Appendix

Second quantization

For readers who have not met it before, I here set out a brief introduction to *second quantization*, the representation of quantum theory in terms of *creation and annihilation operators*, which is used to describe many-body systems of interacting particles. We shall concentrate on fermions, but mention the application to bosons briefly at the end.

A.1 The idea of second quantization

When we have a large number of interacting identical particles, as in the electron liquid in a metal, the wavefunction which describes the system usually becomes extremely complicated, with strong correlations in the positions of the particles produced by the interaction forces. In such a situation we cannot say that particular one-particle states are occupied independently of what other particles may be doing. However, any many-body state function, however complex, may always be expressed as an *expansion* in basis states which *do* have definite one-particle occupations. The idea behind the method of second quantization is to work with such basis states, and to employ operators which act not on the particle coordinates (as in the familiar Schrödinger representation of quantum mechanics) but on the occupation numbers of the basis states.

To be specific, we start by choosing some convenient set of *one-particle states*. (When dealing with superconductivity we frequently, but not necessarily, choose plane-wave states of definite momentum and spin, $\phi_{k,\sigma}$.) The set is to be arranged in some definite order, ϕ_1, ϕ_2, ... We then use as our many-body basis functions the states of definite occupation, $\psi(n_1, n_2, \ldots)$, in which the state variables are the occupation numbers $n_1, n_2, \ldots$ of the various one-particle states. For instance, for fermions the basis function $\psi(0,1,0,0,1,0,1,0,0,0,\ldots)$ represents a state containing three identical fermions in states ϕ_2, ϕ_5 and ϕ_7. (For fermions we, of course, have an *exclusion principle*, i.e. the occupation numbers n_i may only take the values 0 and 1.)

At this point we have to consider the requirements of *particle exchange symmetry*. For fermions, the state function must change sign when we exchange the space and spin coordinates of two identical particles. It follows that the basis functions of definite one-particle occupation cannot be written in Schrödinger representation as simple product functions. We have to use instead the *antisymmetrized products* known as *Slater determinants* such as

$$\begin{aligned}\psi(n_1, n_2 \ldots) &= \psi(0,1,0,0,1,0,1,0,0,0,\ldots) \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_2(a) & \phi_2(b) & \phi_2(c) \\ \phi_5(a) & \phi_5(b) & \phi_5(c) \\ \phi_7(a) & \phi_7(b) & \phi_7(c) \end{vmatrix}. \end{aligned} \tag{A.1}$$

The labels in brackets refer to the *particles*, identified by letter, for example a state such as $\phi_2(a)$ means a one-particle state in which particle a is in state 2, some state of definite orbit and spin. In this example ψ is a state containing three identical fermions labelled a, b and c in states 2, 5 and 7. Because the determinant changes sign when any two columns or any two rows are exchanged, ψ is, as required, antisymmetric under particle exchange (which is equivalent to exchanging the corresponding columns of the determinant). It is also correctly normalized (N is the number of particles present). Notice that to give ψ a definite sign the rows must be written in the proper order.

It is obvious already that we need a formalism which avoids using these Slater determinants explicitly; they would be completely unmanageable for systems containing 10^{23} particles. Moreover, the Schrödinger representation has an unnecessary perversity. The particles are actually indistinguishable, but in the Schrödinger representation we first label the particles as though they were distinguishable and then promptly remove the distinguishability by antisymmetrizing the function. It is this antisymmetrization which introduces the algebraic complexity. The occupation number representation, which never labels the particles, is much simpler and more rational in this respect, as we shall see.

A.2 Creation and annihilation operators

We now define *creation* and *annihilation operators* which act on the occupation numbers of the basis states. We also describe their effects on the corresponding Slater determinants.

> If state i is occupied, the annihilation operator c_i empties it and multiplies by $(-1)^{s(i)}$, where $s(i)$ is the number of filled states which come after i in the standard order. (We may think of this as converting the $N \times N$ Slater determinant to an $(N-1) \times (N-1)$ determinant by first moving the row corresponding to state i to the bottom, which has the effect of multiplying by $(-1)^{s(i)}$, and then removing the final row and the final column, and renormalizing.) If state i is already empty, c_i gives zero.
>
> If state i is empty, the creation operator $c_i^\dagger$ fills it, and multiplies by $(-1)^{s(i)}$ where $s(i)$ is the number of filled states which come after i in the standard order. (We may think of this as converting the $N \times N$ Slater determinant to an $(N+1) \times (N+1)$ determinant by first adding a new state i row at the bottom and a new column on the right and renormalizing and then moving the bottom row up to its correct position, which has the effect of multiplying by $(-1)^{s(i)}$.) If state i is already filled, $c_i^\dagger$ gives zero.

The reason for defining the operators with the $(-1)^{s(i)}$ sign factors will become clear in Section A.4. Note carefully the following algebraic properties.

(i) It is easily seen by inspecting their matrix elements that c_i and $c_i^\dagger$ are Hermitian conjugates.

(ii) It is also easy to see that when $i \neq j$ the operators *anticommute*

$$\begin{aligned} c_i c_j &= -c_j c_i \\ c_i^\dagger c_j &= -c_j c_i^\dagger \\ c_i^\dagger c_j^\dagger &= -c_j^\dagger c_i^\dagger. \end{aligned} \tag{A.2}$$

This happens because the action of the operator corresponding to the *lower* row in the determinant changes by ± 1 the value of s for the *upper* row, and the sign of the product therefore depends on whether this operator acts before or after the operator for the upper row.

(iii) We also find for operators which refer to the same state that

$$c_i c_i = c_i^\dagger c_i^\dagger = 0 \tag{A.3}$$

because we cannot annihilate or create the same state twice, and

$$\begin{aligned} c_i^\dagger c_i &= \hat{n}_i \\ c_i c_i^\dagger &= 1 - \hat{n}_i \end{aligned} \tag{A.4}$$

where $\hat{n}_i$ is the operator for the number of particles in state i, because the first multiplies by 1 if i is occupied and 0 if i is empty, and the second by 0 if occupied and by 1 if empty.

(iv) Combining the results of (ii) and (iii) we find that

$$\{c_i, c_j^\dagger\} = \delta_{ij} \tag{A.5}$$

where $\{\hat{a}, \hat{b}\}$ is the symbol for the *anticommutator* $(\hat{a}\hat{b} + \hat{b}\hat{a})$.

A.3 Representation of states in second quantization

We can do all our calculations using nothing but creation and annihilation operators. We may represent states by letting suitable creation operators act on $|0\rangle$, the *empty state* or *vacuum state*. For instance, the state represented by the Slater determinant (A.1) would be written simply as $c_2^\dagger c_5^\dagger c_7^\dagger|0\rangle$. The Fermi gas ground state is

$$\prod_{k<k_F,\sigma} (c_{k,\sigma}^\dagger)|0\rangle. \tag{A.6}$$

General many-body states of any type may be written using linear combinations of such operators. Notice that we may construct states of *mixed occupation number* such as $(c_2^\dagger c_3^\dagger + c_4^\dagger)|0\rangle$, which are not eigenstates of total particle number and cannot be handled conveniently in Schrödinger representation.

A.4 Representation of operators in second quantization

The next step is to consider the effects of typical operators when they act on the basis functions. In practice what we shall be involved with are *one-particle operators, two-particle operators* and so on. A one-particle operator represents a quantity such as the kinetic energy of all the particles or the total potential energy of all the particles in an external field, which has the form $\hat{F}^{(1)} = \sum_n \hat{f}(r_n, \sigma_n)$, a sum over all particles n of equivalent contributions each of which involves the space and spin coordinates of only one particle. A two-particle operator, such as the mutual potential energy of all the particles, involves a sum over all *pairs* of particles, and so on.

What is the effect of a one-particle operator $\hat{F}^{(1)}$ on a basis function such as (A.1)? In considering this it is helpful to remember that the individual particle operators $\hat{f}$ themselves have definite one-particle matrix elements f_{ji} between the one-particle states ϕ_i and ϕ_j. Let us break the operator $\hat{F}^{(1)}$ down into parts associated with a single one-particle matrix element. Consider for instance the operator $\hat{F}_{62} = \sum_n \hat{f}_{62}(n)$. Here $\hat{f}_{62}(n)$ means the part of $\hat{f}(n)$ associated with the single matrix element f_{62}. It would

be represented by a matrix having a single element, and has the effect of replacing $\phi_2(n)$ by $\phi_6(n)$ and multiplying by f_{62}. (If particle n is not initially in state 2 or if state 6 is occupied by another particle it gives zero.) The overall effect of $\hat{F}_{62}$ on (A.1) is to replace the entire row associated with state 2 by a corresponding row for state 6, and to multiply by f_{62}. Evidently $\hat{F}_{62}$ will have a non-zero matrix element between basis functions provided that the only difference between the initial and final states is that a particle has moved from state 2 to state 6, otherwise the matrix element will be zero. The matrix element will have the value

$$(-1)^{s(6)} f_{62} (-1)^{s(2)}. \tag{A.7}$$

The powers of -1 arise because we have to worry about getting the rows into the correct sequence. To see how this happens, imagine doing the calculation in the following way. First move the state-2 row of the initial state to the bottom of the determinant, which introduces the factor $(-1)^{s(2)}$ where $s(2) = 2$ is the number of filled rows below the state-2 row, then let the operator act, which converts the bottom row into a state-6 row and multiplies by f_{62}, finally convert the result to standard form by moving the state-6 row into its correct position, which introduces a further factor $(-1)^{s(6)}$ where $s(6) = 1$ is the number of filled rows below row 6 in the final state. The matrix element of the whole of $\hat{F}^{(1)}$ may be written down by summing contributions of type (A.7) for all initial and final one-particle states.

At this point we observe that the sign changes included in the definitions of c_i and $c_i^\dagger$ have been chosen in such a way that *the effect of* $\hat{F}_{ji}$ *expressed by* (A.7) *is the same as the effect of the operator* $c_j^\dagger f_{ji} c_i$. This allows us to express the general one-particle operator in terms of creation and annihilation operators. Summing over the one-particle matrix elements, we may make the identification

$$\boxed{\hat{F}^{(1)} = \sum_{j,i} c_j^\dagger f_{ji} c_i} \tag{A.8}$$

for any one-particle operator $\hat{F}^{(1)}$. For instance, if we choose to use basis states of definite momentum the kinetic-energy matrix is diagonal, and the corresponding operator is just

$$\sum_{k,\sigma} c_{k,\sigma}^\dagger c_{k,\sigma} \epsilon_k = \sum_{k,\sigma} \hat{n}_{k,\sigma} \epsilon_k \tag{A.9}$$

where ϵ_k is the one-particle kinetic energy $\hbar^2 k^2 / 2m_e$. Similar results apply to two-particle operators. A general two-particle operator such as the total

mutual energy of all pairs of particles due to their Coulomb interaction may be identified as

$$\boxed{\hat{F}^{(2)} = \frac{1}{2}\sum_{ij,kl} c_i^\dagger c_j^\dagger f_{ij,kl} c_l c_k} \tag{A.10}$$

where $f_{ij,kl}$ is the two-particle matrix element for the simultaneous scattering of a pair of particles in which $k \to i$ and $l \to j$. The factor of $\frac{1}{2}$ avoids counting the starting state twice. Note carefully the orders of the operators in (A.8) and (A.10).

Having written all our states and operators in terms of c_i and $c_i^\dagger$, we have a compact formalism for handling all many-body problems. We may forget about the Slater determinants. All calculations are done simply by using the operator algebraic relations described in Section A.2. The negative signs associated with the antisymmetry of fermions appear automatically because the operators anticommute.

A.5 Localized operators

In many problems it is appropriate to work with the annihilation and creation operators for states of definite momentum $c_{k,\sigma}$ and $c_{k,\sigma}^\dagger$. It is, however, sometimes convenient to work with their Fourier transforms, defined as

$$\begin{aligned}\psi_\sigma(\boldsymbol{r}) &= \sum_k c_{k,\sigma} \frac{\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}}{V^{\frac{1}{2}}} \\ \psi_\sigma^\dagger(\mathbf{r}) &= \sum_k c_{k,\sigma}^\dagger \frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}}{V^{\frac{1}{2}}}\end{aligned} \tag{A.11}$$

where V is the volume of the system. $\psi_\sigma(\boldsymbol{r})$ and $\psi_\sigma^\dagger(\boldsymbol{r})$ are annihilation and creation operators for δ-function one-particle states; they annihilate and create particles at position $\boldsymbol{r}$ with spin σ. It is easy to see from the definitions that for different values of $\boldsymbol{r}$ or σ they anticommute. For particles of the same spin we find that

$$\{\psi_\sigma(\boldsymbol{r}), \psi_\sigma^\dagger(\mathbf{r}')\} = \delta(\boldsymbol{r} - \boldsymbol{r}') \tag{A.12}$$

where $\delta(\boldsymbol{r})$ is a three-dimensional δ-function.

The one- and two-particle operators may be expressed in terms of these localized operators. For instance, the general spin-independent one-particle

operator becomes

$$\boxed{\hat{F}^{(1)} = \sum_\sigma \int \psi_\sigma^\dagger(\boldsymbol{r}) \hat{f}(\boldsymbol{r}) \psi_\sigma(\boldsymbol{r})\, \mathrm{d}^3 r} \tag{A.13}$$

where $\hat{f}$ acts on the $\boldsymbol{r}$ coordinates of the operator $\psi_\sigma(\boldsymbol{r})$.

It is worth commenting on the form of this result. It looks the same as the expression for the expectation value of $\hat{f}$ for a single particle, except that the wavefunction ψ and its complex conjugate ψ^* have been replaced by the operators ψ and $\psi^\dagger$. This is no accident. These localized operators may be regarded as what we get if we *treat the Schrödinger wavefunction ψ itself as an operator*—hence the name *second quantization*—chosen in such a way as to make the eigenvalues of particle number integers. In the same way, the operators c and $c^\dagger$ which appear in (A.8) and (A.10) may be regarded as *operator forms of the state amplitudes* c and c^* of matrix mechanics. Just as the use of energy and other operators in Schrödinger's equation (first quantization) leads to the correct quantization of energy etc, so the representation of ψ itself by an operator (second quantization) leads to the correct quantization of particle number.

A.6 Application to bosons

Although the details of the calculation are different for bosons, the results are very similar, with commutation where we had anticommutation for fermions. We now have no exclusion principle, so there is no limit on the occupation of any state. The basis states of definite occupation are symmetrized product functions such as

$$\begin{aligned}\psi(n_1, n_2, \ldots) &= \psi(0,2,0,0,1,0,1,0,0,\ldots) \\ &= \sqrt{\frac{n_1! n_2! \ldots}{N!}} \sum_{\text{permutations}} \phi_2(a)\phi_2(b)\phi_5(c)\phi_7(d)\end{aligned} \tag{A.14}$$

where the sum is taken over all permutations of particles amongst the occupied states. (In this example we have four identical bosons, two in state 2, one in state 5 and one in state 7.) We define c_i as removing a particle from state i and also multiplying by $\sqrt{n_i}$, and we define $c_i^\dagger$ as adding a particle to state i and also multiplying by $\sqrt{n_i + 1}$. With these definitions it turns out that expressions for general operators such as (A.8), (A.10) and (A.13) are all unchanged. The commutation rules are different,

however. We find that the operators for different states now *commute*; (A.4) is replaced by

$$c_i^\dagger c_i = \hat{n}_i$$
$$c_i c_i^\dagger = \hat{n}_i + 1 \qquad \text{(A.15)}$$

and (A.5) is replaced by

$$[c_i, c_j^\dagger] = \delta_{ij} \qquad \text{(A.16)}$$

where $[c_i, c_j^\dagger]$ is the *commutator* $(c_i c_j^\dagger - c_j^\dagger c_i)$.

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