

2 Wick's theorem

Definition 2.1. Normal ordering. The *normal ordering* of a string $q_1 \cdots q_n$ of particle-hole operators is the mapping $q_1 \cdots q_n \mapsto :q_1 \cdots q_n: \equiv \varepsilon_\pi q_{\pi(1)} \cdots q_{\pi(n)}$ where $\pi \in S_n$ is a permutation that puts the string in normal order. More generally, Φ -normal ordering maps the string into $:q_1 \cdots q_n: \equiv \varepsilon_\sigma q_{\sigma(1)} \cdots q_{\sigma(n)}$ where σ puts the string in Φ -normal order.

Definition 2.2. Contraction. A *contraction* of two particle-hole operators q_1 and q_2 is the difference between their product and its normal-ordering, $:\overline{q_1 q_2}: \equiv q_1 q_2 - :q_1 q_2:$. This associates a scalar value with every pair in $\{a_p\} \cup \{a_p^\dagger\}$.

$$\begin{aligned} :\overline{a_p a_q}: &= a_p a_q - a_p a_q = 0 & :\overline{a_p^\dagger a_q}: &= a_p^\dagger a_q - a_p^\dagger a_q = 0 \\ :\overline{a_p^\dagger a_q^\dagger}: &= a_p^\dagger a_q^\dagger - a_p^\dagger a_q^\dagger = 0 & :\overline{a_p a_q^\dagger}: &= a_p a_q^\dagger + a_q^\dagger a_p = \delta_{pq} \end{aligned} \quad (2.1)$$

More generally, we can define a Φ -normal contraction of two operators by subtracting their Φ -normal-ordering instead, $:\overline{q_1 q_2}: \equiv q_1 q_2 - :q_1 q_2:$. In this case, contractions of like operators still vanish but the mixed cases are more complicated.

$$:\overline{a_p^\dagger a_q}: = \gamma_{pq} \quad :\overline{a_p a_q^\dagger}: = \eta_{pq} \quad \gamma_{pq} \equiv \begin{cases} \delta_{pq} & p, q \text{ occupied in } \Phi \\ 0 & p, q \text{ virtual} \end{cases} \quad \eta_{pq} \equiv \begin{cases} 0 & p, q \text{ occupied in } \Phi \\ \delta_{pq} & p, q \text{ virtual} \end{cases} \quad (2.2)$$

In words, dagger-on-the-left contractions (“hole contractions”) are elements of a matrix γ which is zero everywhere but its occupied block, where $\gamma_{ij} = \delta_{ij}$, whereas daggers-on-the-right contractions (“particle contractions”) are elements of a matrix η which is zero everywhere but its virtual block, $\eta_{ab} = \delta_{ab}$. Noting that $:\overline{q_1 q_2}: = \langle \Phi | q_1 q_2 - :q_1 q_2: | \Phi \rangle = \langle \Phi | q_1 q_2 | \Phi \rangle$, these matrices can be identified as $\gamma_{pq} = \langle \Phi | a_p^\dagger a_q | \Phi \rangle$ and $\eta_{pq} = \langle \Phi | a_p a_q^\dagger | \Phi \rangle$, known as the *one-particle* and *one-hole density matrices* of Φ , respectively.

Notation 2.1. Normal-ordered strings with contractions. Let the notation $:q_1 \cdots \overline{q_i \cdots q_j} \cdots q_n:$ stand for

$$:q_1 \cdots \overline{q_i \cdots q_j} \cdots q_n: \equiv (-)^{j-i-1} \overline{q_i q_j} :q_1 \cdots \cancel{q_i} \cdots \cancel{q_j} \cdots q_n: \quad (2.3)$$

where the phase factor corresponds to the signature of the permutation required to bring q_i and q_j together. The same rule applies for normal-ordered strings with multiple contraction lines.

Problem 2.1. Show that the expansion of $a_p a_q a_s^\dagger a_r^\dagger$ in terms of strings that are in normal order

$$a_p a_q a_s^\dagger a_r^\dagger = a_s^\dagger a_r^\dagger a_p a_q + \delta_{ps} a_r^\dagger a_q - \delta_{pr} a_s^\dagger a_q - \delta_{qs} a_r^\dagger a_p + \delta_{qr} a_s^\dagger a_p - \delta_{ps} \delta_{qr} + \delta_{pr} \delta_{qs} \quad (2.4)$$

can be expressed as follows, using notation 2.1.

$$a_p a_q a_s^\dagger a_r^\dagger = :a_p a_q a_s^\dagger a_r^\dagger: + :\overline{a_p a_q} a_s^\dagger a_r^\dagger: + :\overline{a_p a_q^\dagger} a_s^\dagger a_r^\dagger: + :a_p \overline{a_q a_s^\dagger} a_r^\dagger: + :a_p a_q \overline{a_s^\dagger a_r^\dagger}: + :\overline{a_p a_q} \overline{a_s^\dagger a_r^\dagger}: + :\overline{a_p a_q^\dagger} \overline{a_s^\dagger a_r^\dagger}: \quad (2.5)$$

That is, the string equals its normal-ordering plus all possible contractions. This is one example of a general result known as Wick's theorem, which will be proven below after we introduce some convenient notation.

Notation 2.2. For a particle-hole operator string $Q = q_1 \cdots q_n$, let the $:Q(\overline{q_i q_j}):$ denote $:q_1 \cdots \overline{q_i \cdots q_j} \cdots q_n:$. This is well-defined as long as $i < j$. Let $:\overline{Q}::$ stand for the sum of all unique single, double, triple, etc. contractions of Q

$$:\overline{Q}: \equiv \sum_{k=1}^{\lfloor n/2 \rfloor} \sum_{(i_1 j_1) \cdots (i_k j_k)} \text{Ctr}_k(Q) :Q(\overline{q_{i_1} q_{j_1}} \cdots \overline{q_{i_k} q_{j_k}}):$$

where $\text{Ctr}_k(Q)$ runs over all unique sets $\{(i_1 j_1) \cdots (i_k j_k) \mid i_p < j_p\}$ of k pairs of operator indices in Q and $\lfloor \cdot \rfloor$ is the floor function. Let $:\overline{\overline{Q}}:$ denote the sum of all *complete contractions*: the terms from $:\overline{Q}::$ in which every operator in Q is involved in a contraction. Finally, let $:\overline{Q} \overline{Q'}:$ denote the sum of all single, double, etc. *cross contractions*: those in which all contractions have an operator from Q on the left and one from Q' on the right. In this context, contractions involving two operators from Q or two operators from Q' are called *internal contractions* of Q or Q' . To review, in this notation equation 2.5 would be written as $a_p a_q a_s^\dagger a_r^\dagger = :a_p a_q a_s^\dagger a_r^\dagger: + :\overline{a_p a_q} a_s^\dagger a_r^\dagger:$ and the last two terms on the right equal $:a_p a_q \overline{a_s^\dagger a_r^\dagger}: + :\overline{a_p a_q^\dagger} \overline{a_s^\dagger a_r^\dagger}::$

Lemma 2.1. $:Q:q = :Qq: + \sum_k :Q(\overline{q_k})q:$.

Proof: Let n be the number of operators in Q and begin by assuming that Q is already in normal order, i.e. $:Q: = Q$. If q is an annihilation operator then $:Q:q = Qq = :Qq:$ and all cross-contractions vanish, so the statement holds trivially. If q is a creation operator, note that $:Qq: = (-)^n qQ$. By the anticommutator relation derived in appendix A, we find¹

$$:Q:q = Qq = (-)^n qQ + \sum_{k=1}^n (-)^{n-k} q_1 \cdots [q_k, q]_+ \cdots q_n = :Qq: + \sum_{k=1}^n :Q(\overline{q_k})q:,$$

which completes the proof under our starting assumption. When Q is not in normal order, we can write $:Q: = (-)^p Q'$ and apply the proposition to Q' in order to confirm that it still holds.²

Theorem 2.1. Wick's theorem (vacuum). $Q = :Q: + :\overline{Q}:$

Proof: Let n be the length of Q . The result holds for $n = 2$ since $q_1 q_2 = :q_1 q_2: + \overline{q_1} q_2$ by the definition of contraction. Now, assume it holds for n operators and consider Qq . By our inductive assumption, $Qq = :Q:q + :\overline{Q}:q$. Applying lemma 2.1 to $:Q:q$ gives $:Q:q = :Qq: + \sum_i :Q(\overline{q_i})q:$. Expanding $:\overline{Q}:q$ and applying lemma 2.1 to each term gives

$$\begin{aligned} \sum_{k=1}^{\lfloor n/2 \rfloor} \sum_{(i_1 j_1) \cdots (i_k j_k)}^{\text{Ctr}_k(Q)} :Q(\overline{q_{i_1}} q_{j_1} \cdots \overline{q_{i_k}} q_{j_k}):q &= \sum_{k=1}^{\lfloor n/2 \rfloor} \sum_{(i_1 j_1) \cdots (i_k j_k)}^{\text{Ctr}_k(Q)} :Q(\overline{q_{i_1}} q_{j_1} \cdots \overline{q_{i_k}} q_{j_k})q: + \sum_{k=1}^{\lfloor n/2 \rfloor} \sum_{(i_1 j_1) \cdots (i_k j_k)}^{\text{Ctr}_k(Q)} \sum_{i \notin \{i_1, j_1, \dots, i_k, j_k\}} :Q(\overline{q_{i_1}} q_{j_1} \cdots \overline{q_{i_k}} q_{j_k} \overline{q_i}): \\ &= \sum_{(i_1 j_1)}^{\text{Ctr}_1(Q)} :Q(\overline{q_{i_1}} q_{j_1})q: + \sum_{k=2}^{\lfloor (n+1)/2 \rfloor} \sum_{(i_1 j_2) \cdots (i_k j_k)}^{\text{Ctr}_k(Qq)} :Qq(\overline{q_{i_1}} q_{j_1} \cdots \overline{q_{i_k}} q_{j_k}): \end{aligned}$$

and, combining these results, we find

$$\begin{aligned} Qq = :Q:q + :\overline{Q}:q &= :Qq: + \sum_{i=1}^n :Q(\overline{q_i})q: + \sum_{(i_1 j_1)}^{\text{Ctr}_1(Q)} :Q(\overline{q_{i_1}} q_{j_1})q: + \sum_{k=2}^{\lfloor (n+1)/2 \rfloor} \sum_{(i_1 j_2) \cdots (i_k j_k)}^{\text{Ctr}_k(Qq)} :Qq(\overline{q_{i_1}} q_{j_1} \cdots \overline{q_{i_k}} q_{j_k}): \\ &= :Qq: + \sum_{k=1}^{\lfloor (n+1)/2 \rfloor} \sum_{(i_1 j_2) \cdots (i_k j_k)}^{\text{Ctr}_k(Qq)} :Qq(\overline{q_{i_1}} q_{j_1} \cdots \overline{q_{i_k}} q_{j_k}): \end{aligned}$$

which is $:Qq: + :\overline{Q}q:$. So if the statement holds for strings of length n it must also hold for strings of length $n + 1$. By induction, the theorem holds for Q of arbitrary length.

Theorem 2.2. Wick's theorem (general). $Q = :Q: + :\overline{Q}:$

Proof: Under particle-hole isomorphism, Φ -normal ordering is algebraically identical to vacuum normal ordering.

Corollary 2.1. Wick's theorem for operator products. $:Q::Q': = :QQ': + :\overline{Q}\overline{Q}':$

Proof: By Wick's theorem $:Q::Q': = :QQ': + :(\overline{Q}::\overline{Q}'):$ and since $:Q:$ and $:Q':$ are in normal order their contractions vanish, leaving $:(\overline{Q}::\overline{Q}'): = :\overline{Q}\overline{Q}':$.

Corollary 2.2. Wick's theorem for expectation values. $\langle \Phi | Q | \Phi \rangle = :\overline{Q}:$

Proof: From Wick's theorem $\langle \Phi | Q | \Phi \rangle = \langle \Phi | :Q: | \Phi \rangle + \langle \Phi | :\overline{Q}: | \Phi \rangle$ and any incompletely contracted terms have vanishing expectation values. Therefore, $\langle \Phi | :Q: | \Phi \rangle = 0$ and $\langle \Phi | :\overline{Q}: | \Phi \rangle = :\overline{Q}:$.

Remark 2.1. To recap, let's state Wick's theorem and its corollaries in words as the following three rules.

1. An operator string equals its normal ordering plus all contractions.
2. A product of normal-ordered operators equals the normal ordering of the product plus all cross-contractions.
3. The reference expectation value of a string equals the sum of its complete contractions.

The next proposition provides a convenient rule for evaluating completely contracted operator strings.

Proposition 2.1. The sign of a completely contracted string is $(-)^c$ where c is the number of contraction line intersections.

Proof: Let $\varepsilon_\pi : \overline{q_{\pi(1)}} q_{\pi(2)} \cdots \overline{q_{\pi(n-1)}} q_{\pi(n)} :$ be the disentangled form of a complete contraction of $q_1 \cdots q_n$, where n is an even integer. The phase factor for the contraction, ε_π , is equal to the signature of the disentangling permutation, which is equal to the signature of the inverse permutation π^{-1} , restoring the original ordering of the operators. π^{-1}

¹Note that $(-)^{n-k}$ is the sign factor for bringing q_k and q together, and that $\overline{q_k} q = [q_k, q]_+$ when q is a creation operator.

²For this last step, note that $:(\overline{Q}):q = :Qq:$.

can be expressed as a series of transpositions swapping pairs of operators not connected by a contraction line. Since every operator has a contraction line overhead, each of these transpositions changes the number of line intersections by exactly ± 1 , so $\varepsilon_\pi = (-)^c$ where c is the number of intersections in the original contraction pattern.

Definition 2.3. Correlation component of the Hamiltonian. Using Wick's theorem, we can expand vac-normal one- and two-particle excitations as linear combinations of Φ -normal-ordered ones.

$$a_p^\dagger a_q = :a_p^\dagger a_q: + \gamma_{pq} \quad a_p^\dagger a_q^\dagger a_s a_r = :a_p^\dagger a_q^\dagger a_s a_r: - \gamma_{ps} :a_p^\dagger a_r: + \gamma_{pr} :a_q^\dagger a_s: + \gamma_{qs} :a_p^\dagger a_r: - \gamma_{qr} :a_q^\dagger a_s: + \gamma_{pr} \gamma_{qs} - \gamma_{ps} \gamma_{qr} \quad (2.6)$$

Substituting these into the electronic Hamiltonian leads to an expression for H in terms of Φ -normal operators.

$$H = E_{\text{ref}} + \sum_{pq} f_{pq} :a_p^\dagger a_q: + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle :a_p^\dagger a_q^\dagger a_s a_r: \quad (2.7)$$

$$E_{\text{ref}} \equiv \sum_{pq} h_{pq} \gamma_{pq} + \frac{1}{2} \sum_{pqrs} \langle pq || rs \rangle \gamma_{pr} \gamma_{qs}$$

$$f_{pq} \equiv h_{pq} + \sum_{rs} \langle pr || qs \rangle \gamma_{rs}$$

Note that E_{ref} is another expression for the Hartree-Fock energy, $E_{\text{ref}} = \langle \Phi | \hat{H} | \Phi \rangle$, and f_{pq} is the matrix representation of the Fock operator in the spin-orbital basis, $\mathbf{f} = [f_{pq}]$ where $f_{pq} = \langle \psi_p | \hat{f} | \psi_q \rangle$. The second and third terms in this expression together make up the *correlation component* of the electronic Hamiltonian, $H_c \equiv H - \langle \Phi | H | \Phi \rangle$.

Example 2.1. Derivation of CIS equations. The configuration interaction singles (CIS) equations take the form

$$\sum_{jb} \langle \Phi_i^a | H - E_{\text{ref}} | \Phi_j^b \rangle (\mathbf{c}_k)_b^j = \omega_k (\mathbf{c}_k)_a^i \quad (2.8)$$

where ω_k approximates the excitation energy of the k^{th} state, $\omega_k = E_k - E_{\text{ref}}$. In order to solve the CIS eigenvalue problem, we need to have an expression for the matrix elements $\langle \Phi_i^a | H_c | \Phi_j^b \rangle$ in terms of our known quantities, the one- and two-electron integrals. To do this, we can evaluate $\langle \Phi_i^a | :a_p^\dagger a_q: | \Phi_j^b \rangle$ and $\langle \Phi_i^a | :a_p^\dagger a_q^\dagger a_s a_r: | \Phi_j^b \rangle$ using Wick's theorem.

$$\begin{aligned} \langle \Phi | :a_i^\dagger a_a: :a_p^\dagger a_q: :a_b^\dagger a_j: | \Phi \rangle &= :a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j: + :a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j: = \gamma_{ij} \eta_{ap} \eta_{qb} - \gamma_{iq} \gamma_{pj} \eta_{ab} \\ \langle \Phi | :a_i^\dagger a_a: :a_p^\dagger a_q^\dagger a_s a_r: :a_b^\dagger a_j: | \Phi \rangle &= :a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j: + :a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j: \\ &\quad + :a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j: + :a_i^\dagger a_a a_p^\dagger a_q^\dagger a_s a_r a_b^\dagger a_j: \\ &= -\gamma_{is} \eta_{ap} \gamma_{qj} \eta_{rb} + \gamma_{is} \eta_{aq} \gamma_{pj} \eta_{rb} + \gamma_{ir} \eta_{ap} \gamma_{qj} \eta_{sb} - \gamma_{ir} \eta_{aq} \gamma_{pj} \eta_{sb} \end{aligned}$$

Multiplying these by f_{pq} and $\frac{1}{4} \langle pq || rs \rangle$ and summing over Hamiltonian indices yields the following.

$$\langle \Phi_i^a | H_c | \Phi_j^b \rangle = f_{ab} \gamma_{ij} - f_{ji} \eta_{ab} - \langle aj || bi \rangle$$

A The pull-through relation

Proposition A.1. Pull-through relation. For any non-commuting x_1, \dots, x_n , and y for which addition, subtraction and multiplication are defined, $x_1 \cdots x_n y = (\mp)^n y x_1 \cdots x_n + \sum_{k=1}^n (\mp)^{n-k} x_1 \cdots [x_k, y]_{\pm} \cdots x_n$, where $[x, y]_{\pm} \equiv xy \pm yx$.

Proof: The $n = 1$ case follows from the definition of the commutator brackets: $xy = \mp yx + [x, y]_{\pm}$. Now, assume it holds for n and consider the $n + 1$ case. Since $x_1 \cdots x_{n+1} y = x_1 \cdots x_n (\mp y x_{n+1} + [x_{n+1}, y]_{\pm})$, we find

$$\begin{aligned} x_1 \cdots x_{n+1} y &= \mp \left((\mp)^n y x_1 \cdots x_n + \sum_{k=1}^n (\mp)^{n-k} x_1 \cdots [x_k, y]_{\pm} \cdots x_n \right) x_{n+1} + x_1 \cdots x_n [x_{n+1}, y]_{\pm} \\ &= (\mp)^{n+1} y x_1 \cdots x_{n+1} + \sum_{k=1}^{n+1} (\mp)^{n+1-k} x_1 \cdots [x_k, y]_{\pm} \cdots x_{n+1} \end{aligned}$$

and, by induction, the result holds for all n .