

Algebraic and Diagrammatic Methods in Electronic Structure Theory

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1. Tensors

Definition 1.1. Covariance, contravariance, invariance. Let ϕ be an arbitrary linear function of a vector space V and consider a change of basis $\{e_1, \dots, e_n\} \rightarrow \{\tilde{e}_1, \dots, \tilde{e}_n\}$ defined by $\tilde{e}_j = \sum_i e_i [\mathbf{T}]_{ij}$ where \mathbf{T} is an invertible matrix. If ϕ obeys the same transformation law as the basis elements, it is a *covariant* quantity. If it obeys the opposite transformation law, it is a *contravariant* quantity.

$$\phi(\tilde{e}_j) = \sum_i \phi(e_i) [\mathbf{T}]_{ij} \quad (\text{covariant}) \quad \phi(\tilde{e}_i) = \sum_j [\mathbf{T}^{-1}]_{ij} \phi(e_j) \quad (\text{contravariant}) \quad (1.1)$$

Covariant quantities are typically denoted with subscript indices, $\phi_i = \phi(e_i)$, whereas *contravariant* quantities are denoted with superscript indices, $\phi^i = \phi(e_i)$. Abstract quantities such as vectors and operators are called *invariant*, since they do not depend on the choice of basis.

Example 1.1. Vector coordinates are contravariant. Let $\{v_i\}$ be the coordinates of a vector v in the basis $\{e_i\}$, and let $\{\tilde{v}_j\}$ be its coordinates in $\{\tilde{e}_j = \sum_i e_i [\mathbf{T}]_{ij}\}$. Then the invariance of v implies that the coordinates are contravariant:

$$\sum_i e_i v_i = v = \sum_j \tilde{e}_j \tilde{v}_j = \sum_i e_i \sum_j [\mathbf{T}]_{ij} \tilde{v}_j \implies v_i = \sum_j [\mathbf{T}]_{ij} \tilde{v}_j \implies \tilde{v}_j = \sum_i [\mathbf{T}^{-1}]_{ji} v_i$$

Therefore, vector coordinates should be written with superscript indices $v_i \mapsto v^i$.

Definition 1.2. Linear functional. A *linear functional* $f : V \rightarrow \mathbb{C}$ is a scalar-valued function on V that satisfies $f(v+w) = f(v) + f(w)$ and $f(cv) = cf(v)$ for all $c \in \mathbb{C}$ and all $v, w \in V$. The *null functional* is given by $f_0(v) = 0 \forall v \in V$.

Definition 1.3. Dual space V^* . The *dual space* of V , denoted V^* , is the space of linear functionals on V , which itself forms a vector space with respect to vector addition $(f+g) \in V^*$ and scalar multiplication $(cf) \in V^*$ defined by

$$(f+g)(v) \equiv f(v) + g(v) \quad (cf)(v) \equiv cf(v) \quad (1.2)$$

for all $f, g \in V^*$, $v \in V$, and $c \in \mathbb{C}$. Its dimension is $\dim V^* = \dim V$, which follows from prop 1.1.

Proposition 1.1. The canonical dual basis. If $\{e_1, \dots, e_n\}$ is a basis for V then $\{e^1, \dots, e^n\} \subset V^*$, defined by $e^i(e_j) = \delta_j^i$, is a basis for V^* . This “canonical dual basis” transforms contravariantly relative to $\{e_1, \dots, e_n\}$.

Proof: First, note that $e^j(v) = e^j(\sum_i e_i v^i) = \sum_i e^j(e_i) v^i = v^j$ for any $v \in V$. Therefore, $f(v) = f(\sum_i e_i v^i) = \sum_i f(e_i) v^i = \sum_i f(e_i) e^i(v)$ holds for all $f \in V^*$ and all $v \in V$, which implies that $f = \sum_i f(e_i) e^i$. This shows that $\text{span}\{e^1, \dots, e^n\} = V^*$. Second, assume there exist $c_j \in \mathbb{C}$ such that $\sum_j c_j e^j = f_0$, where f_0 is the null functional. Then $0 = f_0(e_i) = \sum_j c_j e^j(e_i) = c_i$ and all of the coefficients must be zero, showing that $\{e^1, \dots, e^n\}$ is linearly independent.

Since both sets have n elements, $\dim V = \dim V^*$. Since $v^j = e^j(v)$, the dual basis is contravariant.

Remark 1.1. If $\langle \cdot | \cdot \rangle$ is an inner product on V and \mathbf{S} is the matrix of overlaps, $\langle e_i | e_j \rangle = [\mathbf{S}]_{ij}$, then the canonical dual basis is given by $e^i(\cdot) = \sum_j [\mathbf{S}^{-1}]_{ij} \langle e_j | \cdot \rangle$, which simplifies to $e^i(\cdot) = \langle e_i | \cdot \rangle$ when $\{e_1, \dots, e_n\}$ is orthonormal.

Definition 1.4. Linear operator. A linear operator $\hat{T} : V \rightarrow V$ is a vector-valued function on V that satisfies $\hat{T}(v+w) = \hat{T}v + \hat{T}w$ and $\hat{T}(cv) = c\hat{T}v$. The identity operator is given by $\hat{1}v = v$ and the null operator is given by $\hat{0}v = 0$.

Proposition 1.2. Resolution of the identity. Given a basis $\{e_i\}$, the identity operator can be expressed as $\hat{1} = \sum_i e_i e^i$.

Proof: $\hat{1}(v) = v = \sum_i e_i v^i = \sum_i e_i e^i(v)$ holds for all $v \in V$ (see prop 1.1), so $\hat{1} = \sum_i e_i e^i$.

Remark 1.2. Using prop 1.2, we can identify the matrix of a linear operator, $\hat{T}e_j = \sum_i e_i [\mathbf{T}]_{ij}$, with $[\mathbf{T}]_{ij} = e^i(\hat{T}e_j)$. Therefore, the row index of \mathbf{T} should be written as a superscript index, $[\mathbf{T}]_{ij} \mapsto [\mathbf{T}]_j^i$. Using two resolutions of the identity, \hat{T} can be expressed as $\hat{T} = \sum_{ij} [\mathbf{T}]_j^i e_i e^j$, which identifies \mathbf{T} as its coordinates in $V \times V^* = \text{span}\{e_i e^j\}$.

Remark 1.3. The formula for matrix multiplication also follows from prop 1.2: the matrix of $\hat{T}\hat{T}'$ is $e^i(\hat{T}\hat{T}'e_j) = \sum_k e^i(\hat{T}e_k) e^k(\hat{T}'e_j) = \sum_k [\mathbf{T}]_k^i [\mathbf{T}']_j^k$.

Definition 1.5. Direct sum $V \oplus V'$. A direct sum of vector spaces V and V' is $V \oplus V' \equiv \{v \oplus v' \mid v \in V, v' \in V'\}$, a new vector space with vector addition and scalar multiplication defined by

$$v_1 \oplus v'_1 + v_2 \oplus v'_2 = (v_1 + v_2) \oplus (v'_1 + v'_2) \quad c(v \oplus v') = cv \oplus cv'. \quad (1.3)$$

If $\{e_i\}$ and $\{e'_i\}$ are bases for V and V' then $\{e_i \oplus 0'\} \cup \{0 \oplus e'_i\}$ is a basis for $V \oplus V'$, which has dimension $\dim V + \dim V'$.

Definition 1.6. Tensor product $V \otimes V'$. A tensor product of vector spaces V and V' is $V \otimes V' \equiv \{\sum v \otimes v' \mid v \in V, v' \in V'\}$, a new vector space with vector addition and scalar multiplication defined by

$$v_1 \otimes v' + v_2 \otimes v' = (v_1 + v_2) \otimes v' \quad v \otimes v'_1 + v \otimes v'_2 = v \otimes (v'_1 + v'_2) \quad c(v \otimes v') = (cv) \otimes v' = v \otimes (cv') \quad (1.4)$$

If $\{e_i\}$ and $\{e'_i\}$ are bases for V and V' then $\{e_i \otimes e'_i\}$ is a basis for $V \otimes V'$, which has dimension $\dim V \cdot \dim V'$.

Remark 1.4. Since the sum $S + S'$ of two mutually orthogonal subspaces $S, S' \subseteq V$ is isomorphic to their direct sum, $S \oplus S'$ and $S + S'$ are used interchangeably in this context. The reverse is also true. The direct sum of two distinct vector spaces $V \oplus V'$ contains copies of V and V' as mutually orthogonal subspaces, namely $V \simeq V \oplus 0'$ and $V' \simeq 0 \oplus V'$.

Definition 1.7. Direct sums and tensor products of inner product spaces. If V and V' are inner product spaces, then $V \oplus V'$ and $V \otimes V'$ are also inner product spaces with respect to the following inner products.

$$\langle v \oplus v' | w \oplus w' \rangle_{V \oplus V'} \equiv \langle v | w \rangle_V + \langle v' | w' \rangle_{V'} \quad \langle v \otimes v' | w \otimes w' \rangle_{V \otimes V'} \equiv \langle v | w \rangle_V \cdot \langle v' | w' \rangle_{V'} \quad (1.5)$$

Definition 1.8. Tensor. A tensor is a vector in a tensor product space. An n^{th} order tensor lives in a product of n vector spaces, $V_1 \otimes \dots \otimes V_n$. A type- (m, n) tensor on V lives in $\underbrace{V \otimes \dots \otimes V}_{m \text{ times}} \otimes \underbrace{V^* \otimes \dots \otimes V^*}_{n \text{ times}}$, denoted $T_n^m(V)$.

Example 1.2. $T_0^0(V)$ is the scalar field \mathbb{C} , $T_0^1(V)$ is the vector space itself, $T_1^0(V)$ is the dual space V^* , and $T_1^1(V)$ is (up to isomorphism) the space of linear operators $V \otimes V^* \simeq V \times V^*$.

Remark 1.5. A member t of $T_n^m(V)$ can be expanded in the basis $\{e_1, \dots, e_n\}$ as follows.

$$t = \sum_{\substack{i_1 \dots i_m \\ j_1 \dots j_n}} t_{j_1 \dots j_n}^{i_1 \dots i_m} e_{i_1} \otimes \dots \otimes e_{i_m} \otimes e^{j_1} \otimes \dots \otimes e^{j_n} \quad (1.6)$$

Its coordinate array $\mathbf{t} = [t_{j_1 \dots j_n}^{i_1 \dots i_m}]$ is indexed by m contravariant indices and n covariant indices.

Remark 1.6. Just as people often use the term “vector” to refer to the basis-dependent coordinate array v^i rather than v itself, more often than not the word “tensor” refers to the coordinate array $t_{j_1 \dots j_n}^{i_1 \dots i_m}$ rather than the abstract quantity t .

Definition 1.9. Tensor product $t \otimes t'$. The *tensor product* of $t \in T_n^m(V)$ and $t' \in T_{n'}^{m'}(V)$ is $t \otimes t' \in T_{n+n'}^{m+m'}(V)$ with coordinate array $[\mathbf{t} \otimes \mathbf{t}']_{j_1 \dots j_{n+n'}}^{i_1 \dots i_{m+m'}} = t_{j_1 \dots j_n}^{i_1 \dots i_m} t'_{j_{n+1} \dots j_{n+n'}}^{i_{m+1} \dots i_{m+m'}}$. This generalizes the *matrix Kronecker product*.

Definition 1.10. Tensor contraction. A (p, q) *tensor contraction* is a map $\text{tr}_{p,q} : T_n^m(V) \rightarrow T_{n-1}^{m-1}(V)$ given by tracing the p^{th} element in V with the q^{th} element in V^* :

$$\text{tr}_{p,q}(e_{i_1} \otimes \dots \otimes e_{i_p} \otimes \dots \otimes e^{j_q} \otimes \dots \otimes e^{j_n}) = \delta_{i_p}^{j_q} e_{i_1} \otimes \dots \otimes \cancel{e_{i_p}} \otimes \dots \otimes \cancel{e^{j_q}} \otimes \dots \otimes e^{j_n} \quad (1.7)$$

The coordinate array of $\text{tr}_{p,q}(t)$ is $[\text{tr}_{p,q}(\mathbf{t})]_{j_1 \dots j_{n-1}}^{i_1 \dots i_{m-1}} = \sum_{i_p, j_q} \delta_{i_p}^{j_q} t_{j_1 \dots j_n}^{i_1 \dots i_m}$, generalizing the *matrix trace*, $\text{tr}(M) = \sum_i M_i^i$.

Definition 1.11. Cross-contraction. A *cross-contraction* traces a lower index on one tensor with an upper index on another, $\text{tr}_{p,q'} : T_n^m(V) \otimes T_{n'}^{m'}(V) \rightarrow T_{n-1}^m(V) \otimes T_{n'}^{m'-1}(V)$, generalizing the *matrix product* $\text{tr}_{1,1'}(M \otimes M') = \sum_k M_k^i M_j^k$.

Notation 1.1. Einstein summation convention. In the *Einstein summation convention* any index which appears twice in a product, once as a covariant index and once as a contravariant one, is implicitly summed over: $\sum_i a_i b^i \mapsto a_i b^i$. For most purposes, this rule suffices to dispense with summation symbols altogether. The basis expansion of a vector now takes the form $v = e_i v^i$, that of a tensor takes the form $t = t_{j_1 \dots j_n}^{i_1 \dots i_m} e_{i_1} \otimes \dots \otimes e_{i_m} \otimes e^{j_1} \otimes \dots \otimes e^{j_n}$, and resolution of the identity can be written as $\hat{1} = e_i e^i$. The choice of symbol for a *contracted index* is arbitrary, whereas each *free* (uncontracted) *index* symbol must appear once in every term on the right- and left-hand sides of an equation, always with the same co- or contra-variance.

Example 1.3. In Einstein notation, the matrix expression $\mathbf{C} = \mathbf{A}\mathbf{B}$ is written as $C_j^i = A_k^i B_j^k$.

Example 1.4. The expression $a_{ij}^{kl} = \frac{1}{2} b_{ij}^{vx} c_{vx}^{kl} + \frac{1}{6} d_{ijv}^{xyz} e_{xyz}^{klv}$ is a balanced equation with free indices $\overset{kl}{ij}$. Each term is an element of $T_2^2(V)$, so the addition (+) and assignment (=) operations are well-defined.

2. Fock space

2.1 Position-space representation

Definition 2.1. n -electron Hilbert space. If \mathcal{H} is a complete one-electron Hilbert space and $\{\psi_p\}$ is its spin-orbital basis, then $\mathcal{H}^{\otimes n} = \mathcal{H} \otimes \cdots \otimes \mathcal{H}$ (n times) $= \text{span}\{\psi_{p_1} \otimes \cdots \otimes \psi_{p_n}\}$ is an n -electron Hilbert space. The inner product on $\mathcal{H}^{\otimes n}$ is

$$\langle \psi_{p_1} \otimes \cdots \otimes \psi_{p_n} | \psi_{q_1} \otimes \cdots \otimes \psi_{q_n} \rangle = \langle \psi_{p_1} | \psi_{q_1} \rangle \cdots \langle \psi_{p_n} | \psi_{q_n} \rangle. \quad (2.1)$$

Projection onto $\langle 1 \otimes \cdots \otimes n |$, where $|i\rangle = |\mathbf{r}_i, s_i\rangle$ is a space-spin electronic state, reveals that the basis states $\psi_{p_1} \otimes \cdots \otimes \psi_{p_n}$ are abstract representations of ordinary product states, $\langle 1 \otimes \cdots \otimes n | \psi_{p_1} \otimes \cdots \otimes \psi_{p_n} \rangle = \psi_{p_1}(1) \cdots \psi_{p_n}(n)$.

Definition 2.2. n -electron Slater determinant. An n -electron Slater determinant $\Phi_{(p_1 \cdots p_n)}$ is a normalized antisymmetric product of n one-electron states $\psi_{p_1}, \cdots, \psi_{p_n}$

$$\Phi_{(p_1 \cdots p_n)} = \frac{1}{\sqrt{n!}} \sum_{\pi \in S_n} \varepsilon_\pi \psi_{p_{\pi(1)}} \otimes \cdots \otimes \psi_{p_{\pi(n)}} \quad (2.2)$$

where $\pi \in S_n$ is a permutation of $1 \cdots n$ and ε_π is $(-)^{\# \text{ transpositions}}$. Projecting into position space yields its familiar form.

$$\langle 1 \otimes \cdots \otimes n | \Phi_{(p_1 \cdots p_n)} \rangle = \Phi_{(p_1 \cdots p_n)}(1, \cdots, n) = \frac{1}{\sqrt{n!}} \det |\psi_{p_{\pi(1)}}(1) \cdots \psi_{p_{\pi(n)}}(n)|$$

Remark 2.1. A direct derivation of second quantization in position-space representation. Let F_n be the space of n -electron Slater determinants, $\Phi_{(p_1 \cdots p_n)}$, a subspace of $\mathcal{H}^{\otimes n}$. Consider the integral operator $\hat{a}_p : F_n \rightarrow F_{n-1}$ given by

$$\Psi(1, \cdots, n) \mapsto (\hat{a}_p \Psi)(2, \cdots, n) \equiv \sqrt{n} \int d(1) \psi_p^*(1) \Psi(1, 2, \cdots, n). \quad (2.3)$$

This operator acts on Slater determinants as

$$(\hat{a}_p \Phi_{(p_1 \cdots p_n)})(2, \cdots, n) = \frac{1}{\sqrt{(n-1)!}} \sum_{\pi \in S_n} \langle \psi_p | \psi_{p_{\pi(1)}} \rangle \psi_{p_{\pi(2)}}(2) \cdots \psi_{p_{\pi(n)}}(n) = \begin{cases} (-)^{k-1} \Phi_{(p_1 \cdots \cancel{p_k} \cdots p_n)} & p = p_k \in (p_1 \cdots p_n) \\ 0 & \text{otherwise} \end{cases}$$

i.e. it deletes the orbital ψ_p from $\Phi_{(p_1 \cdots p_n)}$ if exists and otherwise kills the determinant. The restriction of \hat{a}_p to the space of antisymmetric functions implies that these operators anticommute, $\hat{a}_p \hat{a}_q = -\hat{a}_q \hat{a}_p$, since

$$\int d(1) d(2) \psi_p^*(1) \psi_q^*(2) \Psi(1, 2, \cdots, n) = \int d(1) d(2) \psi_q^*(1) \psi_p^*(2) \Psi(2, 1, \cdots, n) = - \int d(1) d(2) \psi_q^*(1) \psi_p^*(2) \Psi(1, 2, \cdots, n)$$

by changing dummy variables of integration and plugging in $\Psi(2, 1, \cdots, n) = -\Psi(1, 2, \cdots, n)$. These deletion operators provide the following decomposition of functions in F_n .

$$\Psi(1, \cdots, n) = \frac{1}{\sqrt{n}} \sum_p \psi_p(1) (\hat{a}_p \Psi)(2, \cdots, n) = \frac{1}{\sqrt{n(n-1)}} \sum_{pq} \psi_p(1) \psi_q(2) (\hat{a}_q \hat{a}_p \Psi)(3, \cdots, n) \quad (2.4)$$

Therefore, general matrix elements of the electronic Hamiltonian with respect to $\Psi, \Psi' \in F_n$ can be expressed as

$$\begin{aligned} \langle \Psi | \hat{H}_e | \Psi' \rangle &= \sum_{i=1}^n \langle \Psi | \hat{h}(i) | \Psi' \rangle + \sum_{i < j}^n \langle \Psi | \hat{g}(i, j) | \Psi' \rangle = n \langle \Psi | \hat{h}(1) | \Psi' \rangle + \frac{n(n-1)}{2} \langle \Psi | \hat{g}(1, 2) | \Psi' \rangle \\ &= \sum_{pq} h_{pq} \langle \hat{a}_p \Psi | \hat{a}_q \Psi' \rangle + \frac{1}{2} \sum_{pqrs} \langle pq | rs \rangle \langle \hat{a}_q \hat{a}_p \Psi | \hat{a}_s \hat{a}_r \Psi' \rangle \end{aligned}$$

where $\hat{h}(i) \equiv -\frac{1}{2} \nabla_i^2 + \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}$, $\hat{g}(i, j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$, $h_{pq} \equiv \langle \psi_p(1) | \hat{h}(1) | \psi_q(1) \rangle$, and $\langle pq | rs \rangle \equiv \langle \psi_p(1) \psi_q(2) | \hat{g}(1, 2) | \psi_r(1) \psi_s(2) \rangle$. Therefore, restricting \hat{H}_e to the space of physically realistic (i.e. antisymmetric) functions, we get the following identity

$$\hat{H}_e = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} \langle pq | rs \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \quad (2.5)$$

which is the *second quantized* form of the Hamiltonian, as opposed to the *first quantized* form which is not restricted to antisymmetric functions. A defining feature of the second quantization formalism is that \hat{H}_e is independent of the number of electrons.

2.2 Abstract representation

Definition 2.3. Fock space. Let $F_n(\mathcal{H})$ denote $\text{span}\{\Phi_{(p_1 \dots p_n)}\}$, the antisymmetric subspace of $\mathcal{H}^{\otimes n}$. The fermionic Fock space is the union of all of these spaces, $F(\mathcal{H}) = F_0(\mathcal{H}) \oplus F_1(\mathcal{H}) \oplus F_2(\mathcal{H}) \oplus \dots \oplus F_\infty(\mathcal{H})$, which comprises all possible electronic wavefunctions.

Definition 2.4. The occupation number representation of $F(\mathcal{H})$. In the occupation number representation of Fock space, the basis vectors are represented as lists of 1s and 0s, $|\mathbf{n}\rangle \equiv |n_1, n_2, n_3, \dots, n_\infty\rangle$, where $n_p = 1$ when ψ_p is occupied and $n_p = 0$ when ψ_p is unoccupied in the state. One possible basis for $F(\mathcal{H})$ is given by distributing 1s and 0s over the occupation vector in all possible ways. The state in which no spin-orbitals are occupied is called the *vacuum state*, denoted $|\text{vac}\rangle$, which spans $F_0(\mathcal{H}) \simeq \mathbb{C}$.

Definition 2.5. Particle-hole operators. Particle-hole operators change the occupation numbers of one-particle states. The annihilation operator of ψ_p is a linear mapping $a_p : F_n(\mathcal{H}) \rightarrow F_{n-1}(\mathcal{H})$ defined by

$$a_p |\dots n_p \dots\rangle = (-)^{n_1 + \dots + n_{p-1}} |\dots n_p - 1 \dots\rangle \quad \text{if } n_p = 1 \quad a_p |\dots n_p \dots\rangle = 0 \quad \text{if } n_p = 0 \quad (2.6)$$

and the creation operator of ψ_p is a linear mapping $c_p : F_n(\mathcal{H}) \rightarrow F_{n+1}(\mathcal{H})$ defined by

$$c_p |\dots n_p \dots\rangle = (-)^{n_1 + \dots + n_{p-1}} |\dots n_p + 1 \dots\rangle \quad \text{if } n_p = 0 \quad c_p |\dots n_p \dots\rangle = 0 \quad \text{if } n_p = 1. \quad (2.7)$$

Proposition 2.1. $c_p = a_p^\dagger$. Creation and annihilation operators of the same state ψ_p are adjoints of each other.

Proof: $\langle n'_1 n'_2 \dots | a_p [n_1 n_2 \dots] \rangle$ vanishes unless $n'_p = 0$, $n_p = 1$, and $n'_q = n_q \forall q \neq p$. Likewise for $\langle c_p [n'_1 n'_2 \dots] | n_1 n_2 \dots \rangle$. Therefore, $\langle \Psi | a_p \Psi' \rangle = \langle c_p \Psi | \Psi' \rangle$ for all $\Psi, \Psi' \in F(\mathcal{H})$ and $c_p = a_p^\dagger$ by the definition of adjoint.

Proposition 2.2. $[q, q']_+ = \delta_{q'q^\dagger}$. Particle-hole operators q and q' anticommute unless $q' = q^\dagger$, for which $[q, q^\dagger]_+ = 1$.

Proof: Let q and q' be arbitrary particle-hole operators acting on ψ_p and $\psi_{p'}$, respectively. First, suppose $p \neq p'$. Then

$$qq' |\dots n_p \dots n_{p'} \dots\rangle = (-)^{n_p + \sum_{r=p+1}^{p'} n_r} |\dots \overline{n_p} \dots \overline{n_{p'}} \dots\rangle, \text{ and}$$

$$q'q |\dots n_p \dots n_{p'} \dots\rangle = (-)^{\overline{n_p} + \sum_{r=p+1}^{p'} n_r} |\dots \overline{n_p} \dots \overline{n_{p'}} \dots\rangle$$

where $\overline{n_p}$ and $\overline{n_{p'}}$ are the occupations after applying q and q' . Since n_p and $\overline{n_p}$ differ by one, $qq' = -q'q$. The second case, $p = p'$, implies $q' \in \{q, q^\dagger\}$. If $q' = q$, then $qq' = -q'q = 0$. If $q' = q^\dagger$, either $n_p = 1 \implies (a_p^\dagger a_p + a_p a_p^\dagger) |\dots n_p \dots\rangle = (1+0) |\dots n_p \dots\rangle$ or $n_p = 0 \implies (a_p^\dagger a_p + a_p a_p^\dagger) |\dots n_p \dots\rangle = (0+1) |\dots n_p \dots\rangle$. Either way, $q' = q^\dagger \implies (qq' + q'q) = 1$.

Remark 2.2. Relating the determinant and occupation number representations. When $p_1 < \dots < p_n$, $\Phi_{(p_1 \dots p_n)}$ is equivalent to the occupation vector $|\mathbf{n}_{(p_1 \dots p_n)}\rangle$ with 1s at p_1, \dots, p_n . Otherwise, this determinant is equivalent to $\varepsilon_\pi |\mathbf{n}_{(p_1 \dots p_n)}\rangle$ for $\pi \in S_n$ such that $p_{\pi(1)} < \dots < p_{\pi(n)}$. The actions of a_p and a_p^\dagger on $\Phi_{(p_1 \dots p_n)}$ are given by

$$a_p \Phi_{(p_1 \dots p_n)} = (-)^{k-1} \Phi_{(p_1 \dots \cancel{p_k} \dots p_n)} \text{ if } p = p_k \in (p_1 \dots p_n) \quad a_p \Phi_{(p_1 \dots p_n)} = 0 \text{ if } p \notin (p_1 \dots p_n) \quad (2.8)$$

$$a_p^\dagger \Phi_{(p_1 \dots p_n)} = (-)^{k-1} \Phi_{(p_1 \dots p_{k-1} p p_k \dots p_n)} \text{ if } p \notin (p_1 \dots p_n) \quad a_p^\dagger \Phi_{(p_1 \dots p_n)} = 0 \text{ if } p \in (p_1 \dots p_n) \quad (2.9)$$

which follows directly from eqs (2.6) and (2.7) when $p_1 < \dots < p_n$. Other cases follow from the fact that any sign factors for permuting $(p_1 \dots p_n)$ cancel on both sides of the equation, including the position of insertion or deletion, p_k , whose phase is tracked by $(-)^{k-1}$ on the right. That is, both sides of the equation are antisymmetric to permutations of $(1 \dots n)$. Note that eq (2.8) was also derived in rmk 2.1 using the position-space representation of a_p . One advantage of the determinant basis is that, unlike occupation vectors, determinants translate directly into strings of creations operators

$$|\Phi_{(p_1 \dots p_n)}\rangle = a_{p_1}^\dagger \dots a_{p_n}^\dagger |\text{vac}\rangle \quad (2.10)$$

without any phase ambiguity. Together with the second quantized form of the electronic Hamiltonian (eq (2.5)), this boils much of the grunt work of electronic structure theory down to particle-hole operator algebra.

Definition 2.6. Excitation operators and excited determinants. Operator strings of the form $a_{p_1}^\dagger \dots a_{p_m}^\dagger a_{q_m} \dots a_{q_1}$ are called *excitation operators*. For a given reference determinant Φ , excited determinants can be constructed as

$$\Phi_{i_1 \dots i_m}^{a_1 \dots a_m} = a_{a_1}^\dagger \dots a_{a_m}^\dagger a_{i_m} \dots a_{i_1} \Phi = a_{a_1}^\dagger a_{i_1} \dots a_{a_m}^\dagger a_{i_m} \Phi \quad (2.11)$$

where i_1, \dots, i_m are occupied and a_1, \dots, a_m are virtual indices with respect to Φ .

3. vac-normal ordering

Definition 3.1. vac-normal order. A string $q_1 \cdots q_n$ of particle-hole operators is in *vac-normal order* when all of its creation operators sit to the left of its annihilation operators. That is, a vac-normal string has the form $a_{p_1}^\dagger \cdots a_{p_m}^\dagger a_{r_1} \cdots a_{r_{m'}}.$ This form guarantees that the vacuum expectation value of the string goes to zero, $\langle \text{vac} | q_1 \cdots q_n | \text{vac} \rangle = 0$.

Definition 3.2. vac-normal ordering. The *vac-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 places the string in normal order.

Definition 3.3. vac-normal contraction. A *vac-normal contraction* of two particle-hole operators q_1 and q_2 is defined as $\overline{q_1 q_2} \equiv q_1 q_2 - :q_1 q_2:$. This associates a scalar value with every pair in $\{a_p\} \cup \{a_p^\dagger\}$, of which only $\overline{a_p a_q^\dagger} = a_p a_q^\dagger - :a_p a_q^\dagger: = [a_p, a_q^\dagger]_+ = \delta_{pq}$ is non-zero.

Definition 3.4. n^{th} order density moments. The m^{th} order density moment of a series of particle-hole operators q_1, \dots, q_m is the statistical average of their product, $\langle \Psi | q_1 \cdots q_m | \Psi \rangle$, with respect to a reference state $\Psi \in F(\mathcal{H})$.

Definition 3.5. One-particle and one-hole density matrices. For a state $\Psi \in F_n(\mathcal{H})$ with a definite particle count, the lowest-order non-vanishing density moments are $\gamma_{pq} \equiv \langle \Psi | a_q^\dagger a_p | \Psi \rangle$ and $\eta_{pq} \equiv \langle \Psi | a_p a_q^\dagger | \Psi \rangle$, the *one-particle* and *one-hole density matrices*.

Remark 3.1. vac-normal contractions as pairwise density moments of the vacuum. vac-normal contractions can be identified with pairwise moments of the vacuum state via $\overline{q_1 q_2} = \langle \text{vac} | q_1 q_2 - :q_1 q_2: | \text{vac} \rangle = \langle \text{vac} | q_1 q_2 | \text{vac} \rangle$, since $\langle \text{vac} | :q_1 q_2: | \text{vac} \rangle = 0$ by definition and $\overline{q_2 q_2}$ is a scalar quantity. The only non-vanishing vac-normal contractions are elements of the vac one-hole density matrix, $\overline{a_p a_q^\dagger} = \langle \text{vac} | a_p a_q^\dagger | \text{vac} \rangle = \eta_{pq}$, which evaluates to δ_{pq} .

Notation 3.1. vac-normal-ordered strings with contraction lines. Let the notation $:q_1 \cdots \overline{q_i \cdots q_j} \cdots q_n:$ stand for

$$:q_1 \cdots \overline{q_i \cdots q_j} \cdots q_n: \equiv (-)^{j-i-1} \overline{q_i q_j} :q_1 \cdots \cancel{q_i} \cdots \cancel{q_j} \cdots q_n: \quad (3.1)$$

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

Problem 3.1. Using only the anticommutator relation of prop 2.2, show that $a_p a_q a_s^\dagger a_r^\dagger$ can be expanded into the following linear combination of operator vac-normal operator strings.

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

and then show that the result can also be expressed as follows.

$$a_p a_q a_s^\dagger a_r^\dagger = :a_p a_q a_s^\dagger a_r^\dagger: + \overline{a_p a_q} a_s^\dagger a_r^\dagger + \overline{a_p a_q a_s^\dagger} a_r^\dagger + :a_p a_q a_s^\dagger a_r^\dagger: + :a_p a_q a_s^\dagger a_r^\dagger: + :a_p a_q a_s^\dagger a_r^\dagger: + \overline{a_p a_q a_s^\dagger} a_r^\dagger + \overline{a_p a_q a_s^\dagger} a_r^\dagger:$$

Notation 3.2. 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, if any, from $:\overline{Q}::$ in which every operator in Q is involved in a contraction. Finally, let $:\overline{Q}Q':$ 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' .

Remark 3.2. Note that, using notation 3.2, the result of prob 3.1 can be expressed as $a_p a_q a_s^\dagger a_r^\dagger = :a_p a_q a_s^\dagger a_r^\dagger: + \overline{a_p a_q a_s^\dagger a_r^\dagger}:$. This is a particular case of a more general result known as Wick's theorem, which says that any operator string Q is equal to its normal ordering plus the sum of all of its normal ordered contractions: $Q = :Q: + :\overline{Q}::$. The proof of this result follows in the next section (lem 3.1 and thm 3.1).

3.1 Wick's theorem

Lemma 3.1. $:Q:q = :Qq: + \sum_k :Q(\overline{q_k})q:$.

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 an annihilation operator then $:Qq: = Qq$ and all cross-contractions vanish, so the statement holds trivially. If q is a creation operator then $:Qq: = (-)^n qQ$ and, using the anticommutator relation from prop A.1,

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

since $:Q(\overline{q_k})q: = (-)^{n-k} q_1 \cdots \overline{q_k} q \cdots q_n$ and $\overline{q_k} q = [q_k, q]_+$ when q is a creation operator (see def 3.3).

Theorem 3.1. Wick's theorem (time-independent). $Q = :Q: + :\overline{Q}:$

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 (def 3.3). Now, assume it holds for n operators and consider Qq . By our inductive assumption, $Qq = :Q:q + :\overline{Q}:q$. Applying lem 3.1 to $:Q:q$ gives $:Q:q = :Qq: + \sum_i :Q(\overline{q_i})q:$. Expanding $:\overline{Q}:q$ and applying lem 3.1 to each term gives

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

and, combining these results, we find

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

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.

Corollary 3.1. Wick's theorem for operator products. $:Q::Q': = :QQ': + :\overline{Q}Q':$

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

Corollary 3.2. Wick's theorem for expectation values. $\langle \text{vac}|Q|\text{vac} \rangle = :\overline{Q}:$

Proof: From Wick's theorem $\langle \text{vac}|Q|\text{vac} \rangle = \langle \text{vac}|:Q:|\text{vac} \rangle + \langle \text{vac}|:\overline{Q}:|\text{vac} \rangle$ and any incompletely contracted have vanishing expectation values by the definition of normal ordering. Therefore, $\langle \text{vac}|:Q:|\text{vac} \rangle = 0$ and $\langle \text{vac}|:\overline{Q}:|\text{vac} \rangle = :\overline{Q}:$.

Problem 3.2. Do problem prob 3.1 in reverse: use Wick's theorem to expand $a_p a_q a_s^\dagger a_r^\dagger$ as a linear combination of vac-normal operator strings. Then use cor 3.2 to evaluate $\langle \text{vac}|a_p a_q a_s^\dagger a_r^\dagger|\text{vac} \rangle$.

Proposition 3.1. Sign rule for completely contracted strings. The phase vector of a completely contracted string is given by $(-)^c$ where c is the number of crossings between contraction lines.

Proof: Let $\varepsilon_\pi : \overline{q_{\pi(1)}} \overline{q_{\pi(2)}} \cdots \overline{q_{\pi(n-1)}} \overline{q_{\pi(n)}} :$ 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} can be expressed as a series of transpositions between pairs of adjacent operators that are not contracted together. Since every operator has a contraction line overhead, each such transposition changes the number of crossings by exactly ± 1 , so $\varepsilon_\pi = (-)^c$ where c is the number of crossings in the original contraction pattern.

Problem 3.3. By expanding $|\Phi \rangle$ as $a_{i_1}^\dagger \cdots a_{i_n}^\dagger |\text{vac} \rangle$, use cor 3.2 to show, using verbal arguments where appropriate, that

$$\langle \Phi | a_p^\dagger a_q | \Phi \rangle = \gamma_{pq} \quad \langle \Phi | a_p^\dagger a_q^\dagger a_s a_r | \Phi \rangle = \gamma_{rp} \gamma_{sq} - \gamma_{sp} \gamma_{rq} \quad \gamma_{pq} \equiv \begin{cases} \delta_{pq} & p, q \in \{i_1, \dots, i_n\} \\ 0 & \text{otherwise.} \end{cases}$$

Use your results to derive the first Slater-Condon rule. The solution of this problem will be substantially simplified in the next section by shifting from vac-normal to Φ -normal ordering.

4. Φ -normal ordering

Definition 4.1. Hole-particle isomorphism. The *hole-particle isomorphism* with respect to the reference determinant $|\Phi\rangle = |1 \cdots 1 0 0 \cdots\rangle$ is a mapping $F(\mathcal{H}) \rightarrow F(\mathcal{H})$ that inverts the bits occupied in Φ :

$$|k_1 \cdots k_n k_{n+1} k_{n+2} \cdots\rangle \mapsto |\bar{k}_1 \cdots \bar{k}_n k_{n+1} k_{n+2} \cdots\rangle \quad \text{where } \bar{k}_i = 1 - k_i.$$

Physically, this corresponds to shift in perspective from the *particle frame* to a *quasiparticle frame*, where the first n states are viewed as *holes* rather than *particles*. This makes $|\text{vac}\rangle \mapsto |\bar{1} \cdots \bar{1} 0 0 \cdots\rangle$ a state of n holes and no particles. $|\Phi\rangle \mapsto |\bar{0} \cdots \bar{0} 0 0 \cdots\rangle$ becomes the *quasiparticle vacuum state*, in which all hole and particle states are unoccupied.

Definition 4.2. Quasiparticle creation and annihilation operators. If we apply def 2.5 to the new quasiparticle Fock space, we end up with a new system of *quasiparticle-quasihole operators* $\{b_p\} \cup \{b_p^\dagger\}$, related to the old set via

$$a_i \mapsto b_i^\dagger \quad a_i^\dagger \mapsto b_i \quad a_a \mapsto b_a \quad a_a^\dagger \mapsto b_a^\dagger \quad (4.1)$$

where i and a are occupied and virtual indices with respect to the reference determinant Φ . $\{a_i\} \cup \{a_a\} \mapsto \{b_p\}$ are therefore *quasiparticle annihilation operators* and $\{a_i\} \cup \{a_a^\dagger\} \mapsto \{b_p^\dagger\}$ are *quasiparticle creation operators*.

Definition 4.3. Φ -normal order. A string $q_1 \cdots q_n$ of particle-hole operators is in Φ -normal order when all of its quasiparticle creation operators lie to the left of all of its quasiparticle annihilation operators. That is, it must map to a string of the form $b_{p_1} \cdots b_{p_m}^\dagger b_{r_1} \cdots b_{r_m}$ under the hole-particle isomorphism. This guarantees that the quasiparticle vacuum expectation value of the string goes to zero, $\langle \Phi | q_1 \cdots q_n | \Phi \rangle = 0$.

Definition 4.4. Φ -normal ordering. The Φ -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 places the string in Φ -normal order.

Definition 4.5. Φ -normal contraction. A Φ -normal contraction of two particle-hole operators q_1 and q_2 is defined as $\overline{q_1 q_2} \equiv q_1 q_2 - :q_1 q_2:$. This associates a scalar value with every pair in $\{a_p\} \cup \{a_p^\dagger\}$, of which only those that map to $b_p b_q^\dagger = b_p^\dagger b_q - :b_p b_q: = [b_p^\dagger, b_q]_+ = \delta_{pq}$, namely $\overline{a_a^\dagger a_b} = \delta_{ab}$ and $\overline{a_i^\dagger a_j} = \delta_{ij}$, are non-zero.

Definition 4.6. Φ -normal contractions as pairwise density moments of the quasiparticle vacuum. Φ -normal contractions can be identified with pairwise moments of the quasiparticle vacuum Φ via $\overline{q_1 q_2} = \langle \Phi | q_1 q_2 - :q_1 q_2: | \Phi \rangle = \langle \Phi | q_1 q_2 | \Phi \rangle$ since $\langle \Phi | :q_1 q_2: | \Phi \rangle = 0$ by definition. The non-vanishing contractions are elements of the Φ one-hole density matrix, $\overline{a_p a_q^\dagger} = \eta_{pq}$, or the Φ one-particle density matrix, $\overline{a_p^\dagger a_q} = \gamma_{qp}$. The density matrices η_{pq} and γ_{pq} of a determinant are zero everywhere except the occupied and virtual blocks, respectively, where $\eta_{ab} = \delta_{ab}$ and $\gamma_{ij} = \delta_{ij}$.

Notation 4.1. Φ -normal-ordered strings with contraction lines. As in the vac-normal case, we define

$$:q_1 \cdots \overline{q_i \cdots q_j} \cdots q_n: \equiv (-)^{j-i-1} \overline{q_i q_j} :q_1 \cdots \cancel{q_i} \cdots \cancel{q_j} \cdots q_n: \quad (4.2)$$

where the contraction line now indicates a Φ -normal contraction rather than a vac-normal contraction.

Remark 4.1. Wick's theorem for Φ -normal ordering. Since the particle-hole isomorphism maps Φ -normal ordered products with Φ -normal contractions into vac-normal ordered products with vac-normal contractions, Wick's theorem carries over directly as $Q = :Q: + :\overline{Q}: where $:\overline{Q}: is a sum over all single and multiple Φ -normal contractions. The corollaries $:Q::Q': = :QQ': + :\overline{Q}\overline{Q}':$ and $\langle \Phi | Q | \Phi \rangle = :\overline{Q}: follow.$$$

Problem 4.1. Do prob 3.3 using Wick's theorem for Φ -normal ordering.

Definition 4.7. Φ -normal component of an operator. The Φ -normal component of a Fock-space operator A is the part of A with a vanishing Φ expectation value, $A_c \equiv A - \langle \Phi | A | \Phi \rangle$. Note that this is generally not the same as the Φ -normal ordering $:A:$ of the operator.

Problem 4.2. Using Wick's theorem for Φ -normal ordering, show that vac-normal single and double excitation operators can be expanded in Φ -normal ordered excitation operators as follows.

$$a_p^\dagger a_q = :a_p^\dagger a_q: + \gamma_{qp} \quad a_p^\dagger a_q^\dagger a_s a_r = :a_p^\dagger a_q^\dagger a_s a_r: - \gamma_{sp} :a_q^\dagger a_r: + \gamma_{rp} :a_q^\dagger a_s: + \gamma_{sq} :a_p^\dagger a_r: - \gamma_{rq} :a_p^\dagger a_s: + \gamma_{rp} \gamma_{sq} - \gamma_{sp} \gamma_{rq}$$

Use these results to derive the following expression for Φ -normal component of H_e .

$$H_c \equiv H_e - \langle \Phi | H_e | \Phi \rangle = \sum_{pq} f_{pq} :a_p^\dagger a_q: + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle :a_p^\dagger a_q^\dagger a_s a_r: \quad \begin{aligned} f_{pq} &\equiv h_{pq} + \sum_{rs} \langle pr || qs \rangle \gamma_{sr} \\ \langle pq || rs \rangle &\equiv \langle pq | rs \rangle - \langle pq | sr \rangle \end{aligned} \quad (4.3)$$

5. Kutzelnigg-Mukherjee tensor notation

Notation 5.1. Kutzelnigg-Mukherjee tensor notation. In *Kutzelnigg-Mukherjee (KM) tensor notation*, indices which are covariant with respect to the spin-orbital basis $\{\psi_p\}$ are written as superscripts, whereas contravariant indices are written as subscripts. Note that this reverses the usual convention in multilinear algebra (def 1.1). Furthermore, the Einstein summation convention (nt 1.1) is adopted. As usual, indices i, j, k, l, \dots count over occupied orbitals, indices a, b, c, d, \dots count over virtual orbitals, and indices p, q, r, s, \dots count over the full spin-orbital basis. Creation operators are covariant and are therefore denoted $a_p^\dagger \mapsto a^p$, whereas annihilation operators are contravariant and therefore keep their original notation. The one-particle and one-hole density matrices are written as $\gamma_q^p = \langle \Psi | a^p a_q | \Psi \rangle$ and $\eta_p^q = \langle \Psi | a_p a^q | \Psi \rangle$, respectively. vac-normal ordered and Φ -normal ordered m -fold excitation operators are expressed as tensors in $T_m^m(\mathcal{H})$.

$$a_{q_1 \dots q_m}^{p_1 \dots p_m} \equiv a_{p_1}^\dagger \dots a_{p_m}^\dagger a_{q_m} \dots a_{q_1} \quad \tilde{a}_{q_1 \dots q_m}^{p_1 \dots p_m} \equiv :a_{p_1}^\dagger \dots a_{p_m}^\dagger a_{q_m} \dots a_{q_1}: \quad (5.1)$$

Remark 5.1. Permutational symmetries of KM notation excitation operators. The anticommutation relationships of particle-hole operators impart the following permutational symmetries on KM notation excitation tensors

$$a_{q_1 \dots q_m}^{p_1 \dots p_m} = \varepsilon_\pi a_{q_{\pi(1)} \dots q_{\pi(m)}}^{p_1 \dots p_m} = \varepsilon_\pi a_{q_{\pi(1)} \dots q_{\pi(m)}}^{p_{\pi(1)} \dots p_{\pi(m)}} = a_{q_{\pi(1)} \dots q_{\pi(m)}}^{p_{\pi(1)} \dots p_{\pi(m)}} \quad (5.2)$$

$$\tilde{a}_{q_1 \dots q_m}^{p_1 \dots p_m} = \varepsilon_\pi \tilde{a}_{q_{\pi(1)} \dots q_{\pi(m)}}^{p_1 \dots p_m} = \varepsilon_\pi \tilde{a}_{q_{\pi(1)} \dots q_{\pi(m)}}^{p_{\pi(1)} \dots p_{\pi(m)}} = \tilde{a}_{q_{\pi(1)} \dots q_{\pi(m)}}^{p_{\pi(1)} \dots p_{\pi(m)}} \quad (5.3)$$

for all $\pi \in S_n$. Furthermore, the antisymmetry of normal-ordered operator strings permits the following rearrangements.

$$a_{q_1 \dots q_m}^{p_1 \dots p_m} = :a_{q_1}^{p_1} \dots a_{q_m}^{p_m}: \quad :a_{q_1 \dots q_m}^{p_1 \dots p_m} a_{s_1 \dots s_n}^{r_1 \dots r_n}: = :a_{q_1}^{p_1} \dots a_{q_m}^{p_m} a_{s_1}^{r_1} \dots a_{s_n}^{r_n}: = a_{q_1 \dots q_m s_1 \dots s_n}^{p_1 \dots p_m r_1 \dots r_n} \quad (5.4)$$

$$\tilde{a}_{q_1 \dots q_m}^{p_1 \dots p_m} = :a_{q_1}^{p_1} \dots a_{q_m}^{p_m}: \quad :a_{q_1 \dots q_m}^{p_1 \dots p_m} a_{s_1 \dots s_n}^{r_1 \dots r_n}: = :a_{q_1}^{p_1} \dots a_{q_m}^{p_m} a_{s_1}^{r_1} \dots a_{s_n}^{r_n}: = \tilde{a}_{q_1 \dots q_m s_1 \dots s_n}^{p_1 \dots p_m r_1 \dots r_n} \quad (5.5)$$

These symmetries can be used to our advantage in algebraic manipulations of these operators.

Definition 5.1. m -electron operators in KM notation. An m -electron operator with non-antisymmetric interaction tensor $v_{p_1 \dots p_m}^{q_1 \dots q_m}$ is expressed in KM notation as

$$V = \frac{1}{m!} v_{p_1 \dots p_m}^{q_1 \dots q_m} a_{q_1 \dots q_m}^{p_1 \dots p_m}$$

As shown in prop A.2, any such operator can also be written in terms of an antisymmetrized interaction tensor $\bar{v}_{p_1 \dots p_m}^{q_1 \dots q_m}$ as

$$V = \left(\frac{1}{m!}\right)^2 \bar{v}_{p_1 \dots p_m}^{q_1 \dots q_m} a_{q_1 \dots q_m}^{p_1 \dots p_m}$$

where the elements of \bar{v} satisfy $\bar{v}_{p_1 \dots p_m}^{q_1 \dots q_m} = \varepsilon_\pi \bar{v}_{p_{\pi(1)} \dots p_{\pi(m)}}^{q_1 \dots q_m} = \varepsilon_\pi \bar{v}_{p_1 \dots p_m}^{q_{\pi(1)} \dots q_{\pi(m)}}$.

Example 5.1. The vac-normal and Φ -normal components of the electronic Hamiltonian are expressed as

$$H_e = h_p^q a_q^p + \frac{1}{2} g_{pq}^{rs} a_r^{pq} \quad H_c = f_p^q \tilde{a}_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} \tilde{a}_r^{pq} \quad (5.6)$$

where $h_p^q \equiv \langle \psi_p(1) | \hat{h}(1) | \psi_q(1) \rangle$, $g_{pq}^{rs} \equiv \langle \psi_p(1) \psi_q(2) | \hat{g}(1,2) | \psi_r(1) \psi_s(2) \rangle$, $f_p^q \equiv h_p^q + \bar{g}_{pr}^{qs} \gamma_s^r$, and $\bar{g}_{pq}^{rs} = g_{pq}^{rs} - g_{pq}^{sr}$.

Definition 5.2. Bartlett's index permutation operators. Let $\hat{P}_{(q_1 \dots q_n / \dots / p_1 \dots p_m)}$ denote an *index permutation operator*, which sums over all permutations of the upper and lower indices $p_1 \dots p_m$ and $q_1 \dots q_n$ in a tensor expression, weighted by the permutational signature of each.

$$\hat{P}_{(s_1 \dots s_n / \dots / p_1 \dots p_m)} t_{s_1 \dots s_n}^{p_1 \dots p_m} \equiv \sum_{\pi \in S_m} \sum_{\sigma \in S_n} \varepsilon_\pi \varepsilon_\sigma t_{s_{\sigma(1)} \dots s_{\sigma(n)}}^{p_{\pi(1)} \dots p_{\pi(m)}} \quad (5.7)$$

Furthermore, let $\hat{P}_{(S_1 / \dots / S_N)}^{(P_1 / \dots / P_M)}$, where $P_i = P_i(1) \dots P_i(m_i)$ is a block of indices, denote a sum over all permutations except for those that involve transpositions within one of the blocks.

$$\hat{P}_{(S_1 / \dots / S_N)}^{(P_1 / \dots / P_M)} t_{S_1(1) \dots S_N(n_N)}^{P_1(1) \dots P_M(m_M)} = \sum_{\pi} \sum_{\sigma} \varepsilon_\pi t_{\sigma(S_1(1)) \dots \sigma(S_N(n_N))}^{\pi(P_1(1)) \dots \pi(P_M(m_M))} \quad (5.8)$$

$$\pi(P_i(k)) \begin{cases} = P_i(k) \\ \in \bigcup_{j \neq i} P_j \end{cases} \quad \sigma(S_i(k)) \begin{cases} = S_i(k) \\ \in \bigcup_{j \neq i} S_j \end{cases}$$

That is, the value of $\pi(P_i(k))$ is allowed to be $P_i(k)$ itself or any value in the remaining blocks, P_j with $j \neq i$, but it cannot be any of the other values in P_i , namely $P_i(1), \dots, P_i(k-1), P_i(k+1), \dots, P_i(m_i)$. Finally, arguments separated by vertical bars indicate independent sets of permutations, $\hat{P}_{(S_1 / \dots / S_N)}^{(P_1 / \dots / P_M | P'_1 / \dots / P'_{M'})} = \hat{P}_{(S_1 / \dots / S_N)}^{(P_1 / \dots / P_M)} \hat{P}_{(P'_1 / \dots / P'_{M'})}$.

Notation 5.2. Dot notation for contractions. To allow all of the usual Wick expansions to be expressed, we here augment the traditional KM notation with the following definitions of *particle* \bullet *contractions* and *hole* \circ *contractions*.

$$a_{p\bullet} a^{q\bullet} \equiv \overline{a_p}^q \quad a^{q\bullet} a_{p\bullet} \equiv -\overline{a_p}^q \quad a^{q\circ} a_{p\circ} \equiv \overline{a_p}^q \quad a_{p\circ} a^{q\circ} \equiv -\overline{a_p}^q \quad (5.9)$$

Note that $a_{q\bullet}^{p\bullet} = -\eta_q^p$ and $a_{q\circ}^{p\circ} = \gamma_q^p$. In vac-normal ordering, the hole contractions vanish and the particle contractions become Kronecker deltas. This notation allows for normal ordered strings with contractions to keep all of the permutational symmetries listed in rmk 5.1.

Problem 5.1. Do problem 4.2 in KM notation by first showing that

$$a^p a_q = \tilde{a}_q^p + \gamma_q^p \quad a_{rs}^{pq} = \tilde{a}_{rs}^{pq} + \hat{P}_{(r/s)}^{(p/q)} \gamma_r^p \tilde{a}_s^q + \hat{P}_{(r/s)} \gamma_r^p \gamma_s^q$$

and then plugging these expressions into H_e to derive H_c .

Example 5.2. Derivation of CIS equations in KM notation. A programmable expression for the CI singles Hamiltonian matrix elements, $\langle \Phi_i^a | H_c | \Phi_j^b \rangle$, can be derived in KM notation as follows.

$$\begin{aligned} \langle \Phi | \tilde{a}_a^i \tilde{a}_q^p \tilde{a}_j^b | \Phi \rangle &= :a_{a\bullet}^{i\circ} a_{q\bullet}^{p\bullet} a_{j\circ}^{b\bullet} : + :a_{a\bullet}^{i\circ} a_{q\circ}^{p\circ} a_{j\circ}^{b\bullet} : = \gamma_j^i \eta_a^p \eta_q^b - \gamma_q^i \gamma_j^p \eta_a^b \\ \langle \Phi | \tilde{a}_a^i \tilde{a}_{rs}^{pq} \tilde{a}_j^b | \Phi \rangle &= \hat{P}_{(r/s)}^{(p/q)} : \tilde{a}_{a\bullet}^{i\circ} \tilde{a}_{r\circ}^{p\bullet} \tilde{a}_{s\circ}^{q\circ} a_{j\circ}^{b\bullet} : = \hat{P}_{(r/s)}^{(p/q)} \gamma_r^i \eta_a^p \gamma_s^q \eta_j^b \\ \implies \langle \Phi_i^a | H_c | \Phi_j^b \rangle &= f_p^q (\gamma_j^i \eta_a^p \eta_q^b - \gamma_q^i \gamma_j^p \eta_a^b) + \frac{1}{4} \bar{g}_{pq}^{rs} \left(\hat{P}_{(r/s)}^{(p/q)} \gamma_r^i \eta_a^p \gamma_s^q \eta_j^b \right) = f_a^b \gamma_j^i - f_j^i \eta_a^b + \bar{g}_{aj}^{ib} \end{aligned}$$

which simplifies to $\langle \Phi_i^a | H_c | \Phi_j^b \rangle = f_a^b \delta_j^i - f_j^i \delta_a^b + \bar{g}_{aj}^{ib}$. Here, we have used the fact that $\tilde{a}_i^a = a_i^a$ and $\tilde{a}_a^i = a_a^i$.

Problem 5.2. Derive the following results in KM notation using Wick's theorem for expectation values

$$\begin{aligned} \langle \Phi | a_q^p | \Phi \rangle &= \gamma_q^p & \langle \Phi | a_q^p a_i^a | \Phi \rangle &= \gamma_i^p \eta_q^a & \langle \Phi | a_q^p a_{ij}^{ab} | \Phi \rangle &= 0 & \langle \Phi | a_q^p a_{ijk}^{abc} | \Phi \rangle &= 0 \\ \langle \Phi | a_{rs}^{pq} | \Phi \rangle &= \hat{P}_{(r/s)} \gamma_r^p \gamma_s^q & \langle \Phi | a_{rs}^{pq} a_i^a | \Phi \rangle &= \hat{P}_{(r/s)}^{(p/q)} \gamma_r^p \gamma_i^q \eta_s^a & \langle \Phi | a_{rs}^{pq} a_{ij}^{ab} | \Phi \rangle &= \hat{P}_{(r/s)}^{(p/q)} \gamma_i^p \gamma_j^q \eta_r^a \eta_s^b & \langle \Phi | a_{rs}^{pq} a_{ijk}^{abc} | \Phi \rangle &= 0 \end{aligned}$$

and plug them into $\langle \Phi | H_e | \Phi_{ijk}^{abc\dots} \rangle$ to get the Slater-Condon rules.

Example 5.3. Derivation of CID equations in KM notation. Projecting the CID Schrödinger equation, $H_c \Psi = E_c \Psi$ with $\Psi = (1 + \frac{1}{4} c_{cd}^{kl} \tilde{a}_{kl}^{cd}) \Phi$, by Φ and Φ_{ij}^{ab} gives a system of linear equations

$$\begin{aligned} E_c &= \langle \Phi | H_c (1 + \frac{1}{4} c_{cd}^{kl} \tilde{a}_{kl}^{cd}) | \Phi \rangle & \implies & E_c = \frac{1}{4} \langle \Phi | H_c | \Phi_{kl}^{cd} \rangle c_{cd}^{kl} \\ E_c c_{ab}^{ij} &= \langle \Phi_{ij}^{ab} | H_c (1 + \frac{1}{4} c_{cd}^{kl} \tilde{a}_{kl}^{cd}) | \Phi \rangle & \implies & E_c c_{ab}^{ij} = \langle \Phi_{ij}^{ab} | H_c | \Phi \rangle + \frac{1}{4} \langle \Phi_{ij}^{ab} | H_c | \Phi_{kl}^{cd} \rangle c_{cd}^{kl} \end{aligned}$$

which can be simplified into programmable expressions as follows.

$$\begin{aligned} \langle \Phi | \tilde{a}_{rs}^{pq} \tilde{a}_{kl}^{cd} | \Phi \rangle &= \hat{P}_{(r/s)}^{(p/q)} \gamma_r^p \gamma_l^q \eta_r^c \eta_s^d \\ \langle \Phi | \tilde{a}_{ab}^{ij} \tilde{a}_q^p \tilde{a}_{kl}^{cd} | \Phi \rangle &= \hat{P}_{(a/b|k/l)}^{(c/d)} : \tilde{a}_{a\bullet}^{i\circ 1} \tilde{a}_{b\bullet}^{j\circ 2} \tilde{a}_{q\bullet}^{p\bullet 1} \tilde{a}_{k\circ 1 l\circ 2}^{c\bullet 2 d\bullet 3} : + \hat{P}_{(k/l)}^{(i/j|c/d)} : \tilde{a}_{a\bullet}^{i\circ 1} \tilde{a}_{b\bullet}^{j\circ 3} \tilde{a}_{q\circ 1}^{p\circ 2} \tilde{a}_{k\circ 2 l\circ 3}^{c\bullet 1 d\bullet 2} : \\ &= \hat{P}_{(a/b|k/l)}^{(c/d)} \eta_a^p \eta_q^c \eta_b^d \gamma_k^i \gamma_l^j - \hat{P}_{(k/l)}^{(i/j|c/d)} \gamma_q^i \gamma_k^p \gamma_l^j \eta_a^c \eta_b^d \\ \langle \Phi | \tilde{a}_{ab}^{ij} \tilde{a}_{rs}^{pq} \tilde{a}_{kl}^{cd} | \Phi \rangle &= \hat{P}_{(a/b|k/l)}^{(c/d)} : \tilde{a}_{a\bullet}^{i\circ 1} \tilde{a}_{b\bullet}^{j\circ 2} \tilde{a}_{r\bullet}^{p\bullet 1} \tilde{a}_{s\bullet}^{q\bullet 2} \tilde{a}_{k\circ 1 l\circ 2}^{c\bullet 3 d\bullet 4} : + \hat{P}_{(k/l)}^{(i/j|c/d)} : \tilde{a}_{a\bullet}^{i\circ 1} \tilde{a}_{b\bullet}^{j\circ 2} \tilde{a}_{r\circ 1 s\circ 2}^{p\circ 3 q\circ 4} \tilde{a}_{k\circ 3 l\circ 4}^{c\bullet 1 d\bullet 2} : + \hat{P}_{(r/s|k/l|a/b)}^{(p/q|i/j|c/d)} : \tilde{a}_{a\bullet}^{i\circ 1} \tilde{a}_{b\bullet}^{j\circ 3} \tilde{a}_{r\circ 1 s\circ 2}^{p\circ 2 q\bullet 1} \tilde{a}_{k\circ 2 l\circ 3}^{c\bullet 2 d\bullet 3} : \\ &= \hat{P}_{(a/b|k/l)}^{(c/d)} \eta_a^p \eta_b^q \eta_r^c \eta_s^d \gamma_k^i \gamma_l^j + \hat{P}_{(k/l)}^{(i/j|c/d)} \gamma_r^i \gamma_s^j \gamma_k^p \gamma_l^q \eta_a^c \eta_b^d - \hat{P}_{(r/s|k/l|a/b)}^{(p/q|i/j|c/d)} \gamma_r^i \gamma_k^p \gamma_l^j \eta_a^q \eta_s^c \eta_b^d \\ \implies E_c &= \frac{1}{4} \bar{g}_{kl}^{cd} c_{cd}^{kl} & E_c c_{ab}^{ij} &= \bar{g}_{ab}^{ij} + \hat{P}_{(a/b)} f_a^c c_{cb}^{ij} - \hat{P}_{(i/j)} f_k^i c_{ab}^{kj} + \frac{1}{2} \bar{g}_{ab}^{cd} c_{cd}^{ij} + \frac{1}{2} \bar{g}_{kl}^{ij} c_{ab}^{kl} + \hat{P}_{(a/b)} \bar{g}_{ak}^{ic} c_{bc}^{jk} \end{aligned}$$

Problem 5.3. Derive the Φ -normal Wick expansion for triple excitations

$$a_{stu}^{pqr} = \tilde{a}_{stu}^{pqrs} + \hat{P}_{(s/tu)}^{(p/qr)} \gamma_s^p \tilde{a}_{tu}^{qr} + \hat{P}_{(s/t/u)}^{(pq/r)} \gamma_s^p \gamma_t^q \tilde{a}_u^r + \hat{P}_{(s/t/u)} \gamma_s^p \gamma_t^q \gamma_u^r$$

where $\hat{P}_{(p/q/r)} t_{pqr} = t_{pqr} - t_{prq} - t_{qpr} + t_{qrp} + t_{rpq} - t_{rqp}$ and $\hat{P}_{(p/qr)} t_{pqr} = t_{pqr} - t_{qpr} - t_{rqp}$.

6. Diagram notation

Notation 6.1. Particle-hole operators in diagram notation. In diagram notation, particle-hole operators are written as oriented lines extending from a vertex. Particle annihilation operators enter the vertex from below, particle creation operators leave the vertex extending upward, and single-excitation operators have both creation and annihilation lines. Contractions of are represented by joining particle-hole lines with compatible position and orientation.

$$\begin{array}{cccc}
 \begin{array}{c} p \\ \circ \\ \uparrow \end{array} \equiv a_p &
 \begin{array}{c} \uparrow \\ \circ \\ p \end{array} \equiv a_p^\dagger &
 \begin{array}{c} p \\ \uparrow \\ \circ \\ \uparrow \\ q \end{array} \equiv a_p^\dagger a_q &
 \begin{array}{c} p \\ \uparrow \\ \circ \\ \downarrow \\ q \end{array} \equiv \overline{a_p a_q^\dagger} = \delta_{pq}
 \end{array}$$

Note that the vanishing contractions are not expressible in diagram notation. This has the advantage of simplifying the evaluation of Wick expansions without any loss of generality.

Remark 6.1. Spin-orbital labels in diagram notation. When using generic placeholder indices, the spin-orbital labels are dispensed with wherever possible. The removal of placeholder indices supports the primary objective of diagram notation: stripping an expression of all extraneous details to reveal its essential information content.

$$\begin{array}{cccc}
 \begin{array}{c} \circ \\ \uparrow \end{array} \mapsto a_p &
 \begin{array}{c} \uparrow \\ \circ \end{array} \mapsto a_p^\dagger &
 \begin{array}{c} \uparrow \\ \circ \\ \uparrow \end{array} \mapsto a_p^\dagger a_q &
 \begin{array}{c} \circ \\ \uparrow \\ \downarrow \end{array} \mapsto \overline{a_p a_q^\dagger}
 \end{array}$$

Notation 6.2. Quasiparticle-quasihole operators in diagram notation. Diagram notation with respect to Φ is expressed in the quasiparticle operator basis, which is indicated by the use of closed- rather than open-circle vertices. For particles, annihilation operators enter the vertex from below while creation operators leave the vertex extending upward. For holes, annihilation operators leave the vertex extending downward while creation operators enter from above.

$$\begin{array}{cccc}
 \begin{array}{c} \bullet \\ \uparrow \end{array} \mapsto b_a &
 \begin{array}{c} \uparrow \\ \bullet \end{array} \mapsto b_a^\dagger &
 \begin{array}{c} \bullet \\ \downarrow \end{array} \mapsto b_i &
 \begin{array}{c} \downarrow \\ \bullet \end{array} \mapsto b_i^\dagger
 \end{array}$$

That is, the hole operator diagrams are rotated by 180° . In this basis, there are two possible contractions

$$\begin{array}{c} \bullet \\ \uparrow \end{array} \mapsto \overline{b_a b_b^\dagger} \qquad \begin{array}{c} \bullet \\ \downarrow \end{array} \mapsto \overline{b_i b_j^\dagger}$$

and the single-excitation operator $a_p^\dagger a_q$ splits into four distinct parts.

$$\begin{array}{cccc}
 \begin{array}{c} \uparrow \\ \bullet \\ \uparrow \end{array} \mapsto b_a^\dagger b_b = a_a^\dagger a_b &
 \begin{array}{c} \swarrow \\ \bullet \\ \searrow \end{array} \mapsto b_a^\dagger b_i^\dagger = a_a^\dagger a_i &
 \begin{array}{c} \swarrow \\ \bullet \\ \swarrow \end{array} \mapsto b_i b_a = a_i^\dagger a_a &
 \begin{array}{c} \downarrow \\ \bullet \\ \downarrow \end{array} \mapsto b_i b_j^\dagger = a_i^\dagger a_j
 \end{array}$$

Definition 6.1. Bubble contractions. A *bubble contraction* is an internal contraction of a single-excitation operator.

$$\begin{array}{c} \circ \\ \uparrow \\ \downarrow \\ \circ \end{array} \mapsto \overline{b_i b_j^\dagger}$$

By convention bubble contractions are defined to represent only hole contractions, since excitation operators have no internal particle contractions.

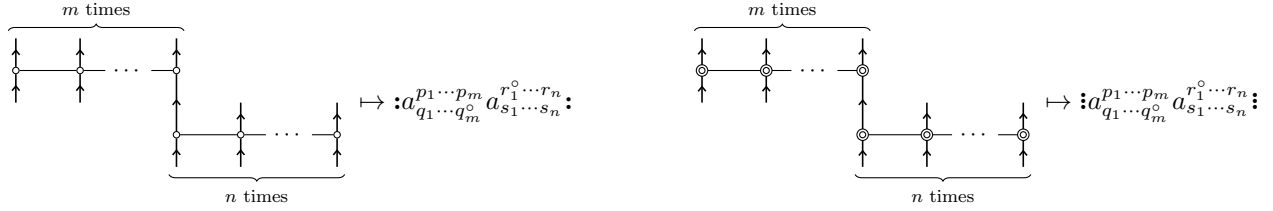
Example 6.1. The vac-normal Wick expansion of $a_p a_q^\dagger$ can be expressed diagram notation as follows.

$$a_p a_q^\dagger = -a_q^\dagger a_p + \overline{a_p a_q^\dagger} \quad \leftrightarrow \quad \begin{array}{c} \circ \\ \uparrow \\ \downarrow \\ \circ \end{array} = - \begin{array}{c} \uparrow \\ \circ \\ \uparrow \end{array} + \begin{array}{c} \circ \\ \uparrow \end{array}$$

Note that the operators in a diagram are ordered from top-to-bottom rather than left-to-right [fig 6(a)].

$$\underbrace{\begin{array}{c} \updownarrow \\ \circ \\ \hline \circ \\ \hline \updownarrow \end{array}}_{m \text{ times}} \mapsto :a_{q_1}^{p_1} a_{q_2}^{p_2} \cdots a_{q_m}^{p_m}: = a_{q_1 \cdots q_m}^{p_1 \cdots p_m}$$

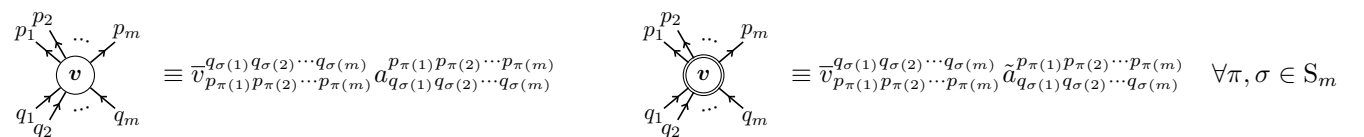
Notation 6.4. *Diagram notation for normal-ordered products of excitation operators.* A pair of excitation operators connected by one or more cross-contractions is implicitly normal-ordered together.


$$\begin{array}{c}
 \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \quad \cdots \quad \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \quad \cdots \quad \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \quad \cdots \quad \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \\
 \underbrace{\hspace{10em}}_{m \text{ times}} \quad \underbrace{\hspace{10em}}_{n \text{ times}}
 \end{array}
 \mapsto :a_{q_1 \dots q_m}^{p_1 \dots p_m} a_{s_1 \dots s_n}^{r_1 \dots r_n}:
 \end{array}
 \qquad
 \begin{array}{c}
 \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \quad \cdots \quad \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \quad \cdots \quad \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \quad \cdots \quad \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \quad \begin{array}{c} \uparrow \\ \bigcirc \\ \downarrow \end{array} \\
 \underbrace{\hspace{10em}}_{m \text{ times}} \quad \underbrace{\hspace{10em}}_{n \text{ times}}
 \end{array}
 \mapsto :a_{q_1 \dots q_m}^{p_1 \dots p_m} a_{s_1 \dots s_n}^{r_1 \dots r_n}:$$

Definition 6.2. Operator element. For an m -electron operator V , we will use the term *operator element* to refer to a single element of V 's interaction tensor times its corresponding excitation operator, i.e. $v_{p_1 p_2 \dots p_m}^{q_1 q_2 \dots q_m} a_{q_1 q_2 \dots q_m}^{p_1 p_2 \dots p_m}$ (no summation) or $\bar{v}_{p_1 p_2 \dots p_m}^{q_1 q_2 \dots q_m} a_{q_1 q_2 \dots q_m}^{p_1 p_2 \dots p_m}$ (no summation). Note that operator elements with antisymmetric interaction tensors are invariant to all permutations of $p_1 \dots p_m$ and $q_1 \dots q_m$, because the phase factors from the interaction tensor and the excitation operator cancel.

$$\begin{array}{c} p_1 \quad p_2 \quad \dots \quad p_m \\ \uparrow \quad \uparrow \quad \dots \quad \uparrow \\ \boxed{v} - \bigcirc - \bigcirc - \dots - \bigcirc \\ \uparrow \quad \uparrow \quad \dots \quad \uparrow \\ q_1 \quad q_2 \quad \dots \quad q_m \end{array} \equiv \bar{v}_{p_1 p_2 \dots p_m} a_{q_1 q_2 \dots q_m}^{p_1 p_2 \dots p_m}
\quad
\begin{array}{c} p_1 \quad p_2 \quad \dots \quad p_m \\ \uparrow \quad \uparrow \quad \dots \quad \uparrow \\ \boxed{v} - \bigcirc - \bigcirc - \dots - \bigcirc \\ \uparrow \quad \uparrow \quad \dots \quad \uparrow \\ q_1 \quad q_2 \quad \dots \quad q_m \end{array} \equiv \bar{v}_{p_1 p_2 \dots p_m} \tilde{a}_{q_1 q_2 \dots q_m}^{p_1 p_2 \dots p_m} \quad (\text{no summation})$$

Notation 6.6. *Hughenoltz operator element.* In Hughenoltz notation, an element of an operator V is depicted as a single labeled vertex with several outgoing and incoming lines.



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Unlike the Goldstone element, the correspondence between a Hugenholtz element and an algebraic operator element is non-unique, reflecting the symmetry of the operator element with respect to its indices. However, a Hugenholtz operator can always be directly translated into a Goldstone operator by simply choosing an arbitrary ordering for the outgoing and incoming lines.

Definition 6.3. Connected pairs, removable sets, connected sets. A pair of operators is *connected* if they have at least one cross-contraction running between them. A set S of operators with no connections to operators outside of S is called *removable*. A set of operators is *connected* if it has no removable subsets.

Definition 6.4. Degeneracy. Given a connected product of operators

$$\sum_{\text{Einstein}} \vdots \left(v_{uv}^{wx} a_{w\bullet x}^{u\circ\circ v} \right) \left(w_{yz}^{\alpha\beta} a_{\alpha\circ\circ\beta}^{y\bullet z\bullet\bullet} \right) \left(z_{\gamma\delta\varepsilon}^{\phi\eta\theta} a_{\phi\eta}^{\gamma\delta\bullet\bullet\bullet\varepsilon} \right) \vdots \quad (\text{for example})$$

consider taking the summand and permuting the summed-over index symbols in all possible ways. The number of index permutations which can be rearranged back into the original summand using only the permutational degrees of freedom of the operator elements is the *degeneracy* of this summand. The degeneracy of a general product is given by the product of the degeneracies of its connected subsets.

Example 6.2. The following expression has a degeneracy of $2^3 = 8$

$$\sum_{\text{Einstein}} \vdots \left(v_{uv}^{wx} a_{w\bullet x}^{uv} \right) \left(w_{yz}^{\alpha\beta} a_{\alpha\beta}^{y\bullet z\bullet\bullet} \right) \vdots$$

because the summand is invariant to $u \leftrightarrow v$ transpositions, simultaneous $\begin{smallmatrix} w \leftrightarrow x \\ y \leftrightarrow z \end{smallmatrix}$ transpositions, and $\alpha \leftrightarrow \beta$ transpositions.

Definition 6.5. Inequivalent contraction lines. Lines with vertices on both ends are called *contraction lines*. Contraction lines with the same orientation that terminate on particle-hole operators at the same vertical level in a diagram are called *inequivalent contraction lines*.

Definition 6.6. Diagram. A *diagram* is a vertically-arranged [fig 6(a)] visual representation of a product of one or more m -electron operators, particle-hole operators, and excitation operators [fig 6(b)] with zero or more contractions. A diagram translates into an algebraic expression as follows.

1. Sum over all unlabeled m -electron operator lines (Einstein summation)
2. Multiply the expression by D^{-1} where D is the degeneracy of the summation
3. For each maximal set of inequivalent contraction lines, multiply the expression by an index permutation operator $\hat{P}(\alpha\beta\gamma\cdots)$ where $\alpha\beta\gamma\cdots$ are the labels on those lines

The factor D^{-1} will be referred to as the *degeneracy factor* of the diagram. Note that these rules are reversible: any algebraic term can be translated into a diagram times a scalar factor.

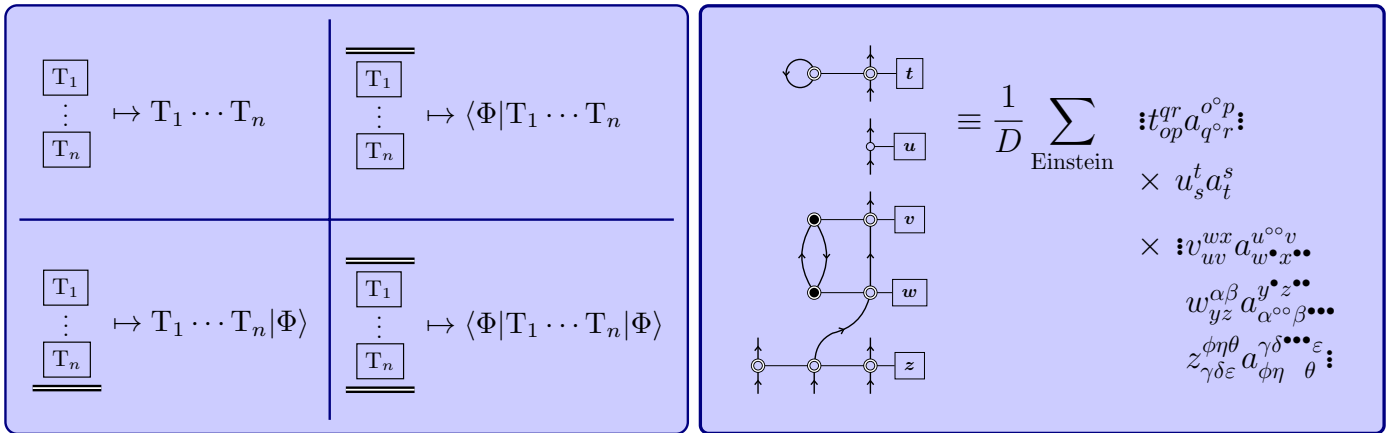


Figure 1: (a) vertical ordering of a diagram, showing four possible cases of vacuum state bra/ket bookends. (b) a generic example of a diagram, along with its corresponding algebraic term.

Example 6.3. The degeneracy of the product in fig 6(b) is $D = 2!2!3!$, so the diagram's degeneracy factor is $1/D = 1/24$.

Example 6.4. Applying the rules of interpretation to a single un-contracted Goldstone operator: 1. tells us that all lines are summed over, 3. tells us that the expression has a factor of $\frac{1}{(m!)^2}$ in front

$$\boxed{v} \begin{array}{c} \uparrow \\ \downarrow \end{array} \begin{array}{c} \uparrow \\ \downarrow \end{array} \cdots \begin{array}{c} \uparrow \\ \downarrow \end{array} \equiv \left(\frac{1}{m!}\right)^2 \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}} \boxed{v} \begin{array}{c} \uparrow \\ \downarrow \end{array} \begin{array}{c} \uparrow \\ \downarrow \end{array} \cdots \begin{array}{c} \uparrow \\ \downarrow \end{array} \equiv \left(\frac{1}{m!}\right)^2 \sum_{\text{Einstein}} \bar{v}_{p_1 p_2 \cdots p_m}^{q_1 q_2 \cdots q_m} a_{q_1 q_2 \cdots q_m}^{p_1 p_2 \cdots p_m}$$

which shows that the diagram is exactly equal to V , including the correct summations and the correct scalar factor.

Example 6.5. Similarly, for a diagram consisting of a single Hugenholtz operator, we get

$$\begin{array}{c} \cdots \\ \nearrow \\ \circ v \\ \searrow \\ \cdots \end{array} \equiv \left(\frac{1}{m!}\right)^2 \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}} \begin{array}{c} p_1 \quad p_2 \quad \cdots \quad p_m \\ \nearrow \quad \nearrow \quad \cdots \quad \nearrow \\ \circ v \\ \searrow \quad \searrow \quad \cdots \quad \searrow \\ q_1 \quad q_2 \quad \cdots \quad q_m \end{array} \equiv \left(\frac{1}{m!}\right)^2 \sum_{\text{Einstein}} \bar{v}_{p_1 p_2 \cdots p_m}^{q_1 q_2 \cdots q_m} a_{q_1 q_2 \cdots q_m}^{p_1 p_2 \cdots p_m}$$

where we have assigned dummy indices of summation in left-to-right order.

Definition 6.7. External and internal lines. An *external line* is an un-labeled line connected to a single m -electron operator, whereas an *internal line* is an un-labeled line connecting one m -electron operator to another.

Definition 6.8. Equivalent lines. Two un-labeled lines with the same direction and orientation are called *equivalent* if they are (a) external lines leaving or entering the same m -electron operator, or (b) internal lines connected leaving the same m -electron operator and entering the same m -electron operator.

Definition 6.9. Equivalent operators. Two copies of the an m -electron operator in a diagram are considered *equivalent* if they are connected to the same set of operators in the same way and their external lines match in orientation.

Derivation 6.1. Counting the degeneracy of a diagram. Consider a connected diagram. First, suppose a diagram has no repeated m -electron operators. A permutation of the summation symbols associated with a pair of equivalent lines applies a transposition to the operator symbols within the operators that they leave and enter. Since this operation can be undone using the permutational degrees of freedom of the operator elements, these permutations contribute to the overall degeneracy. Permutations of the summation symbols associated with inequivalent lines, on the other hand, permute symbols between operators and so cannot be undone using their individual permutational degrees of freedom. Therefore, if L is the set of lines in the diagram and $\{L_1, \dots, L_g\}$ is the partitioning of L into equivalent lines then the degeneracy of the diagram is the following.

$$D = |L_1|! \cdots |L_g|! \quad (6.1)$$

Definition 6.10. Redundancy of a contraction pattern. Given a connected diagram with a specific contraction pattern, the number of distinct contractions that can be transformed into the original contraction pattern by relabeling summation indices and using the permutational degrees of freedom of the operator elements is the *redundancy* R of the pattern. This is equivalent to the number of contributions in a Wick expansion that are equal to the term with the reference term.

Derivation 6.2. Counting the redundancy of a contraction pattern. Imagine forming the contraction pattern of a connected diagram step-by-step. First, consider a diagram in which all of the contractions have been removed. Partition the set of lines L in this diagram into equivalent lines $\{L_1, \dots, L_g\}$. Now, partition each L_i into subsets $\{L_i(0), L_i(1), \dots, L_i(g)\}$ where $L_i(0)$ become external lines and $L_i(j)$ are joined and contracted with $L_j(i)$ in the final diagram. Note that $|L_i(j)| = |L_j(i)|$ and $|L_i(j)| = 0$ unless L_i and L_j have compatible orientations. The number of equivalent partitionings is therefore

$$\prod_{i=1}^g \binom{|L_i|}{|L_i(0)|, |L_i(1)|, \dots, |L_i(g)|}$$

where $\binom{n}{k_1, \dots, k_m} \equiv \frac{n!}{k_1! \cdots k_m!}$ are multinomial coefficients. Finally, consider joining together these partitioned sets of equivalent lines into contractions. For each $L_i(j)$ - $L_j(i)$ pair, there are $|L_i(j)|! = |L_j(i)|!$ equivalent ways of contracting

the lines, so the total redundancy of the contraction pattern is

$$R = \prod_{i=1}^g \binom{|L_i|}{|L_i(0)|, |L_i(1)|, \dots, |L_i(g)|} \times \prod_{i=1}^g \prod_{j=i+1}^g |S_i(j)|!$$

which simplifies to the following.

$$R = \prod_{i=1}^g \frac{|L_i|!}{|L_i(0)|!} \left(\prod_{j=1}^{i-1} \frac{1}{|L_i(j)|!} \right) \quad (6.2)$$

Theorem 6.1. Wick's theorem for diagrams. *The Wick expansion of a product of m -electron operators is given by a normal-ordered sum over all unique contracted diagrams, each corresponding to a single algebraic term, without any minus signs or scalar factors.*

Proof: Clearly, every term in the Wick expansion corresponds to a diagram, and no minus sign is necessary because the phase is defined by the contracted operator string. Therefore, it remains to be shown that a single unique diagram is equal to the sum over all redundant contractions corresponding to the pattern. That is, the final degeneracy factor $1/D'$ for a given term must be equal to the redundancy R of its contraction pattern times the original degeneracy factor $1/D$ of the component diagrams. Evaluating the latter, we get

$$\frac{R}{D} = \prod_{i=1}^g \frac{|L_i|!}{|L_i(0)|!} \left(\prod_{j=1}^{i-1} \frac{1}{|L_i(j)|!} \right) \times \left(\prod_{i=1}^g |L_i|! \right)^{-1} = \prod_{i=1}^g \frac{1}{|L_i(0)|!} \left(\prod_{j=1}^{i-1} \frac{1}{|L_i(j)|!} \right)$$

but $\{L_i(0)\} \cup \{L_i(j) \mid j < i\}$ is precisely equal the partitioning of the final diagram into equivalent lines, so

$$D' = \prod_{i=1}^g |L_i(0)|! \left(\prod_{j=1}^{i-1} |L_i(j)|! \right) = \frac{D}{R}$$

which completes the proof.

Definition 6.11. Adjacent. Two that share a vertex are called *adjacent*.

Definition 6.12. Path. A sequence of adjacent lines is called a *path*. Each path has either two external lines, in which case it is an *open path*, or none, in which case it is a *closed path*. A closed path is also known as a *loop*.

Proposition 6.1. Phase factor for a path.

Corollary 6.1. Phase factor for a loop.

Corollary 6.2. Phase factor for a completely contracted diagram.

A. Parenthetical results

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 .

Proposition A.2. Expressing m -electron operators in terms of ordinary and antisymmetrized integrals. *A first-quantized m -electron operator $\hat{V} = \sum_{i_1 < \dots < i_m} \hat{v}(i_1 \cdots i_m)$ can be expressed in two equivalent second-quantized forms*

$$V = \frac{1}{m!} \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}} \langle p_1 \cdots p_m | \hat{v} | q_1 \cdots q_m \rangle a_{p_1}^{\dagger} \cdots a_{p_m}^{\dagger} a_{q_m} \cdots a_{q_1} = \left(\frac{1}{m!} \right)^2 \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}} \langle p_1 \cdots p_m | \hat{v} | q_{[1} \cdots q_m]} \rangle a_{p_1}^{\dagger} \cdots a_{p_m}^{\dagger} a_{q_m} \cdots a_{q_1}$$

where $\langle p_1 \cdots p_m | \hat{v} | q_{[1} \cdots q_m]} \rangle \equiv \sum \varepsilon_{\pi} \langle p_1 \cdots p_m | \hat{v} | q_{\pi(1)} \cdots q_{\pi(m)} \rangle$ are antisymmetrized m -electron integrals and the original m -electron integrals are given by $\langle p_1 \cdots p_m | \hat{v} | q_1 \cdots q_m \rangle \equiv \int d(1 \cdots m) \psi_{p_1}^*(1) \cdots \psi_{p_m}^*(m) \hat{v}(1 \cdots m) \psi_{q_1}(1) \cdots \psi_{q_m}(m)$.

Proof: It follows from rmk 2.1 that any function Ψ in Fock space can be decomposed as

$$\Psi(1, \dots, n) = \frac{1}{\sqrt{m!}} \sum_{p_1 \cdots p_m} \psi_{p_1}(1) \cdots \psi_{p_m}(m) (\hat{a}_{p_m} \cdots \hat{a}_{p_1} \Psi)(m, \dots, n)$$

and therefore the following holds for all $\Psi, \Psi' \in F(\mathcal{H})$

$$\begin{aligned} \langle \Psi | \hat{V} \Psi' \rangle &= \sum_{i_1 < \dots < i_m}^n \langle \Psi | \hat{v}(i_1 \cdots i_m) \Psi' \rangle = \frac{n!}{m!(n-m)!} \langle \Psi | \hat{v}(1 \cdots m) \Psi' \rangle \\ &= \frac{1}{m!} \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}}^{\infty} \langle p_1 \cdots p_m | \hat{v} | q_1 \cdots q_m \rangle \langle \hat{a}_{p_m} \cdots \hat{a}_{p_1} \Psi | \hat{a}_{q_m} \cdots \hat{a}_{q_1} \Psi' \rangle \end{aligned}$$

which gives the first part of the proposition.

$$V = \frac{1}{m!} \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}} \langle p_1 \cdots p_m | \hat{v} | q_1 \cdots q_m \rangle a_{p_1}^{\dagger} \cdots a_{p_m}^{\dagger} a_{q_m} \cdots a_{q_1}$$

The antisymmetrized form can then be derived by the following rearrangement

$$\begin{aligned} V &= \frac{1}{m!} \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}} \langle p_1 \cdots p_m | \hat{v} | q_1 \cdots q_m \rangle a_{p_1}^{\dagger} \cdots a_{p_m}^{\dagger} a_{q_m} \cdots a_{q_1} \\ &= \left(\frac{1}{m!} \right)^2 \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}} \sum_{\pi \in S_m} \langle p_1 \cdots p_m | \hat{v} | q_{\pi(1)} \cdots q_{\pi(m)} \rangle a_{p_1}^{\dagger} \cdots a_{p_m}^{\dagger} a_{q_{\pi(m)}} \cdots a_{q_{\pi(1)}} \\ &= \left(\frac{1}{m!} \right)^2 \sum_{\substack{p_1 \cdots p_m \\ q_1 \cdots q_m}} \sum_{\pi \in S_m} \varepsilon_{\pi} \langle p_1 \cdots p_m | \hat{v} | q_{\pi(1)} \cdots q_{\pi(m)} \rangle a_{p_1}^{\dagger} \cdots a_{p_m}^{\dagger} a_{q_m} \cdots a_{q_1} \end{aligned}$$

where the first step follows from simply relabeling the dummy indices of summation $q_1 \cdots q_m$ in $m!$ different ways and the second step follows from the fact that annihilation operators anticommute with other annihilation operators.