Appendix C. Second Quantization

C.1 Rules

C.1.1 States

Begin with a complete orthonormal set of basis functions ψ_l. Any collection of identical particles can be described by sums of products of these functions. In the formalism of second quantization, one focuses upon many-body basis functions, which describe how many particles are in each state. For example,

$$|0, 2, 3, 10, \ldots\rangle \tag{C.1}$$

means that no particles are in state ψ_1, two particles are in state ψ_2, three are in state ψ_3, and so on. The integers describing the numbers of particles are called *occupation numbers.*

C.1.2 Operators

The operators of second quantization change the numbers of particles in these quantum states. There is a *creation operator* with index l that adds one particle to state l and an *annihilation operator* with index l that takes one particle away from state l.

Fermions. The Pauli principle prohibits more than one electron from occupying any given quantum state, so the occupation numbers all are zero or one. The creation and annihilation operators are usually denoted by $\hat{c}_l^\dagger$ and $\hat{c}_l$ respectively. The way they operate is

$$\hat{c}_l|n_1 n_2 \ldots n_l \ldots\rangle = \begin{cases} 0 & \text{if } n_l = 0 \\ |n_1 n_2 \ldots 0 \ldots\rangle & \text{if } n_l = 1 \end{cases} \tag{C.2a}$$

$$\hat{c}_l^\dagger|n_1 n_2 \ldots n_l \ldots\rangle = \begin{cases} 0 & \text{if } n_l = 1 \\ |n_1 n_2 \ldots 1 \ldots\rangle & \text{if } n_l = 0. \end{cases} \tag{C.2b}$$

The operators anticommute:

$$\hat{c}_l^\dagger \hat{c}_{l'}^\dagger + \hat{c}_{l'}^\dagger \hat{c}_l^\dagger = 0 \tag{C.3a}$$

$$\hat{c}_l \hat{c}_{l'} + \hat{c}_{l'} \hat{c}_l = 0 \tag{C.3b}$$

$$\hat{c}_l \hat{c}_{l'}^\dagger + \hat{c}_{l'}^\dagger \hat{c}_l = \delta_{ll'}. \tag{C.3c}$$

Bosons. Bosons can inhabit any quantum state as often as they please, so the occupation numbers range over all non-negative integers. The creation and annihilation operators are usually denoted by $\hat{a}_l^\dagger$ and $\hat{a}_l$ respectively. The way they operate is

$$\hat{a}_l|n_1n_2\ldots n_l\ldots\rangle = \sqrt{n_l}|n_1n_2\ldots n_l-1\ldots\rangle \tag{C.4a}$$

$$\hat{a}_l^\dagger|n_1n_2\ldots n_l\ldots\rangle = \sqrt{n_l+1}|n_1n_2\ldots n_l+1\ldots\rangle. \tag{C.4b}$$

The operators commute:

$$\hat{a}_l^\dagger\hat{a}_{l'}^\dagger - \hat{a}_{l'}^\dagger\hat{a}_l^\dagger = 0 \tag{C.5a}$$

$$\hat{a}_l\hat{a}_{l'} - \hat{a}_{l'}\hat{a}_l = 0 \tag{C.5b}$$

$$\hat{a}_l\hat{a}_{l'}^\dagger - \hat{a}_{l'}^\dagger\hat{a}_l = \delta_{ll'}. \tag{C.5c}$$

C.1.3 Hamiltonians

A Hamiltonian that is given as a sum of operators on single particles can be rewritten in second quantized notation as

$$\hat{\mathcal{H}} = \sum_j \hat{f}_j \tag{C.6}$$

f_j means an operator such as $f(\vec{r}_j)$ that acts in some identical fashion upon each particle j in turn.

$$= \sum_{ll'} \hat{c}_l^\dagger \langle\psi_l(1)|\hat{f}_1|\psi_{l'}(1)\rangle\hat{c}_{l'}. \tag{C.7}$$

The wave functions ψ_l and operator $\hat{f}$ all act on particle 1. The expression for bose operators is identical.

The notation $|\psi_{l'}(1)\rangle$ means that particle number 1 is in state $\psi_{l'}$. For example, if $\hat{f}$ is the kinetic energy operator and ψ_l is the product of a Wannier function w_l and a spin function χ_l, then

$$\langle\psi_l(1)|\hat{f}_1|\psi_{l'}(1)\rangle = \delta_{\chi_l\chi_{l'}} \int d\vec{r}_1\; w_l^*(\vec{r}_1)\frac{-\hbar^2\nabla_1^2}{2m}w_{l'}(\vec{r}_1) \tag{C.8}$$

The leading delta function requires the spins of the two states to be the same. The Laplacian ∇_1^2 acts on variable $\vec{r}_1$.

A Hamiltonian that is given as a sum of operators on pairs of particles can be rewritten in second quantized notation as

$$\hat{\mathcal{H}} = \sum_{j\neq j'} \hat{f}_{jj'} \tag{C.9}$$

$f_{jj'}$ means an operator such as $f(\vec{r}_j, \vec{r}_{j'})$ that acts in some identical fashion upon pairs of particles.

$$= \sum_{ll'l''l'''} \hat{c}_l^\dagger\hat{c}_{l'}^\dagger\hat{c}_{l'''}\hat{c}_{l''}\langle\psi_l(1)\psi_{l'}(2)|\hat{f}_{12}|\psi_{l''}(1)\psi_{l'''}(2)\rangle \tag{C.10}$$

For example, if f_{12} is the Coulomb interaction and ψ_l is the product of some spatial wave function ϕ_l and a spin function χ_l, then

$$\langle\psi_l(1)\psi_{l'}(2)|\hat{f}_{12}|\psi_{l''}(1)\psi_{l'''}(2)\rangle$$

$$= \delta_{\chi_l\chi_{l''}}\delta_{\chi_{l'}\chi_{l'''}} \int d\vec{r}_1 d\vec{r}_2\; \phi_l^*(\vec{r}_1)\phi_{l'}^*(\vec{r}_2)\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\phi_{l''}(\vec{r}_1)\phi_{l'''}(\vec{r}_2). \tag{C.11}$$

Often one does not write down spin sums or spin delta functions explicitly and just multiplies the final answer by appropriate factors of two.

C.2 Derivations

C.2.1 Bosons

A collection of Bose particles can be described by a wave function of the form

$$|n_1 n_2 n_3 \ldots\rangle = \sqrt{\frac{1}{N! n_1! n_2! \ldots}} \sum_{\text{Permutations } s_j} \prod_{j=1}^{N} |\psi_{l(j)}(s_j)\rangle. \tag{C.12}$$

The function s_j gives some permutation of the integers j, and by summing over all permutations the wave function is guaranteed to be symmetric under interchange of all indices.

The function $l(j)$ is some function into the positive integers. The idea is that the states ψ_l are numbered in a way that may be quite arbitrary. Suppose one decides to build a many-body state with one particle in state 1 and two particles in state 3. The function $l(j)$ could then be

$$l(1) = 3, \quad l(2) = 1 \quad l(3) = 3. \tag{C.13}$$

Notation of the form $|\psi_2(6)\rangle$ means that particle number 6 is in state ψ_2.

The number of times a certain integer $l(j)$ appears as j ranges from 1 to N is n_l, so n_l gives the number of particles in state l. The factors of $n_1! n_2! \ldots$ account for the fact that any given term in the sum where n_1 particles are in state 1 appears $n_1!$ times. To illustrate that the factorials are correctly employed, suppose first of all that there is only one particle in each distinct state. Then there are $N!$ distinct orthogonal functions appearing in the sum (C.12), and the normalization must be $1/\sqrt{N!}$. On the other hand, suppose all particles are in state ψ_1. Then all the $N!$ terms in the sum are identical, and the sum must be divided by $N!$ to produce a normalized wave function.

To study the behavior of this wave function, it is helpful to define the operator

$$\hat{E}_{l \leftarrow l'} = \sum_j |\psi_l(j)\rangle\langle\psi_{l'}(j)|. \tag{C.14}$$

The effect of this operator is to search one at a time for each particle in state $\psi_{l'}$ and move it to state ψ_l.

To use this operator, consider a Hamiltonian of the form (C.6),

$$\hat{\mathcal{H}} = \sum_{j=1}^{N} \hat{f}_j = \sum_{ll'j} |\psi_l(j)\rangle\langle\psi_l(j)|\hat{f}_j|\psi_{l'} j\rangle\langle\psi_{l'}(j)| \tag{C.15}$$

$$= \sum_{ll'} \hat{E}_{l\leftarrow l'} \langle\psi_l(1)|\hat{f}_1|\psi_{l'}(1)\rangle. \tag{C.16}$$

The matrix elements of the one-particle operator $\hat{f}$ do not depend upon which particle is involved, so the label 1 can be used instead of j.

Let $\hat{E}_{l\leftarrow l'}$ act upon $|n_1 n_2 \ldots\rangle$. If state $\psi_{l'}$ is not occupied, the result is zero. If it is occupied, then in every term of (C.12), there will be precisely $n_{l'}$ values of j

for which there is a nonzero result, with the population of state l' being reduced by 1 and the population of state l being increased by 1. The result will not be properly normalized because $\sqrt{n_{l'}!n_l!}$ is in the denominator rather than $\sqrt{(n_{l'}-1)!(n_l+1)!}$, and a factor of $n_{l'}$ has been acquired along the way. So

$$\hat{E}_{l\leftarrow l'}|n_1n_2\ldots\rangle = \sqrt{n_{l'}(n_l+1)}|\ldots n_{l'}-1\ldots n_l+1\ldots\rangle. \tag{C.17}$$

For this reason, define

$$\hat{a}_l^\dagger|n_1, n_2\ldots\rangle = \sqrt{n_l+1}|\ldots n_l+1\ldots\rangle \tag{C.18a}$$

$$\hat{a}_l|n_1, n_2\ldots\rangle = \sqrt{n_l}|\ldots n_l-1\ldots\rangle \tag{C.18b}$$

so that

$$\hat{E}_{l\leftarrow l'} = \hat{a}_l^\dagger\hat{a}_{l'}. \tag{C.19}$$

It is easy from Eq. (C.18) to check the commutation relations (C.5) by allowing the creation and annihilation operators to act in various orders upon general states $|n_1n_2\ldots\rangle$.

C.2.2 Fermions

The wave function describing a collection of fermions must be antisymmetric under interchange of arguments, and it consists of sums of terms of the form

$$\Psi = |n_1n_2\ldots\rangle = \sqrt{\frac{1}{N!}}\sum_{\text{Permutations } s_j}(-1)^s\prod_{j=1}^{N}|\psi_{l(j)}(s_j)\rangle, \tag{C.20}$$

where the sum is over all permutations s_j of $j=1\ldots N$, with s the sign of the permutation. In order for Ψ not to equal zero, no more than one electron is allowed to inhabit each individual state. If an electron is in state l, then n_l is one and otherwise it is zero.

Given the occupation numbers n_l for each state ψ_l, the wave function that can be formed from the collection is almost unique. There is only one ambiguity, which has to do with the overall sign of the wave function. The ambiguity is avoided by requiring that $l(j)$ be an increasing function of j.

Consider again a Hamiltonian of the form (C.15), acting on antisymmetric wave functions Ψ as in Eq. (C.20). It is sufficient to examine the behavior of a single term in the sum (C.15). For example, look at

$$\langle\Psi_a|\psi_l(1)\rangle\langle\psi_{l'}(1)|\Psi_b\rangle. \tag{C.21}$$

(C.21) is nonzero only if in $|\Psi_b\rangle$ $\psi_{l'}$ is occupied, ψ_l unoccupied, while in $|\Psi_a\rangle$ $\psi_{l'}$ is unoccupied, ψ_l is occupied, and otherwise Ψ_a and Ψ_b are identical. To be explicity, let

$$|\Psi_a\rangle = \sum_s(-1)^s\frac{1}{\sqrt{3!}}|\psi_1(s_1)\rangle|\psi_2(s_2)\rangle|\psi_3(s_3)\rangle \tag{C.22}$$

$$|\Psi_b\rangle = \sum_s(-1)^s\frac{1}{\sqrt{3!}}|\psi_1(s_1)\rangle|\psi_3(s_2)\rangle|\psi_4(s_3)\rangle \tag{C.23}$$

and look at

$$\langle\Psi_a|\psi_2(1)\rangle\langle\psi_4(1)|\Psi_b\rangle. \tag{C.24}$$

The parts of the wave functions that survive are

$$\frac{1}{3!}\Big[\langle\psi_3(2)|\langle\psi_1(3)| - \langle\psi_1(2)|\langle\psi_3(3)|\Big] \left\{\begin{array}{l}\langle\psi_2(1)|\psi_2(1)\rangle\\ \langle\psi_4(1)|\psi_4(1)\rangle\end{array}\right\} \Big[|\psi_1(2)\rangle|\psi_3(3)\rangle \quad -|\psi_3(2)\rangle|\psi_1(3)\rangle\Big] \tag{C.25}$$

$$= -\frac{1}{3}. \tag{C.26}$$

The general lesson to learn from this example is that one must permute ψ_l past all the states below it in the ordering scheme to produce the term $|\psi_l(1)\rangle$, obtaining a factor of

$$(-1)^{\sum_{j=1}^{l-1} n_j}, \tag{C.27}$$

where n_l is 1 if state l is occupied in Ψ_a and zero otherwise. One also has a factor

$$(-1)^{\sum_{j=1}^{l'-1} n_j} \tag{C.28}$$

similarly, so that

$$\sum_{j=1}^{N}\langle\Psi_a|\psi_l(j)\rangle\langle\psi_{l'}(j)|\Psi_b\rangle = (-1)^{\sum_{j=1}^{l'-1} n_j}(-1)^{\sum_{j=1}^{l-1} n_j} \tag{C.29}$$

if it is not zero.

Therefore, one can again define the operator $\hat{E}_{l\leftarrow l'}$ from Eq. (C.14). Write wave functions in the occupation number representation

$$|\Psi\rangle = |n_1 n_2 n_3 \ldots\rangle, \tag{C.30}$$

where each n_i can be either zero or one. In the example above,

$$|\Psi_a\rangle = |1110000\ldots\rangle \tag{C.31}$$

$$|\Psi_b\rangle = |1011000\ldots\rangle. \tag{C.32}$$

In acting on such a wave function

$$\hat{E}_{l\leftarrow l'}|n_1 n_2 n_3 \ldots\rangle = (-1)^{\sum_{j=1}^{l'-1} n_j}(-1)^{\sum_{j=1}^{l-1} n_j}\delta_{n_{l'}1}\delta_{n_l 0}|n_1 n_2 n_3 \ldots n_{l'}-1 \ldots n_l+1\ldots\rangle. \tag{C.33}$$

The creation and annihilation operators are defined so that

$$\hat{E}_{l\leftarrow l'} = \hat{c}_l^\dagger \hat{c}_{l'}. \tag{C.34}$$

More explicitly,

$$\hat{c}_l|n_1n_2n_3\ldots\rangle = \delta_{1,n_l}(-1)^{\sum_{j=1}^{l-1} n_j}|n_1n_2n_3\ldots n_{l-1}\;0\;n_{l+1}\ldots\rangle \quad \text{(C.35a)}$$

$$\hat{c}_l^\dagger|n_1n_2n_3\ldots\rangle = \delta_{0,n_l}(-1)^{\sum_{j=1}^{l-1} n_j}|n_1n_2n_3\ldots n_{l-1}\;1\;n_{l+1}\ldots\rangle. \quad \text{(C.35b)}$$

The anti-commutation relations in Eq. (C.3) can be verified explicitly from this definition.

A final relation that should be verified is Eq. (C.10). The special ordering of the creation and annihilation operators results from the condition $j \neq j'$ in the sum over particle numbers. Write

$$\sum_{j\neq j'} \hat{f}_{jj'}$$
$$= \sum_{\substack{ll'l''l'''\\ j\neq j'}} |\psi_l(j)\rangle|\psi_{l'}(j')\rangle\langle\psi_l(j)\psi_{l'}(j')|\hat{f}_{jj'}|\psi_{l''}(j)\psi_{l'''}(j')\rangle\langle\psi_{l''}(j)|\langle\psi_{l'''}(j')| \quad \text{(C.36)}$$

$$= \sum_{\substack{ll'l''l'''\\ jj'}} [|\psi_l(j)\rangle\langle\psi_{l''}(j)|]\,[|\psi_{l'}(j')\rangle\langle\psi_{l'''}(j')|]\,\langle\psi_l(j)\psi_{l'}(j')|\hat{f}_{jj'}|\psi_{l''}(j)\psi_{l'''}(j')\rangle$$
$$- \sum_{\substack{ll'l''l'''\\ j}} \delta_{l'l''}[|\psi_l(j)\rangle\langle\psi_{l'''}(j)|]\,\langle\psi_l(j)\psi_{l'}(j)|\hat{f}_{jj}|\psi_{l''}(j)\psi_{l'''}(j)\rangle \quad \text{(C.37)}$$

$$= \sum_{ll'l''l'''} \hat{E}_{l\leftarrow l''}\hat{E}_{l'\leftarrow l'''}\langle\psi_l(1)\psi_{l'}(2)|\hat{f}_{12}|\psi_{l''}(1)\psi_{l'''}(2)\rangle$$
$$- \sum_{ll'l''l'''} \delta_{l'l''}\,\hat{E}_{l\leftarrow l'''}\,\langle\psi_l(1)\psi_{l'}(2)|\hat{f}_{12}|\psi_{l''}(1)\psi_{l'''}(2)\rangle \quad \text{(C.38)}$$

$$= \sum_{ll'l''l'''} \hat{c}_l^\dagger\hat{c}_{l''}\hat{c}_{l'}^\dagger\hat{c}_{l'''}\langle\psi_l(1)\psi_{l'}(2)|\hat{f}_{12}|\psi_{l''}(1)\psi_{l'''}(2)\rangle$$
$$- \sum_{ll'l''l'''} \delta_{l'l''}\,\hat{c}_l^\dagger\hat{c}_{l'''}\,\langle\psi_l(1)\psi_{l'}(2)|\hat{f}_{12}|\psi_{l''}(1)\psi_{l'''}(2)\rangle \quad \text{(C.39)}$$

$$= \sum_{ll'l''l'''} \hat{c}_l^\dagger\hat{c}_{l'}^\dagger\hat{c}_{l'''}\hat{c}_{l''}\langle\psi_l(1)\psi_{l'}(2)|\hat{f}_{12}|\psi_{l''}(1)\psi_{l'''}(2)\rangle. \quad \text{(C.40)}$$