

1 Second Quantization

Definition 1.1. Slater determinant. An *Slater determinant* is a normalized antisymmetric product of spin-orbitals

$$\Phi_{(p_1 \dots p_n)}(1, \dots, n) = \frac{1}{\sqrt{n!}} \sum_{\pi \in S_n} \varepsilon_\pi \psi_{p_{\pi(1)}}(1) \cdots \psi_{p_{\pi(n)}}(n) \quad (1.1)$$

where $\pi \in S_n$ is a permutation of $1 \dots n$ with signature ε_π .¹

1.1 Deriving the second-quantized Hamiltonian from first quantization

Let \mathcal{F}_n denote the span of n -electron determinants and consider the integral operator $\hat{a}_p : \mathcal{F}_n \rightarrow \mathcal{F}_{n-1}$ given by

$$(\hat{a}_p \Psi)(2, \dots, n) \equiv \sqrt{n} \int d(1) \psi_p^*(1) \Psi(1, 2, \dots, n). \quad (1.2)$$

This operator acts on Slater determinants as follows.

$$(\hat{a}_p \Phi_{(p_1 \dots p_n)})(2, \dots, n) = \begin{cases} (-)^{k-1} \Phi_{(p_1 \dots \cancel{p_k} \dots p_n)}(2, \dots, n) & p = p_k \in (p_1 \dots p_n) \\ 0 & \text{otherwise} \end{cases} \quad (1.3)$$

In words, it deletes ψ_p from $\Phi_{(p_1 \dots p_n)}$ if present, otherwise killing the determinant. The restriction to an antisymmetric space makes these operators anticommute, $\hat{a}_p \hat{a}_q = -\hat{a}_q \hat{a}_p$, since it can be shown that for $\Psi \in \mathcal{F}_n$

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

by swapping integration variables. These operators can be used to generate the following decompositions.²

$$\Psi(1, \dots, n) = \frac{1}{\sqrt{n}} \sum_p \psi_p(1) (\hat{a}_p \Psi)(2, \dots, n) \quad (1.4)$$

$$= \frac{1}{\sqrt{n(n-1)}} \sum_{pq} \psi_p(1) \psi_q(2) (\hat{a}_q \hat{a}_p \Psi)(3, \dots, n) \quad (1.5)$$

Therefore, matrix elements of the electronic Hamiltonian with respect to $\Psi, \Psi' \in \mathcal{F}_n$ can be expressed as

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

in terms of the usual one- and two-electron integrals. Since Ψ and Ψ' are arbitrary elements of \mathcal{F}_n , this implies

$$\hat{H}_e \Big|_{\mathcal{F}_n} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} \langle pq | rs \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \quad (1.6)$$

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, because eq (1.6) holds for all n .

¹The signature of a permutation is $(-)^{\# \text{ transpositions }}$.

²These follow from substituting in the definition of \hat{a}_p and applying resolution of the identity to each argument.

1.2 Formal treatment of second quantization

Definition 1.2. Direct sums and products. The *direct sum*, \oplus , and *direct product*³, \otimes , are operations defining two different ways of combining vector spaces. Each operation takes a vector from one space and a vector the other to form an ordered pair, but they behave differently under vector addition and scalar multiplication. In a direct sum space $V \oplus V' \equiv \{v \oplus v' \mid v \in V, v' \in V'\}$, vector addition and scalar multiplication are defined by

$$v_1 \oplus v'_1 + v_2 \oplus v'_2 = (v_1 + v_2) \oplus (v'_1 + v'_2) \quad c(v \oplus v') = cv \oplus cv', \quad (1.7)$$

whereas, in a direct product space $V \otimes V' \equiv \{\sum v \otimes v' \mid v \in V, v' \in V'\}$, they are defined as follows.

$$v_1 \otimes v' + v_2 \otimes v' = (v_1 + v_2) \otimes v' \quad v \otimes v'_1 + v \otimes v'_2 = v \otimes (v'_1 + v'_2) \quad c(v \otimes v') = (cv) \otimes v' = v \otimes (cv') \quad (1.8)$$

Note that \oplus behaves like addition and \otimes behaves like multiplication. If $\{e_i\}$ and $\{e'_i\}$ are basis sets for V and V' , respectively, then $\{e_i \oplus 0'\} \cup \{0 \oplus e'_i\}$ is a basis for their direct sum and $\{e_i \otimes e'_i\}$ is a basis for their direct product. The dimension of the direct sum space is the sum of their dimensions, $\dim V + \dim V'$, and that of the direct product space is the product of their dimensions, $\dim V \cdot \dim V'$. Finally, if $\langle \cdot | \cdot \rangle_V$ and $\langle \cdot | \cdot \rangle_{V'}$ are inner products on V and V' , then the following are inner products on the combined spaces.

$$\langle v \oplus v' | w \oplus w' \rangle_{V \oplus V'} \equiv \langle v | w \rangle_V + \langle v' | w' \rangle_{V'} \quad \langle v \otimes v' | w \otimes w' \rangle_{V \otimes V'} \equiv \langle v | w \rangle_V \cdot \langle v' | w' \rangle_{V'} \quad (1.9)$$

Definition 1.3. Hilbert space. If \mathcal{H} is a one-electron Hilbert space spanned by a set of spin-orbitals $\{\psi_p\}$, then $\mathcal{H}^{\otimes n} = \mathcal{H} \otimes \cdots \otimes \mathcal{H} = \text{span}\{\psi_{p_1} \otimes \cdots \otimes \psi_{p_n}\}$ is an n -electron Hilbert space.⁴

Definition 1.4. Fock space. Let $\mathcal{F}_n(\mathcal{H})$ denote $\text{span}\{\Phi_{(p_1 \dots p_n)}\}$,⁵ the antisymmetric subspace of $\mathcal{H}^{\otimes n}$. *Fock space* is the union of these spaces, $\mathcal{F}(\mathcal{H}) = \mathcal{F}_0(\mathcal{H}) \oplus \mathcal{F}_1(\mathcal{H}) \oplus \mathcal{F}_2(\mathcal{H}) \oplus \cdots \oplus \mathcal{F}_\infty(\mathcal{H})$, comprising all possible electronic wavefunctions.

Definition 1.5. Occupation vectors. In the *occupation number formalism*, Fock space basis states are represented as *occupation vectors*. These are denoted by a series of bits, $|\mathbf{n}\rangle \equiv |n_1, n_2, n_3, \dots, n_\infty\rangle$, where $n_p = 1$ when ψ_p is occupied and $n_p = 0$ when it isn't. The fully unoccupied state is called the *vacuum*, denoted $|\text{vac}\rangle$, which spans $\mathcal{F}_0(\mathcal{H})$.

Definition 1.6. Particle-hole operators. *Particle-hole operators* change the occupation numbers of one-particle states. The *annihilation operator* of ψ_p is a linear mapping $a_p : \mathcal{F}_n(\mathcal{H}) \rightarrow \mathcal{F}_{n-1}(\mathcal{H})$ defined by

$$a_p |\cdots n_p \cdots\rangle = (-)^{n_1 + \cdots + n_{p-1}} |\cdots n_p - 1 \cdots\rangle \quad \text{if } n_p = 1 \quad a_p |\cdots n_p \cdots\rangle = 0 \quad \text{if } n_p = 0 \quad (1.10)$$

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

$$c_p |\cdots n_p \cdots\rangle = (-)^{n_1 + \cdots + n_{p-1}} |\cdots n_p + 1 \cdots\rangle \quad \text{if } n_p = 0 \quad c_p |\cdots n_p \cdots\rangle = 0 \quad \text{if } n_p = 1. \quad (1.11)$$

Proposition 1.1. $c_p = a_p^\dagger$. Creation and annihilation operators of the same state ψ_p are adjoints of each other.

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

Proposition 1.2. $[q, q']_+ = \delta_{q'q^\dagger}$. Particle-hole operators q and q' anticommute unless $q' = q^\dagger$, for which $[q, q^\dagger]_+ = 1$.⁶

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

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

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 $n_p = 1 \implies (a_p^\dagger a_p + a_p a_p^\dagger) |\cdots n_p \cdots\rangle = (1+0) |\cdots n_p \cdots\rangle$ or $n_p = 0 \implies (a_p^\dagger a_p + a_p a_p^\dagger) |\cdots n_p \cdots\rangle = (0+1) |\cdots n_p \cdots\rangle$. Either way, $q' = q^\dagger \implies (qq' + q'q) = 1$.

³Also known as a *tensor product*

⁴These basis vectors are abstract representations spin-orbital product functions, $(1 \otimes \cdots \otimes n | \psi_{p_1} \otimes \cdots \otimes \psi_{p_n}) = \psi_{p_1}(1) \cdots \psi_{p_n}(n)$, which are known as *Hartree products*.

⁵These basis vectors are Slater determinants, abstracted from position space: $\Phi_{(p_1 \dots p_n)} = \frac{1}{\sqrt{n!}} \sum_{\pi \in S_n} \psi_{p_{\pi(1)}} \otimes \cdots \otimes \psi_{p_{\pi(n)}}$. Equation 1.1 corresponds to $\langle 1 \otimes \cdots \otimes n | \Phi_{(p_1 \dots p_n)} \rangle = \Phi_{(p_1 \dots p_n)}(1, \dots, n)$.

⁶These are anticommutator brackets, $[q, q']_+ \equiv qq' + q'q$.

Remark 1.1. Relating the determinant and occupation number formalisms. 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

$$a_p \Phi_{(p_1 \dots p_n)} = (-)^{k-1} \Phi_{(p_1 \dots \cancel{p_k} \dots p_n)} \text{ if } p = p_k \in (p_1 \dots p_n) \quad a_p \Phi_{(p_1 \dots p_n)} = 0 \text{ if } p \notin (p_1 \dots p_n) \quad (1.12)$$

$$a_p^\dagger \Phi_{(p_1 \dots p_n)} = (-)^{k-1} \Phi_{(p_1 \dots p_{k-1} p p_k \dots p_n)} \text{ if } p \notin (p_1 \dots p_n) \quad a_p^\dagger \Phi_{(p_1 \dots p_n)} = 0 \text{ if } p \in (p_1 \dots p_n) \quad (1.13)$$

which follows directly from Eqs (1.10) and (1.11) 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 (1.12) was also derived in Section 1.1 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

$$|\Phi_{(p_1 \dots p_n)}\rangle = a_{p_1}^\dagger \dots a_{p_n}^\dagger |\text{vac}\rangle \quad (1.14)$$

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

Definition 1.7. 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

$$\Phi_{i_1 \dots i_m}^{a_1 \dots a_m} = a_{a_1}^\dagger \dots a_{a_m}^\dagger a_{i_m} \dots a_{i_1} \Phi = a_{a_1}^\dagger a_{i_1} \dots a_{a_m}^\dagger a_{i_m} \Phi \quad (1.15)$$

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

Definition 1.8. Particle-hole isomorphism. The *particle-hole isomorphism* with respect to the reference determinant $|\Phi\rangle = |1 \dots 1 0 0 \dots\rangle_{n \text{ times}}$ is a mapping $F(\mathcal{H}) \rightarrow F(\mathcal{H})$ that inverts the bits occupied in Φ :

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

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 $|\text{vac}\rangle \mapsto |\bar{1} \dots \bar{1} 0 0 \dots\rangle_{n \text{ times}}$ a state of n holes and no particles.

$|\Phi\rangle \mapsto |\bar{0} \dots \bar{0} 0 0 \dots\rangle_{n \text{ times}}$ becomes the *quasiparticle vacuum state*, in which all hole and particle states are unoccupied.

Definition 1.9. Quasiparticle creation and annihilation operators. If we apply Def 1.6 to the new quasiparticle Fock space, we end up with a new system of *quasi-particle-hole operators* $\{b_p\} \cup \{b_p^\dagger\}$, related to the old set via

$$a_i \mapsto b_i^\dagger \quad a_i^\dagger \mapsto b_i \quad a_a \mapsto b_a \quad a_a^\dagger \mapsto b_a^\dagger \quad (1.16)$$

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*.

Remark 1.2. The standard expression for the second-quantized Hamiltonian is

$$H_e = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r \quad (1.17)$$

where the summations run over the full set of spin-orbitals. Note that this matches Eq (1.6), except that we have rearranged the second term to express it in terms of antisymmetrized integrals. In terms of quasi-particle-hole operators,

$$\begin{aligned} H_e = & \sum_{ab} h_{ab} b_a^\dagger b_b + \sum_{ai} h_{ai} b_a^\dagger b_i^\dagger + \sum_{ia} h_{ia} b_i b_a + \sum_{ij} h_{ij} b_i b_j^\dagger \\ & + \frac{1}{4} \sum_{abcd} \langle ab || cd \rangle b_a^\dagger b_b^\dagger b_d b_c + \frac{1}{2} \sum_{abci} \langle ab || ci \rangle b_a^\dagger b_b^\dagger b_i^\dagger b_c + \frac{1}{2} \sum_{aibc} \langle ai || bc \rangle b_a^\dagger b_i b_c b_b + \frac{1}{4} \sum_{abij} \langle ab || ij \rangle b_a^\dagger b_b^\dagger b_j^\dagger b_i + \sum_{aibj} \langle ai || bj \rangle b_a^\dagger b_i b_j^\dagger b_b \\ & + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle b_i b_j b_b b_a + \frac{1}{2} \sum_{iajk} \langle ia || jk \rangle b_i b_a^\dagger b_k^\dagger b_j^\dagger + \frac{1}{2} \sum_{ijka} \langle ij || ka \rangle b_i b_j b_a b_k^\dagger + \frac{1}{4} \sum_{ijkl} \langle ij || kl \rangle b_i b_j b_l^\dagger b_k^\dagger \end{aligned} \quad (1.18)$$

where we have split the full summations above into summations over occupied and virtual orbitals and grouped like terms.

Definition 1.10. Normal order. A string $q_1 \cdots q_n$ of particle-hole operators is in *normal order* when all of its creation operators sit to the left of its annihilation operators. That is, when the string has the form $a_{p_1}^\dagger \cdots a_{p_m}^\dagger a_{r_1} \cdots a_{r_{m'}}$. This guarantees that its vacuum expectation value vanishes, $\langle \text{vac} | q_1 \cdots q_n | \text{vac} \rangle = 0$. More generally, we say that $q_1 \cdots q_n$ is in Φ -*normal order* if it maps into a string of the form $b_{p_1}^\dagger \cdots b_{p_m}^\dagger b_{r_1} \cdots b_{r_{m'}}$ under particle-hole isomorphism referenced to Φ , since this guarantees that $\langle \Phi | q_1 \cdots q_n | \Phi \rangle = 0$.

Example 1.1. In second quantization, any operator string can be expanded as a linear combination of strings which are in normal order. The expectation value of a string is always equal to the constant term in this expansion. For example:

$$a_p a_q^\dagger = -a_q^\dagger a_p + \delta_{pq} \implies \langle \text{vac} | a_p a_q^\dagger | \text{vac} \rangle = \delta_{pq}$$

$$a_p a_q a_s^\dagger a_r^\dagger = a_r^\dagger a_s^\dagger a_q a_p + \delta_{pq} a_r^\dagger a_q - \delta_{pr} a_s^\dagger a_q - \delta_{qs} a_r^\dagger a_p + \delta_{qr} a_s^\dagger a_p - \delta_{pq} \delta_{sr} + \delta_{pq} \delta_{qs} \implies \langle \text{vac} | a_p a_q a_s^\dagger a_r^\dagger | \text{vac} \rangle = \delta_{pq} \delta_{qs} - \delta_{pq} \delta_{sr}$$

where we have made repeated use of Prop 1.2 to arrive at these expansions. This strategy becomes unwieldy for expectation values of a reference determinant Φ , in which case it is more convenient to use particle-hole isomorphism. For example, consider the following matrix element of the core Hamiltonian.

$$\sum_{pq} h_{pq} \langle \Phi | a_p^\dagger a_q | \Phi_i^a \rangle = \sum_{bc} h_{bc} \langle \Phi | \cancel{b_b^\dagger b_c^\dagger b_a^\dagger b_i^\dagger} | \Phi \rangle + \sum_{bj} h_{bj} \langle \Phi | \cancel{b_b^\dagger b_j^\dagger b_a^\dagger b_i^\dagger} | \Phi \rangle + \sum_{jb} h_{jb} \langle \Phi | \cancel{b_j b_b b_a^\dagger b_i^\dagger} | \Phi \rangle + \sum_{jk} h_{jk} \langle \Phi | \cancel{b_j b_k^\dagger b_a^\dagger b_i^\dagger} | \Phi \rangle = h_{ia}$$

Only the third term survives, because the others generate a ket state with a different number of quasi-particles from the bra state.