8.3: Multiparticle Systems

Leaving several other problems on two-particle systems for the reader's exercise, let me proceed to the discussion of systems with $N > 2$ indistinguishable particles, whose list notably includes atoms, molecules, and condensed-matter systems. In this case, Eq. (7) for fermions is generalized as

$$\hat{\mathcal{P}}_{kk'} |\alpha_-\rangle = -|\alpha_-\rangle, \text{for all } k, k' = 1, 2, \ldots, N, \tag{8.3.1}$$

where the operator $\hat{P}_{kk}$ permutes particles with numbers k and k '. As a result, for systems with nondirectly-interacting fermions, the Pauli principle forbids any state in which any two particles have similar single-particle wavefunctions. Nevertheless, it permits two fermions to have similar orbital wavefunctions, provided that their spins are in the singlet state (18), because this satisfies the permutation requirement (55). This fact is of paramount importance for the ground state of the systems whose Hamiltonians do not depend on spin because it allows the fermions to be in their orbital singleparticle ground states, with two electrons of the spin singlet sharing the same orbital state. Hence, for the limited (but very important!) goal of finding ground-state energies of multi-fermion systems with negligible direct interaction, we may ignore the actual singlet spin structure, and reduce the Pauli exclusion principle to the simple picture of single-particle orbital energy levels, each "occupied with two fermions".

As a very simple example, let us find the ground energy of five fermions, confined in a hardwall, cubic-shaped 3D volume of side a, ignoring their direct interaction. From Sec. 1.7, we know the single-particle energy spectrum of the system:

$$\varepsilon_{n_x,n_y,n_z} = \varepsilon_0 \left(n_x^2 + n_y^2 + n_z^2\right), \quad \text{with } \varepsilon_0 \equiv \frac{\pi^2\hbar^2}{2ma^2}, \quad \text{and } n_x, n_y, n_z = 1, 2, \ldots \tag{8.3.2}$$

so that the lowest-energy states are:

- one ground state with $\{n_x, n_y, n_z\} = \{1, 1, 1\}$, and energy $\varepsilon_{111} = \left(1^2 + 1^2 + 1^2\right)\varepsilon_0 = 3\varepsilon_0$, and
- three excited states, with $\{n_x, n_y, n_z\}$ equal to either $\{2, 1, 1\}$, or $\{1, 2, 1\}$, or $\{1, 1, 2\}$, with equal energies $\varepsilon_{211} = \varepsilon_{121} = \varepsilon_{112} = \left(2^2 + 1^2 + 1^2\right)\varepsilon_0 = 6\varepsilon_0$.

According to the above simple formulation of the Pauli principle, each of these orbital energy levels can accommodate up to two fermions. Hence the lowest-energy (ground) state of the five-fermion system is achieved by placing two of them on the ground level $\varepsilon_{111} = 3\varepsilon_0$, and the remaining three particles, in any of the degenerate "excited" states of energy $6\varepsilon_0$, so that the ground-state energy of the system is

$$E_g = 2 \times 3\varepsilon_0 + 3 \times 6\varepsilon_0 \equiv 24\varepsilon_0 \equiv \frac{12\pi^2\hbar^2}{ma^2}. \tag{8.3.3}$$

Moreover, in many cases, relatively weak interaction between fermions does not blow up such a simple quantum state classification scheme qualitatively, and the Pauli principle allows tracing the order of single-particle state filling. This is exactly the simple approach that has been used in our discussion of atoms in Sec. 3.7. Unfortunately, it does not allow for a more specific characterization of the ground states of most atoms, in particular the evaluation of the corresponding values of the quantum numbers S, L, and J that characterize the net angular momenta of the atom, and hence its response to an external magnetic field. These numbers are defined by relations similar to Eqs. (48), each for the corresponding vector operator of the net angular momenta:

$$\hat{\mathbf{S}} \equiv \sum_{k=1}^{N} \hat{\mathbf{s}}_k, \quad \hat{\mathbf{L}} \equiv \sum_{k=1}^{N} \hat{\mathbf{l}}_k, \quad \hat{\mathbf{J}} \equiv \sum_{k=1}^{N} \hat{\mathbf{j}}_k; \tag{8.3.4}$$

note that these definitions are consistent with Eq. (5.170) applied both to the angular momenta $\mathbf{s}_k$, $\mathbf{l}_k$, and $\mathbf{j}_k$ of each particle, and to the full vectors $\mathbf{S}$, $\mathbf{L}$, and $\mathbf{J}$. When the numbers S, L, and J for a state are known, they are traditionally recorded in the form of the so-called Russell-Saunders symbols: [20]

$$^{2S+1}\mathscr{L}_J \tag{8.3.5}$$

where S and J are the corresponding values of these quantum numbers, while $\mathscr{L}$ is a capital letter, encoding the quantum number L - via the same spectroscopic notation as for single particles (see Sec. 3.6): $\mathscr{L} = S$ for $L = 0$, $\mathscr{L} = P$ for $L = 1$, $\mathscr{L} = D$ for $L = 2$, etc. (The reason why the front superscript of the Russel-Saunders symbol lists $2S + 1$ rather than just S, is that according to the last of Eqs. (48), it shows the number of possible values of the quantum number M_S, which characterizes the state's spin degeneracy, and is called its multiplicity.)

For example, for the simplest, hydrogen atom $(Z=1)$, with its single electron in the ground $1s$ state, $L=l=0, S=s=1/2$, and $J=S=1/2$, so that its Russell-Saunders symbol is $2S_{1/2}$. Next, the discussion of the helium atom $(Z=2)$ in the previous section has shown that in its ground state $L=0$ (because of the $1s$ orbital state of both electrons), and $S=0$ (because of the singlet spin state), so that the total angular momentum also vanishes: $J=0$. As a result, the Russell-Saunders symbol is ${}^1S_0$. The structure of the next atom, lithium $(Z=3)$ is also easy to predict, because, as was discussed in Sec. 3.7, its ground-state electron configuration is $1s^2 2s^1$, i.e. includes two electrons in the "helium shell", i.e. on the $1s$ orbitals (now we know that they are actually in a singlet spin state), and one electron in the $2s$ state, of higher energy, also with zero orbital momentum, $l=0$. As a result, the total L in this state is evidently equal to 0, and S is equal to $1/2$, so that $J=1/2$, meaning that the Russell-Saunders symbol of lithium is ${}^2P_{1/2}$. Even in the next atom, beryllium $(Z=4)$, with the ground state configuration $1s^2 2s^2$, the symbol is readily predictable, because none of its electrons has non-zero orbital momentum, giving $L=0$. Also, each electron pair is in the singlet spin state, i.e. we have $S=0$, so that $J=0$ - the quantum number set described by the Russell-Saunders symbol ${}^1S_0$ - just as for helium.

However, for the next, boron atom $(Z=5)$, with its ground-state electron configuration $1s^2 2s^2 2p^1$ (see, e.g., Fig. 3.24), there is no obvious way to predict the result. Indeed, this atom has two pairs of electrons, with opposite spins, on its two lowest s-orbitals, giving zero contributions to the net S, L, and J. Hence these total quantum numbers may be only contributed by the last, fifth electron with $s=1/2$ and $l=1$, giving $S=1/2, L=1$. As was discussed in Sec. 5.7 for the single-particle case, the vector addition of the angular momenta $\mathbf{S}$ and $\mathbf{L}$ enables two values of the quantum number J : either $L+S=3/2$ or $L-S=1/2$. Experiment shows that the difference between the energies of these two states is very small $(\sim 2$ meV), so that at room temperature (with $k_{\mathrm{B}}T \approx 26\mathrm{meV}$) they are both occupied, with the genuine ground state having $J=1/2$, so that its Russell-Saunders symbol is ${}^2P_{1/2}$.

Such energy differences, which become larger for heavier atoms, are determined both by the Coulomb and spin-orbit [21] interactions between the electrons. Their quantitative analysis is rather involved (see below), but the results tend to follow simple phenomenological Hund rules, with the following hierarchy:

Rule 1. For a given electron configuration, the ground state has the largest possible S, and hence the largest multiplicity $2S+1$.

Rule 2. For a given S, the ground state has the largest possible L.

Rule 3. For given S \text { and } L, J \text { has its smallest possible value, }|L-S| \text {, if the given sub-shell }\{n, l\}\) is filled not more than by half, while in the opposite case, J has its largest possible value, $L+S$.

Let us see how these rules work for the boron atom we have just discussed. For it, the Hund Rules 1 and 2 are satisfied automatically, while the sub-shell $\{n=2, l=1\}$, which can house up to $2\times(2l+1)=6$ electrons, is filled with just one $2p$ electron, i.e. by less than a half of the maximum value. As a result, the Hund Rule 3 predicts the ground state's value $J=1/2$, in agreement with experiment.

Generally, for lighter atoms, the Hund rules are well obeyed. However, the lower down the Hund rule hierarchy, the less "powerful" the rules are, i.e. the more often they are violated in heavier atoms.

Now let us discuss possible approaches to a quantitative theory of multiparticle systems - not only atoms. As was discussed in Sec. 1, if fermions do not interact directly, the stationary states of the system have to be the antisymmetric eigenstates of the permutation operator, i.e. satisfy Eq. (55). To understand how such states may be formed from the single-electron ones, let us return for a minute to the case of two electrons, and rewrite Eq. (11) in the following compact form:

$$\begin{array}{c} \text{state 1 state 2} \\ \downarrow\downarrow \\ |\alpha_-\rangle \equiv \frac{1}{\sqrt{2}}\left(|\beta\rangle\otimes|\beta'\rangle - |\beta'\rangle\otimes|\beta\rangle\right) \equiv \frac{1}{\sqrt{2}}\left\|\begin{array}{ll} |\beta\rangle & |\beta'\rangle| \\ |\beta\rangle & |\beta'\rangle| \end{array}\right\rangle \begin{array}{l} \\ \leftarrow \text{ particle number 1,} \\ \leftarrow \text{ particle number 2,} \end{array} \end{array}$$

where the direct product signs are just implied. In this way, the Pauli principle is mapped on the wellknown property of matrix determinants: if any of two columns of a matrix coincide, its determinant vanishes. This Slater determinant approach [22] may be readily generalized to N fermions occupying any N (not necessarily the lowest-energy) single-particle states β, β', β', etc:

$$|\alpha_-\rangle = \frac{1}{(N!)^{1/2}} \begin{array}{c} \text{state list} \rightarrow \\ \begin{array}{cccc} \beta\rangle & |\beta'\rangle & |\beta''\rangle & \dots \\ \beta\rangle & |\beta'\rangle & |\beta''\rangle & \dots \\ \beta\rangle & |\beta'\rangle & |\beta''\rangle & \dots \\ \dots & \dots & \dots & \dots \end{array} \end{array} \begin{array}{l} \\ \\ \\ \\ \text{particle} \\ \\ \\ \\ \underbrace{\qquad\qquad\qquad\qquad}_{N} \end{array} \tag{8.3.6}$$

The Slater determinant form is extremely nice and compact - in comparison with direct writing of a sum of $N!$ products, each of N ket factors. However, there are two major problems with using it for practical calculations:

(i) For the calculation of any bra-ket product (say, within the perturbation theory) we still need to spell out each bra- and ket-vector as a sum of component terms. Even for a limited number of electrons (say $N \sim 10^2$ in a typical atom), the number $N! \sim 10^{160}$ of terms in such a sum is impracticably large for any analytical or numerical calculation.

(ii) In the case of interacting fermions, the Slater determinant does not describe the eigenvectors of the system; rather the stationary state is a superposition of such basis functions, i.e. of the Slater determinants - each for a specific selection of N states from the full set of single-particle states – that is generally larger than N.

For atoms and simple molecules, whose filled-shell electrons may be excluded from an explicit analysis (by describing their effects, approximately, with effective pseudo-potentials), the effective number N may be reduced to a smaller number N_{ef} of the order of 10 , so that $N_{\text{ef}}! < 10^6$, and the Slater determinants may be used for numerical calculations - for example, in the Hartree-Fock theory - see the next section. However, for condensed-matter systems, such as metals and semiconductors, with the number of free electrons is of the order of 10^{23} per cm^3, this approach is generally unacceptable, though with some smart tricks (such as using the crystal's periodicity) it may be still used for some approximate (also mostly numerical) calculations.

These challenges make the development of a more general theory that would not use particle numbers (which are superficial for indistinguishable particles to start with) a must for getting any final analytical results for multiparticle systems. The most effective formalism for this purpose, which avoids particle numbering at all, is called the second quantization. [23] Actually, we have already discussed a particular version of this formalism, for the case of the 1D harmonic oscillator, in Sec. 5.4. As a reminder, after the definition (5.65) of the "creation" and "annihilation" operators via those of the particle's coordinate and momentum, we have derived their key properties (5.89),

$$\hat{a}|n\rangle = n^{1/2}|n-1\rangle, \quad \hat{a}^\dagger|n\rangle = (n+1)^{1/2}|n+1\rangle, \tag{8.3.7}$$

where n are the stationary (Fock) states of the oscillator. This property allows an interpretation of the operators' actions as the creation/annihilation of a single excitation with the energy $\hbar\omega_0$ - thus justifying the operator names. In the next chapter, we will show that such excitation of an electromagnetic field mode may be interpreted as a massless boson with $s = 1$, called the photon.

In order to generalize this approach to arbitrary bosons, not appealing to a specific system, we may use relations similar to Eq. (61) to define the creation and annihilation operators. The definitions look simple in the language of the so-called Dirac states, described by ket-vectors

$$|N_1, N_2, \dots N_j, \dots\rangle, \tag{8.3.8}$$

where N_j is the state occupancy, i.e. the number of bosons in the single-particle state j. Let me emphasize that here the indices $1, 2, \dots j, \dots$ number single-particle states (including their spin parts) rather than particles. Thus the very notion of an individual particle's number is completely (and for indistinguishable particles, very relevantly) absent from this formalism. Generally, the set of singleparticle states participating in the Dirac state may be selected arbitrarily, provided that it is full and orthonormal in the sense

$$\left\langle N_1', N_2' \dots, N_j', \dots \mid N_1, N_2 \dots, N_j, \dots \right\rangle = \delta_{N_1 N_1'} \delta_{N_2 N_2'} \dots \delta_{N_j N'_j} \dots \tag{8.3.9}$$

though for systems of non- (or weakly) interacting bosons, using the stationary states of individual particles in the system under analysis is almost always the best choice.

Now we can define the particle annihilation operator as follows:

$$\hat{a}_j \, |N_1, N_2, \dots N_j, \dots\rangle \equiv N_j^{1/2} \, |N_1, N_2, \dots N_j - 1, \dots\rangle \tag{8.3.10}$$

Note that the pre-ket coefficient, similar to that in the first of Eqs. (61), guarantees that any attempt to annihilate a particle in an initially unpopulated state gives the non-existing ("null") state:

$$\hat{a}_j \left| N_1, N_2, \ldots 0_j, \ldots \right\rangle = 0, \tag{8.3.11}$$

where the symbol 0_j means zero occupancy of the j^{th} state. According to Eq. (63), an equivalent way to write Eq. (64) is

$$\left\langle N_1', N_2', \ldots, N_j', \ldots \left| \hat{a}_j \right| \cdot N_1, N_2, .., N_j, \ldots \right\rangle = N_j^{1/2} \delta_{N_1 N_1'} \delta_{N_2 N_2'} \ldots \delta_{N_j', N_j - 1} \ldots \tag{8.3.12}$$

According to the general Eq. (4.65), the matrix element of the Hermitian conjugate operator $\hat{a}_j^\dagger$ is

$$\begin{aligned} &\left\langle N_1', N_2', \ldots, N_j', \ldots \left| \hat{a}_j^\dagger \right| N_1, N_2, \ldots N_j, \ldots \right\rangle = \left\langle N_1, N_2, \ldots, N_j, \ldots \left| \hat{a}_j \right| N_1', N_2', \ldots, N_j', \ldots \right\rangle^* \\ &= \left\langle N_1, N_2, \ldots, N_j, \ldots \left| \left(N_j' \right)^{1/2} \right| N_1', N_2', \ldots, N_j' - 1, \ldots \right\rangle = \left(N_j' \right)^{1/2} \delta_{N_1 N_1'} \delta_{N_2 N_2'} \ldots \delta_{N_j, N' - 1} \ldots \\ &= \left(N_j + 1 \right)^{1/2} \delta_{N_1 N_1'} \delta_{N_2 N_2'} \ldots \delta_{N_j + 1, N_j'} \ldots \end{aligned}$$

meaning that

$$\hat{a}_j^\dagger \left| N_1, N_2, \ldots, N_j, \ldots \right\rangle = \left(N_j + 1 \right)^{1/2} \left| N_1, N_2, \ldots, N_j + 1, \ldots \right\rangle \tag{8.3.13}$$

in total compliance with the second of Eqs. (61). In particular, this particle creation operator allows the description of the generation of a single particle from the vacuum (not null!) state $|0, 0, \ldots\rangle$:

$$\hat{a}_j^\dagger \left| 0, 0, \ldots, 0_j, \ldots, 0 \right\rangle = \left| 0, 0, \ldots, 1_j, \ldots 0 \right\rangle, \tag{8.3.14}$$

and hence a product of such operators may create, from the vacuum, a multiparticle state with an arbitrary set of occupancies: [24]

$$\underbrace{\hat{a}_1^\dagger \hat{a}_1^\dagger \ldots \hat{a}_1^\dagger}_{N_1 \text{ times}} \underbrace{\hat{a}_2^\dagger \hat{a}_2^\dagger \ldots \hat{a}_2^\dagger}_{N_2 \text{ times}} \ldots \left| 0, 0, \ldots \right\rangle = \left(N_1! N_2! \ldots \right)^{1/2} \left| N_1, N_2, \ldots \right\rangle. \tag{8.3.15}$$

Next, combining Eqs. (64) and (68), we get

$$\hat{a}_j^\dagger \hat{a}_j \left| N_1, N_2, \ldots N_j, \ldots \right\rangle = N_j \left| N_1, N_2, \ldots, N_j, \ldots \right\rangle, \tag{8.3.16}$$

so that, just as for the particular case of harmonic oscillator excitations, the operator

$$\hat{N}_j \equiv \hat{a}_j^\dagger \hat{a}_j \tag{8.3.17}$$

"counts" the number of particles in the j^{th} single-particle state, while preserving the whole multiparticle state. Acting on a state by the creation-annihilation operators in the reverse order, we get

$$\hat{a}_j \hat{a}_j^\dagger \left| N_1, N_2, \ldots, N_j, \ldots \right\rangle = \left(N_j + 1 \right) \left| N_1, N_2, \ldots, N_j, \ldots \right\rangle. \tag{8.3.18}$$

Eqs. (71) and (73) show that for any state of a multiparticle system (which may be represented as a linear superposition of Dirac states with all possible sets of numbers N_j), we may write

$$\hat{a}_j \hat{a}_j^\dagger - \hat{a}_j^\dagger \hat{a}_j \equiv \left[\hat{a}_j, \hat{a}_j^\dagger \right] = \hat{I}, \tag{8.3.19}$$

again in agreement with what we had for the 1D oscillator – cf. Eq. (5.68). According to Eqs. (63), (64), and (68), the creation and annihilation operators corresponding to different single-particle states do commute, so that Eq. (74) may be generalized as

$$\left[\hat{a}_j, \hat{a}_{j'}^\dagger \right] = \hat{I} \, \delta_{ij'}, \tag{8.3.20}$$

while the similar operators commute, regardless of which states do they act upon:

$$\left[\hat{a}_j^\dagger, \hat{a}_{j'}^\dagger \right] = \left[\hat{a}_j, \hat{a}_{j'} \right] = \hat{0}. \tag{8.3.21}$$

commutation relations

As was mentioned earlier, a major challenge in the Dirac approach is to rewrite the Hamiltonian of a multiparticle system, that naturally carries particle numbers k (see, e.g., Eq. (22) for $k = 1, 2$), in the second quantization language, in which there are no these numbers. Let us start with single-particle components of such Hamiltonians, i.e. operators of the type

$$\hat{F} = \sum_{k=1}^{N} \hat{f}_k. \tag{8.3.22}$$

where all N operators $\hat{f}_k$ are similar, besides that each of them acts on one specific $\left(k^{\text{th}}\right)$ particle, and N is the total number of particles in the system, which is evidently equal to the sum of single-particle state occupancies:

$$N = \sum_j N_j. \tag{8.3.23}$$

The most important examples of such operators are the kinetic energy of N similar single particles, and their potential energy in an external field:

$$\hat{T} = \sum_{k=1}^{N} \frac{\hat{p}_k^2}{2m}, \quad \hat{U} = \sum_{k=1}^{N} \hat{u}\left(\mathbf{r}_k\right). \tag{8.3.24}$$

For bosons, instead of the Slater determinant (60), we have to write a similar expression, but without the sign alternation at permutations:

$$|N_1, \ldots N_j, \ldots\rangle = \left(\frac{N_1! \ldots N_j! \ldots}{N!}\right)^{1/2} \sum_P |\underbrace{\ldots \beta\beta'\beta'' \ldots}_{N \text{ operands}}\rangle, \tag{8.3.25}$$

sometimes called the permanent. Note again that the left-hand side of this relation is written in the Dirac notation (that does not use particle numbering), while on its right-hand side, just in relations of Secs. 1 and 2 , the particle numbers are coded with the positions of the single-particle states inside the state vectors, and the summation is over all different permutations of the states in the ket - cf. Eq. (10). (According to the basic combinatorics, [25] there are $N!/\left(N_1! \ldots N_j! \ldots\right)$ such permutations, so that the front coefficient in Eq. (80) ensures the normalization of the Dirac state, provided that the single-particle states $\beta, \beta', \ldots$ are normalized.) Let us use Eq. (80) to spell out the following matrix element for a system with $(N-1)$ particles:

$$\begin{aligned}
&\left\langle \ldots N_j, \ldots N_{j'} - 1, \ldots \middle| \hat{F} \middle| \ldots N_j - 1, \ldots N_{j'}, \ldots \right\rangle \\
&= \frac{N_1! \ldots (N_j - 1)! \ldots \left(N_{j'} - 1\right)! \ldots}{(N-1)!} \left(N_j N_{j'}\right)^{1/2} \sum_{P\langle N-1|} \sum_{P|N-1\rangle} \left\langle \ldots \beta\beta'\beta'' \ldots \middle| \sum_{k=1}^{N-1} \hat{f}_k \middle| \ldots \beta\beta'\beta'' \ldots \right\rangle
\end{aligned}$$

where all non-specified occupation numbers in the corresponding positions of the bra- and ket-vectors are equal to each other. Each single-particle operator $\hat{f}_k$ participating in the operator sum, acts on the bra- and ket-vectors of states only in one $\left(k^{\text{th}}\right)$ position, giving the following result, independent of the position number:

$$\left\langle \beta_j|_{\text{in}}\, k^{\text{th}} \text{ position } \hat{f}_k \mid \beta_{j'} \right\rangle_{\text{in}} k^{\text{th}} \text{ position } = \left\langle \beta_j | \hat{f} | \beta_{j'} \right\rangle \equiv f_{jj'}. \tag{8.3.26}$$

Since in both permutation sets participating in Eq. (81), with $(N-1)$ state vectors each, all positions are equivalent, we can fix the position (say, take the first one) and replace the sum over k with the multiplication by of the bracket by $(N-1)$. The fraction of permutations with the necessary bra-vector (with number j) in that position is $N_j/(N-1)$, while that with the necessary ket-vector (with number j ') in the same position is $N_j/(N-1)$. As the result, the permutation sum in Eq. (81) reduces to

$$(N-1) \frac{N_j}{N-1} \frac{N_{j'}}{N-1} f_{jj'} \sum_{P\langle N-2|P|N-2\rangle} \sum \langle \ldots \beta\beta'\beta'' \ldots | \ldots \beta\beta'\beta'' \ldots \rangle \tag{8.3.27}$$

where our specific position k is now excluded from both the bra- and ket-vector permutations. Each of these permutations now includes only $(N_j - 1)$ states j and $(N_j, -1)$ states j ', so that, using the state orthonormality, we finally arrive at a very simple result:

$$\left\langle \ldots N_j, \ldots N_{j'}-1, \ldots \left|\hat{F}\right| \ldots N_j-1, \ldots N_{j'}, \ldots \right\rangle$$
$$= \frac{N_1! \ldots (N_j-1)! \ldots \left(N_{j'}-1\right)! \ldots}{(N-1)!} \left(N_j N_{j'}\right)^{1/2} (N-1) \frac{N_j}{N-1} \frac{N_{j'}}{N-1} f_{ij'} \frac{(N-2)!}{N_1! \ldots (N_j-1)! \ldots \left(N_{j'}-1\right)! \ldots}$$
$$\equiv \left(N_j N_{j'}\right)^{1/2} f_{ij'}$$

On the other hand, let us calculate matrix elements of the following operator:

$$\sum_{j,j'} f_{ij'} \hat{a}_j^\dagger \hat{a}_{j'} \tag{8.3.28}$$

A direct application of Eqs. (64) and (68) shows that the only non-vanishing of the elements are

$$\left\langle \ldots N_j, \ldots N_{j'}-1, \ldots \left| f_{ij'} \hat{a}_j^\dagger \hat{a}_{j'} \right| \ldots N_j-1, \ldots, N_{j'}, \ldots \right\rangle = \left(N_j N_{j'}\right)^{1/2} f_{jj'}. \tag{8.3.29}$$

But this is exactly the last form of Eq. (84), so that in the basis of Dirac states, the operator (77) may be single- represented as

$$(8.87) \tag{8.3.30}$$

$$\hat{F} = \sum_{j,j'} f_{jj'} \hat{a}_j^\dagger \hat{a}_{j'} \tag{8.3.31}$$

This beautifully simple relation is the key formula of the second quantization theory, and is essentially the Dirac-language analog of Eq. (4.59) of the single-particle quantum mechanics. Each term of the sum (87) may be described by a very simple mnemonic rule: for each pair of single-particle states j and j ', annihilate a particle in the state j ', create one in the state j, and weigh the result with the corresponding single-particle matrix element. One of the corollaries of Eq. (87) is that the expectation value of an operator whose eigenstates coincide with the Dirac states is

$$\langle F \rangle \equiv \left\langle \ldots N_j, \ldots \left|\hat{F}\right| \ldots N_j, \ldots \right\rangle = \sum_j f_{ij} N_j \tag{8.3.32}$$

with an evident physical interpretation as the sum of single-particle expectation values over all states, weighed by the occupancy of each state.

Proceeding to fermions, which have to obey the Pauli principle, we immediately notice that any occupation number N_j may only take two values, 0 or 1 . To account for that, and also make the key relation (87) valid for fermions as well, the creation-annihilation operators are defined by the following relations:

$$\hat{a}_j \left|N_1, N_2, \ldots, 0_j, \ldots\right\rangle = 0, \quad \hat{a}_j \left|N_1, N_2, \ldots, 1_j, \ldots\right\rangle = (-1)^{\Sigma(1,j-1)} \left|N_1, N_2, \ldots, 0_j, \ldots\right\rangle$$
$$\hat{a}_j^\dagger \left|N_1, N_2, \ldots, 0_j, \ldots\right\rangle = (-1)^{\Sigma(1,j-1)} \left|N_1, N_2, \ldots, 1_j, \ldots\right\rangle, \quad \hat{a}_j^\dagger \left|N_1, N_2, \ldots, 1_j, \ldots\right\rangle = 0$$

where the symbol $\Sigma\left(J, J'\right)$ means the sum of all occupancy numbers in the states with numbers from J to J', including the border points:

$$\Sigma\left(J, J'\right) \equiv \sum_{j=J}^{J'} N_j, \tag{8.3.33}$$

so that the sum participating in Eqs. (89)-(90) is the total occupancy of all states with the numbers below j. (The states are supposed to be numbered in a fixed albeit arbitrary order.) As a result, these relations may be conveniently summarized in the following verbal form: if an operator replaces the j^{th} state's occupancy with the opposite one (either 1 with 0 , or vice versa), it also changes the sign before the result if (and only if) the total number of particles in the states with j ' $< j$ is odd.

Let us use this (perhaps somewhat counter-intuitive) sign alternation rule to spell out the ketvector $|11\rangle$ of a completely filled two-state system, formed from the vacuum state $|00\rangle$ in two different ways. If we start by creating a fermion in the state 1 , we get

$$\hat{a}_1^\dagger |0,0\rangle = (-1)^0 |1,0\rangle \equiv |1,0\rangle, \quad \hat{a}_2^\dagger \hat{a}_1^\dagger |0,0\rangle = \hat{a}_2^\dagger |1,0\rangle = (-1)^1 |1,1\rangle \equiv -|1,1\rangle, \tag{8.3.34}$$

while if the operator order is different, the result is

$$\hat{a}_2^\dagger |0,0\rangle = (-1)^0 |0,1\rangle \equiv |0,1\rangle, \quad \hat{a}_1^\dagger \hat{a}_2^\dagger |0,0\rangle = \hat{a}_1^\dagger |0,1\rangle = (-1)^0 |1,1\rangle \equiv |1,1\rangle, \tag{8.3.35}$$

so that

$$\left(\hat{a}_1^\dagger \hat{a}_2^\dagger + \hat{a}_2^\dagger \hat{a}_1^\dagger\right)|0,0\rangle = 0. \tag{8.3.36}$$

Since the action of any of these operator products on any initial state rather than the vacuum one also gives the null ket, we may write the following operator equality:

$$\hat{a}_1^\dagger \hat{a}_2^\dagger + \hat{a}_2^\dagger \hat{a}_1^\dagger \equiv \left\{\hat{a}_1^\dagger, \hat{a}_2^\dagger\right\} = \hat{0}. \tag{8.3.37}$$

It is straightforward to check that this result is valid for Dirac vectors of an arbitrary length, and does not depend on the occupancy of other states, so that we may generalize it as

$$\left\{\hat{a}_j^\dagger, \hat{a}_{j'}^\dagger\right\} = \left\{\hat{a}_j, \hat{a}_{j'}\right\} = \hat{0} \tag{8.3.38}$$

$$\left\{\hat{a}_j, \hat{a}_{j'}^\dagger\right\} = \hat{I}\,\delta_{jj'} \tag{8.3.39}$$

These equations look very much like Eqs. (75)-(76) for bosons, "only" with the replacement of commutators with anticommutators. Since the core laws of quantum mechanics, including the operator compatibility (Sec. 4.5) and the Heisenberg equation (4.199) of operator evolution in time, involve commutators rather than anticommutators, one might think that all the behavior of bosonic and fermionic multiparticle systems should be dramatically different. However, the difference is not as big as one could expect; indeed, a straightforward check shows that the sign factors in Eqs. (89)-(90) just compensate those in the Slater determinant, and thus make the key relation (87) valid for the fermions as well. (Indeed, this is the very goal of the introduction of these factors.)

To illustrate this fact on the simplest example, let us examine what does the second quantization formalism say about the dynamics of non-interacting particles in the system whose single-particle properties we have discussed repeatedly, namely two nearly-similar potential wells, coupled by tunneling through the separating potential barrier - see, e.g., Figs. 2.21 or 7.4. If the coupling is so small that the states localized in the wells are only weakly perturbed, then in the basis of these states, the single-particle Hamiltonian of the system may be represented by the 2×2 matrix (5.3). With the energy reference selected at the middle between the energies of unperturbed states, the coefficient b vanishes, this matrix is reduced to

$$\mathrm{h} = \mathbf{c}\cdot\boldsymbol{\sigma} \equiv \begin{pmatrix} c_z & c_- \\ c_+ & -c_z \end{pmatrix}, \quad \text{with } c_\pm \equiv c_x \pm i c_y \tag{8.3.40}$$

and its eigenvalues to

$$\varepsilon_\pm = \pm c, \quad \text{with } c \equiv |\mathbf{c}| \equiv \left(c_x^2 + c_y^2 + c_z^2\right)^{1/2}. \tag{8.3.41}$$

Now following the recipe (87), we can use Eq. (97) to represent the Hamiltonian of the whole system of particles in terms of the creation-annihilation operators:

$$\hat{H} = c_z \hat{a}_1^\dagger \hat{a}_1 + c_- \hat{a}_1^\dagger \hat{a}_2 + c_+ \hat{a}_2^\dagger \hat{a}_1 - c_z \hat{a}_2^\dagger \hat{a}_2, \tag{8.3.42}$$

where $\hat{a}_{1,2}^\dagger$ and $\hat{a}_{1,2}$ are the operators of creation and annihilation of a particle in the corresponding potential well. (Again, in the second quantization approach the particles are not numbered at all!) As Eq. (72) shows, the first and the last terms of the right-hand side of Eq. (99) describe the particle energies $\varepsilon_{1,2} = \pm c_z$ in uncoupled wells,

$$c_z \hat{a}_1^\dagger \hat{a}_1 = c_z \hat{N}_1 \equiv \varepsilon_1 \hat{N}_1, \quad -c_z \hat{a}_2^\dagger \hat{a}_2 = -c_z \hat{N}_2 \equiv \varepsilon_2 \hat{N}_2, \tag{8.3.43}$$

while the sum of the middle two terms is the second-quantization description of tunneling between the wells.

Now we can use the general Eq. (4.199) of the Heisenberg picture to spell out the equations of motion of the creation-annihilation operators. For example,

$$i\hbar \dot{\hat{a}}_1 = \left[\hat{a}_1, \hat{H}\right] = c_z\left[\hat{a}_1, \hat{a}_1^\dagger \hat{a}_1\right] + c_-\left[\hat{a}_1, \hat{a}_1^\dagger \hat{a}_2\right] + c_+\left[\hat{a}_1, \hat{a}_2^\dagger \hat{a}_1\right] - c_z\left[\hat{a}_1, \hat{a}_2^\dagger \hat{a}_2\right]. \tag{8.3.44}$$

Since the Bose and Fermi operators satisfy different commutation relations, one could expect the righthand side of this equation to be different for bosons and fermions. However, it is not so. Indeed, all commutators on the right-hand side of Eq. (101) have the following form:

$$\left[\hat{a}_j, \hat{a}^\dagger_{j'}\hat{a}_{j''}\right] \equiv \hat{a}_j\hat{a}^\dagger_{j'}\hat{a}_{j''} - \hat{a}^\dagger_{j'}\hat{a}_{j''}\hat{a}_j. \tag{8.3.45}$$

As Eqs. (74) and (94) show, the first pair product of operators on the right-hand side may be recast as

$$\hat{a}_j\hat{a}^\dagger_{j'} = \hat{I}\,\delta_{jj'} \pm \hat{a}^\dagger_{j'}\hat{a}_j, \tag{8.3.46}$$

where the upper sign pertains to bosons and the lower one to fermions, while according to Eqs. (76) and (95), the very last pair product in Eq. (102) is

$$\hat{a}_{j''}\hat{a}_j = \pm\hat{a}_j\hat{a}_{j''}, \tag{8.3.47}$$

with the same sign convention. Plugging these expressions into Eq. (102), we see that regardless of the particle type, there is a universal (and generally very useful) commutation relation

$$\left[\hat{a}_j, \hat{a}^\dagger_{j'}\hat{a}_{j''}\right] = \hat{a}_{j''}\delta_{jj'}, \tag{8.3.48}$$

valid for both bosons and fermions. As a result, the Heisenberg equation of motion for the operator $\hat{a}_1$, and the equation for $\hat{a}_2$ (which may be obtained absolutely similarly), are also universal:27

$$i\hbar\dot{\hat{a}}_1 = c_z\hat{a}_1 + c_-\hat{a}_2,$$
$$i\hbar\dot{\hat{a}}_2 = c_+\hat{a}_1 - c_z\hat{a}_2.$$

This is a system of two coupled, linear differential equations, which is similar to the equations for the c-number probability amplitudes of single-particle wavefunctions of a two-level system - see, e.g., Eq. (2.201) and the model solution of Problem 4.25. Their general solution is a linear superposition

$$\hat{a}_{1,2}(t) = \sum_{\pm} \hat{\alpha}^{(\pm)}_{1,2}\exp\{\lambda_\pm t\}. \tag{8.3.49}$$

As usual, to find the exponents $\lambda_\pm$, it is sufficient to plug in a particular solution $\hat{a}_{1,2}(t) = \hat{\alpha}_{1,2}\exp\{\lambda t\}$ into Eq. (106) and require that the determinant of the resulting homogeneous, linear system for the "coefficients" (actually, time-independent operators) $\hat{\alpha}_{1,2}$ equals zero. This gives us the following characteristic equation

$$\begin{vmatrix} c_z - i\hbar\lambda & c_- \\ c_+ & -c_z - i\hbar\lambda \end{vmatrix} = 0, \tag{8.3.50}$$

with two roots $\lambda_\pm = \pm i\Omega/2$, where $\Omega \equiv 2c/\hbar - cf$. Eq. (5.20). Now plugging each of the roots, one by one, into the system of equations for $\hat{\alpha}_{1,2}$, we can find these operators, and hence the general solution of system (98) for arbitrary initial conditions.

Let us consider the simple case $c_y = c_z = 0$ (meaning in particular that the wells are exactly aligned, see Fig. 2.21), so that $\hbar\Omega/2 \equiv c = c_x$; then the solution of Eq. (106) is

$$\hat{a}_1(t) = \hat{a}_1(0)\cos\frac{\Omega t}{2} - i\hat{a}_2(0)\sin\frac{\Omega t}{2}, \quad \hat{a}_2(t) = -i\hat{a}_1(0)\sin\frac{\Omega t}{2} + \hat{a}_2(0)\cos\frac{\Omega t}{2}. \tag{8.3.51}$$

Multiplying the first of these relations by its Hermitian conjugate, and ensemble-averaging the result, we get

$$\langle N_1\rangle \equiv \left\langle \hat{a}^\dagger_1(t)\hat{a}_1(t)\right\rangle = \left\langle \hat{a}^\dagger_1(0)\hat{a}_1(0)\right\rangle \cos^2\frac{\Omega t}{2} + \left\langle \hat{a}^\dagger_2(0)\hat{a}_2(0)\right\rangle \sin^2\frac{\Omega t}{2}$$
$$- i\left\langle \hat{a}^\dagger_1(0)\hat{a}_2(0) + \hat{a}^\dagger_2(0)\hat{a}_1(0)\right\rangle \sin\frac{\Omega t}{2}\cos\frac{\Omega t}{2}.$$

Let the initial state of the system be a single Dirac state, i.e. have a definite number of particles in each well; in this case, only the two first terms on the right-hand side of Eq. (110) are different from zero, giving: [28]

$$\langle N_1\rangle = N_1(0)\cos^2\frac{\Omega t}{2} + N_2(0)\sin^2\frac{\Omega t}{2}. \tag{8.3.52}$$

For one particle, initially placed in either well, this gives us our old result (2.181) describing the usual quantum oscillations of the particle between two wells with the frequency Ω. However, Eq. (111) is valid for any set of initial occupancies; let us use this fact. For example, starting from two particles, with initially one particle in each well, we get $\langle N_1\rangle = 1$, regardless of time. So, the occupancies do not oscillate, and no experiment may detect the quantum oscillations, though their frequency Ω is still formally

present in the time evolution equations. This fact may be interpreted as the simultaneous quantum oscillations of two particles between the wells, exactly in anti-phase. For bosons, we can go on to even larger occupancies by preparing the system, for example, in the state with $N_1(0) = N, N_2(0) = 0$. The result (111) says that in this case, we see that the quantum oscillation amplitude increases N-fold; this is a particular manifestation of the general fact that bosons can be (and evolve in time) in the same quantum state. On the other hand, for fermions we cannot increase the initial occupancies beyond 1, so that the largest oscillation amplitude we can get is if we initially fill just one well.

The Dirac approach may be readily generalized to more complex systems. For example, Eq. (99) implies that an arbitrary system of potential wells with weak tunneling coupling between the adjacent wells may be described by the Hamiltonian

$$\hat{H} = \sum_j \varepsilon_j a_j^\dagger \hat{a}_j + \sum_{\{j,j'\}} \delta_{jj'} a_j^\dagger \hat{a}_{j'} + \text{h.c.}, \tag{8.3.53}$$

where the symbol $\{j, j'\}$ means that the second sum is restricted to pairs of next-neighbor wells - see, e.g., Eq. (2.203) and its discussion. Note that this Hamiltonian is still a quadratic form of the creationannihilation operators, so the Heisenberg-picture equations of motion of these operators are still linear, and its exact solutions, though possibly cumbersome, may be studied in detail. Due to this fact, the Hamiltonian (112) is widely used for the study of some phenomena, for example, the very interesting Anderson localization effects, in which a random distribution of the localized-site energies ε_j prevents tunneling particles, within a certain energy range, from spreading to unlimited distances. [29]

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[20] Named after H. Russell and F. Saunders, whose pioneering (circa 1925) processing of experimental spectralline data has established the very idea of vector addition of the electron spins, described by the first of Eqs. (58).

[21] In light atoms, the spin-orbit interaction is so weak that it may be reasonably well described as an interaction of the total momenta $\mathbf{L}$ and $\mathbf{S}$ of the system - the so-called LS (or "Russell-Saunders") coupling. On the other hand, in very heavy atoms, the interaction is effectively between the net momenta $\mathbf{j}_k = \mathbf{l}_k + \mathbf{s}_k$ of the individual electrons - the so-called jj coupling. This is the reason why in such atoms the Hund rule 3 may be violated.

[22] It was suggested in 1929 by John C. Slater.

[23] It was invented (first for photons and then for arbitrary bosons) by P. Dirac in 1927, and then modified in 1928 for fermions by E. Wigner and P. Jordan. Note that the term "second quantization" is rather misleading for the non-relativistic applications we are discussing here, but finds certain justification in the quantum field theory.

[24] The resulting Dirac state is not an eigenstate of every multiparticle Hamiltonian. However, we will see below that for a set of non-interacting particles it is a stationary state, so that the full set of such states may be used as a good basis in perturbation theories of systems of weakly interacting particles.

[25] See, e.g., MA Eq. (2.3).

[26] A by-product of this calculation is proof that the operator defined by Eq. (72) counts the number of particles N_j (now equal to either 1 or 0), just at it does for bosons.

[27] Equations of motion for the creation operators $\hat{a}_{1,2}^\dagger$ are just the Hermitian-conjugates of Eqs. (106), and do not add any new information about the system's dynamics.

[28] For the second well's occupancy, the result is complementary, $N_2(t) = N_1(0) \sin^2 \Omega t + N_2(0) \cos^2 \Omega t$, giving in particular a good sanity check: $N_1(t) + N_2(t) = N_1(0) + N_2(0) =$ const.

[29] For a review of the 1D version of this problem, see, e.g., J. Pendry, *Adv.* Phys. 43,461 (1994).
