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In condensed matter physics we often have to deal with systems of many particles. We can describe such a system starting from the wavefunctions of the single particles $|\psi_k\rangle$, where the particle is in the eigenstate of eigenvalue k of an operator $\hat{K}$. We suppose this set of vectors to be orthonormal. We could initially write the total state vector as the product of the single ones.

$$|\Psi\rangle = \left|\psi_{P[k_1]}\right\rangle \left|\psi_{P[k_2]}\right\rangle \dots \left|\psi_{P[k_N]}\right\rangle \tag{2.1}$$

However, the former expression does not take into account the indistinguishability of quantum particles. In fact, the physics of the system must be invariant under the exchange of two particles. This is possible only if $|\Psi\rangle$ is symmetric or antisymmetric for the exchange of two particles. The former case is true for bosons, the latter for fermions.

In order to satisfy this condition, we have to modify Eq. (2.1). An appropriate linear combination of the products of the single kets, compatible with the symmetry constraints required by Bose and Fermi statistics is given by

$$|\Psi\rangle = |\psi_{k_1}, \psi_{k_2}, \dots, \psi_{k_N}\rangle = \sqrt{\frac{1}{N!}} \sum_P \xi^P \left|\psi_{P[k_1]}\right\rangle \left|\psi_{P[k_2]}\right\rangle \dots \left|\psi_{P[k_N]}\right\rangle \tag{2.2}$$

where the sum is extended to all the $N!$ permutations P of $k_1, k_2, \dots k_N$. $\xi = 1$ for bosons and $\xi = -1$ for fermions, so that for fermions $\xi^P = 1$ for even permutations and $\xi^P = -1$ for odd permutations. This construction assures that the total wavefunction is symmetric for the exchange of two bosons and antisymmetric for the exchange of two fermions. It is important to notice that Eq. (2.2) has an ambiguity in the phase of the final vector. To remove it, we chose the permutation to be even when $k_1 < k_2 < \dots k_N$.

It is useful to compute the product of a base bra and a base ket of two total state vectors.

$$
\begin{aligned}
\langle \psi_{m_1}, \ldots, \psi_{m_N} | \psi_{k_1}, \ldots, \psi_{k_N} \rangle &= \frac{1}{N!} \\
&= \sum_P \sum_{P'} \xi^{P+P'} \left\langle \psi_{P[m_1]} \right| \left\langle \psi_{P[m_2]} \right| \ldots \left\langle \psi_{P[m_N]} \right| \times \left| \psi_{P'[k_1]} \right\rangle \left| \psi_{P'[k_2]} \right\rangle \ldots \left| \psi_{P'[k_N]} \right\rangle \\
&= \sum_{P''} \xi^{P''} \left\langle \psi_{m_1} \middle| \psi_{P''[k_1]} \right\rangle \ldots \left\langle \psi_{m_N} \middle| \psi_{P''[k_N]} \right\rangle \\
&= \begin{vmatrix} \langle \psi_{m_1} | \psi_{k_1} \rangle & \langle \psi_{m_1} | \psi_{k_2} \rangle & \ldots & \langle \psi_{m_1} | \psi_{k_N} \rangle \\ \langle \psi_{m_2} | \psi_{k_2} \rangle & \langle \psi_{m_2} | \psi_{k_2} \rangle & \ldots & \langle \psi_{m_2} | \psi_{k_N} \rangle \\ \ldots & \ldots & \ldots & \ldots \\ \langle \psi_{m_N} | \psi_{k_1} \rangle & \langle \psi_{m_N} | \psi_{k_2} \rangle & \ldots & \langle \psi_{m_N} | \psi_{k_N} \rangle \end{vmatrix}_\xi
\end{aligned}
\tag{2.3}
$$

where $|\cdot|_{\xi=1}$ represents a permanent and $|\cdot|_{\xi=-1}$ a determinant. Given the orthonormality of the single state kets, the only terms of the sum that differ from zero are the ones where

$$P''\{k_1, \ldots, k_N\} = \{m_1, \ldots, m_N\} \tag{2.4}$$

If a state ψ_j appears n_j times, the norm of the state vector will be

$$\langle \psi_{k_1}, \ldots, \psi_{k_N} | \psi_{k_1}, \ldots, \psi_{k_N} \rangle = n_1! n_2! \ldots n_N! \tag{2.5}$$

Thus, the normalized state vector is

$$|\psi_{k_1}, \ldots, \psi_{k_N}\rangle_n = \frac{1}{\sqrt{n_1! n_2! \ldots n_N!}} |\psi_{k_1}, \ldots, \psi_{k_N}\rangle \tag{2.6}$$

Given the indisinguishibility of the particles, a simpler way to describe this state vector is using only the number n_j of particles that are in the state ψ_{k_j}.

$$|n_1, n_2, ...n_i, ...\rangle = |\psi_{k_1}, \ldots, \psi_{k_N}\rangle_n \tag{2.7}$$

where ψ_{k_j} is repeated n_j times. This eliminates the inconvenience of having multiple kets describing the same state as we had before. This representation is called occupation number representation, and the kets are said to be elements of the Fock space.

Two special cases of states in the Fock space are the following. The vacuum state

$$|0, 0, \ldots 0\rangle = |\mathbf{0}\rangle \tag{2.8}$$

is a state with no particles in any single-particle states. The second is

$$|0, 0, \ldots, n_i = 1, \ldots\rangle = |\psi_{k_i}\rangle \tag{2.9}$$

where there is exactly one particle in the k_i state.

2.1.2 Creation and annihilation operators

Now that we have defined the base kets, we can introduce two operators that are used to transform the kets. We define a *creation operator* as

$$\hat{a}_i^\dagger \left|\psi_{k_1}, \psi_{k_2}, \dots\right\rangle = \left|\psi_{k_i}, \psi_{k_1}, \psi_{k_2}, \dots\right\rangle \tag{2.10}$$

Below we show several properties that derive from these definition, but its essential role can be understood applying it to the vacuum state.

$$\hat{a}_i^\dagger \left|\mathbf{0}\right\rangle = \left|\psi_{k_i}\right\rangle \tag{2.11}$$

Its effect is to add a particle in k_i state to the system. It is easy to interpret its adjoint as an *annihilation operator*, in fact

$$1 = \left\langle\psi_{k_i}\middle|\psi_{k_i}\right\rangle = \left\langle\mathbf{0}\right| \hat{a}_i \hat{a}_i^\dagger \left|\mathbf{0}\right\rangle = \left\langle\mathbf{0}\right| \hat{a}_i \left|\psi_{k_i}\right\rangle \tag{2.12}$$

which implies that

$$\hat{a}_i \left|\psi_{k_i}\right\rangle = \left|\mathbf{0}\right\rangle \tag{2.13}$$

We now try to prove these properties on a general base ket. We consider the transition matrix element

$$\begin{aligned}\mathcal{A} &= \left\langle\phi_{m_1}, \dots, \phi_{m_{N-1}}\right| \hat{a}_i \left|\psi_{k_1}, \dots, \psi_{k_N}\right\rangle = \\ &= \left\langle\psi_{k_1}, \dots, \psi_{k_N}\right| \hat{a}_i^\dagger \left|\phi_{m_1}, \dots, \phi_{m_{N-1}}\right\rangle^* = \left\langle\psi_{k_1}, \dots, \psi_{k_N}\middle|\psi_{k_i}, \phi_{m_1}, \dots, \phi_{m_{N-1}}\right\rangle^*\end{aligned} \tag{2.14}$$

using Eq. (2.3)

$$\mathcal{A} = \begin{vmatrix} \left\langle\psi_{k_1}\middle|\psi_{k_i}\right\rangle & \left\langle\psi_{k_1}\middle|\phi_{m_1}\right\rangle & \dots & \left\langle\psi_{k_1}\middle|\phi_{m_{N-1}}\right\rangle \\ \left\langle\psi_{k_2}\middle|\psi_{k_i}\right\rangle & \left\langle\psi_{k_2}\middle|\phi_{m_1}\right\rangle & \dots & \left\langle\psi_{k_2}\middle|\phi_{m_{N-1}}\right\rangle \\ \dots & \dots & \dots & \dots \\ \left\langle\psi_{k_N}\middle|\psi_{k_i}\right\rangle & \left\langle\psi_{k_N}\middle|\phi_{m_1}\right\rangle & \dots & \left\langle\psi_{k_N}\middle|\phi_{m_{N-1}}\right\rangle \end{vmatrix}_\xi^* \tag{2.15}$$

and developing it along the first column

$$\begin{aligned}\mathcal{A} &= \left(\sum_{j=1}^{N} \xi^{j+1} \left\langle\psi_{k_j}\middle|\psi_{k_i}\right\rangle \begin{vmatrix} \left\langle\psi_{k_1}\middle|\phi_{m_1}\right\rangle & \dots & \left\langle\psi_{k_1}\middle|\phi_{m_{N-1}}\right\rangle \\ \left\langle\psi_{k_2}\middle|\phi_{m_1}\right\rangle & \dots & \left\langle\psi_{k_2}\middle|\phi_{m_{N-1}}\right\rangle \\ \dots & (\text{no } \psi_{k_j}) & \dots \\ \left\langle\psi_{k_N}\middle|\phi_{m_1}\right\rangle & \dots & \left\langle\psi_{k_N}\middle|\phi_{m_{N-1}}\right\rangle \end{vmatrix}_\xi\right)^* \\ &= \sum_{j=1}^{N} \xi^{j+1} \left\langle\psi_{k_i}\middle|\psi_{k_j}\right\rangle \left\langle\psi_{k_1}, \dots (\text{no } \psi_{k_j}), \psi_{k_N}\middle|\phi_{m_1}, \dots, \phi_{m_{N-1}}\right\rangle^* \\ &= \sum_{j=1}^{N} \xi^{j+1} \delta_{k_i k_j} \left\langle\phi_{m_1}, \dots, \phi_{m_{N-1}}\middle|\psi_{k_1}, \dots (\text{no } \psi_{k_j}), \psi_{k_N}\right\rangle\end{aligned} \tag{2.16}$$

Confronting it with Eq. (2.14) we conclude

$$\hat{a}_i \left|\psi_{k_1}, \dots, \psi_{k_N}\right\rangle = \sum_{j=1}^{N} \xi^{j+1} \left\langle \psi_{k_i} \middle| \psi_{k_j} \right\rangle \left|\psi_{k_1}, \dots (\text{no } \psi_{k_j}), \psi_{k_N}\right\rangle$$
$$= \sum_{j=1}^{N} \xi^{j+1} \delta_{k_i k_j} \left|\psi_{k_1}, \dots (\text{no } \psi_{k_j}), \psi_{k_N}\right\rangle \quad (2.17)$$

If k_i is not present in $|\psi_{k_1}, \dots, \psi_{k_N}\rangle$, $\delta_{k_i k_j} = 0$ and overall $\hat{a}_i |\psi_{k_1}, \dots, \psi_{k_N}\rangle = 0$. On the other hand, if k_i is included in the ket n times, there will be n_i non-null terms in the sum.

In the case of bosons,

$$\hat{a}_i |\psi_{k_1}, \dots, \psi_{k_N}\rangle = n_i |\psi_{k_1}, \dots (\text{one less } \psi_{k_i}), \psi_{k_N}\rangle \tag{2.18}$$

We can use Eq. (2.7) to express the last relation in the occupation number representation.

$$\hat{a}_i |n_1, n_2, \dots, n_i, \dots\rangle = \hat{a}_i |\psi_{k_1}, \dots, \psi_{k_N}\rangle_n$$
$$= \hat{a}_i \left(\prod_{j=1}^{N} \sqrt{n_j!}\right)^{-1} |\psi_{k_1}, \dots, \psi_{k_N}\rangle = n_i \left(\prod_{j=1}^{N} \sqrt{n_j!}\right)^{-1} |\psi_{k_1}, \dots (\text{one less } \psi_{k_i}), \psi_{k_N}\rangle$$
$$= \sqrt{n_i} |\psi_{k_1}, \dots (\text{one less } \psi_{k_i}), \psi_{k_N}\rangle_n = \sqrt{n_i} |n_1, n_2, \dots, n_i - 1, \dots\rangle \quad (2.19)$$

The same argument, developed for the creation operator $\hat{a}_i{}^\dagger$, leads to

$$\hat{a}_i{}^\dagger |n_1, n_2, \dots, n_i, \dots\rangle = \sqrt{n_i + 1} |n_1, n_2, \dots, n_i + 1, \dots\rangle \tag{2.20}$$

For fermions, the occupation numbers can either be 1 or 0. The creation operator $\hat{a}_i{}^\dagger$ returns a phase factor of 0 if $n_i = 1$ and ± 1 if $n_i = 0$ The annihilation operator $\hat{a}_i$ does the opposite.

It is useful defining a new operator, the number operator $\hat{N}_i = \hat{a}_i{}^\dagger \hat{a}_i$. If we apply it to base ket of a system made of bosons

$$\hat{N}_i |n_1, n_2, \dots, n_i, \dots\rangle = \hat{a}_i{}^\dagger \hat{a}_i |n_1, n_2, \dots, n_i, \dots\rangle$$
$$= \hat{a}_i{}^\dagger \sqrt{n_i} |n_1, n_2, \dots, n_i - 1, \dots\rangle = n_i |n_1, n_2, \dots, n_i, \dots\rangle \quad (2.21)$$

2.1.3 Commutation relations

Applying $\hat{a_k^\dagger} \hat{a_{k'}^\dagger}$ on a base ket, using Eq. (2.10)

$$\hat{a_{k'}^\dagger} \hat{a_k^\dagger} |\psi_{k_1}, \psi_{k_2}, \dots\rangle = |\psi_{k'} \psi_k, \psi_{k_1}, \psi_{k_2}, \dots\rangle$$
$$= \xi |\psi_k \psi_{k'}, \psi_{k_1}, \psi_{k_2}, \dots\rangle = \hat{a_k^\dagger} \hat{a_{k'}^\dagger} |\psi_{k_1}, \psi_{k_2}, \dots\rangle \quad (2.22)$$

We have proven the (anti)commutation relation

$$[\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger]_\xi = 0 \tag{2.23}$$

where $[A, B]_1 = \{A, B\} = AB + BA$ and $[A, B]_{-1} = AB - BA$. We see that for bosons the creation operators always commute, while for fermions they anti-commute.

Let's now investigate the commutator of a creation and an annihilation operator. Using Eq. (2.10) and Eq. (2.17)

$$\begin{aligned} \hat{a_{k'}} \hat{a}_k^\dagger \left|\psi_{k_1}, \psi_{k_2}, \ldots\right\rangle &= \hat{a_{k'}} \left|\psi_k, \psi_{k_1}, \psi_{k_2}, \ldots\right\rangle \\ &= \langle\psi_{k'}|\psi_k\rangle \left|\psi_{k_1}, \psi_{k_2}, \ldots\right\rangle + \sum_j \xi^j \left\langle\psi_{k'}\middle|\psi_{k_j}\right\rangle \left|\psi_k, \psi_{k_1}, \psi_{k_2}, (\text{no } \psi_{k_j}) \ldots\right\rangle \end{aligned} \tag{2.24}$$

$$\begin{aligned} \hat{a}_k^\dagger \hat{a_{k'}} \left|\psi_{k_1}, \psi_{k_2}, \ldots\right\rangle &= \hat{a}_k^\dagger \sum_j \xi^{j+1} \left\langle\psi_{k'}\middle|\psi_{k_j}\right\rangle \left|\psi_{k_1}, \psi_{k_2}, (\text{no } \psi_{k_j}) \ldots\right\rangle \\ &= \sum_j \xi^{j+1} \left\langle\psi_{k'}\middle|\psi_{k_j}\right\rangle \left|\psi_k, \psi_{k_1}, \psi_{k_2}, (\text{no } \psi_{k_j}) \ldots\right\rangle \end{aligned} \tag{2.25}$$

thus

$$(\hat{a_{k'}} \hat{a}_k^\dagger - \xi \hat{a}_k^\dagger \hat{a_{k'}}) = \langle\psi_{k'}|\psi_k\rangle \left|\psi_{k_1}, \psi_{k_2}, \ldots\right\rangle \tag{2.26}$$

and

$$[\hat{a_{k'}}, \hat{a}_k^\dagger]_\xi = \langle\psi_{k'}|\psi_k\rangle = \delta_{kk'} \tag{2.27}$$

The former equation is of fundamental importance in second quantization formalism. If we have a set of single-state base kets $|\psi_k\rangle$ and we define a creation and annihilation operator that satisfy Eq. (2.27), we obtain multi-particle base kets $|\psi_{k_1}, \psi_{k_2}, \ldots\rangle$ that automatically satisfy the symmetry condition of Fermi and Bose statistics. The kets can then be expressed in the more compact occupation number representation $|n_{k_1}, n_{k_2}, \ldots\rangle$.

2.1.4 Dynamical variables

We now investigate how operators different from the ones we have already encountered can be expressed in second quantization. We focus our discussion on additive single-particle operator. Examples are momentum, kinetic energy or single body potentials. In these cases, the total value of the operator is simply the sum over all the particles.

Given an operator $\hat{K}$ of eigenkets $|k_i\rangle$ and a state vector

$$|\Psi\rangle = |n_1, n_2, \ldots\rangle \tag{2.28}$$

the result of applying $\hat{K}$ to $|\Psi\rangle$ is simply

$$\hat{K}\,|\Psi\rangle = \left(\sum_i n_i k_i\right)|\Psi\rangle \tag{2.29}$$

Confronting this expression with the definition of the number operator expressed in Eq. (2.21) we can write $\hat{K}$ as

$$\hat{K} = \sum_i k_i N_i = \sum_i k_i \hat{a}_i^\dagger \hat{a}_i \tag{2.30}$$

It could happen that we have a state ket expressed in base different from the eigenkets of our operator of interest. If we suppose this base to be formed by $|l_j\rangle$, using completeness

$$|k_i\rangle = \sum_j |l_j\rangle \langle l_j|k_i\rangle \tag{2.31}$$

It makes then sense to write

$$\hat{a}_i^\dagger = \sum_j \hat{b}_j^\dagger \langle l_j|k_i\rangle \tag{2.32}$$

which implies

$$\hat{a}_i = \sum_j \hat{b}_j \langle k_i|l_j\rangle \tag{2.33}$$

where operators $\hat{b}_j^\dagger$ and $\hat{b}_j$ create and annihilate the single-particle states $|l_j\rangle$. The result of applying Eq. (2.32) on the vacuum state is then

$$\hat{a}_i^\dagger\,|\mathbf{0}\rangle = \sum_j \hat{b}_j^\dagger \langle l_j|k_i\rangle\,|\mathbf{0}\rangle = \sum_j |l_j\rangle \langle l_j|k_i\rangle = |k_i\rangle \tag{2.34}$$

in agreement with Eq. (2.31).

We are now ready to express the operator $\hat{K}$ in the basis $|l_j\rangle$.

$$\begin{aligned}\hat{K} = \sum_i k_i \hat{a}_i^\dagger \hat{a}_i &= \sum_i k_i \sum_{mn} \hat{b}_m^\dagger \hat{b}_n \langle l_m|k_i\rangle \langle k_i|l_n\rangle \\ &= \sum_{mn} \hat{b}_m^\dagger \hat{b}_n \sum_i \langle l_m|k_i\rangle\, k_i \,\langle k_i|l_n\rangle = \sum_{mn} \hat{b}_m^\dagger \hat{b}_n \langle l_m| \left[\hat{K} \sum_i |k_i\rangle\langle k_i|\right] |l_n\rangle \\ &= \sum_{mn} \langle l_m|\,\hat{K}\,|l_n\rangle\, \hat{b}_m^\dagger \hat{b}_n \end{aligned} \tag{2.35}$$

This allow us to write every additive operator in terms of the creation and annihilation operators. It is then possible to write the Hamiltonian for a non-interacting system of particles, where the potential and the kinetic energy satisfy the additivity requirement.

$$\hat{H} = \sum_{mn} \langle l_m | \hat{T} + \hat{V}_1 | l_n \rangle \hat{b}_m^\dagger \hat{b}_n \tag{2.36}$$

where V_1 is the non-interacting (single particle) potential.

2.2 Electrons and phonons in a crystal

In this section we will briefly describe how free electrons and phonons behave in a crystal, starting with a description of a crystal lattice. The interaction between two electrons and two phonons will not be considered. The electron-phonon interaction will be discussed in the following section.

2.2.1 Crystal lattice

Solid state physics deals with materials made of huge numbers of atoms, of the order of the Avogadro number. We have just developed a mathematical formalism (second quantization) with which it is possible to treat such systems. However, it is clearly impossible to solve the equations for a general N-body system. Luckily, X-ray diffraction experiments showed that many solids exhibit particular symmetry properties. The most important is translation symmetry.

It was discovered that many materials, called crystals, can be described as an organized collection of atoms sitting in a lattice, usually called Bravais lattice. A lattice is a collection of points translationally invariant. This means that given any two points described by two vectors $\mathbf{R_1}$ and $\mathbf{R_2}$, the difference between them is

$$\mathbf{R}_1 - \mathbf{R}_2 = \mathbf{R}_n \tag{2.37}$$

with $\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$. The three vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are called basis vectors and n_1, n_2, n_3 are integers. Every property $f(\mathbf{r})$ of the lattice is then invariant under a translation of a lattice vector $\mathbf{R}_n$

$$f(\mathbf{r} + \mathbf{R}_n) = f(\mathbf{r}) \tag{2.38}$$

We will see that applying this principle to the potential generated by the ions of the crystal will have important implications on the description of the electrons.

Associated to the Bravais lattice, there is a second one called reciprocal lattice. It is defined by three other base vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$, with

$$\mathbf{b}_1 = \frac{2\pi}{V}\,\mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{b}_2 = \frac{2\pi}{V}\,\mathbf{a}_3 \times \mathbf{a}_1 \quad \mathbf{b}_3 = \frac{2\pi}{V}\,\mathbf{a}_1 \times \mathbf{a}_2 \tag{2.39}$$

where $V = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$. A vector in the reciprocal lattice is usually written as $\mathbf{G}_m = m_1\mathbf{a}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$. From Eq. (2.39) it is easy to see that the product of a base Bravais lattice vector $\mathbf{a}_i$ and a base reciprocal lattice vector $\mathbf{b}_j$ is

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \tag{2.40}$$

2.2.2 Electrons in crystals