

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.

$$H_c \Psi_{CC} = E_c \Psi_{CC} \quad \Psi_{CC} \equiv \exp(T)\Phi \quad T \equiv T_1 + T_2 + \cdots + T_n \quad T_k \equiv \left(\frac{1}{k!}\right)^2 t_{a_1 \dots a_k}^{i_1 \dots i_k} \tilde{a}_{i_1 \dots i_k}^{a_1 \dots a_k} \quad (5.1)$$

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

$$\langle \Phi | H_c | \Psi_{CC} \rangle = E_c \quad \langle \Phi | H_c | \Psi_{CC} \rangle = E_c t_{ab \dots}^{ij \dots} \quad (5.2)$$

which specify the coupled-cluster energy and the *amplitudes*, $t_{ab \dots}^{ij \dots}$. 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

$$\bar{H}_c \Phi = E_c \Phi \quad \bar{H}_c \equiv \exp(-T) H_c \exp(T) \quad (5.3)$$

to define an *effective Hamiltonian*, \bar{H}_c . The eigenvalue of this similarity-transformed¹ 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, \bar{H}_c is non-Hermitian. Projection onto the determinant basis yields energy and amplitude equations

$$\langle \Phi | \bar{H}_c | \Phi \rangle = E_c \quad \langle \Phi | \bar{H}_c | \Phi \rangle = 0 \quad (5.4)$$

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 $E_c t_{ab \dots}^{ij \dots}$ 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. $e^X Y e^{-X} = \sum_{n=0}^{\infty} \frac{1}{n!} [X, \cdot]^n(Y)$

Proof: This follows from a direct Taylor expansion of the exponentials, along with proposition A.1.²

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

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, $[:Q:, :Q':] = :\bar{Q}Q': - :Q'\bar{Q}:.$

Proof: By Wick's theorem, $:Q::Q': - :Q':Q: = :QQ': + :\bar{Q}Q': - :Q'\bar{Q}: - :\bar{Q}'Q':.$ 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

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

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

$$\bar{H}_c = H_c + :\bar{H}_c T: + \frac{1}{2!} :\bar{H}_c \overbrace{TT}^2: + \frac{1}{3!} :\bar{H}_c \overbrace{TTT}^3: + \frac{1}{4!} :\bar{H}_c \overbrace{TTTT}^4: = (H_c e^T)_C$$

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.

$$\langle \Phi | H_c \exp(T) | \Phi \rangle_C = E_c \quad \langle \Phi | H_c \exp(T) | \Phi \rangle_C = 0 \quad (5.5)$$

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

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

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

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

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

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

A Nested commutator relation

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

Proof: We proceed by induction on n . For $n = 1$ 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

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

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.