 1s-orbital in the correlation treatment. Collect the results in a table and discuss the observed trends regarding method and basis set. Compare the results with the experimental values and discuss the origins of the observed deviations and their relevance.

File	E_{tot} (Hartree)	E_{corr} (Hartree)	$d(\text{C-H})$ (Å)
HF_D.out	-40.1987119772	—	1.090785
HF_T.out	-40.2134659225	—	1.082128
HF_Q.out	-40.2163017843	—	1.081531
MP2_D.out	-40.3601751411	-0.16166748	1.099507
MP2_T.out	-40.4116665308	-0.19822849	1.085351
MP2_Q.out	-40.4263062515	-0.21002249	1.084120
CCSD_D.out	-40.3838491098	-0.18551121	1.102620
CCSD_T.out	-40.4318218267	-0.21843898	1.087703
CCSD_Q.out	-40.4439747283	-0.22773978	1.086528

Table 2: Total energies, correlation energies and average C–H bond lengths for methane computed at HF, MP2 and CCSD levels using cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets.

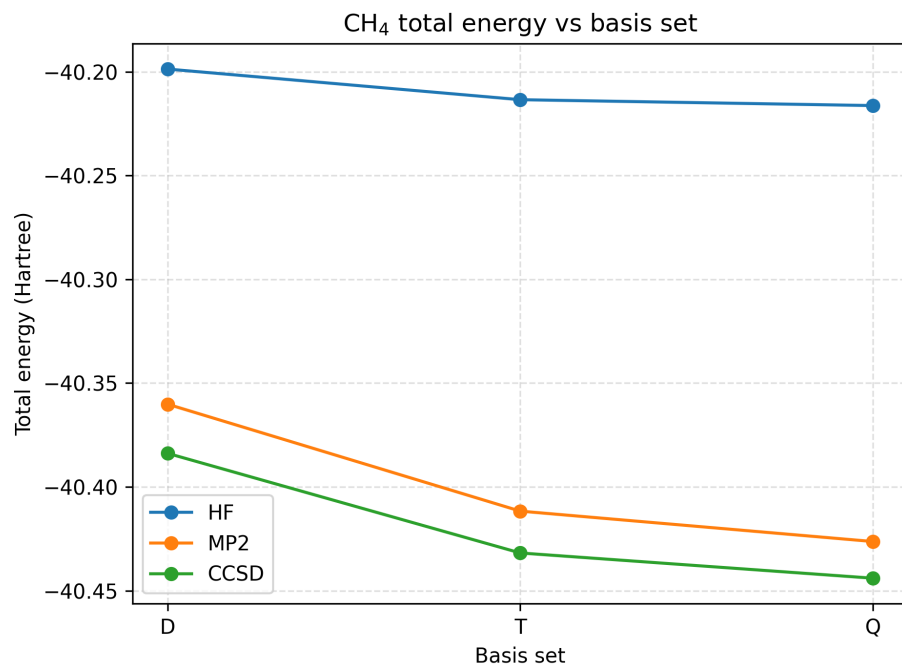


Figure 3: Total energies of methane as a function of the basis set for HF, MP2 and CCSD methods.

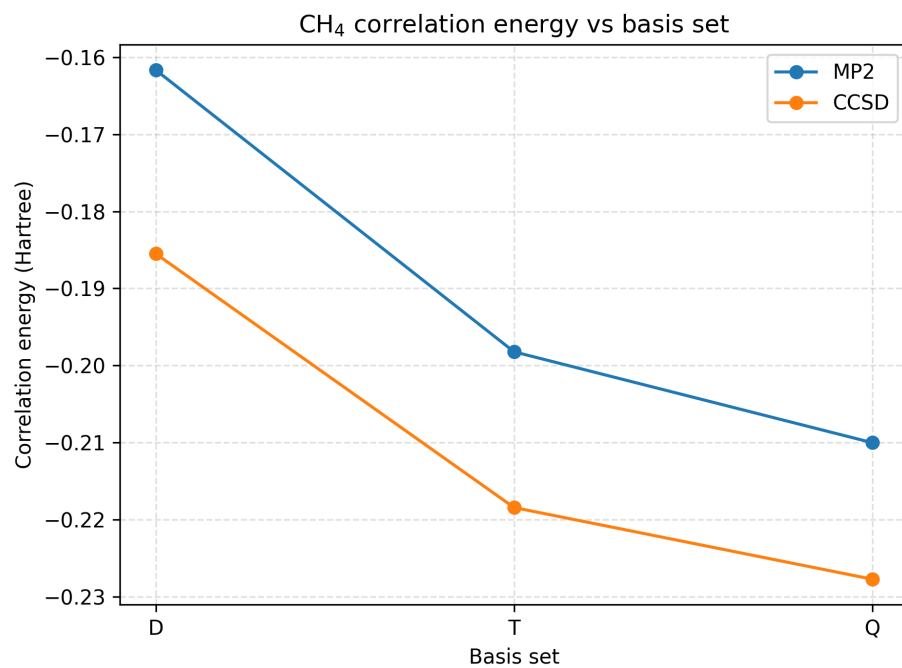


Figure 4: Correlation energies of methane as a function of the basis set for MP2 and CCSD methods.

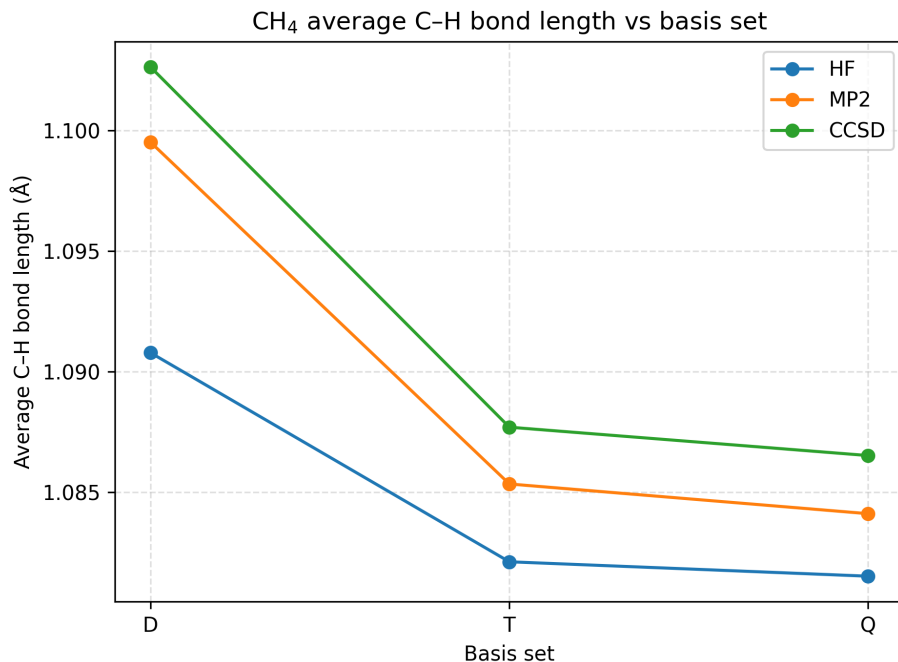


Figure 5: Average C–H bond length of methane as a function of the basis set for HF, MP2 and CCSD methods.

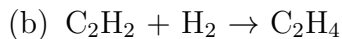
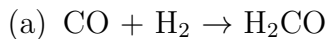
Figures 3, 4 and 5 show the trends of total energies, correlation energies and average C–H bond lengths of methane with respect to the basis set size and the level of theory. For all methods, the total energy decreases systematically when going from smaller to larger basis sets ($D \rightarrow T \rightarrow Q$), indicating an improved description of the electronic wavefunction as the basis becomes more complete. At a given basis set, Hartree–Fock yields the highest energies because electron correlation is not included. MP2 introduces a first correction to the HF reference by accounting for electron correlation at second order, which leads to a significant lowering of the total energy. CCSD further improves the description by including higher-order correlation effects, resulting in an additional stabilization with respect to MP2.

This behavior is consistent with the correlation-energy trends shown in Figure 4, where the correlation energy becomes more negative both with increasing basis set size and when moving from MP2 to CCSD.

Regarding the optimized structures, the average C–H bond length increases when electron correlation is included, with MP2 and CCSD predicting longer bond lengths than Hartree–Fock. This trend can be attributed to the inclusion of electron correlation, which leads to a more realistic description of electron–electron repulsion and results in a slight bond elongation. For a given method, increasing the basis set from cc-pVDZ to cc-pVTZ produces a significant decrease in the C–H bond length. When the basis set is further enlarged to cc-pVQZ, the bond length decreases only slightly, suggesting that the structural parameters are already close to convergence at the triple-zeta level.

3 Reaction energies

Compute reaction energies for the following chemical reactions at the HF and CCSD levels of theory using the cc-pVDZ and cc-pVTZ basis sets:



Do not include the 1s-orbitals of oxygen and carbon in the correlation treatment. Note that you need to optimize the structures of all involved molecules. Also note that methanol has two conformers; you need to use the structure with the lower energy.

Collect all results in a table and discuss the observed trends; in particular, discuss the differences to Exercises 1 and 2 (total energies and equilibrium structures).

Note that the energies that you compute are purely electronic, whereas tabulated reaction energies include contributions from vibration, rotation, and translation to the partition function. Therefore, compare your results with the following purely electronic reference values: (a) -4.7 kcal/mol; (b) -48.1 kcal/mol; (c) -29.3 kcal/mol.

Table 3: Total electronic energies (Hartree) for all molecules, methods and basis sets.

Molecule	Method	Basis	E (Hartree)
H ₂	HF	cc-pVDZ	-1.128746110
	HF	cc-pVTZ	-1.132989711
	CCSD	cc-pVDZ	-1.163672960
	CCSD	cc-pVTZ	-1.172336670
CO	HF	cc-pVDZ	-112.750150619
	HF	cc-pVTZ	-112.781812561
	CCSD	cc-pVDZ	-113.043969439
	CCSD	cc-pVTZ	-113.138548675
H ₂ CO	HF	cc-pVDZ	-113.877222699
	HF	cc-pVTZ	-113.913225391
	CCSD	cc-pVDZ	-114.208910991
	CCSD	cc-pVTZ	-114.317299477
C ₂ H ₂	HF	cc-pVDZ	-76.826043100
	HF	cc-pVTZ	-76.850623924
	CCSD	cc-pVDZ	-77.099263808
	CCSD	cc-pVTZ	-77.171184228
C ₂ H ₄	HF	cc-pVDZ	-78.040165294
	HF	cc-pVTZ	-78.064420067
	CCSD	cc-pVDZ	-78.345632817
	CCSD	cc-pVTZ	-78.423802588
CH ₃ OH (eclipsed)	HF	cc-pVDZ	-115.047611595
	HF	cc-pVTZ	-115.088443143
	CCSD	cc-pVDZ	-115.410623545
	CCSD	cc-pVTZ	-115.534279459
CH ₃ OH (staggered)	HF	cc-pVDZ	-115.049733368
	HF	cc-pVTZ	-115.090198660
	CCSD	cc-pVDZ	-115.412920970
	CCSD	cc-pVTZ	-115.536026726

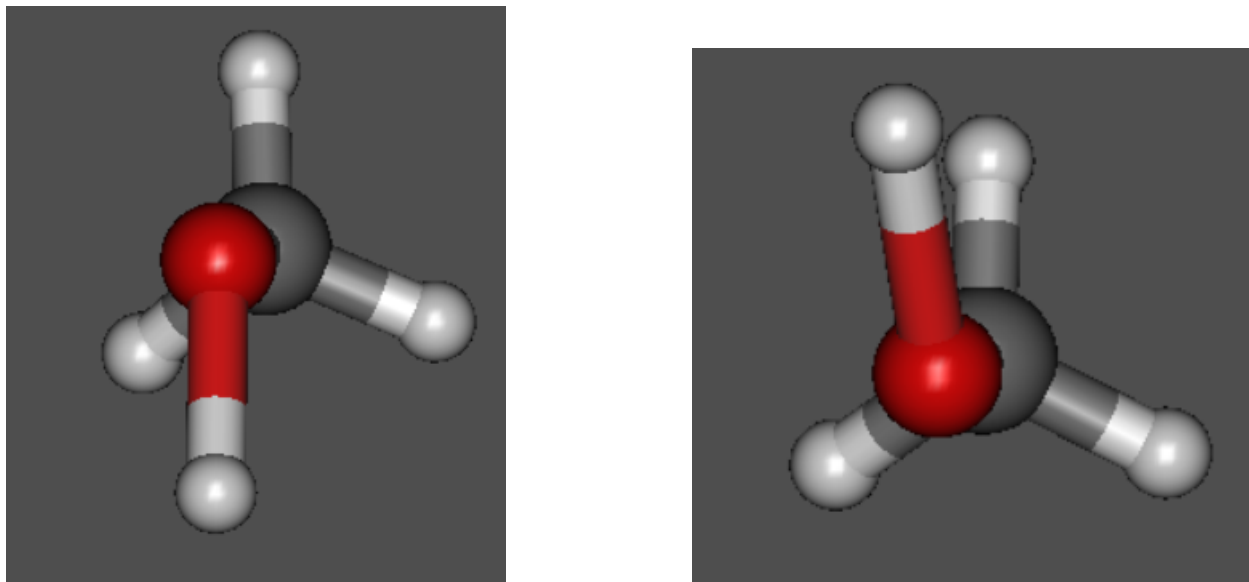


Figure 6: Staggered (left) and eclipsed (right) conformations of methanol.

After collecting the total electronic energies of all molecules, it is observed that the staggered conformation of methanol is consistently lower in energy than the eclipsed conformation at all levels of theory and basis sets considered. This energy difference can be explained by the reduced steric and electronic repulsion in the staggered structure.

$$1 \text{ Hartree} = 627.509474 \text{ kcal mol}^{-1}$$

$$\Delta E = \sum E_{\text{products}} - \sum E_{\text{reactants}}$$



HF/cc-pVDZ

$$\Delta E = -113.877222699 + 112.750150619 + 1.128746110 = 0.001674030 \text{ Hartree}$$

$$\Delta E = 0.001674030 \times 627.509474 = 1.05 \text{ kcal mol}^{-1}$$

HF/cc-pVTZ

$$\Delta E = -113.913225391 + 112.781812561 + 1.132989711 = 0.001577214 \text{ Hartree}$$

$$\Delta E = 0.001577214 \times 627.509474 = 0.99 \text{ kcal mol}^{-1}$$

CCSD/cc-pVDZ

$$\Delta E = -114.208910991 + 113.043969439 + 1.163672960 = -0.001268593 \text{ Hartree}$$

$$\Delta E = -0.001268593 \times 627.509474 = -0.80 \text{ kcal mol}^{-1}$$

CCSD/cc-pVTZ

$$\Delta E = -114.317299477 + 113.138548675 + 1.172336670 = -0.006414132 \text{ Hartree}$$

$$\Delta E = -0.006414132 \times 627.509474 = -4.02 \text{ kcal mol}^{-1}$$

(b) C₂H₂ + H₂ → C₂H₄**HF/cc-pVDZ**

$$\Delta E = -78.040165294 + 76.826043100 + 1.128746110 = -0.085376084 \text{ Hartree}$$

$$\Delta E = -0.085376084 \times 627.509474 = -53.57 \text{ kcal mol}^{-1}$$

HF/cc-pVTZ

$$\Delta E = -78.064420067 + 76.850623924 + 1.132989711 = -0.080806432 \text{ Hartree}$$

$$\Delta E = -0.080806432 \times 627.509474 = -50.71 \text{ kcal mol}^{-1}$$

CCSD/cc-pVDZ

$$\Delta E = -78.345632817 + 77.099263808 + 1.163672960 = -0.082696049 \text{ Hartree}$$

$$\Delta E = -0.082696049 \times 627.509474 = -51.89 \text{ kcal mol}^{-1}$$

CCSD/cc-pVTZ

$$\Delta E = -78.423802588 + 77.171184228 + 1.172336670 = -0.080281690 \text{ Hartree}$$

$$\Delta E = -0.080281690 \times 627.509474 = -50.38 \text{ kcal mol}^{-1}$$

(c) H₂CO + H₂ → CH₃OH

(Using CH₃OH staggered.)

HF/cc-pVDZ

$$\Delta E = -115.049733368 + 113.877222699 + 1.128746110 = -0.043764559 \text{ Hartree}$$

$$\Delta E = -0.043764559 \times 627.509474 = -27.46 \text{ kcal mol}^{-1}$$

HF/cc-pVTZ

$$\Delta E = -115.090198660 + 113.913225391 + 1.132989711 = -0.043983558 \text{ Hartree}$$

$$\Delta E = -0.043983558 \times 627.509474 = -27.60 \text{ kcal mol}^{-1}$$

CCSD/cc-pVDZ

$$\Delta E = -115.412920970 + 114.208910991 + 1.163672960 = -0.040337019 \text{ Hartree}$$

$$\Delta E = -0.040337019 \times 627.509474 = -25.31 \text{ kcal mol}^{-1}$$

CCSD/cc-pVTZ

$$\Delta E = -115.536026726 + 114.317299477 + 1.172336670 = -0.046390579 \text{ Hartree}$$

$$\Delta E = -0.046390579 \times 627.509474 = -29.11 \text{ kcal mol}^{-1}$$

Table 4: Reaction energies ΔE_{rxn} (kcal mol⁻¹) computed at HF and CCSD levels with cc-pVDZ and cc-pVTZ basis sets.

Reaction	Method	Basis	ΔE_{rxn} (kcal mol ⁻¹)
(a) CO + H ₂ → H ₂ CO	HF	cc-pVDZ	+1.05
	HF	cc-pVTZ	+0.99
	CCSD	cc-pVDZ	-0.80
	CCSD	cc-pVTZ	-4.02
(b) C ₂ H ₂ + H ₂ → C ₂ H ₄	HF	cc-pVDZ	-53.57
	HF	cc-pVTZ	-50.71
	CCSD	cc-pVDZ	-51.89
	CCSD	cc-pVTZ	-50.38
(c) H ₂ CO + H ₂ → CH ₃ OH	HF	cc-pVDZ	-27.46
	HF	cc-pVTZ	-27.60
	CCSD	cc-pVDZ	-25.31
	CCSD	cc-pVTZ	-29.11

Table 4 summarizes the electronic reaction energies computed for reactions (a)–(c) at the HF and CCSD levels with cc-pVDZ and cc-pVTZ basis sets. Overall, the best agreement with the purely electronic reference values is obtained with CCSD/cc-pVTZ for all three reactions, which is consistent with Exercises 1 and 2: using a larger basis set systematically improves total energies, and including electron correlation (moving from HF to correlated methods) typically improves the relative energetics of different molecules.

For reaction (a) (CO + H₂ → H₂CO), HF predicts a slightly endothermic reaction (+1.05 and +0.99 kcal mol⁻¹ with cc-pVDZ and cc-pVTZ), while the electronic reference value is exothermic (-4.7 kcal mol⁻¹). This sign error indicates that HF does not provide a balanced description of reactants and products for this reaction because it neglects electron correlation. When correlation is included at the CCSD level, the reaction becomes exothermic (-0.80 and -4.02 kcal mol⁻¹), and CCSD/cc-pVTZ nearly reproduces the reference value. This behavior matches the trend observed in Exercises 1 and 2.

For reaction (b) (C₂H₂ + H₂ → C₂H₄). The results show that improving the basis set from cc-pVDZ to cc-pVTZ has a clear effect, and in this case HF/cc-pVTZ (-50.71

kcal mol⁻¹) is closer to the reference (-48.1 kcal mol⁻¹) than CCSD/cc-pVDZ (-51.89 kcal mol⁻¹). This suggests that for this reaction, basis set incompleteness can be a dominant source of error, and a larger basis may be more important than adding correlation with a small basis. However, when both improvements are combined (CCSD/cc-pVTZ), the closest result is obtained (-50.38 kcal mol⁻¹).

For reaction (c) ($\text{H}_2\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH}$), the reference electronic reaction energy is -29.3 kcal mol⁻¹. HF gives values around -27.5 kcal mol⁻¹, while CCSD improves the description, and CCSD/cc-pVTZ (-29.11 kcal mol⁻¹) is very close to the reference. This again supports the conclusion that a correlated method with a sufficiently large basis set provides the most reliable reaction energies.

Finally, compared to Exercises 1 and 2, the key difference is that reaction energies depend on energy differences between multiple molecules, so error cancellation becomes important. In some cases like reaction (b), a larger basis at HF can outperform a smaller basis with correlation. In contrast, when correlation effects differ significantly between reactants and products (reaction (a)), not taking into account the correlation can even give the wrong sign.

4 Electronic excitation energies

Compute excitation energies for the 5 lowest excited states of the methane molecule at the CIS and EOM-CCSD levels of theory using the cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, and aug-cc-pVTZ basis sets. In addition, use the HOMO-LUMO gap as an estimate for the excitation energy. Use the same molecular structure as in Exercise 1. Do not include the carbon 1s-orbital in the correlation treatment. Collect all results in a table and discuss the observed trends. Under which irreducible representations do the computed states transform? And are they singlet or triplet states? (Note that some programs compute only singlet states by default. Set the appropriate keywords to get triplet states as well.)

Method	Basis	Rank	State (S/T)	E_{exc} (eV)
CIS	aug-cc-pVDZ	1	T1	10.2671
		2	T2	10.2686
		3	T3	10.2686
		4	T4	11.0035
		5	S1	11.0239
CIS	aug-cc-pVTZ	1	T1	10.2757
		2	T2	10.2772
		3	T3	10.2772
		4	T4	11.0071
		5	S1	11.0425
CIS	cc-pVDZ	1	T1	11.0455
		2	T2	11.0466
		3	T3	11.0466
		4	T4	11.5082
		5	S1	12.7195
CIS	cc-pVTZ	1	T1	10.7455
		2	T2	10.7467
		3	T3	10.7467
		4	T4	11.3655
		5	S1	12.0732
EOM-CCSD	aug-cc-pVDZ	1	T1	10.1014
		2	T2	10.1029
		3	T3	10.1030
		4	S1	10.5146
		5	S2	10.5163
EOM-CCSD	aug-cc-pVTZ	1	T1	10.1993
		2	T2	10.2009
		3	T3	10.2009
		4	S1	10.6115
		5	S2	10.6132
EOM-CCSD	cc-pVDZ	1	T1	11.2093
		2	T2	11.2106
		3	T3	11.2106
		4	T4	11.8514
		5	S1	12.2807
EOM-CCSD	cc-pVTZ	1	T1	10.8553
		2	T2	10.8566
		3	T3	10.8567
		4	S1	11.6342
		5	S2	11.6360

Table 5: Five lowest vertical excitation energies for CH_4 (singlet + triplet manifold merged and sorted) for each method and basis set.

Vertical excitation energies of CH_4 were computed using the same fixed molecular geometry as in Exercise 1. For each excited state, the vertical excitation energy was obtained

as

$$E_{\text{exc}} = E_{\text{tot}}(\text{excited state}) - E_{\text{tot}}(\text{ground state}), \quad (49)$$

Calculations were performed at the CIS and EOM-CCSD levels of theory using the cc-pVDZ, cc-pVTZ, aug-cc-pVDZ and aug-cc-pVTZ basis sets. In the correlated calculations, the carbon $1s$ orbital was excluded from the correlation treatment. Singlet and triplet excited states were computed separately and combined after in order to identify the five lowest excited states for each method and basis set.

For all methods and basis sets, the lowest excited states are found to be triplet states. In particular, the three lowest states are nearly degenerate, followed by higher triplet or singlet state depending on the level of theory and basis set.

Systematic differences are observed between CIS and EOM-CCSD excitation energies. CIS tends to give higher excitation energies because it lacks a consistent description of electron correlation in both the ground and excited states. In contrast, EOM-CCSD generally predicts lower excitation energies than CIS since it is based on a correlated CCSD ground state and provides a more balanced treatment of excited states.

The inclusion of diffuse functions has a pronounced effect on the excitation energies. Moving from cc-pVXZ to aug-cc-pVXZ basis sets results in a significant lowering of the lowest excitation energies. Increasing the from double- ζ to triple- ζ produces a more moderate effect, generally leading to a slight stabilization of the excitation energies and improved basis-set convergence.

Table 6: HOMO–LUMO gaps obtained from Hartree–Fock orbital energies ($\Delta_{\text{HL}} = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$).

Basis set	$\varepsilon_{\text{HOMO}}$ (Ha)	$\varepsilon_{\text{LUMO}}$ (Ha)	Gap (Ha)	Gap (eV)
cc-pVDZ	-0.5425	0.1930	0.7355	20.01
cc-pVTZ	-0.5445	0.1434	0.6879	18.72
aug-cc-pVDZ	-0.5436	0.0370	0.5806	15.80
aug-cc-pVTZ	-0.5445	0.0308	0.5753	15.65

These HOMO–LUMO gaps are significantly larger than the vertical excitation energies obtained with CIS and EOM-CCSD. This discrepancy is expected, because the HOMO–LUMO gap is calculated as the difference in the orbital energies of the Hartree–Fock calculation which neglects electron correlation, orbital relaxation, and configuration mixing, and therefore cannot be interpreted as true excitation energies. Nevertheless, the HOMO–LUMO gap reproduces qualitative trends with respect to the basis set, in particular the strong reduction observed upon inclusion of diffuse functions.

Irreducible representations of the excited states

In the present work, all calculations were performed without imposing molecular symmetry, using the C_1 point group. In this point group, only the irreducible representation A exists. All computed electronic states, both singlet and triplet, transform according to the A irreducible representation.

Methane, however, belongs to the T_d point group in its ideal equilibrium geometry. In this higher symmetry group, several of the lower excited states are expected to be degenerate and to transform according to multidimensional irreducible representations, such as T_2 or E . When the symmetry is reduced to C_1 , these degeneracies are broken, and each component of a degenerate manifold appears as a separate electronic state with very similar excitation energies.

This effect is clearly observed in the computed excitation spectra, where groups of nearly degenerate roots correspond to symmetry-degenerate excited states in the T_d point group. Although these states are all labeled as A in C_1 symmetry, their energetic proximity reflects the real higher molecular symmetry of methane.

All calculations were performed using the Q-Chem quantum chemistry package [1].

References

- [1] Y. Shao *et al.*, *Advances in molecular quantum chemistry contained in the Q-Chem 4 program package*, Molecular Physics **113**, 184–215 (2015).