Second Quantization Formalism*

Juan Carlos Paniagua

E-mail: juancapani@gmail.com

Departament de Ciència de Materials i Química Física &
Institut de Química Teòrica i Computacional (IQTC-UB)
Universitat de Barcelona

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1 Introduction

Quantum chemists we are seldom concern with phenomena involving variations in the number of particles, so they do not need to resort to quantum field theories to lay the foundations of their work (one exception are certain spectroscopic phenomena with require a quantum description of electromagnetic radiation). The standard quantum mechanic theory for material particles is then a sufficient basis for their purposes. In this

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theory, the wave function norm remains constant over time, which implies the conservation of the number of particles of every type. However, even in this context it is often convenient to use some tools of quantum field theories—in particular, the creation and annihilation operators—to state certain mathematical developments, particularly in the study of solid-state and molecular electronic structure. This way of formulating the theory is known as second quantization formalism.¹

2 The Fock space

Creation and annihilation operators are applications that, when applied to a state of an n-particle system, produce a state of an (n + 1)- and an (n − 1)-particle system, respectively. Therefore they act in a broader Hilbert space that those considered so far, which is known as the Fock space (F). If all of the variable-number particles are of the same type the Fock space is the direct sum of every fixed-particle-number space.²

In the particular case of an electron system (or any system made of identical fermions) the Fock space is:

\[ F = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_1^{\otimes 2} \oplus \cdots \]

where \( \mathcal{H}_0 \) and \( \mathcal{H}_1 \) are, respectively, the zero-electron and one-electron Hilbert spaces. \( \mathcal{H}_0 \) is a one-dimensional space containing a normalized vector \( |0\rangle \) that represents a state with no electrons (the vacuum state), which is different from the zero vector (0). Let us choose a normalized discrete basis set \( \{\psi_1, \ldots, \psi_i, \cdots\} \) in \( \mathcal{H}_1 \). The set \( \{n\Phi_I\} \) of all n-electron Slater determinants

\[ n\Phi_I = \langle (\psi_{i_1} \cdots \psi_{i_n})_n \rangle \]

is then a normalized basis of \( \mathcal{H}_1^{\otimes n} \), and the collection of all these basis for every value of n

\[ \{0\Phi, \{1\Phi\}, \{2\Phi\}, \cdots \{n\Phi\}, \cdots\} \]

is a normalized basis of \( F \).

When referring to state vectors as elements of the Fock space an occupation number representation is often used, in which each basis vector \( n\Phi_I \) is identified by a sequence of occupation numbers \( n_i \) that take the value 1 for the spin-orbitals present in \( n\Phi_I \) and 0 for all the other:

\[ n\Phi_I = |n_1, \cdots, n_i, \cdots\rangle \quad \text{with} \quad n = \sum_i n_i \]

For instance, if \( \psi_1 \cdots \psi_n \) are the first n spin-orbitals of the one-electron basis set, then \( n\Phi_0 = |(\psi_1 \cdots \psi_n)_n\rangle = |1, \cdots, 1, 0, 0, \cdots\rangle \). The vacuum state has all the occupation numbers equal to zero: \( |\rangle = |0, \cdots, 0, \cdots\rangle \). In the case of boson systems the occupation numbers can take any natural value (including zero).

3 Electron creation and annihilation operators

The annihilation operator \( \hat{a}_i \) of an electron in the spin-orbital \( \psi_i \) is conveniently defined in the occupation number representation as

\[ \hat{a}_i |n_1, \cdots, n_i, \cdots\rangle = (-1)^{\nu_i} n_i |n_1, \cdots, 1 - n_i, \cdots\rangle \]

where \( \nu_i = \sum_{j=1}^{i-1} n_j \) and \( \nu_1 = 0 \). The reason for the term “annihilation” will become clear by applying this definition to some particular cases:

\[ \hat{a}_1 |n_1, n_2, \cdots, n_i, \cdots\rangle = |0, n_2, \cdots, n_i, \cdots\rangle \]
\[ \hat{a}_1 |0, n_2, \cdots, n_i, \cdots\rangle = 0 \]
\[ \hat{a}_2 |0, 1, n_1, \cdots, n_i, \cdots\rangle = |0, 0, n_1, \cdots, n_i, \cdots\rangle \]
\[ \hat{a}_2 |1, 1, n_i, \cdots, \cdots\rangle = -|1, 0, \cdots, n_i, \cdots\rangle \]

¹While in quantum electrodynamics the energy associated to the classical electromagnetic fields becomes a quantized observable, in the present formalism a certain type of quantization will emerge from the quantum wave functions, hence the term “second quantization”.

²One could wonder why to use direct products to build de Hilbert space of a many-particle system from the one-particle spaces and direct sums to express the Fock space in terms of fixed-particle spaces. In the first case we have a complex system that can be divided into different subsystems, and these are different from their union. On the other hand, the Fock space is the Hilbert space of a single system in which the number of particles is not a fixed parameter, as in standard quantum mechanics, but an observable that can take different values, may evolve in time, and may even not be well defined. In the Hilbert space containing the states of this system there are subspaces that correspond to different eigenvalues of the "number of particles operator", in the same way that there are subspaces corresponding to different values of any other observable, and the direct sum of all of these subspaces gives the whole Hilbert space.
That is, if the spin-orbital $\psi_i$ is occupied in $|n_1, \cdots, n_i, \cdots \rangle$ then $\hat{a}_i$ annihilates an electron in that spin-orbital, and it changes the sign of the many-electron state vector if $\psi_i$ was in an even position among the occupied states. So, from an $n$-electron state we obtain an $(n-1)$-electron state. If $\psi_i$ is empty in $|n_1, \cdots, n_i, \cdots \rangle$ the result of applying $\hat{a}_i$ to this many-electron vector is zero.

When we represent the many-electron basis vector as a Slater determinant then the effect of the annihilation operator $\hat{a}_i$ over a determinant containing $\psi_i$ takes the form:

$$\hat{a}_i \langle \psi_j \cdots \psi_i \cdots \psi_k \rangle = (-1)^{\nu_i} \langle \psi_j \cdots \psi' \cdots \psi_k \rangle$$

where $\nu_i$ is again the position number of $\psi_i$ minus 1, and $\psi'$ means that $\psi_i$ is absent in the determinant. $\nu_i$ is also the number of transpositions needed to bring $\psi_i$ to the first position of the determinant, so that we can obtain the effect of $\hat{a}_i$ by first bringing $\psi_i$ to the first position and then dropping it from the determinant. The application of $\hat{a}_i$ would give zero if $\psi_i$ were not occupied in the determinant:

$$\hat{a}_i \langle \psi_j \cdots \psi' \cdots \psi_k \rangle = 0$$

Likewise, the creation operator $\hat{a}_i^\dagger$ of an electron in the spin-orbital $\psi_i$ is defined by

$$\hat{a}_i^\dagger |n_{1}, \cdots, n_i, \cdots \rangle = (-1)^{\nu_i}(1 - n_i) |n_1, \cdots, 1 - n_i, \cdots \rangle$$

Some examples reveal that this operator creates an electron in the spin-orbital $\psi_i$ if this was empty, and introduces a change of sign if the creation takes place in an even position among the occupied spin-orbitals:

$$\hat{a}_1^\dagger |0, n_2, \cdots, n_i, \cdots \rangle = |1, n_2, \cdots, n_i, \cdots \rangle$$
$$\hat{a}_1^\dagger |1, n_2, \cdots, n_i, \cdots \rangle = 0$$
$$\hat{a}_2^\dagger |0, 0, \cdots, n_i, \cdots \rangle = |0, 1, \cdots, n_i, \cdots \rangle$$
$$\hat{a}_2^\dagger |1, 0, \cdots, n_i, \cdots \rangle = -|1, 1, \cdots, n_i, \cdots \rangle$$

Any many-electron basis vector can be obtained from the vacuum state by successive application of creation operators:

$$|n_{1}, \cdots, n_i, \cdots \rangle = (\hat{a}_1^\dagger)^{n_i} \cdots (\hat{a}_i^\dagger)^{n_i} \cdots |0, 0, \cdots \rangle$$

In terms of Slater determinants the effect of the creation operator $\hat{a}_i^\dagger$ over a product not containing $\psi_i$ is:

$$\hat{a}_i^\dagger \langle \psi_j \cdots \psi' \cdots \psi_k \rangle = (-1)^{\nu_i} \langle \psi_j \cdots \psi_i \cdots \psi_k \rangle$$

and

$$\hat{a}_i^\dagger \langle \psi_j \cdots \psi_i \cdots \psi_k \rangle = 0$$

In the right hand side of the first equation we can bring $\psi_i$ to the first position of the product by making $\nu_i$ transpositions, so that we also can say that $\hat{a}_i^\dagger$ creates an electron in the spin-orbital $\psi_i$ and in the first position of the determinant:

$$\hat{a}_i^\dagger \langle \psi_j \cdots \psi' \cdots \psi_k \rangle = \langle \psi_i \psi_j \cdots \psi_k \rangle$$

Let us now show that $\hat{a}_i^\dagger$ is the adjoint of $\hat{a}_i$. From now on we will assume that the one-electron basis $\{\psi_1, \cdots, \psi_i, \cdots \}$ is orthonormal, but most of the results are general. We want to prove the equality

$$\langle n_{1}', \cdots n_{i}', \cdots | \hat{a}_i | n_{1}, \cdots, n_i, \cdots \rangle = \langle \hat{a}_i^\dagger (n_{1}', \cdots, n_{i}', \cdots) | n_{1}, \cdots n_i, \cdots \rangle$$

for any two sequences of occupation numbers $\{n_{1}', \cdots, n_{i}', \cdots \}$ and $\{n_{1}, \cdots, n_i, \cdots \}$. By using the above definition of $\hat{a}_i^\dagger$ the right hand side member becomes

$$(-1)^{\nu_i}(1 - n_i')\delta_{n_{1}', n_1} \cdots \delta_{1 - n_{i}', n_i} \cdots$$

since the many-electron basis vectors are orthonormal. Likewise, the left hand side member is

$$(-1)^{\nu_i}n_i\delta_{n_{1}', n_1} \cdots \delta_{n_{i}', 1 - n_i} \cdots$$

This two expressions vanish unless $n_{1}' = n_1, \cdots n_{i}' = 1 - n_i, \cdots$, in which case they coincide.
3.1 Number operators

The product
\[ \hat{a}_i \hat{a}_i^\dagger \equiv \hat{n}_i \]

is known as occupation number operator of the spin-orbital \( \psi \), for reasons that will now become evident:
\[ \hat{a}_i \hat{a}_i^\dagger |n_1, \cdots n_i, \cdots \rangle = \hat{a}_i^\dagger (-1)^{n_i} n_i |n_1, \cdots 1 - n_i, \cdots \rangle = (-1)^{n_i} (-1)^{n_i} (1 - (1 - n_i)) |n_1, \cdots n_i, \cdots \rangle \]

Since \( n_i \) can only take the values 1 and 0, \( n_i^2 = n_i \) and
\[ \hat{n}_i |n_1, \cdots n_i, \cdots \rangle = n_i |n_1, \cdots n_i, \cdots \rangle \]

That is, \( |n_1, \cdots n_i, \cdots \rangle \) is an eigenvector of \( \hat{n}_i \), and its eigenvalue is the occupation number of the state \( \psi \).

Occupation number operators are self-adjoint:
\[ \langle n'_1, \cdots n'_i, \cdots | \hat{a}_i \hat{a}_i^\dagger | n_1, \cdots n_i, \cdots \rangle = \langle \hat{a}_i \hat{a}_i^\dagger | n_1, \cdots n_i, \cdots | n'_1, \cdots n'_i, \cdots \rangle = \langle \hat{a}_i^\dagger \hat{a}_i | n'_1, \cdots n'_i, \cdots | n_1, \cdots n_i, \cdots \rangle \]

and they commute among themselves, since, for \( i \neq j \),
\[ \hat{a}_i \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_j = \hat{a}_i \hat{a}_j^\dagger \hat{a}_j \hat{a}_i = \hat{a}_j \hat{a}_i^\dagger \hat{a}_i \hat{a}_j \]

Their eigenvalues univocally determine a complete set of state vectors, so that they are a CSCO. On the other hand they are idempotent (\( \hat{n}_i^2 = \hat{n}_i \) for the basis set \{ \( \{n_1, \cdots n_i, \cdots \}\) \}), so that they are projection operators. \( \hat{n}_i \) projects onto the the subspace spanned by the many-electron basis vectors in which \( \psi \) is occupied.

The sum of occupation number operators for every spin-orbital is known as the electron number operator for obvious reasons:
\[ \hat{n} = \sum_i \hat{n}_i \]
\[ \hat{n} |n_1, \cdots n_i, \cdots \rangle = \sum_i n_i |n_1, \cdots n_i, \cdots \rangle = n |n_1, \cdots n_i, \cdots \rangle \]

Different \( \hat{n}_i \) do not project onto orthogonal subspaces, since \( \hat{n}_i \hat{n}_j |n_1, \cdots n_i, \cdots \rangle \neq 0 \) if \( n_i = n_j = 1 \), so, according to theorem 7, \( \hat{n} \) is not a projection operator. 3

In general, linear combinations of Slater determinants \( ^n \Psi \), such as Configuration Interaction wavefunctions, are not eigenfunctions of the occupation number operators, but their expected value can still be used to assign an occupation number to each spin-orbital in the wave function, also referred to as the population of the spin-orbital:
\[ \langle n_i \rangle_{^n \Psi} = \langle ^n \Psi | \hat{n}_i | ^n \Psi \rangle = \sum_I C_I^n \Phi_I \hat{n}_i \sum_J C_J^n \Phi_J = \sum_I C_I^n \Phi_I (\hat{n}_i | ^n \Phi_I \rangle \langle ^n \Phi_I | n_i \Phi_I \rangle) \]

Since \( \hat{n}_i | \Phi_I \rangle = 1 | \Phi_I \rangle \) if \( ^n \Phi_I \) contains \( \psi \), and vanishes otherwise, we can restrict the summation over \( J \) to the determinants containing that spin-orbital:
\[ \langle n_i \rangle_{^n \Psi} = \sum_I C_I^n \Phi_I (\hat{n}_i | ^n \Phi_I \rangle \langle ^n \Phi_I | n_i \Phi_I \rangle) = \sum_I |C_I|^2 \leq 1 \]

Thus, populations are, in general, less than 1 for multiconfigurational wavefunctions. Since all of the \( n \)-electron determinants are eigenfunctions of the electron number operator \( \hat{n} \) with eigenvalue \( n \), the same applies to \( ^n \Psi \).

3.2 Anticommutation rules

Electron creation and annihilation operators fulfill the following anticommutation rules:
\[ [\hat{a}_i, \hat{a}_j^\dagger]_+ = \delta_{ij} \quad [\hat{a}_i, \hat{a}_j]_+ = [\hat{a}_i^\dagger, \hat{a}_j^\dagger]_+ = 0 \]

where the anticommutator is defined as \([\hat{A}, \hat{B}]_+ \equiv \hat{A}\hat{B} + \hat{B}\hat{A}\).

Let us prove the first rule. For \( i < j \) we have

3The restrictions of the operators \( \hat{n}_i \) to \( H_1 \) do project onto orthogonal subspaces, so that the restriction of \( \hat{n} \) to \( H_1 \) is a projection operator which, in fact, is the identity operator in that subspace.
over the spin-orbitals of the one-electron basis

convenient for some mathematical developments and, in particular, for infinite systems such as solids.

We will now obtain an expression of the hamiltonian operator of a many-electron system in terms of creation

operators anticommute if they correspond to different states:

but \( \hat{a}_i \) does not anticommute (nor commute) with \( \hat{a}_i \):

An immediate consequence of these rules is that we cannot create two of them in the same state:

in accordance with the fermionic character of the electrons.

\[ (\hat{a}_i^\dagger)^2 = \frac{1}{2} [\hat{a}_i^\dagger, \hat{a}_i]_+ = 0 \]

exercise

Use the second quantized form of Slater determinants to show that

\[ \langle (\psi_i \psi_j) - | (\psi_k \psi_l) - \rangle = \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}. \]

Hint: Write the determinants as creation operators acting on the vacuum state; then move the creation operators from the left to the right-hand side of the scalar product; then move the resulting annihilation operators to the right until they operate directly on the vacuum state.

4 The many-electron hamiltonian in second quantization

We will now obtain an expression of the hamiltonian operator of a many-electron system in terms of creation and annihilation operators that is independent of the number of electrons in the system. This makes it quite convenient for some mathematical developments and, in particular, for infinite systems such as solids.

The non-relativistic electronic hamiltonian of a system with \( n \) electron and \( N \) nuclei is a sum of one-electron and two-electron terms:

\[ \hat{H} = \sum_{i=1}^{n} h(i) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{1}{r_{ij}} \]

where \( \hat{h}(i) = -\frac{\nabla_i^2}{2} - \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} \). We want to show that the second quantization formalism allows to put it in the form

\[ \hat{H} = \sum_{rs} h_{rs} \hat{a}_r^\dagger \hat{a}_s + \frac{1}{2} \sum_{rstu} g_{rstu} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u \hat{a}_t \]

where \( h_{rs} = \langle \psi_r | \hat{h} | \psi_s \rangle \) and \( g_{rstu} = \langle \psi_r(1) \psi_s(2) | \frac{1}{r_{12}} \psi_t(1) \psi_u(2) \rangle \). To be precise, \( \hat{H} \) is the projection of \( \hat{H} \) onto the \( n \)-electron subspace of \( \mathcal{F} \), also referred to as the restriction of \( \hat{H} \) to that subspace. The sums extend over the spin-orbitals of the one-electron basis \( \{ \psi_r \} \), there being no reference to \( n \).
To prove the preceding statement we will show that $\hat{H}$ and $\tilde{H}$ (restricted to $\mathcal{H}^R$) have the same matrix elements for a given $n$-electron basis set. Let us first consider the one-electron part of $\tilde{H}$. Its matrix element are:

$$
\left\langle \psi_k \cdots \psi_l \right| \sum_{rs} h_{rs} \hat{a}_r^+ \hat{a}_s \left| \psi_k \cdots \psi_l \right\rangle = \sum_{rs} h_{rs} \left\langle \hat{a}_r \left| \psi_k \cdots \psi_l \right\rangle \right| \hat{a}_s \left| \psi_k \cdots \psi_l \right\rangle
$$

This vanishes unless $r \in \{k' \cdots l'\}$ and $s \in \{k \cdots l\}$. If both $n$-electron basis vectors are equal the only non-vanishing terms in the double sum correspond to $r = s$, and the corresponding diagonal matrix element reduces to

$$
\sum_{r \in \{k \cdots l\}} h_{rr} \left\langle \hat{a}_r \left| \psi_k \cdots \psi_l \right\rangle \right| \hat{a}_r \left| \psi_k \cdots \psi_l \right\rangle = \sum_{r \in \{k \cdots l\}} h_{rr}
$$

If the two basis vectors differ in one spin-orbital —say $\psi_a$ in the former is replaced by $\psi_b$ in the latter— then the only surviving term in the double sum is the one with $r = a$ and $s = b$; that is $h_{ab}$. If there are two or more differing spin-orbitals the matrix element vanishes. These results are the Slater-Condon rules for the one-electron-type operator $\sum_{i=1}^n h(i)$.

Let us now consider the two-electron terms of the second quantized hamiltonian. For a diagonal matrix element we have

$$
\left\langle \psi_k \cdots \psi_l \right| \frac{1}{2} \sum_{rstu} g_{rstu} \hat{a}_r^+ \hat{a}_s^+ \hat{a}_t^+ \hat{a}_u \left| \psi_k \cdots \psi_l \right\rangle = \frac{1}{2} \sum_{rstu} g_{rstu} \left\langle \hat{a}_r \hat{a}_t \right| \hat{a}_s \hat{a}_u \left| \psi_k \cdots \psi_l \right\rangle
$$

The terms in this sum vanish unless $r = t \in \{k \cdots l\}$ and $s = u \in \{k \cdots l\}$ or $r = u \in \{k \cdots l\}$ and $s = t \in \{k \cdots l\}$. Thus, the diagonal matrix element reduces

$$
= \frac{1}{2} \sum_{r,s \in \{k \cdots l\}} g_{rsrs} - g_{rsst} = \sum_{r \in \{k \cdots l\}} \sum_{s \in \{k \cdots l\}, s > r} g_{rsrs} - g_{rsst}
$$

where we have taken into account the anticommutativity of the annihilation operators. Similar deductions can be applied for non-diagonal matrix elements. The expressions resulting for all these matrix elements are the Slater-Condon rules for the two-electron-type operator $\sum_{i=1}^n \sum_{j=i+1}^n \frac{1}{r_{ij}}$.

The diagonal matrix element of $\tilde{H}$ corresponding to the Hartree-Fock Slater determinant $^n\Phi_0$ is the Hartree-Fock energy:

$$
E^{HF} = \left\langle ^n\Phi_0 \right| \tilde{H} \left| ^n\Phi_0 \right\rangle = \sum_{rs} h_{rs} \left\langle ^n\Phi_0 \right| \hat{a}_r^+ \hat{a}_s \left| ^n\Phi_0 \right\rangle + \frac{1}{2} \sum_{rstu} g_{rstu} \left\langle ^n\Phi_0 \right| \hat{a}_r^+ \hat{a}_t^+ \hat{a}_u \hat{a}_s \left| ^n\Phi_0 \right\rangle
$$

where the sums extend over the occupied spin-orbitals of $^n\Phi_0$. Although the number of electrons does not appear explicitly in this expression, it is implied in the list of occupation numbers of $^n\Phi_0 = \{n_1, \cdots , n_i, \cdots \}$: $n = \sum_{i} n_i$.

In the above demonstration we have assumed that the spin-orbitals $\psi_i$ form a complete set. For computational reasons a finite subset must be used, so that the second quantized hamiltonian is, in fact, the projection of the exact Hamiltonian onto the subspace spanned by that subset.

Similar expressions to those obtained for $\sum_{i=1}^n h(i)$ and $\sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{r_{ij}}$ can be used to write the second quantized form of any one- or two-electron-type operator.

**Exercise**

Use the anticommutation rules to show that a one-electron-type operator of an $n$-electron system, $\hat{F} = \sum_{i=1}^n f(i)$, can be cast into the form of a two-electron-type operator:

$$
\hat{F} = \frac{1}{n-1} \sum_{rstu} f_{rt} \delta_{su} \hat{a}_r^+ \hat{a}_s^+ \hat{a}_u \hat{a}_t = \frac{1}{n-1} \sum_{rstu} \delta_{rt} f_{su} \hat{a}_r^+ \hat{a}_s^+ \hat{a}_u \hat{a}_t
$$

(these being restricted to the $n$-electron subspace).
4.1 Restricted spin-orbitals

Usually the spin-orbitals $\psi_r$ are chosen as products of an orbital $\phi_r$ and a spin vector $\sigma$ or $\bar{\sigma}$. Then $D_{r} \psi_r = 0$ unless $\psi_r$ and $\psi_s$ have the same spin factor, and $D_{r} \psi_s = 0$ unless $\psi_r$ and $\psi_t$ on the one hand, and $\psi_s$ and $\psi_u$ on the other, have the same spin factor. By carrying out the scalar products of the spin factors we are left with scalar products involving only orbitals. Thus, for a closed-shell determinant the electronic hamiltonian takes the form:

$$\hat{H} = \sum_{rs} h_{rs} \sum_{\sigma=\alpha,\beta} a_{r\sigma}^\dagger a_{s\sigma} + \frac{1}{2} \sum_{rstu} g_{rstu} \sum_{\sigma,\tau=\alpha,\beta} a_{r\sigma}^\dagger a_{s\tau}^\dagger a_{u\tau} a_{t\sigma}$$

where $h_{rs} = \langle \phi_r | \hat{h} | \phi_s \rangle$, $g_{rstu} = \langle \phi_r(1)\phi_s(2) | \frac{1}{r_{12}} \phi_t(1)\phi_u(2) \rangle$ and the indexes $r$, $s$, $t$ and $u$ extend over the orbital basis. As told before, this basis set must be truncated in practice to a finite number $m$, so that we work on a $2m$-dimensional subspace of $\mathcal{H}_1$. Then the sums over $r$, $s$, $t$ and $u$ in the preceding equation extend over those $m$ orbitals and the resulting second-quantized operator is an approximation to the true hamiltonian $\hat{H}$.

5 Non-fixed-particle systems

It is clear that the second quantized operator of any observable in fixed-particle quantum mechanics must contain an equal number of creation and annihilation operators, so that these should always appear in pairs of either type. However, single operators that create or annihilate photons are needed to study spectroscopic phenomena in which the quantum nature of light plays a relevant role, such as the spontaneous emission of radiation or the Raman scattering. Since photons have spin 1 they are bosons and the corresponding creation and annihilation operators are defined otherwise (see, for instance, Quantum electrodynamics by José A. N. F. Gomes and Juan C. Paniagua, in Computational Chemistry: Structure, Interactions and Reactivity, ed. by S. Fraga. Studies in Physical and Theoretical Chemistry, vol. 77 (B). Elsevier, Amsterdam (1992)).

6 Particles and holes

Electron creation and annihilation operators are sometimes referred to a Fermi vacuum (or Fermi sea) instead of the zero-electron vacuum. The Fermi vacuum is the independent-electron ground state, in which all the electrons occupy the lowest-energy spin-orbitals. The energy of the highest occupied spin-orbital is known as the Fermi level. The independent-particle excited states are identified by specifying their occupation number differences with respect to that state vector; that is, the holes created in the Fermi sea by the operators $\hat{a}_q^\dagger$ and the particles created above the Fermi level by operators such as $\hat{a}_q$. That is, an operator that annihilates an electron below the Fermi level is viewed as a hole creation operator. A hole acts as a particle (a quasi-particle) with positive charge $e$, and a neutral pair formed by an electron and a hole interacting by electrostatic attraction is sometimes called an exciton.

The language of particles and holes is common in solid-state theory, and it is also sometimes used for finite systems, particularly in the statement of some post-Hartree-Fock methods such as configuration interaction or coupled cluster.