

Chapter 2

Second Quantization for Fermions

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The object of quantum chemistry consists of interacting many particle systems of electrons and nuclei. An accurate description of such systems requires the solution of the many-particle Schrödinger equation. In principle, the n-body wave function in configuration space contains all possible information, but a direct solution of the Schrödinger equation is impractical. It is therefore necessary to resort to approximate techniques, and to work within the framework of more convenient representation of the quantum mechanic operators and wave functions: the Second Quantization.

In a relativistic theory, the concept of Second Quantization is essential to describe the creation and destruction of particles¹. However, even in a non-relativistic theory, Second Quantization greatly simplifies the discussion of many identical interacting particles²². This formalism has several distinct advantages: the second-quantized operators incorporate the statistics (Fermi in our case) at each step, which contrasts with the more cumbersome

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approach of using antisymmetrized products of single-particle wave functions. It also allows us to concentrate on the few matrix elements of interest, thus avoiding the need for dealing directly with the many-particle wave functions and the coordinates of all the remaining particles. Finally, the Green's functions and density matrices, which contain the most important physical information concerning to the ground-state energy, the energy and lifetime of excited states, and other molecular properties, are easily expressed in this formalism.

The Schrödinger equation

Any problem on non-relativistic electronic structure requires the solution of the Schrödinger equation,

$$\hat{H}\Psi = E\Psi \quad (1)$$

where \hat{H} and Ψ represent the Hamiltonian and the wave function of the system respectively. In the Born-Oppenheimer approximation, the electronic Hamiltonian for atoms and molecules (the systems of our interest) takes the form

$$\hat{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=1}^n \hat{\nabla}_i^2 - \sum_{i=1}^n \sum_{I=1}^N \frac{Z_I}{r_{iI}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{r_{ij}} = \sum_{i=1}^n \hat{h}_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{r_{ij}} \quad (2)$$

where \hat{h}_i is the h-core operator, which contains the kinetic energy and the potential energy of interaction between nuclei and electrons. We should observe that this term is composed by the sum of operators involving the coordinates of the particles one at a time hence, it belongs to the group of the symmetric one-particle operators:

$$\hat{A}_n = \sum_{i=1}^n \hat{h}_i \quad (3)$$

The second term represents the potential energy of interaction between every pair of particles therefore; it belongs to the so-called symmetric two-particle operators,

$$\hat{B}_n = \sum_{i=1}^{n-1} \sum_{j=i+1}^n r_{ij}^{-1} = \frac{1}{2} \sum_{i,j=1}^n r_{ij}^{-1} \quad (4)$$

Here, all pairs of particles are counted once, which accounts for the factor of $\frac{1}{2}$, and the double sum runs over the indices 'i' and 'j' separately, excluding the value 'i' equal 'j'.

These two kinds of operators are the most frequently ones in almost all cases of interest in quantum chemistry.

The Undistinguished Principle

It is well known that for a correct description of a system with 'n' identical particles is not enough to solve for the Schrödinger equation, it is necessary to incorporate the statistics of the particles. In the case of an assembly of fermions, the many-particle wave function is assumed to have the following property

$$\Psi(x_1, x_2, \dots, x_i, x_j, \dots, x_n) = -\Psi(x_1, x_2, \dots, x_j, x_i, \dots, x_n) \quad (5)$$

where x_i denotes the coordinates of the *i*th particle, including the spatial coordinate \mathbf{r}_i and any discrete variable such as the *z* component of spin. Equation (5) shows that the wave function must be antisymmetric under the interchange of the coordinates of any two particles.

For a system with 'n' independent particles, we can easily satisfy the antisymmetric restriction using the Slater normalized determinant

$$\Psi(x_1, x_2, \dots, x_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \dots & \psi_n(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \dots & \psi_n(x_2) \\ \dots & \dots & \dots & \dots \\ \psi_1(x_n) & \psi_2(x_n) & \dots & \psi_n(x_n) \end{vmatrix} \quad (6)$$

where $\psi_1(x), \psi_2(x), \dots, \psi_n(x)$ are the orthonormal single-particle wave functions occupied by all particles. We should note that there exist single-particle states but we do not know exactly which particle occupies each state. Moreover, it is satisfied rigorously the Pauli exclusion principle. Consequently, we can consider a complete set of orthonormal time-independent single-particle wave functions

$$\{\psi_i(x)\} \quad , \quad i = 1, 2, \dots, \infty \quad ; \quad \int \psi_i(x) \psi_j(x) dx = \delta_{ij} \quad (7)$$

and the occupation numbers for each state (n_i) must be taken 0 or 1.

On the other hand, if we have a complete orthonormal set of one-particle functions $\{\psi_i(x)\}$ then, the set of all determinants $\{\Psi_I\}$ built on these functions, equation (6), constitutes also a complete and orthonormal n -particle basis. Therefore, we can now expand any interacting many-body wave functions as follows:

$$\Psi = \sum_{I=1}^{\infty} C_I \Psi_I \quad (8)$$

This expression is completely general since it is simply the expansion of the wave function in a complete set of states.

From the First to the Second Quantization

Let us now analyze the simplest possible fermion system: two electrons in a symmetric potential well. We will take as single-particle functions those obtained solving the one-particle problem for this potential, and numbered in the increasing order of energy.

The states of the system corresponding to Slater determinants can be written as

$$\Psi_{ij} = \frac{1}{\sqrt{2}} \{\psi_i(x_1) \psi_j(x_2) - \psi_j(x_1) \psi_i(x_2)\} \quad , \quad i \neq j \quad ; \quad i, j = 1, 2, 3, \dots \quad (9)$$

where $\{\psi_i(x)\}$ are the single-particle functions, which satisfy equation (7).

The symmetric one-particle operator takes the form

$$\hat{A} = V(x_1) + V(x_2) \quad (10)$$

where V could be an external potential, and an example of its matrix element is

$$\begin{aligned} \langle \Psi_{13} | \hat{A} | \Psi_{12} \rangle &= \frac{1}{2} \iint [\psi_1^*(x_1) \psi_3^*(x_2) - \psi_3^*(x_1) \psi_1^*(x_2)] (V(x_1) + V(x_2)) \times \\ &\quad \times [\psi_1(x_1) \psi_2(x_2) - \psi_2(x_1) \psi_1(x_2)] dx_1 dx_2 = \int \psi_3^*(x) V(x) \psi_2(x) dx \end{aligned} \quad (11)$$

In the previous result, it was taken into account the orthonormality of the single-particle functions.

Let us now observe that for a symmetric operator, the matrix element does not change if we hold only antisymmetric one of wave functions, eliminating further the normalization coefficient, that is,

$$\begin{aligned} \langle \Psi_{13} | \hat{A} | \Psi_{12} \rangle &= \iint [\psi_1^*(x_1) \psi_3^*(x_2)] [V(x_1) + V(x_2)] \times \\ &\times [\psi_1(x_1) \psi_2(x_2) - \psi_2(x_1) \psi_1(x_2)] dx_1 dx_2 = \int \psi_3^*(x) V(x) \psi_2(x) dx \end{aligned} \quad (12)$$

The next step is to introduce the matrix notation. For the sake of simplicity, we will restrain our space to three states

$$\Psi_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \Psi_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \Psi_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad V_i = \begin{pmatrix} \langle 1|V|1 \rangle & \langle 1|V|2 \rangle & \langle 1|V|3 \rangle \\ \langle 2|V|1 \rangle & \langle 2|V|2 \rangle & \langle 2|V|3 \rangle \\ \langle 3|V|1 \rangle & \langle 3|V|2 \rangle & \langle 3|V|3 \rangle \end{pmatrix}_i \quad (13)$$

where $\langle t|V|s \rangle = \int \psi_t^*(x) V(x) \psi_s(x) dx$, $A = V_1 + V_2$

In this notation, the matrix element discussed above is expressed as

$$\begin{aligned} \langle \Psi_{13} | \hat{A} | \Psi_{12} \rangle &= \left\{ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}_2 \right\}^+ \left[\begin{pmatrix} \langle 1|V|1 \rangle & \langle 1|V|2 \rangle & \langle 1|V|3 \rangle \\ \langle 2|V|1 \rangle & \langle 2|V|2 \rangle & \langle 2|V|3 \rangle \\ \langle 3|V|1 \rangle & \langle 3|V|2 \rangle & \langle 3|V|3 \rangle \end{pmatrix}_1 + \right. \\ &\left. + \begin{pmatrix} \langle 1|V|1 \rangle & \langle 1|V|2 \rangle & \langle 1|V|3 \rangle \\ \langle 2|V|1 \rangle & \langle 2|V|2 \rangle & \langle 2|V|3 \rangle \\ \langle 3|V|1 \rangle & \langle 3|V|2 \rangle & \langle 3|V|3 \rangle \end{pmatrix}_2 \right] \left\{ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_2 \right\} \end{aligned} \quad (14)$$

Here, the sub-indices 1 and 2 identify the particles. Note that in the wave function on the left, as well as in the first term of the wave function on the right, when the particle identifier increases, the occupation number 1 in columns gets down. We will say that these functions are in a normal form. On the contrary, the last term of the function Ψ_{12} is non-normal. Performing the matrix product we get

$$\langle \Psi_{13} | \hat{A} | \Psi_{12} \rangle = \langle 3|V|2 \rangle \quad (15)$$

Furthermore, we have to note that matrix V_1 differs from V_2 only in the particle identifier, since both matrices are equal. It is more convenient to introduce a new matrix e_{ts} defined by all elements equal zero except one in row 't' and column 's', for example,

$$e_{12} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (16)$$

Thus, we can write matrix V_i in the form

$$V_i = \sum_{t,s=1}^3 \langle t|V|s \rangle e_{ts}^i \quad (17)$$

As a consequence, the one-particle operator becomes

$$A = \sum_{i=1}^2 \sum_{t,s=1}^3 \langle t|V|s \rangle e_{ts}^i = \sum_{t,s=1}^3 \langle t|V|s \rangle E_{ts}, \quad E_{ts} = \sum_{i=1}^2 e_{ts}^i \quad (18)$$

Equation (18) shows an important result: matrix E_{ts} does not depend on the particle identifier. This is a crucial point in the whole treatment, instead of performing a sum over particles, we can well sum over states.

The original wave functions can now be rewritten as follows

$$\left\{ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}_2 \right\} = \Phi_{101} \quad \left\{ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_2 \right\} = \tilde{\Phi}_{110} \quad (19)$$

Φ_{101} represents that only the first and the third states are occupied, while the first and the second states occur in $\tilde{\Phi}_{110}$. The wave under the last function denotes that it is anti-symmetrized. This result shows that wave functions are characterized by the occupation numbers of each state, which are equal either zero or one. Thus, we have obtained an occupation number representation.

Let us now concentrate our attention in the matrix elements of E_{ts} . It is easy to see that matrix E_{ts} has to act on a wave function at the right side with an occupied state 's', and similarly on a wave function at the left side with an occupied state 't'. In particular,

$$(\Phi_{101}, E_{32} \tilde{\Phi}_{110}) = 1 \quad (20)$$

Thus, it is convenient to simplify the notation by representing matrix E_{ts} as a product of two new operators, i.e.,

$$E_{ts} = \hat{a}_t^+ \hat{a}_s \quad (21)$$

where \hat{a}_s is an operator that annihilates a particle in the state 's' on the right side, as long as \hat{a}_t^+ destroys a particle in the state 't' on the left one.

However, we have to consider a little complicated detail: some matrix elements of E_{ts} involve a minus sign, for example

$$\begin{aligned} (\Phi_{011}, E_{31} \tilde{\Phi}_{110}) = & \left\{ \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}_2 \right\}^+ \left[\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}_1 + \right. \\ & \left. + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}_2 \right] \left\{ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}_2 - \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}_1 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_2 \right\} = -1 \end{aligned} \quad (22)$$

The appearance of a phase factor, which changes the sign of matrix elements is because of the non-normal form of the second term on the right side that has an occupied state 's' corresponding to an occupied state 't' on the left.

In general, we can regard that matrix E_{ts} moves a particle from the single state 's' to the state 't', and the phase factor concerns to the number of particles necessary to permute in this procedure. Consequently, we can determine the phase factor of $(\Phi, E_{ts} \Phi)$ by the expression

$$(-1)^{n_{ts}} \quad , \quad n_{ts} = \sum_{r=s+1}^{t-1} n_r \quad (23)$$

where n_r is the occupation number of the state 'r'.

Including the phase factor on the new operators which define matrix E_{ts} one can get

$$\hat{a}_s \Leftrightarrow (-1)^{\sum_{r=1}^{s-1} n_r} \quad , \quad \hat{a}_t^+ \Leftrightarrow (-1)^{\sum_{r=1}^{t-1} n_r} \quad (24)$$

$$\hat{a}_t^+ \hat{a}_s \Leftrightarrow (-1)^{\sum_{r=1}^{t-1} n_r} (-1)^{\sum_{r=1}^{s-1} n_r} = (-1)^{\sum_{r=1}^{s-1} 2n_r} (-1)^{n_s} (-1)^{n_{ts}} = (-1)^{n_{ts}} \quad (25)$$

In the previous result, we have supposed that 't > s', and n_s corresponds to the occupation number of the final state of the system. This value should be zero since the final state is obtained after the annihilation by the operator \hat{a}_s of the single state 's' in the initial state of the system.

The inclusion of the phase factor in the operator excludes the requirement on the antisymmetrization of the wave function at the right side. Thus, we finally can generalize our result, and write out the matrix elements of the one-particle symmetric operator as:

$$\left(\Phi_{n'_1 n'_2 n'_3 \dots} \sum_{t,s} \langle t | V | s \rangle \hat{a}_t^+ \hat{a}_s \Phi_{n_1 n_2 n_3 \dots} \right) \quad (26)$$

where $\{n\}$ denotes the occupation numbers of single-particle states in the initial wave function of the system, while $\{n'\}$ represents the occupation numbers of these one-particle states concerning the final one.

Let us now analyze matrix elements of the symmetric two-particle operators

$$\hat{B} = \sum_{i=1}^{n-1} \sum_{j=i+1}^n V(x_i, x_j) = \frac{1}{2} \sum_{i,j=1}^n V(x_i, x_j) \quad (27)$$

For this simple system formed by two particles, the operator (27) is only one V, which could be the Coulomb interaction.

The matrix element is for instance,

$$\begin{aligned} \langle \Psi_{13} | \hat{B} | \Psi_{12} \rangle &= \iint \Psi_3^*(x_1) \Psi_1^*(x_2) V(x_1, x_2) \Psi_2(x_1) \Psi_1(x_2) dx_1 dx_2 - \\ &\quad - \iint \Psi_1^*(x_1) \Psi_3^*(x_2) V(x_1, x_2) \Psi_2(x_1) \Psi_1(x_2) dx_1 dx_2 \end{aligned} \quad (28)$$

Introducing matrix notation, similarly we did before for one-particle operators, one can obtain

$$\hat{B} = \frac{1}{2} \sum_{t,s,t',s'} \langle t's' | V | ts \rangle E_{t't} E_{s's} \quad (29)$$

$$\text{where} \quad \langle t's' | V | ts \rangle = \iint \Psi_{t'}^*(x_1) \Psi_{s'}^*(x_2) V(x_1, x_2) \Psi_t(x_1) \Psi_s(x_2) dx_1 dx_2 \quad (30)$$

Here the expression $E_{t't} E_{s's}$ is a function of the new operators \hat{a}^+ and \hat{a} which should be obtained. There are four possible kinds of products of these operators in our example, that is,

$$\begin{pmatrix} s=1 \\ t=2 \\ s'=1 \\ t'=3 \end{pmatrix} \quad \begin{pmatrix} s=2 \\ t=1 \\ s'=3 \\ t'=1 \end{pmatrix} \quad \begin{pmatrix} s=1 \\ t=2 \\ s'=3 \\ t'=1 \end{pmatrix} \quad \begin{pmatrix} s=2 \\ t=1 \\ s'=1 \\ t'=3 \end{pmatrix} \quad (31)$$

The calculation shows that the first two variants give same results as last ones, but preceding by a phase factor -1 . The cause of this is

$$\langle 31 | V | 21 \rangle = \langle 13 | V | 12 \rangle \quad , \quad \langle 13 | V | 21 \rangle = \langle 31 | V | 12 \rangle \quad (32)$$

Taking into account the phase factor one can write:

$$E_{t't} E_{s's} = \hat{a}_s^+ \hat{a}_t^+ \hat{a}_t \hat{a}_s \quad (33)$$

In fact, for our system of two particles we have

$$\langle \Phi_{101}, \hat{a}_1^+ \hat{a}_3^+ \hat{a}_2 \hat{a}_1 \Phi_{110} \rangle = 1 \quad \langle \Phi_{101}, \hat{a}_3^+ \hat{a}_1^+ \hat{a}_1 \hat{a}_2 \Phi_{110} \rangle = (-1)(-1) = 1 \quad (34)$$

$$\langle \Phi_{101}, \hat{a}_3^+ \hat{a}_1^+ \hat{a}_2 \hat{a}_1 \Phi_{110} \rangle = -1 \quad \langle \Phi_{101}, \hat{a}_1^+ \hat{a}_3^+ \hat{a}_1 \hat{a}_2 \Phi_{110} \rangle = -1$$

The rest of terms only afford zeros. Then,

$$\begin{aligned} \left(\Phi_{101}, \frac{1}{2} \sum_{t,s,t',s'} \langle t's' | V | ts \rangle \hat{a}_s^+ \hat{a}_t^+ \hat{a}_t \hat{a}_s \Phi_{110} \right) &= \frac{1}{2} \{ \langle 31 | V | 21 \rangle + \langle 13 | V | 12 \rangle - \\ &\quad - \langle 13 | V | 21 \rangle - \langle 31 | V | 12 \rangle \} = \langle 31 | V | 21 \rangle - \langle 13 | V | 21 \rangle \end{aligned} \quad (35)$$

Generalizing this result, the matrix elements of two-particle symmetric operators can be written as

$$\left(\Phi_{n_1' n_2' n_3' \dots}, \frac{1}{2} \sum_{t,s,t',s'} \langle t's' | V | ts \rangle \hat{a}_s^+ \hat{a}_t^+ \hat{a}_t \hat{a}_s \Phi_{n_1 n_2 n_3 \dots} \right) \quad (36)$$

Creation and destruction operators

The just introduced operators satisfy some properties. Let us note that the action of the pairs of operators $\hat{a}_s \hat{a}_t$ and $\hat{a}_t \hat{a}_s$ over a same function differ only in a sign, due to phase factors associated to each operator. Accordingly to this, operators \hat{a}^+ and \hat{a} satisfy the anticommutation rules

$$[\hat{a}_s^+, \hat{a}_t^+] = \hat{a}_s \hat{a}_t + \hat{a}_t \hat{a}_s = 0 \quad (37)$$

$$[\hat{a}_s, \hat{a}_t] = \hat{a}_s^+ \hat{a}_t^+ + \hat{a}_t^+ \hat{a}_s^+ = 0 \quad (38)$$

On the other hand, we can observe that operator \hat{a}^+ , which annihilates a particle on the left, gives the same result if we consider that it creates a particle acting on the wave function at the right side. Hence, we will call this kind of operators as creators.

Following a similar procedure like before, one can obtain the last anticommutation rule for these operators, that is,

$$\begin{aligned} \hat{a}_s \hat{a}_t^+ + \hat{a}_t^+ \hat{a}_s &= 0, \quad s \neq t & \hat{a}_s \hat{a}_s^+ + \hat{a}_s^+ \hat{a}_s &= 1 \\ \text{or} & & [\hat{a}_s, \hat{a}_t^+] &= \delta_{st} \end{aligned} \quad (39)$$

Let us now represent the occupation number states through the creation and destruction operators. For this purpose, we introduce the vacuum wave function $\Phi_{0000\dots}$, in which there are not particles. Accordingly, for every destruction operator one can obtain

$$\hat{a}_s \Phi_{0000\dots} = 0 \quad (40)$$

Any wave function of a system can be obtained creating particles by the action of \hat{a}^+ operators on the vacuum. Some examples are:

$$\Phi_{101} = \hat{a}_1^+ \hat{a}_3^+ \Phi_{000} \quad \Phi_{110} = \hat{a}_1^+ \hat{a}_2^+ \Phi_{000} \quad (41)$$

Usually, to gain in generality the occupation number states are represented as time-independent abstract state vectors

$$|\alpha_1 \alpha_2 \alpha_3 \dots \alpha_n\rangle \quad (42)$$

where the notation means that (42) is a state of 'n' particles, in which, there is a particle in the eigenstate α_1 , another one in the eigenstate α_2 , etc, of a complete orthonormal set of single-particle states $\{|\alpha_k\rangle\}$. The eigenstates of this set which do not appear in (42) are empty.

Correspondingly, the vacuum state is represented as $|0\rangle$, and the creation and destruction operators satisfy the following equations:

$$\hat{a}_k^+ |0\rangle = |\alpha_k\rangle, \quad \langle 0 | \hat{a}_k^+ = 0 \quad (43)$$

$$\hat{a}_k |0\rangle = 0, \quad \langle 0 | \hat{a}_k = \langle \alpha_k | \quad (44)$$

It is easily seen that the set of anticommutation rules (37)–(39) produces the correct statistics:

1. $\hat{a}_s^2 = \hat{a}_s^{+2} = 0$, therefore $\hat{a}_s^+ \hat{a}_s^+ |0\rangle = 0$, which prevents two particles from occupying the same state.
2. $\hat{a}_s^+ \hat{a}_s = 1 - \hat{a}_s \hat{a}_s^+$, therefore $(\hat{a}_s^+ \hat{a}_s)^2 = 1 - 2\hat{a}_s \hat{a}_s^+ + \hat{a}_s \hat{a}_s^+ \hat{a}_s \hat{a}_s^+ = 1 - 2\hat{a}_s \hat{a}_s^+ + \hat{a}_s (1 - \hat{a}_s \hat{a}_s^+) \hat{a}_s^+ = \hat{a}_s^+ \hat{a}_s$ or $\hat{a}_s^+ \hat{a}_s (1 - \hat{a}_s^+ \hat{a}_s) = 0$. This last relation implies that the number operator for the sth mode is $\hat{n}_s = \hat{a}_s^+ \hat{a}_s$, and it has the eigenvalues zero and one, as required. Thus, the particle number operator is $\hat{n} = \sum_s \hat{a}_s^+ \hat{a}_s$.

$$3. \hat{a}_k |\alpha_1 \alpha_2 \dots \alpha_n\rangle = \hat{a}_k \hat{a}_1^+ \hat{a}_2^+ \dots \hat{a}_n^+ |0\rangle = \begin{cases} (-1)^{k-1} |\alpha_1 \alpha_2 \dots (\text{not } \alpha_k) \dots \alpha_n\rangle & \text{si } \alpha_k \in \Omega \\ 0 & \text{si } \alpha_k \notin \Omega \end{cases}, \quad \Omega \equiv \{\alpha_1 \alpha_2 \dots \alpha_n\}.$$

Example: The Hartree-Fock energy

Nowadays, one of the most useful methods in Quantum Chemistry is the Hartree-Fock (HF) approximation. In this method, the ground-state function is taken as an independent n-particle state, which in the second quantization formalism takes the form

$$|\Psi_{\text{HF}}\rangle = \prod_{i=1}^n \hat{a}_i^+ |0\rangle = |\alpha_1 \alpha_2 \alpha_3 \dots \alpha_n\rangle, \quad \Omega \equiv \{\alpha_1 \alpha_2 \dots \alpha_n\} \quad (45)$$

Taking into account that Hamiltonian (2) is now represented as

$$\hat{H} = \sum_{t,s} \langle t | \hat{h} | s \rangle \hat{a}_t^+ \hat{a}_s + \frac{1}{2} \sum_{t,s,t',s'} \langle t' s' | ts \rangle \hat{a}_s^+ \hat{a}_t^+ \hat{a}_t \hat{a}_s \quad (46)$$

one can very easily calculate the ground state energy. Certainly,

$$\langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle = \sum_{t,s} \langle t | \hat{h} | s \rangle \langle \Psi_{\text{HF}} | \hat{a}_t^+ \hat{a}_s | \Psi_{\text{HF}} \rangle + \frac{1}{2} \sum_{t,s,t',s'} \langle t' s' | ts \rangle \langle \Psi_{\text{HF}} | \hat{a}_s^+ \hat{a}_t^+ \hat{a}_t \hat{a}_s | \Psi_{\text{HF}} \rangle \quad (47)$$

where $\langle \Psi_{\text{HF}} | \hat{a}_t^+ \hat{a}_s | \Psi_{\text{HF}} \rangle$ and $\langle \Psi_{\text{HF}} | \hat{a}_s^+ \hat{a}_t^+ \hat{a}_t \hat{a}_s | \Psi_{\text{HF}} \rangle$ are the so-called first and second order Reduced Density Matrices (1- and 2-RDM) respectively.

In the 1-RDM, the state 's' has to be present in the set of the HF single-particle states Ω on the contrary, the operator \hat{a}_s acting on the left yields zero. At the same time, the operator \hat{a}_t^+ should create a particle in the recent annihilated 's' state to obtain again the HF function, due to the orthogonality of the one-particle states. Thus, one gets

$$\langle \Psi_{\text{HF}} | \hat{a}_t^+ \hat{a}_s | \Psi_{\text{HF}} \rangle = \delta_{ts} \delta_{si}, \quad i \in \Omega \quad (48)$$

The situation for the 2-RDM is very similar: the operators \hat{a}_t and \hat{a}_s have to annihilate two particles in states belonging to the set Ω , while operators \hat{a}_t^+ and \hat{a}_s^+ must create these states to generate again the HF function in view of the orthogonality. There are two different ways of satisfying this condition, that afford the following

$$\langle \Psi_{\text{HF}} | \hat{a}_s^+ \hat{a}_t^+ \hat{a}_t \hat{a}_s | \Psi_{\text{HF}} \rangle = (\delta_{tt'} \delta_{ss'} - \delta_{st'} \delta_{ts'}) \delta_{ij} \delta_{si}, \quad i, j \in \Omega \quad (49)$$

Substituting the results (48) and (49) obtained for the HF 1- and 2-RDM into equation (47), one can obtain

$$\langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle = \sum_{i=1}^n \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i,j=1}^n [\langle ji | ji \rangle - \langle ij | ji \rangle] \quad (50)$$

Fields

It is often convenient to form the linear combination of the creation and destruction operators

$$\hat{\psi}(x) \equiv \sum_k \psi_k(x) \hat{a}_k \quad (51)$$

$$\hat{\psi}^+(x) \equiv \sum_k \psi_k(x)^* \hat{a}_k^+ \quad (52)$$

where the coefficients are the single-particle wave functions and the sum is over the complete set of single-particle quantum numbers. Here, the index 'k' may denote now the set of quantum numbers $\{\mathbf{k}, s_z\}$.

These quantities $\hat{\psi}$ and $\hat{\psi}^+$ are called field operators. They are operators because they depend on the creation and destruction operators. The field operators satisfy simple anticommutation relations

$$[\hat{\psi}(x), \hat{\psi}^+(x')] = \sum_k \hat{\psi}_k(x) \hat{\psi}_k(x')^* = \delta(x - x') \quad (53)$$

$$[\hat{\psi}(x), \hat{\psi}(x')] = [\hat{\psi}^+(x), \hat{\psi}^+(x')] = 0 \quad (54)$$

These equalities follow from the anticommutation relations for the creation and destruction operators, and the completeness of the single-particle wave functions.

The hamiltonian operator (2) can be rewritten in terms of these field operators as follow:

$$\hat{H} = \int dx \hat{\psi}^+(x) h(x) \hat{\psi}(x) + \frac{1}{2} \iint dx dx' \hat{\psi}^+(x) \hat{\psi}^+(x') V(x, x') \hat{\psi}(x') \hat{\psi}(x) \quad (55)$$

This expression is readily verified since the integration over spatial and spin coordinates produces the corresponding matrix elements, leaving a sum of these ones multiplied by the appropriate creation and destruction operators. Note carefully the ordering of the last two field operators in the Coulomb potential energy, which ensures that the hamiltonian is hermitian. In this form, the hamiltonian suggests the name of second quantization since the above expression looks like the expectation value of the hamiltonian taken between wave functions. The quantities $\hat{\psi}$ and $\hat{\psi}^+$ are not wave functions, however, but field operators, thus in second quantization the fields are the operators and the potential and kinetic energy are just complex coefficients.

Closing Remarks

The second quantization is a good representation of the quantum mechanic operators and wave functions through the creation and destruction operators. Strictly speaking, there is not really another quantization. It is quantum formalism very useful for treating many identical interacting particles systems.

The main advantage of this formalism is the guarantee of the undistinguished principle, which is implicitly in the anticommutation relations of the operators \hat{a}^+ and \hat{a} . Thus, one avoids the cumbersome work of using antisymmetrized products of single-particle wave functions.

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