1 Second Quantization

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

$$\Phi_{(p_1\cdots p_n)}(1,\dots,n) = \tfrac{1}{\sqrt{n!}} \sum_{\pi\in \mathrm{S}_n} \varepsilon_\pi \psi_{p_{\pi(1)}}(1)\cdots\psi_{p_{\pi(n)}}(n) \tag{1.1}$$

where $\pi \in \mathrm{S}_n$ is a permutation of $1\cdots n$ 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 $\hat{a}_p : \mathcal{F}_n \to \mathcal{F}_{n-1}$ given by

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

This operator acts on Slater determinants as follows.

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

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

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

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

$$\Psi(1,\cdots,n) = \tfrac{1}{\sqrt{n}}\sum_p^\infty \psi_p(1)\,(\hat{a}_p\Psi)\,(2,\cdots,n) \tag{1.4}$$

$$= \tfrac{1}{\sqrt{n(n-1)}}\sum_{pq}^\infty \psi_p(1)\psi_q(2)(\hat{a}_q\hat{a}_p\Psi)(3,\cdots,n) \tag{1.5}$$

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

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

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

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

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.

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

[2] These 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 $V \oplus V' \equiv \{v \oplus v' \,|\, v \in V,\, v' \in V'\}$, vector addition and scalar multilication are defined by

$$v_1 \oplus v_1' + v_2 \oplus v_2' = (v_1 + v_2) \oplus (v_1' + v_2') \qquad c(v \oplus v') = cv \oplus cv' \,, \tag{1.7}$$

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

$$v_1 \otimes v' + v_2 \otimes v' = (v_1 + v_2) \otimes v' \qquad v \otimes v_1' + v \otimes v_2' = v \otimes (v_1' + v_2') \qquad c(v \otimes v') = (cv) \otimes v' = v \otimes (cv') \tag{1.8}$$

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.

$$\langle v \oplus v' | w \oplus w' \rangle_{V \oplus V'} \equiv \langle v|w \rangle_V + \langle v'|w' \rangle_{V'} \qquad \langle v \otimes v' | w \otimes w' \rangle_{V \otimes V'} \equiv \langle v|w \rangle_V \cdot \langle v'|w' \rangle_{V'} \tag{1.9}$$

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

Definition 1.4. ***Fock space.*** Let $\mathcal{F}_n(\mathcal{H})$ denote $\mathrm{span}\{\Phi_{(p_1 \cdots p_n)}\}$,[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, $|\mathbf{n}\rangle \equiv |n_1, n_2, n_3, \cdots, n_\infty\rangle$, 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 $|\mathrm{vac}\rangle$, 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 $a_p : \mathcal{F}_n(\mathcal{H}) \to \mathcal{F}_{n-1}(\mathcal{H})$ defined by

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

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

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

Proposition 1.1. $\boldsymbol{c_p = a_p^\dagger}$**.** *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. $\boldsymbol{[q, q']_+ = \delta_{q' q^\dagger}}$**.** *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, $q' = q^\dagger \implies (qq' + q'q) = 1$.

[3] Also known as a *tensor product*

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

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

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

Remark 1.1. ***Relating the determinant and occupation number formalisms.*** 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

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

$$a_p^\dagger\Phi_{(p_1\cdots p_n)} = (-)^{k-1}\Phi_{(p_1\cdots p_{k-1}pp_k\cdots p_n)} \text{ if } p \notin (p_1\cdots p_n) \qquad a_p^\dagger\Phi_{(p_1\cdots p_n)} = 0 \text{ if } p \in (p_1\cdots p_n) \tag{1.13}$$

which follows directly from Eqs (1.10) and (1.11) 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 (1.12) 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

$$|\Phi_{(p_1\cdots p_n)}\rangle = a_{p_1}^\dagger\cdots a_{p_n}^\dagger|\mathrm{vac}\rangle \tag{1.14}$$

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 $a_{p_1}^\dagger\cdots a_{p_m}^\dagger a_{q_m}\cdots a_{q_1}$ are called *excitation operators*. For a given reference determinant Φ, excited determinants can be constructed as

$$\Phi_{i_1\cdots i_m}^{a_1\cdots a_m} = a_{a_1}^\dagger\cdots a_{a_m}^\dagger a_{i_m}\cdots a_{i_1}\Phi = a_{a_1}^\dagger a_{i_1}\cdots a_{a_m}^\dagger a_{i_m}\Phi \tag{1.15}$$

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

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

$$|k_1\cdots k_nk_{n+1}k_{n+1}\cdots\rangle \mapsto |\overline{k}_1\cdots\overline{k}_nk_{n+1}k_{n+2}\cdots\rangle \qquad \text{where } \overline{k}_i = 1 - k_i.$$

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 $|\mathrm{vac}\rangle \mapsto |\underbrace{\overline{1}\cdots\overline{1}}_{n\text{ times}}0\,0\cdots\rangle$ a state of n holes and no particles. $|\Phi\rangle \mapsto |\underbrace{\overline{0}\cdots\overline{0}}_{n\text{ times}}0\,0\cdots\rangle$ 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

$$a_i \mapsto b_i^\dagger \qquad a_i^\dagger \mapsto b_i \qquad a_a \mapsto b_a \qquad a_a^\dagger \mapsto b_a^\dagger \tag{1.16}$$

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

$$H_e = \sum_{pq} h_{pq}\, a_p^\dagger a_q + \tfrac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\, a_p^\dagger a_q^\dagger a_s a_r \tag{1.17}$$

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,

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

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 $a_{p_1}^\dagger \cdots a_{p_m}^\dagger a_{r_1} \cdots q_{r_{m'}}$. This guarantees that its vacuum expectation value vanishes, $\langle \mathrm{vac}|q_1 \cdots q_n|\mathrm{vac}\rangle = 0$. 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:

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

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

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.

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

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