5 Traditional coupled-cluster theory

Definition 5.1. *Traditional coupled-cluster theory.* A *wave operator* maps a determinant into a correlated wavefunction, $\Psi = \Omega\Phi$. The *coupled-cluster Ansatz* is characterized by an exponential parametrization of the wave operator.

$$H_c \Psi_{CC} = E_c \Psi_{CC} \qquad \Psi_{CC} \equiv \exp(T)\Phi \qquad T \equiv T_1 + T_2 + \cdots + T_n \qquad T_k \equiv (\tfrac{1}{k!})^2 t^{i_1 \cdots i_k}_{a_1 \cdots a_k} \tilde{a}^{a_1 \cdots a_k}_{i_1 \cdots i_k} \tag{5.1}$$

The coupled-cluster Schrödinger equation can be projected onto the determinant basis to arrive at a series of equations

$$\langle \Phi | H_c | \Psi_{CC} \rangle = E_c \qquad\qquad \langle \Phi^{ab\cdots}_{ij\cdots} | H_c | \Psi_{CC} \rangle = E_c\, t^{ij\cdots}_{ab\cdots} \tag{5.2}$$

which specify the coupled-cluster energy and the *amplitudes*, $t^{ij\cdots}_{ab\cdots}$. A different approach, known as *traditional coupled-cluster (TCC) theory*, first multiplies the Schrödinger equation on the left by the inverse of the wave operator

$$\overline{H}_c \Phi = E_c \Phi \qquad\qquad \overline{H}_c \equiv \exp(-T) H_c \exp(T) \tag{5.3}$$

to define an *effective Hamiltonian*, $\overline{H}_c$. The eigenvalue of this similarity-transformed[1] Hamiltonian is the exact correlation energy, E_c, but its eigenstate is the reference determinant, Φ, rather than the correlated wavefunction. Note that, unlike the true Hamiltonian, $\overline{H}_c$ is non-Hermitian. Projection onto the determinant basis yields energy and amplitude equations

$$\langle \Phi | \overline{H}_c | \Phi \rangle = E_c \qquad\qquad \langle \Phi^{ab\cdots}_{ij\cdots} | \overline{H}_c | \Phi \rangle = 0 \tag{5.4}$$

which look similar to equation 5.2, except that the right-hand side of the amplitude equations is now zero. The next few results lead up to remark 5.1, which says that the effect of the TCC similarity transformation is to remove disconnected contributions to the amplitude equations, of which $E_c t^{ij\cdots}_{ab\cdots}$ is an example.

Notation 5.1. Nested commutators will here be denoted by $[X, \cdot]^n(Y) \equiv [X, \cdots [X, [X, Y]] \cdots]$ with $[X, \cdot]^0(Y) \equiv Y$.

Theorem 5.1. *The Hausdorff Expansion.* $\quad e^X Y e^{-X} = \sum\limits_{n=0}^{\infty} \dfrac{1}{n!} [X, \cdot]^n(Y)$

    Proof: This follows from a direct Taylor expansion of the exponentials, along with proposition A.1.[2]

$$e^X Y e^{-X} = \sum_{h=0}^{\infty} \sum_{k=0}^{\infty} \frac{1}{h!\,k!}(-)^k X^h Y X^k = \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{k=0}^{n} \frac{n!}{(n-k)!\,k!}(-)^k X^{n-k} Y X^k = \sum_{n=0}^{\infty} \frac{1}{n!}[X, \cdot](Y)$$

    In the second step, we have rearranged the sum to run over $n = h + k$ and k and inserted $1 = n!/n!$.

Proposition 5.1. If Q or Q' contains an even number of operators, $[{:}Q{:}, {:}Q'{:}] = {:}\overline{QQ'}{:} - {:}\overline{Q'Q}{:}$.

    Proof: By Wick's theorem, ${:}Q{:}{:}Q'{:} - {:}Q'{:}{:}Q{:} = {:}QQ'{:} + {:}\overline{QQ'}{:} - {:}Q'Q{:} - {:}\overline{Q'Q}{:}$. The proposition follows from the fact that, if one of these strings contains an even number of operators, then ${:}QQ'{:} = {:}Q'Q{:}$.

Remark 5.1. The Hausdorff expansion can be used to express the TCC effective Hamiltonian in powers of T.[3]

$$\overline{H}_c = e^{-T} H_c\, e^T = H_c + [H_c, T] + \tfrac{1}{2!}[[H_c, T], T] + \tfrac{1}{3!}[[[H_c, T], T], T] + \cdots$$

Proposition 5.1 implies that $[H_c, T] = {:}\overline{H_c T}{:}$ and more generally $[\cdot, T]^n(H_c) = {:}\overline{H_c T T \cdots T}{:}$, since T has no non-vanishing contractions with operators to its right.[4] This leads to a new expression for the effective Hamiltonian.[5]

$$\overline{H}_c = H_c + {:}\overline{H_c T}{:} + \tfrac{1}{2!}{:}\overline{H_c T T}{:} + \tfrac{1}{3!}{:}\overline{H_c T T T}{:} + \tfrac{1}{4!}{:}\overline{H_c T T T T}{:} = (H_c\, e^T)_C$$

This expansion naturally truncates at the fourth power, since each T must have at least one contraction with the Hamiltonian and the electron repulsion operator only has four operators available for contraction. Substituting this result into equation 5.4 leads to a new expression for the TCC energy and amplitude equations.

$$\langle \Phi | H_c \exp(T) | \Phi \rangle_C = E_c \qquad\qquad \langle \Phi^{ab\cdots}_{ij\cdots} | H_c \exp(T) | \Phi \rangle_C = 0 \tag{5.5}$$

Note that the subscript C here means specifically that that the cluster operators are connected to the Hamiltonian. Connection through the bare excitation operator $\tilde{a}^{ij\cdots}_{ab\cdots}$ is excluded.

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[1]See https://en.wikipedia.org/wiki/Matrix_similarity.

[2]For a slick alternative to this proof, see Helgaker, Jørgensen, and Olsen, *Molecular Electronic-Structure Theory* (2000), p. 100.

[3]Note that $[X, \cdot]^n(Y) = [\cdot, -X]^n(Y)$.

[4]This is easily seen from the diagram. It comes from the fact that T is composed entirely of quasi-particle creation operators.

[5]Subscript C denotes the connected part, i.e. the connected graphs in a term's Wick expansion.

Remark 5.2. It can be shown that the determinant basis forms an eigenbasis for the diagonal part of the Fock operator.[6]

$$H_0 \Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k} = \mathcal{E}_{i_1 \cdots i_k}^{a_1 \cdots a_k} \Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k} \qquad\qquad H_0 \equiv f_p^p \tilde{a}_p^p \qquad\qquad \mathcal{E}_{q_1 \cdots q_k}^{p_1 \cdots p_k} \equiv \sum_{r=1}^{k} f_{p_r}^{p_r} - \sum_{r=1}^{k} f_{q_r}^{q_r} \qquad (5.6)$$

Noting that H_0 is Hermitian, this implies $\langle \Phi_{ij\cdots}^{ab\cdots}|H_0 \exp(T)|\Phi\rangle = \mathcal{E}_{ij\cdots}^{ab\cdots}\langle \Phi_{ij\cdots}^{ab\cdots}|\exp(T)|\Phi\rangle = \mathcal{E}_{ij\cdots}^{ab\cdots} t_{ab\cdots}^{ij\cdots}$. This can be used to rearrange the amplitude equation in (5.5) as follows, which defines the working equations used to iteratively solve TCC.

$$t_{ab\cdots}^{ij\cdots} = (\mathcal{E}_{ab\cdots}^{ij\cdots})^{-1} \langle \Phi_{ab\cdots}^{ij\cdots}|V_c \exp(T)|\Phi\rangle_C \qquad\qquad V_c \equiv H_c - H_0 = f_p^q(1 - \delta_p^q)\tilde{a}_q^p + \tfrac{1}{4}\bar{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} \qquad (5.7)$$

In Møller-Plesset perturbation theory, H_0 is known the *zeroth order Hamiltonian* and V_c is the *perturbation*. These operators are also known as the *model Hamiltonian* and *fluctuation potential*, respectively.

Notation 5.2. The following is suggested notation for the diagonal and off-diagonal contributions to the Fock operator.

$$\otimes\!\!-\!\!\phi = \odot\!\!-\!\!\phi + \oplus\!\!-\!\!\phi \qquad\qquad \odot\!\!-\!\!\phi \equiv H_0 \qquad\qquad \oplus\!\!-\!\!\phi \equiv f_p^q(1 - \delta_p^q)\tilde{a}_q^p \qquad (5.8)$$

so that $H_e = E_0 + \odot\!\!-\!\!\phi + \oplus\!\!-\!\!\phi + \phi\!\!\sim\!\!\!\sim\!\!\phi$ is the full electronic Hamiltonian and $V_c = \oplus\!\!-\!\!\phi + \phi\!\!\sim\!\!\!\sim\!\!\phi$.

Definition 5.2. *Excitation level.* The *excitation level* of a graph equals the net number of particles or quasi-particles it creates, divided by two. For example, the quasi-particle excitation levels of the T_1, T_2 and T_3 operators are one, two, and three, respectively, and that of $\tilde{a}_{abcd}^{ijkl}$ is -4. A convenient rule for evaluating reference expectation values is that the total excitation level of a closed graph must balance out to zero.

Example 5.1. The excitation levels in the quasi-particle expansions of one- and two-particle operators are as follows.

Example 5.2. *The CCSDT equations.* Truncating the cluster operator at triple excitations, $T \approx T_1 + T_2 + T_3$, leads to the CCSDT approximation. The singles, doubles, and triples amplitude equations are given by the following

$$t_a^i = (\mathcal{E}_a^i)^{-1}\langle\Phi_i^a|V_c(1 + T_2 + T_1 + T_1 T_2 + \tfrac{1}{2}T_1^2 + \tfrac{1}{3!}T_1^3 + T_3)|\Phi\rangle_C \qquad (5.9)$$

$$t_{ab}^{ij} = (\mathcal{E}_{ab}^{ij})^{-1}\langle\Phi_{ij}^{ab}|V_c(1 + T_2 + \tfrac{1}{2}T_2^2 + T_1 + T_1 T_2 + \tfrac{1}{2}T_1^2 + \tfrac{1}{2}T_1^2 T_2 + \tfrac{1}{3!}T_1^3 + \tfrac{1}{4!}T_1^4 + T_3 + T_1 T_3)|\Phi\rangle_C \qquad (5.10)$$

$$t_{abc}^{ijk} = (\mathcal{E}_{abc}^{ijk})^{-1}\langle\Phi_{ijk}^{abc}|V_c(T_2 + T_3 + \tfrac{1}{2}T_2^2 + T_1 T_2 + T_2 T_3 + T_1 T_3 + \tfrac{1}{2}T_1^2 T_2 + \tfrac{1}{2}T_1 T_2^2 + \tfrac{1}{2}T_1^2 T_3 + \tfrac{1}{3!}T_1^3 T_2)|\Phi\rangle_C \qquad (5.11)$$

where several contributions to $\exp(T_1 + T_2 + T_3)$ have been omitted either because the excitation levels do not balance or because they require one of the cluster operators to be disconnected from the Hamiltonian.

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[6]The proof is as follows. First, note that $a_p^p \Phi_\mu = n_p^\mu \Phi_\mu$, where n_p^μ denotes the occupation of ψ_p in Φ_μ. By Wick's theorem, $a_p^p = \tilde{a}_p^p + n_p^0$, where n_p^0 denotes the occupation of ψ_p in Φ. Therefore, $\tilde{a}_p^p \Phi_\mu = (n_p^\mu - n_p^0)\Phi_\mu$ and $H_0 \Phi_\mu = \left(\sum_{p \in \Phi_\mu} f_p^p - \sum_{p \in \Phi} f_p^p\right)\Phi_\mu$.

A   Nested commutator relation

Proposition A.1. *Nested commutator relation.* $[X, \cdot]^n(Y) = \sum_{k=0}^{n}(-)^k \binom{n}{k} X^{n-k}YX^k.$

Proof: We proceed by induction on n. For $n = 0$ this follows from the definition of the commutator, $[X,Y] = XY - YX$. Assuming the proposition holds for $n-1$ nested commutators, we can express the n-fold nested commutator as

$$[X, \cdot]^n(Y) = X[X, \cdot]^{n-1}(Y) - [X, \cdot]^{n-1}(Y)\,X = X^kY + \sum_{k=1}^{n-1}(-)^k \left(\binom{n-1}{k} + \binom{n-1}{k-1}\right) X^{n-k}YX^k + (-)^nYX^n$$

by expanding $[X, \cdot]^{n-1}(Y)$ twice and substituting k for $k-1$ in the second summation. Combining factorials as follows

$$\binom{n-1}{k} + \binom{n-1}{k-1} = \frac{n-k}{n-k}\cdot\frac{(n-1)!}{k!(n-1-k)!} + \frac{k}{k}\cdot\frac{(n-1)!}{(k-1)!(n-k)!} = \binom{n}{k}$$

shows that the proposition also holds for n, completing the proof by induction.