# 1 Second Quantization

## 1.1 Position-space representation

**Definition 1.1.** ***n*-electron Hilbert space.** If $\mathcal{H}$ is a complete one-electron Hilbert space and $\{\psi_p\}$ is its spin-orbital basis, then $\mathcal{H}^{\otimes n} = \underbrace{\mathcal{H} \otimes \cdots \otimes \mathcal{H}}_{n \text{ times}} = \operatorname{span}\{\psi_{p_1} \otimes \cdots \otimes \psi_{p_n}\}$ is an *n-electron Hilbert space*.[1] The inner product on $\mathcal{H}^{\otimes n}$ is

$$\langle \psi_{p_1} \otimes \cdots \otimes \psi_{p_n} | \psi_{q_1} \otimes \cdots \otimes \psi_{q_n} \rangle = \langle \psi_{p_1} | \psi_{q_1} \rangle \cdots \langle \psi_{p_n} | \psi_{q_n} \rangle \,. \tag{1.1}$$

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 abstact 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 1.2.** ***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 $\psi_{p_1}, \cdots, \psi_{p_n}$

$$\Phi_{(p_1 \cdots p_n)} = \tfrac{1}{\sqrt{n!}} \sum_{\pi \in \mathrm{S}_n} \varepsilon_\pi \psi_{p_{\pi(1)}} \otimes \cdots \otimes \psi_{p_{\pi(n)}} \tag{1.2}$$

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

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

**Remark 1.1.** ***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 $\hat{a}_p : F_n \to F_{n-1}$ given by

$$\Psi(1, \cdots, n) \mapsto (\hat{a}_p \Psi)(2, \cdots, n) \equiv \sqrt{n} \int d(1) \psi_p^*(1) \Psi(1, 2, \cdots, n) \,. \tag{1.3}$$

This operator acts on Slater determinants as

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

i.e. it deletes the orbital $\psi_p$ 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 $F_n$.

$$\Psi(1, \cdots, n) = \tfrac{1}{\sqrt{n}} \sum_p^\infty \psi_p(1) \left(\hat{a}_p \Psi\right)(2, \cdots, n) = \tfrac{1}{\sqrt{n(n-1)}} \sum_{pq}^\infty \psi_p(1) \psi_q(2) (\hat{a}_q \hat{a}_p \Psi)(3, \cdots, n) \tag{1.4}$$

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

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

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

$$\hat{H}_e = \sum_{pq}^\infty h_{pq} \hat{a}_p^\dagger \hat{a}_q + \tfrac{1}{2} \sum_{pqrs}^\infty \langle pq|rs \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \tag{1.5}$$

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.

[1] See **??** for the definition of a tensor product.

## 1.2 Abstract representation

**Definition 1.3.** ***Fock space.*** Let $F_n(\mathcal{H})$ denote $\mathrm{span}\{\Phi_{(p_1\cdots p_n)}\}$, the antisymmetric subspace of $\mathcal{H}^{\otimes n}$. The fermionic *Fock space* is the union of all of these spaces, $F(\mathcal{H}) = F_0(\mathcal{H}) \oplus F_1(\mathcal{H}) \oplus F_2(\mathcal{H}) \oplus \cdots \oplus F_\infty(\mathcal{H})$, which comprises all possible electronic wavefunctions.

**Definition 1.4.** ***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, $|\mathbf{n}\rangle \equiv |n_1, n_2, n_3, \cdots, n_\infty\rangle$, where $n_p = 1$ when $\psi_p$ is occupied and $n_p = 0$ when $\psi_p$ 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 $|\mathrm{vac}\rangle$, which spans $F_0(\mathcal{H}) \simeq \mathbb{C}$.

**Definition 1.5.** ***Particle-hole operators.*** *Particle-hole operators* change the occupation numbers of one-particle states. The *annihilation operator* of $\psi_p$ is a linear mapping $a_p : F_n(\mathcal{H}) \to F_{n-1}(\mathcal{H})$ defined by

$$a_p|\cdots n_p \cdots\rangle = (-)^{n_1+\cdots+n_{p-1}}|\cdots n_p - 1 \cdots\rangle \quad \text{if } n_p = 1 \qquad a_p|\cdots n_p \cdots\rangle = 0 \quad \text{if } n_p = 0 \tag{1.6}$$

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

$$c_p|\cdots n_p \cdots\rangle = (-)^{n_1+\cdots+n_{p-1}}|\cdots n_p + 1 \cdots\rangle \quad \text{if } n_p = 0 \qquad c_p|\cdots n_p \cdots\rangle = 0 \quad \text{if } n_p = 1. \tag{1.7}$$

**Proposition 1.1.** $\boldsymbol{c_p = a_p^\dagger}$**.** *Creation and annihilation operators of the same state $\psi_p$ 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 $\Psi, \Psi' \in F(\mathcal{H})$ and $c_p = a_p^\dagger$ by the definition of adjoint.

**Proposition 1.2.** $\boldsymbol{[q, q']_+ = \delta_{q'q^\dagger}}$**.** *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 $\psi_p$ and $\psi_{p'}$, respectively. First, suppose $p \neq p'$. Then

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

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, $q' = q^\dagger \implies (qq' + q'q) = 1$.

**Remark 1.2.** ***Relating the determinant and occupation number representations.*** When $p_1 < \cdots < p_n$, $\Phi_{(p_1\cdots p_n)}$ is equivalent to the occupation vector $|\mathbf{n}_{(p_1\cdots p_n)}\rangle$ with 1s at $p_1, \cdots, p_n$. Otherwise, this determinant is equivalent to $\varepsilon_\pi|\mathbf{n}_{(p_1\cdots p_n)}\rangle$ for $\pi \in \mathrm{S}_n$ such that $p_{\pi(1)} < \cdots < p_{\pi(n)}$. The actions of $a_p$ and $a_p^\dagger$ on $\Phi_{(p_1\cdots p_n)}$ are given by

$$a_p\Phi_{(p_1\cdots p_n)} = (-)^{k-1}\Phi_{(p_1\cdots \cancel{p_k} \cdots p_n)} \text{ if } p = p_k \in (p_1 \cdots p_n) \qquad a_p\Phi_{(p_1\cdots p_n)} = 0 \text{ if } p \notin (p_1 \cdots p_n) \tag{1.8}$$

$$a_p^\dagger\Phi_{(p_1\cdots p_n)} = (-)^{k-1}\Phi_{(p_1\cdots p_{k-1} p p_k \cdots p_n)} \text{ if } p \notin (p_1 \cdots p_n) \qquad a_p^\dagger\Phi_{(p_1\cdots p_n)} = 0 \text{ if } p \in (p_1 \cdots p_n) \tag{1.9}$$

which follows directly from Eqs (1.6) and (1.7) when $p_1 < \cdots < p_n$. Other cases follow from the fact that any sign factors for permuting $(p_1 \cdots p_n)$ 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 $(1 \cdots n)$. Note that Eq (1.8) was also derived in Rmk 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

$$|\Phi_{(p_1\cdots p_n)}\rangle = a_{p_1}^\dagger \cdots a_{p_n}^\dagger|\mathrm{vac}\rangle \tag{1.10}$$

without any phase ambiguity. Together with the second quantized form of the electronic Hamiltonian (Eq (1.5)), this boils much of the grunt work of electronic structure theory down to particle-hole operator algebra.

**Definition 1.6.** ***Excitation operators and excited determinants.*** Operator strings of the form $a_{p_1}^\dagger \cdots a_{p_m}^\dagger a_{q_m} \cdots a_{q_1}$ are called *excitation operators*. For a given reference determinant $\Phi$, excited determinants can be constructed as

$$\Phi_{i_1\cdots i_m}^{a_1\cdots a_m} = a_{a_1}^\dagger \cdots a_{a_m}^\dagger a_{i_m} \cdots a_{i_1}\Phi = a_{a_1}^\dagger a_{i_1} \cdots a_{a_m}^\dagger a_{i_m}\Phi \tag{1.11}$$

where $i_1, \cdots, i_m$ are occupied and $a_1, \cdots, a_m$ are virtual indices with respect to $\Phi$.