

## Chapter 3 Second Quantization

### The Hilbert Space and Fock Space

In the previous chapter we showed that there is a one-to-one mapping of the symmetric products (for bosons) and determinants (for fermions) to the occupation number representation. For a given number of particle,  $N$ , we then define the Hilbert space of  $N$  particles as

$$H_N = \left\{ |\mathbf{n}\rangle, \sum_j n_j = N \right\}. \quad (30)$$

For practical reason we also introduce the Hilbert space containing zero particles, consisting of only one element, the vacuum state

$$H_0 \equiv |0, 0, \dots\rangle = |-\rangle. \quad (31)$$

The direct sum of all the Hilbert spaces leads to the Fock space

$$F_F \equiv \bigoplus_{N=0}^{\infty} H_N \quad (32)$$

capable of describing systems with a variable number of particles.

In the Fock space the overlap of two states with the same number of particles is defined as

$$\langle \mathbf{n} | \mathbf{m} \rangle = \prod_{j=1}^{\infty} \delta_{n_j, m_j}, \quad (33)$$

while for two states with a different number of particles it is zero. For the vacuum state we define

$$\langle - | - \rangle = 1. \quad (34)$$

## Second Quantization

We now want to introduce operators that allow us to describe N-particle states, in essence we would like to write a certain state, described by the occupation vector, in terms of an operator  $\hat{\Theta}$  that creates bosons or fermions out of the vacuum

$$|\Psi\rangle = \hat{\Theta} |-\rangle. \quad (35)$$

The easiest way to approach this problem is by looking at states containing only one particle. We can make the correspondence

$$|0 \dots 1_j \dots\rangle = \begin{cases} \hat{b}_j^+ |-\rangle & \text{for bosons} \\ \hat{a}_j^+ |-\rangle & \text{for fermions} \end{cases}, \quad (36)$$

that defines the creation operator  $\hat{a}_j^+$ , and introduce the annihilation operators  $\hat{a}_j$ , defined to satisfy

$$\begin{aligned} \hat{a}_j \hat{a}_j^+ |-\rangle &= |-\rangle \\ \hat{a}_j |-\rangle &= 0 \end{aligned} \quad (37)$$

Bosonic and fermionic second quantization is intrinsically different because these two families of particle belong to two different representation of the symmetric group. This is not reflected in the occupation number representation of the symmetric products and the determinants but rather on the commutator and anticommutator of the creation and annihilation operators. Thus we have that for bosons

$$\begin{aligned} [\hat{b}_i, \hat{b}_j]_- &= [\hat{b}_i^+, \hat{b}_j^+]_- = 0 \\ [\hat{b}_i, \hat{b}_j^+]_- &= \delta_{ij} \end{aligned} \quad (38)$$

while for fermions we have

$$\begin{aligned} [\hat{a}_i, \hat{a}_j]_+ &= [\hat{a}_i^+, \hat{a}_j^+]_+ = 0 \\ [\hat{a}_i, \hat{a}_j^+]_+ &= \delta_{ij} \end{aligned} \quad (39)$$

Let us show this property in the case of fermions. Consider a system containing two particle in orbitals  $j$  and  $k$ , with  $j < k$ . The determinant corresponding to this state is

$$\Phi_{jk}^F(x_1, x_2) \leftrightarrow \hat{a}_j^+ \hat{a}_k^+ |-\rangle. \quad (40)$$

According to Pauli's principle

$$\Phi_{jk}^F(x_1, x_2) = -\Phi_{jk}^F(x_2, x_1) = \Phi_{kj}^F(x_2, x_1) = -\Phi_{kj}^F(x_1, x_2) \quad (41)$$

we also have that

$$\Phi_{kj}^F(x_1, x_2) \leftrightarrow \hat{a}_k^+ \hat{a}_j^+ |-\rangle, \quad (42)$$

and so

$$(\hat{a}_k^+ \hat{a}_j^+ + \hat{a}_j^+ \hat{a}_k^+) |-\rangle = 0. \quad (43)$$

Moreover using Eq. (37) we have the other commutator

$$\hat{a}_k \hat{a}_j^+ |-\rangle + \hat{a}_j^+ \hat{a}_k |-\rangle = \delta_{jk} |-\rangle. \quad (44)$$

## Operators in Fock space

Second quantization come quite handy when we want to represent the effect of one and two particles operators because we can derive a general form independent of the number of particles in the system. Say we have  $N$  particles, then we want to express the operators

$$\begin{aligned} \hat{h}_1^N &= \sum_{j=1}^N h(x_j) \\ \hat{h}_2^N &= \frac{1}{2} \sum_{j=1}^N \sum_{\substack{k=1 \\ k \neq j}}^N g(x_j, x_k) \end{aligned} \quad (45)$$

as operators involving only matrix elements and the creation and annihilation operators.

The results are

$$\begin{aligned} \hat{h}_1^{SQ} &= \sum_{pq} \langle \varphi_p | \hat{h} | \varphi_q \rangle \hat{a}_p^+ \hat{a}_q \\ \hat{h}_2^{SQ} &= \frac{1}{2} \sum_{pqrs} \langle \varphi_p \varphi_q | \hat{g} | \varphi_r \varphi_s \rangle \hat{a}_q^+ \hat{a}_p^+ \hat{a}_r \hat{a}_s \end{aligned} \quad (46)$$

where the indices  $p$ ,  $q$ ,  $r$ , and  $s$  run over all the basis functions.

To keep the notation short it is common to write the one and two electron integrals as

$$\begin{aligned} h_{pq} &= \langle \varphi_p | \hat{h} | \varphi_q \rangle = \int \varphi_p^*(x) \hat{h}(x) \varphi_q(x) dx \\ \langle pq | rs \rangle &= \langle \varphi_p \varphi_q | \hat{g} | \varphi_r \varphi_s \rangle = \int \varphi_p^*(x_1) \varphi_q^*(x_2) \hat{g}(x_1, x_2) \varphi_r(x_1) \varphi_s(x_2) dx_1 dx_2 \end{aligned} \quad (47)$$

**Exercise. Show that for the energy of the determinant**

$$|0\rangle = \prod_{j=1}^N \hat{a}_j^+ |-\rangle \quad (48)$$

**is given by**

$$\langle 0 | \hat{H} | 0 \rangle = \sum_{i=1}^N h_{pq} + \frac{1}{2} \sum_{i,j}^N [\langle ij | ij \rangle - \langle ij | ji \rangle] \quad (49)$$

The two-particle operator is sometimes written in terms of antisymmetrized two electron integrals

$$\langle ij || ij \rangle = \langle ij | ij \rangle - \langle ij | ji \rangle, \quad (50)$$

as

$$\hat{h}_2^{SQ} = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \hat{a}_q^+ \hat{a}_p^+ \hat{a}_r \hat{a}_s. \quad (51)$$