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 $\pi \in \mathrm{S}_n$ is a permutation that puts the string in normal order. More generally, Φ-*normal ordering* maps the string into $\vdots q_1 \cdots q_n \vdots \equiv \varepsilon_\sigma q_{\sigma(1)} \cdots q_{\sigma(n)}$ where σ puts the string in Φ-normal order.

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

$$
\begin{aligned}
{:}\wick{\c a_p \c a_q}{:} &= a_p a_q - a_p a_q = 0 & \qquad {:}\wick{\c a_p^\dagger \c a_q}{:} &= a_p^\dagger a_q - a_p^\dagger a_q = 0 \\
{:}\wick{\c a_p^\dagger \c a_q^\dagger}{:} &= a_p^\dagger a_q^\dagger - a_p^\dagger a_q^\dagger = 0 & \qquad {:}\wick{\c a_p \c a_q^\dagger}{:} &= a_p a_q^\dagger + a_q^\dagger a_p = \delta_{pq}
\end{aligned}
\tag{2.1}
$$

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

$$
\vdots\wick{\c a_p^\dagger \c a_q}\vdots = \gamma_{pq} \qquad \vdots\wick{\c a_p \c a_q^\dagger}\vdots = \eta_{pq} \qquad \gamma_{pq} \equiv \begin{cases} \delta_{pq} & p,q \text{ occupied in } \Phi \\ 0 & p,q \text{ virtual} \end{cases} \qquad \eta_{pq} \equiv \begin{cases} 0 & p,q \text{ occupied in } \Phi \\ \delta_{pq} & p,q \text{ virtual} \end{cases}
\tag{2.2}
$$

In words, dagger-on-the-left contractions ("hole contractions") are elements of a matrix $\boldsymbol{\gamma}$ 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 $\boldsymbol{\eta}$ which is zero everywhere but its virtual block, $\eta_{ab} = \delta_{ab}$. Noting that $\vdots\wick{\c q_1 \c q_2}\vdots = \langle\Phi|q_1 q_2 - \vdots q_1 q_2 \vdots|\Phi\rangle = \langle\Phi|q_1 q_2|\Phi\rangle$, 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 $\vdots\wick{q_1 \cdots \c q_i \cdots \c q_j \cdots q_n}\vdots$ stand for

$$
\vdots\wick{q_1 \cdots \c q_i \cdots \c q_j \cdots q_n}\vdots \equiv (-)^{j-i-1}\, \wick{\c q_i \c q_j}\, \vdots q_1 \cdots \cancel{q_i} \cdots \cancel{q_j} \cdots q_n \vdots
\tag{2.3}
$$

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

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

can be expressed as follows, using notation 2.1.

$$
a_p a_q a_s^\dagger a_r^\dagger = {:}a_p a_q a_s^\dagger a_r^\dagger{:} + {:}\wick{\c a_p a_q \c a_s^\dagger a_r^\dagger}{:} + {:}\wick{\c a_p a_q a_s^\dagger \c a_r^\dagger}{:} + {:}\wick{a_p \c a_q \c a_s^\dagger a_r^\dagger}{:} + {:}\wick{a_p \c a_q a_s^\dagger \c a_r^\dagger}{:} + {:}\wick{\c1 a_p \c2 a_q \c1 a_s^\dagger \c2 a_r^\dagger}{:} + {:}\wick{\c1 a_p \c2 a_q \c2 a_s^\dagger \c1 a_r^\dagger}{:}
\tag{2.5}
$$

That is, the string equals its normal-ordering plus all possible contractions. This is one example of a general a 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 $\vdots Q(\wick{\c q_i \c q_j})\vdots$ denote $\vdots\wick{q_1 \cdots \c q_i \cdots \c q_j \cdots q_n}\vdots$. This is well-defined as long as $i < j$. Let $\vdots\overline{Q}\vdots$ stand for the sum of all unique single, double, triple, etc. contractions of Q

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

where $\mathrm{Ctr}_k(Q)$ runs over all unique sets $\{(i_1 j_2)\cdots(i_k j_k)\,|\,i_p < j_p\}$ of k pairs of operator indices in Q and $\lfloor\cdot\rfloor$ is the floor function. Let $\vdots\overline{\overline{Q}}\vdots$ denote the sum of all *complete contractions*: the terms from $\vdots\overline{Q}\vdots$ in which every operator in Q is involved in a contraction. Finally, let ${:}\wick{\c Q \c Q'}{:}$ 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 ${:}\overline{\overline{a_p a_q a_s^\dagger a_r^\dagger}}{:}$.

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

Proof: Let n be the number of operators in Q and assume, without loss of generality, that Q is already in normal order so that ${:\!Q\!:} = Q$. If q is a quasiparticle annihilation operator then ${:\!Qq\!:} = Qq$ and all cross-contractions vanish, so the statement holds trivially. If q is a quasiparticle creation operator then ${:\!Qq\!:} = (-)^n qQ$ and, using an anticommutator relation derived in the appendix (prop A.1),

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

since ${:\!Q(\overbracket{q_k)q}\!:} = (-)^{n-k} {:\!q_1 \cdots \overbracket{q_k q} \cdots q_n\!:}$ and $\overbracket{q_k q} = [q_k, q]_+$ when q is a quasiparticle creation operator (see def 2.2).

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 $q_1 q_2 = {:\!q_1 q_2\!:} + \overbracket{q_1 q_2}$ 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 ${:\!Q\!:}q = {:\!Qq\!:} + \sum_i {:\!Q(\overbracket{q_i)q}\!:}$. Expanding ${:\!\overline{Q}\!:}q$ and applying lemma 2.1 to each term gives

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

and, combining these results, we find

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

which is ${:\!Qq\!:} + {:\!\overline{Qq}\!:}$. 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).*** $Q = {\vdots Q \vdots} + {\vdots \overline{Q} \vdots}$

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

Corollary 2.1. ***Wick's theorem for operator products.*** ${\vdots Q \vdots}{\vdots Q' \vdots} = {\vdots QQ' \vdots} + {\vdots \overbracket{QQ'} \vdots}$

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

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

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

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 $\varepsilon_\pi {\vdots \overbracket{q_{\pi(1)} q_{\pi(2)}} \cdots \overbracket{q_{\pi(n-1)} q_{\pi(n)}} \vdots}$ 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} 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.

$$a_p^\dagger a_q = \vdots a_p^\dagger a_q \vdots + \gamma_{pq} \qquad a_p^\dagger a_q^\dagger a_s a_r = \vdots a_p^\dagger a_q^\dagger a_s a_r \vdots - \gamma_{ps} \vdots a_q^\dagger a_r \vdots + \gamma_{pr} \vdots a_q^\dagger a_s \vdots + \gamma_{qs} \vdots a_p^\dagger a_r \vdots - \gamma_{qr} \vdots a_p^\dagger a_s \vdots + \gamma_{pr}\gamma_{qs} - \gamma_{ps}\gamma_{qr} \tag{2.6}$$

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

$$H = E_{\mathrm{ref}} + \sum_{pq}^{\infty} f_{pq} \vdots a_p^\dagger a_q \vdots + \tfrac{1}{4} \sum_{pqrs}^{\infty} \langle pq||rs\rangle \vdots a_p^\dagger a_q^\dagger a_s a_r \vdots \qquad \begin{aligned} E_{\mathrm{ref}} &\equiv \sum_{pq}^{\infty} h_{pq}\gamma_{pq} + \tfrac{1}{2}\sum_{pqrs}^{\infty} \langle pq||rs\rangle \gamma_{pr}\gamma_{qs} \\ f_{pq} &\equiv h_{pq} + \sum_{rs}^{\infty} \langle pr||qs\rangle \gamma_{rs} \end{aligned} \tag{2.7}$$

Note that E_{ref} is another expression for the Hartree-Fock energy, $E_{\mathrm{ref}} = \langle \Phi|\hat{H}|\Phi\rangle$, and f_{pq} is the matrix representation of the Fock operator in the spin-orbital basis, $\boldsymbol{f} = [f_{pq}]$ 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, $H_{\mathrm{c}} \equiv H - \langle \Phi|H|\Phi\rangle$.

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

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

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

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

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

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

A The pull-through relation

Proposition A.1. ***Pull-through relation.*** *For any non-commuting $x_1, \ldots, x_n$, 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.