Second Quantization Formalism*

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Contents

1 Introduction

Material particles can be created or destroyed in processes such as the conversion of a gamma photon into an electron-positron pair. To deal such phenomena we need to resort to quantum electrodynamics, that treats the interplay between electrons, positrons and photons. In this theory operators that create or destroy particles play a central role. In ordinary chemical processes the number of particles is kept constant, so no creation and annihilation operators are needed to describe them.[1] The standard quantum mechanic theory for material particles, in which the number of particles of every type does not change over time, is then a suitable theoretical framework. However, even in this context it is often convenient to use some tools of quantum field theories — specifically, the creation and annihilation operators— to state certain mathematical developments, particularly in the study of infinite systems. This way of formulating the theory is known as *second quantization formalism*.[2]

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* ($\mathcal{F}$). 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.[3]

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

$$\mathcal{F} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_1^{\otimes^a 2} \oplus \cdots \mathcal{H}_1^{\otimes^a n} \oplus \cdots$$

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 ${}^0\Phi = |\rangle$ 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 $\{\psi_1, \cdots \psi_i, \cdots\}$ in $\mathcal{H}_1$. The set $\{{}^n\Phi_I\}$ of all n-electron Slater determinants

$${}^n\Phi_I \equiv \left|(\psi_{1_I} \cdots \psi_{n_I})_-\right\rangle$$

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

$$\left\{{}^0\Phi, \left\{{}^1\Phi_I\right\}, \left\{{}^2\Phi_I\right\} \cdots \left\{{}^n\Phi_I\right\} \cdots\right\}$$

is a normalized basis of $\mathcal{F}$.

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:

$${}^n\Phi_I = |n_1, \cdots n_i, \cdots\rangle \qquad \text{with} \qquad n = \sum_i n_i$$

For instance, if $\psi_1 \cdots \psi_n$ are the first n spin-orbitals of the one-electron basis set, then ${}^n\Phi_0 = \left|(\psi_1 \cdots \psi_n)_-\right\rangle = |\underbrace{1, \cdots 1}_{n}, 0, 0, \cdots\rangle$. For the vacuum state all the occupation numbers are 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* $\widehat{a}_i$ of an electron in the spin-orbital ψ_i is conveniently defined in the occupation-number representation as

$$\boxed{\widehat{a}_i\,|n_1, \cdots n_i, \cdots\rangle = (-1)^{\nu_i} n_i\,|n_1, \cdots 1 - n_i, \cdots\rangle}$$

[1] One exception are certain spectroscopic phenomena that require a quantum description of electromagnetic radiation, in which photons can be created (radiation emission) and destroyed (radiation absorption).

[2] While 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".

[3] One 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.

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:

$$\begin{aligned} \widehat{a_1}\,|1, n_2, \cdots n_i, \cdots\rangle &= |0, n_2, \cdots n_i, \cdots\rangle \\ \widehat{a_2}\,|0, 1, \cdots n_i, \cdots\rangle &= |0, 0, \cdots n_i, \cdots\rangle \\ \widehat{a_2}\,|1, 1, \cdots n_i, \cdots\rangle &= -\,|1, 0, \cdots n_i, \cdots\rangle \end{aligned}$$

That is, if the spin-orbital ψ_i is occupied in the many-electron vector $|n_1, \cdots n_i, \cdots\rangle$ then $\widehat{a_i}$ annihilates an electron in that spin-orbital. So, from an n-electron vector we obtain an (n-1)-electron vector. Besides, it changes the sign of the vector if ψ_i was in an even position among the occupied states. If ψ_i is empty in $|n_1, \cdots n_i, \cdots\rangle$ the result of applying $\widehat{a_i}$ to this vector is zero. Thus

$$\widehat{a_1}\,|0, n_2, \cdots n_i, \cdots\rangle = 0$$

When we use the usual occupied-spin-orbitals-only notation for the Slater determinants then the effect of the annihilation operator $\widehat{a_i}$ over a determinant containing ψ_i takes the form:

$$\boxed{\widehat{a_i}\,\Big|(\psi_j \cdots \psi_i \cdots \psi_k)_-\Big\rangle = (-1)^{\nu_i}\,\Big|\big(\psi_j \cdots \cancel{\psi_i} \cdots \psi_k\big)_-\Big\rangle}$$

where ν_i is again the position number of ψ_i minus 1, and $\cancel{\psi_i}$ means that ψ_i is absent in the determinant. ν_i is also the number of transpositions needed to bring ψ_i to the first position of the determinant.[4] Since every transposition introduces a change of sign, we can obtain the effect of $\widehat{a_i}$ by first bringing ψ_i to the first position and then dropping it from the determinant.

For a determinant that does not contain ψ_i it is clear that

$$\widehat{a_i}\,\Big|\big(\psi_j \cdots \cancel{\psi_i} \cdots \psi_k\big)_-\Big\rangle = 0$$

The *creation operator* $\widehat{a_i}^\dagger$ of an electron in the spin-orbital ψ_i is defined by

$$\boxed{\widehat{a_i}^\dagger\,|n_1, \cdots n_i, \cdots\rangle = (-1)^{\nu_i}(1 - n_i)\,|n_1, \cdots 1 - n_i, \cdots\rangle}$$

Some examples reveal that this operator creates an electron in the spin-orbital ψ_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:

$$\begin{aligned} \widehat{a_1}^\dagger\,|0, n_2, \cdots n_i, \cdots\rangle &= |1, n_2, \cdots n_i, \cdots\rangle \\ \widehat{a_2}^\dagger\,|0, 0, \cdots n_i, \cdots\rangle &= |0, 1, \cdots n_i, \cdots\rangle \\ \widehat{a_2}^\dagger\,|1, 0, \cdots n_i, \cdots\rangle &= -\,|1, 1, \cdots n_i, \cdots\rangle \end{aligned}$$

Therefore, it produces an (n+1)-electron vector from an n-electron one. If ψ_i is occupied in $|n_1, \cdots n_i, \cdots\rangle$ the result of applying $\widehat{a_i}^\dagger$ to this vector is zero; for instance:

$$\widehat{a_1}^\dagger\,|1, n_2, \cdots n_i, \cdots\rangle = 0$$

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

$$|n_1, \cdots n_i, \cdots\rangle = \left(\widehat{a_1}^\dagger\right)^{n_1} \cdots \left(\widehat{a_i}^\dagger\right)^{n_i} \cdots |0, \cdots 0, \cdots\rangle$$

In terms of the occupied-spin-orbitals-only notation the effect of the creation operator $\widehat{a_i}^\dagger$ over a determinant not containing ψ_i is:

$$\widehat{a_i}^\dagger\,\Big|\big(\psi_j \cdots \cancel{\psi_i} \cdots \psi_k\big)_-\Big\rangle = (-1)^{\nu_i}\,\Big|(\psi_j \cdots \psi_i \cdots \psi_k)_-\Big\rangle$$

where ν_i is the position in which ψ_i has been made to appear minus 1. ν_i is also the number of transpositions needed to bring ψ_i to the first position of the determinant:

$$\widehat{a_i}^\dagger\,\Big|(\psi_j \cdots \psi_{i-1}\psi_{i+1} \cdots \psi_k)_-\Big\rangle = (-1)^{\nu_i}\,\Big|(\psi_j \cdots \psi_{i-1}\psi_i\psi_{i+1} \cdots \psi_k)_-\Big\rangle = \Big|(\psi_i\psi_j \cdots \psi_{i-1}\psi_{i+1} \cdots \psi_k)_-\Big\rangle$$

so that we can also say that $\widehat{a_i}^\dagger$ creates an electron in the spin-orbital ψ_i placed in the first position of the determinant:

$$\boxed{\widehat{a_i}^\dagger\,\Big|\big(\psi_j \cdots \cancel{\psi_i} \cdots \psi_k\big)_-\Big\rangle = \Big|(\psi_i\psi_j \cdots \psi_k)_-\Big\rangle}$$

[4] When the Slater determinants are represented by sequences of occupation numbers the spin-orbital ordering must be the same for all of them, but in the occupied-spin-orbitals-only notation this ordering can be altered.

Then, if we want to advance it ν_i positions we have to introduce ν_i changes of sign; that is, we have to multiply the determinant by $(-1)^{\nu_i}$.

It is evident that

$$\widehat{a_i}^\dagger \left| (\psi_j \cdots \psi_i \cdots \psi_k)_- \right\rangle = 0$$

Let us now show that $\widehat{a_i}^\dagger$ *is the adjoint of* $\widehat{a_i}$. *From now on we will assume that the one-electron basis* $\{\psi_1, \cdots \psi_i, \cdots\}$ *is orthonormal*, although some of the results that will be obtained are independent of this assumption.

We want to prove the equality

$$\langle n'_1, \cdots n'_i, \cdots | \widehat{a_i} | \, n_1, \cdots n_i, \cdots \rangle = \left\langle \widehat{a_i}^\dagger (n'_1, \cdots n'_i, \cdots) \right| \, n_1, \cdots n_i, \cdots \right\rangle$$

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 $\widehat{a_i}^\dagger$ the right hand side member becomes

$$(-1)^{\nu'_i}(1 - n'_i) \, \langle n'_1, \cdots 1 - n'_i, \cdots | \, n_1, \cdots n_i, \cdots \rangle = (-1)^{\nu'_i}(1 - n'_i)\delta_{n'_1, n_1} \cdots \delta_{1-n'_i, n_i} \cdots$$

Likewise, the left hand side member is

$$\langle n'_1, \cdots n'_i, \cdots | (-1)^{\nu_i} n_i | \, n_1, \cdots 1 - n_i, \cdots \rangle = (-1)^{\nu_i} n_i \delta_{n'_1, n_1} \cdots \delta_{n'_i, 1-n_i} \cdots$$

This two expressions vanish unless $n'_1 = n_1, \cdots n'_i = 1 - n_i \cdots$, in which case they coincide.

Exercise
Let $\Phi = \left| (\psi_1 \cdots \psi_i \cdots \psi_n)_- \right\rangle$ be the Hartree-Fock Slater determinant of an n-electron system and let Φ_i^k be the determinant that results upon changing in Φ the occupied spin-orbital ψ_i by an empty one ψ_k. The spin-orbitals are assumed orthonormal.

- Write Φ_i^k in terms of Φ by applying on this the proper creation and annihilation operators.
- Use the resulting expression to show that $\left\langle \Phi \left| \Phi_i^k \right. \right\rangle = 0$.

3.1 Number operators

The product

$$\boxed{\widehat{a_i}^\dagger \widehat{a_i} \equiv \widehat{n_i}}$$

is known as *occupation number operator* of the spin-orbital ψ_i for reasons that will now become evident:

$$\widehat{a_i}^\dagger \widehat{a_i} \, | n_1, \cdots n_i, \cdots \rangle = \widehat{a_i}^\dagger (-1)^{\nu_i} n_i \, | n_1, \cdots 1 - n_i, \cdots \rangle = (-1)^{\nu_i} n_i (-1)^{\nu_i} (1 - (1 - n_i)) \, | n_1, \cdots n_i, \cdots \rangle$$

Since n_i can only take the values 1 and 0, $n_i^2 = n_i$ and

$$\widehat{n_i} \, | n_1, \cdots n_i, \cdots \rangle = n_i \, | n_1, \cdots n_i, \cdots \rangle$$

That is, $| n_1, \cdots n_i, \cdots \rangle$ is an eigenvector of $\widehat{n_i}$, and its eigenvalue is the occupation number of the state ψ_i.

Occupation number operators are self-adjoint:

$$\left\langle n'_1, \cdots n'_i, \cdots \left| \widehat{a_i}^\dagger \widehat{a_i} \right| \, n_1, \cdots n_i, \cdots \right\rangle = \langle \widehat{a_i}(n'_1, \cdots n'_i, \cdots) \, | \widehat{a_i} | \, n_1, \cdots n_i, \cdots \rangle = \left\langle \widehat{a_i}^\dagger \widehat{a_i}(n'_1, \cdots n'_i, \cdots) | n_1, \cdots n_i, \cdots \right\rangle$$

and they commute among themselves, since, for $i \neq j$,

$$\widehat{a_i}^\dagger \widehat{a_i} \widehat{a_j}^\dagger \widehat{a_j} = \widehat{a_i}^\dagger \widehat{a_j}^\dagger \widehat{a_j} \widehat{a_i} = \widehat{a_j}^\dagger \widehat{a_j} \widehat{a_i}^\dagger \widehat{a_i}$$

Their eigenvalues univocally determine a complete set of state vectors, so that they are a complete set of commuting observables. On the other hand they are idempotent ($\widehat{n_i}^2 = \widehat{n_i}$ for the basis set $\{| n_1, \cdots n_i, \cdots \rangle\}$), so that they are projection operators. $\widehat{n_i}$ projects onto the the subspace spanned by all the Slater determinants containing ψ_i.

The sum of occupation number operators for every spin-orbital is known as the *electron number operator* for obvious reasons:

$$\boxed{\widehat{n} = \sum_i \widehat{n_i}}$$

$$\widehat{n}\,|n_1,\cdots n_i,\cdots\rangle = \sum_i n_i\,|n_1,\cdots n_i,\cdots\rangle = n\,|n_1,\cdots n_i,\cdots\rangle$$

Different $\widehat{n_i}$ do not project onto orthogonal subspaces, since $\widehat{n_i}\widehat{n_j}\,|n_1,\cdots n_i,\cdots\rangle \neq 0$ if $n_i = n_j = 1$, so that theorem 7 cannot be applied[5] and, in fact, their sum $\widehat{n}$ is not a projection operator. The restrictions of the operators $\widehat{n_i}$ to $\mathcal{H}_1$ do project onto orthogonal one-dimensional subspaces, so that the definition of $\widehat{n}$ is a resolution of the identity in that subspace, and $\widehat{n}$ restricted to $\mathcal{H}_1$ is the identity operator in the spin-orbital subspace.

In general, linear combinations of Slater determinants ${}^n\Psi$ —such as multiconfigurational wavefunctions— are not eigenvectors 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:

$$\langle n_i\rangle_{{}^n\Psi} = \langle {}^n\Psi\,|\widehat{n_i}\;{}^n\Psi\rangle = \left\langle \sum_I C_I\,{}^n\Phi_I\,|\widehat{n_i}\sum_J C_J\,{}^n\Phi_J\right\rangle = \sum_{IJ} C_I^* C_J\,\langle {}^n\Phi_I\,|\widehat{n_i}\;{}^n\Phi_J\rangle$$

Since $\widehat{n_i}\,{}^n\Phi_J = {}^n\Phi_J$ if ${}^n\Phi_J$ contains ψ_i and vanishes otherwise, we can restrict the summation over J to the determinants containing that spin-orbital:

$$\langle n_i\rangle_{{}^n\Psi} = \sum_{I,J\ni i} C_I^* C_J\,\langle {}^n\Phi_I\,|{}^n\Phi_J\rangle = \sum_{I\ni i}|C_I|^2 \leq 1$$

Thus, spin-orbital populations are, in general, less than 1 for multiconfigurational wave functions. Certainly, all of the n-electron determinants are eigenfunctions of the electron number operator $\widehat{n}$ with eigenvalue n, so that the same applies to ${}^n\Psi$.

3.2 Anticommutation rules

Electron creation and annihilation operators fulfill the following anticommutation rules:

$$\boxed{\left[\widehat{a_i},\widehat{a_j}^\dagger\right]_+ = \delta_{ij} \qquad [\widehat{a_i},\widehat{a_j}]_+ = \left[\widehat{a_i}^\dagger,\widehat{a_j}^\dagger\right]_+ = 0}$$

where the anticommutator is defined as $\left[\widehat{A},\widehat{B}\right]_+ \equiv \widehat{A}\widehat{B} + \widehat{B}\widehat{A}$.

Let us prove the first rule. For $i < j$ we have

$$\begin{aligned}\left(\widehat{a_i}\widehat{a_j}^\dagger + \widehat{a_j}^\dagger\widehat{a_i}\right)|n_1,\cdots n_i,\cdots\rangle &= \widehat{a_i}(-1)^{\nu_j}(1-n_j)\,|n_1,\cdots 1-n_j,\cdots\rangle + \widehat{a_j}^\dagger(-1)^{\nu_i}n_i\,|n_1,\cdots 1-n_i,\cdots\rangle \\ &= (-1)^{\nu_j}(1-n_j)(-1)^{\nu_i}n_i\,|n_1,\cdots 1-n_i,\cdots 1-n_j,\cdots\rangle \\ &\quad +(-1)^{\nu_i}n_i(-1)^{\nu'_j}(1-n_j)\,|n_1,\cdots 1-n_i,\cdots 1-n_j,\cdots\rangle = 0\end{aligned}$$

since $\nu'_j = \nu_j \pm 1$, depending on n_i being 0 or 1 respectively. For $i = j$

$$\begin{aligned}\left(\widehat{a_i}\widehat{a_i}^\dagger + \widehat{a_i}^\dagger\widehat{a_i}\right)|n_1,\cdots n_i,\cdots\rangle &= \widehat{a_i}(-1)^{\nu_i}(1-n_i)\,|n_1,\cdots 1-n_i,\cdots\rangle + n_i\,|n_1,\cdots n_i,\cdots\rangle \\ &= (-1)^{2\nu_i}(1-n_i)^2\,|n_1,\cdots n_i,\cdots\rangle + n_i\,|n_1,\cdots n_i,\cdots\rangle = |n_1,\cdots n_i,\cdots\rangle\end{aligned}$$

since n_i or $1-n_i$ must vanish.

According to these rules, if we commute a pair of annihilation or creation operators we have to introduce a change of sign; that is, those pairs of operators anticommute:

$$\widehat{a_i}\widehat{a_j} = -\widehat{a_j}\widehat{a_i} \qquad \widehat{a_i}^\dagger\widehat{a_j}^\dagger = -\widehat{a_j}^\dagger\widehat{a_i}^\dagger$$

If the two operators are of either type then

$$\widehat{a_i}\widehat{a_j}^\dagger = \delta_{ij} - \widehat{a_j}^\dagger\widehat{a_i}$$

so that they anticommute if they correspond to different states:

$$\widehat{a_i}\widehat{a_j}^\dagger = -\widehat{a_j}^\dagger\widehat{a_i} \qquad \text{for } i \neq j$$

but $\widehat{a_i}$ does not anticommute (nor commute) with $\widehat{a_i}^\dagger$:

$$\widehat{a_i}\widehat{a_i}^\dagger = 1 - \widehat{a_i}^\dagger\widehat{a_i}$$

[5] A linear combination of projectors onto orthogonal subspaces is a projector if and only if all the coefficients are equal to 1.

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

$$\left(\widehat{a_i}^\dagger\right)^2 = \frac{1}{2}\left[\widehat{a_i}^\dagger, \widehat{a_i}^\dagger\right]_+ = 0$$

in accordande with the fermionic character of these particles.

Exercise
Use the occupation-number representation of the 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 non-relativistic many-electron hamiltonian in second quantization

We will now obtain an expression of the non-relativistic 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:

$$^n\widehat{H} = \sum_{i=1}^{n} h(i) + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \frac{1}{r_{ij}}$$

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

$$\boxed{\widehat{H} = \sum_{rs} h_{rs}\widehat{a_r}^\dagger\widehat{a_s} + \frac{1}{2}\sum_{rstu} g_{rstu}\widehat{a_r}^\dagger\widehat{a_s}^\dagger\widehat{a_u}\widehat{a_t}}$$

where $h_{rs} = \left\langle \psi_r \middle| \widehat{h}\ \psi_s \right\rangle$ and $g_{rstu} = \left\langle \psi_r(1)\psi_s(2) \middle| \frac{1}{r_{12}}\ \psi_t(1)\psi_u(2) \right\rangle$. To be precise, $^n\widehat{H}$ is the projection of $\widehat{H}$ onto the n-electron subspace of $\mathcal{F}$, also referred to as the *restriction* of $\widehat{H}$ 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 $^n\widehat{H}$ and $\widehat{H}$ (restricted to $\mathcal{H}_1^{\otimes^a n}$) have the same matrix elements for a given n-electron basis set. Let us first consider the one-electron part of $\widehat{H}$. Its matrix element are:

$$\left\langle (\psi_{k'}\cdots\psi_{l'})_- \middle| \sum_{rs} h_{rs}\widehat{a_r}^\dagger\widehat{a_s} \middle| (\psi_k\cdots\psi_l)_- \right\rangle = \sum_{rs} h_{rs} \left\langle \widehat{a_r}\,(\psi_{k'}\cdots\psi_{l'})_- \,|\widehat{a_s}\ (\psi_k\cdots\psi_l)_- \right\rangle$$

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

$$\sum_{r\in\{k\cdots l\}} h_{rr} \left\langle \widehat{a_r}\,(\psi_k\cdots\psi_l)_- \,|\widehat{a_r}\ (\psi_k\cdots\psi_l)_- \right\rangle = \sum_{r\in\{k\cdots l\}} h_{rr}$$

If the two basis vectors differ in one spin-orbital —say ψ_a in the former is replaced by ψ_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

$$\left\langle (\psi_k\cdots\psi_l)_- \middle| \frac{1}{2}\sum_{rstu} g_{rstu}\widehat{a_r}^\dagger\widehat{a_s}^\dagger\widehat{a_u}\widehat{a_t} \middle| (\psi_k\cdots\psi_l)_- \right\rangle = \frac{1}{2}\sum_{rstu} g_{rstu} \left\langle \widehat{a_s}\widehat{a_r}\,(\psi_k\cdots\psi_l)_- \,|\widehat{a_u}\widehat{a_t}\ (\psi_k\cdots\psi_l)_- \right\rangle$$

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, this diagonal element reduces

$$\begin{aligned}
&\frac{1}{2} \sum_{r,s \in \{k \cdots l\}} g_{rsrs} \left\langle \widehat{a_s} \widehat{a_r} \left(\psi_k \cdots \psi_l\right)_- \left| \widehat{a_s} \widehat{a_r} \left(\psi_k \cdots \psi_l\right)_- \right\rangle + g_{rssr} \left\langle \widehat{a_s} \widehat{a_r} \left(\psi_k \cdots \psi_l\right)_- \left| \widehat{a_r} \widehat{a_s} \left(\psi_k \cdots \psi_l\right)_- \right\rangle \right. \\
&= \frac{1}{2} \sum_{r,s \in \{k \cdots l\}} g_{rsrs} - g_{rssr} = \sum_{r,s \in \{k \cdots l\}, r > s} g_{rsrs} - g_{rssr}
\end{aligned}$$

where we have taken into account the anticommutativity of the annihilation operators. Similar deductions can be applied for non-diagonal matrix elements, leading to the Slater-Condon rules for the two-electron-type operator $\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{1}{r_{ij}}$. This completes the proof.

In the above demonstration we have assumed that the spin-orbitals ψ_r 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
Show that the second quantized form of the first-order reduced density operator $\widehat{\gamma}$ in an arbitrary orthonormal spin-orbital basis set is

$$\widehat{\gamma} = \sum_{rs} \gamma_{rs} \widehat{a_r}^\dagger \widehat{a_s}$$

and, for the natural spin-orbital basis,

$$\widehat{\gamma} = \sum_{i} n_i \widehat{a_i}^\dagger \widehat{a_i} = \sum_{i} n_i \widehat{n_i}$$

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

$$\widehat{F} = \frac{1}{n-1} \sum_{rstu} f_{rt} \delta_{su} \widehat{a_r}^\dagger \widehat{a_s}^\dagger \widehat{a_u} \widehat{a_t} = \frac{1}{n-1} \sum_{rstu} \delta_{rt} f_{su} \widehat{a_r}^\dagger \widehat{a_s}^\dagger \widehat{a_u} \widehat{a_t}$$

both being restricted to the n-electron subspace of the Fock space. *Hint*: use the anticommutation rules to bring $\widehat{a_t}$ next to $\widehat{a_r}^\dagger$ to obtain $\sum_{rt} f_{rt} \widehat{a_r}^\dagger \widehat{a_t} = \widehat{F}$; use also $\widehat{n} = \sum_s \widehat{n_s}$.
Use this result to write the n-electron hamiltonian as a sum of two-electron operators:

$$\widehat{H} = \sum_{rstu} w_{rstu} \widehat{a_r}^\dagger \widehat{a_s}^\dagger \widehat{a_u} \widehat{a_t} \quad \text{with} \quad w_{rstu} = \frac{1}{n-1} h_{rt} \delta_{su} \widehat{a_r}^\dagger \widehat{a_s}^\dagger \widehat{a_u} \widehat{a_t} + \frac{1}{2} g_{rstu}$$

The expected value of the hamiltonian for any n-electron state ${}^n\Psi$ in in the second quantization formalism is

$$\begin{aligned}
\left\langle {}^n\Psi \left| \widehat{H} \right| {}^n\Psi \right\rangle &= \sum_{rs} h_{rs} \left\langle {}^n\Psi \left| \widehat{a_r}^\dagger \widehat{a_s} \right| {}^n\Psi \right\rangle + \frac{1}{2} \sum_{rstu} g_{rstu} \left\langle {}^n\Psi \left| \widehat{a_r}^\dagger \widehat{a_s}^\dagger \widehat{a_u} \widehat{a_t} \right| {}^n\Psi \right\rangle \\
&= \sum_{rs} h_{rs} \left\langle \widehat{a_r}\ {}^n\Psi \left| \widehat{a_s} \right| {}^n\Psi \right\rangle + \frac{1}{2} \sum_{rstu} g_{rstu} \left\langle \widehat{a_s} \widehat{a_r}\ {}^n\Psi \left| \widehat{a_u} \widehat{a_t} \right| {}^n\Psi \right\rangle
\end{aligned}$$

For the particular case of a single-determinant wave function ${}^n\Phi$ the only non-vanishing terms in the above summations are those for which r, s, t and u correspond to spin-orbitals that are occupied in the determinant,

and the usual Hartree-Fock-type energy expression is readily obtained:

$$\begin{aligned}\left\langle {}^n\Phi \left| \widehat{H} \right| {}^n\Phi \right\rangle &= \sum_{rs}^{occ} h_{rs} \left\langle \widehat{a_r}\ {}^n\Phi \left| \widehat{a_s} \right| {}^n\Phi \right\rangle + \frac{1}{2} \sum_{rstu}^{occ} g_{rstu} \left\langle \widehat{a_s}\widehat{a_r}\ {}^n\Phi \left| \widehat{a_u}\widehat{a_t} \right| {}^n\Phi \right\rangle \\ &= \sum_{r}^{occ} h_{rr} + \frac{1}{2} \sum_{rs}^{occ} g_{rsrs} - g_{rssr} \\ &= \sum_{r}^{occ} h_{rr} + \sum_{r<s}^{occ} g_{rsrs} - g_{rssr}\end{aligned}$$

Although the number of electrons does not appear explicitly in the above expressions, it is implied in the lists of occupation numbers of the n-electron basis vectors ${}^n\Phi_I = |n_1, \cdots n_i, \cdots\rangle$: $n = \sum_i n_i$.

4.1 Restricted spin-orbitals

Usually the spin-orbitals ψ_r are chosen as products of an orbital ϕ_r and a spin vector α or β. Then $\left\langle \psi_r \left| \widehat{h}\ \psi_s \right\rangle \right. = 0$ unless ψ_r and ψ_s have the same spin factor, and $\left\langle \psi_r\psi_s \left| \frac{1}{r_{12}}\ \psi_t\psi_u \right\rangle \right. = 0$ unless ψ_r and ψ_t on the one hand, and ψ_s and ψ_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:

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

where $h_{rs} = \left\langle \phi_r \left| \widehat{h}\ \phi_s \right\rangle \right.$, $g_{rstu} = \left\langle \phi_r(1)\phi_s(2) \left| \frac{1}{r_{12}}\ \phi_t(1)\phi_u(2) \right\rangle \right.$ 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 ${}^n\widehat{H}$.

5 Change of spin-orbital basis set

For each spin-orbital basis set there is a corresponding set of creation and annihilation operators, and different sets can be connected by using the appropriate resolutions of the identity. So, the operators $\widehat{a'_r}^\dagger$ corresponding to a new basis set $\{\psi'_1, \cdots \psi'_r, \cdots\}$ should satisfy the equation

$$\widehat{a'_r}^\dagger |\rangle = \psi'_r = \left(\sum_i |\psi_i\rangle \langle\psi_i| \right) \psi'_r = \sum_i \langle \psi_i | \psi'_r \rangle\, \widehat{a_i}^\dagger |\rangle$$

which is clearly fulfilled if

$$\widehat{a'_r}^\dagger = \sum_i \langle \psi_i | \psi'_r \rangle\, \widehat{a_i}^\dagger$$

By applying his relationship to each basis vector of the Fock space it can be shown to be general. This relationship is, in fact, the same that connects the elements of the two basis sets:

$$\psi'_r = \sum_i \langle \psi_i | \psi'_r \rangle\, \psi_i$$

By taking adjoints in both sides of the transformation equation for creation operators one obtains the corresponding relation for the annihilation operators:

$$\widehat{a'_r} = \sum_i \langle \psi'_r | \psi_i \rangle\, \widehat{a_i}$$

5.1 Field operators

If we change to a continuous basis set, as the position eigenvectors $\{|\vec{r}, \omega\rangle\}$, the resulting creation and annihilation operators will be functions of a continuous index ($\vec{r}$), and they are called *field operators* or *quantum field operators*. The preceding equation then becomes

$$\widehat{a}(\vec{r}, \omega) = \sum_i \langle \vec{r}, \omega | \psi_i \rangle\, \widehat{a_i} = \sum_i \psi_i(\vec{r}, \omega) \widehat{a_i}$$

and, by taking adjoints,

$$\widehat{a}^\dagger(\vec{r},\omega) = \sum_i \psi_i^*(\vec{r},\omega)\widehat{a_i}^\dagger$$

$\widehat{a}^\dagger(\vec{r},\omega)$ creates a particle at point $\vec{r}$ with spin ω:

$$\widehat{a}^\dagger(\vec{r},\omega)\,|\rangle = \sum_i \langle\,\psi_i|\,\vec{r},\omega\rangle\,\widehat{a_i}^\dagger\,|\rangle = \sum_i |\psi_i\rangle\,\langle\,\psi_i|\,\vec{r},\omega\rangle = |\vec{r},\omega\rangle$$

The expression $\widehat{a_i}$ of in terms of the field operator $\widehat{a}(\vec{r},\omega)$ can be readily obtained from the expression of this operator in terms of the $\widehat{a_j}$'s:

$$\sum_{\omega=\alpha,\beta}\int_{\vec{r}} \psi_i^*(\vec{r},\omega)\widehat{a}(\vec{r},\omega)d\vec{r} = \sum_{\omega=\alpha,\beta}\int_{\vec{r}} \psi_i^*(\vec{r},\omega)\sum_j \psi_j(\vec{r},\omega)\widehat{a_j}d\vec{r} = \sum_j \delta_{ij}\widehat{a_j} = \widehat{a_i}$$

By taking adjoints in both sides of this equation the corresponding expression for $\widehat{a_i}^\dagger$ is obtained:

$$\sum_{\omega=\alpha,\beta}\int_{\vec{r}} \psi_i(\vec{r},\omega)\widehat{a}^\dagger(\vec{r},\omega)d\vec{r} = \widehat{a_i}^\dagger$$

Field operators fulfill similar anticommutation relationships than discrete creation and annihilation operators:

$$\begin{aligned}\left[\widehat{a}(\vec{r},\omega),\widehat{a}^\dagger(\vec{r}',\omega')\right]_+ &= \left[\sum_i \psi_i(\vec{r},\omega)\widehat{a_i},\sum_j \psi_j^*(\vec{r}',\omega')\widehat{a_j}^\dagger\right]_+ = \sum_{i,j}\psi_i(\vec{r},\omega)\psi_j^*(\vec{r}',\omega')\left[\widehat{a_i},\widehat{a_j}^\dagger\right]_+ \\ &= \sum_{i,j}\psi_i(\vec{r},\omega)\psi_j^*(\vec{r}',\omega')\delta_{ij} = \sum_i \langle\,\vec{r},\omega|\,\psi_i\rangle\,\langle\,\psi_i|\,\vec{r}',\omega'\rangle = \langle\,\vec{r},\omega|\,\vec{r}',\omega'\rangle\end{aligned}$$

that, is

$$\left[\widehat{a}(\vec{r},\omega),\widehat{a}^\dagger(\vec{r}',\omega')\right]_+ = \delta_{\omega\omega'}\delta(\vec{r},\vec{r}')$$

In the same way

$$[\widehat{a}(\vec{r},\omega),\widehat{a}(\vec{r}',\omega')]_+ = \sum_{i,j}\psi_i(\vec{r},\omega)\psi_j(\vec{r}',\omega')\,[\widehat{a_i},\widehat{a_j}]_+ = 0$$

and, by taking adjoints:

$$\left[\widehat{a}^\dagger(\vec{r},\omega),\widehat{a}^\dagger(\vec{r}',\omega')\right]_+ = 0$$

Field operators are usually denoted by $\widehat{\psi}(\vec{r},\omega)$ and $\widehat{\psi}^\dagger(\vec{r},\omega)$. Many texts omit the accent $\widehat{\ }$ in the notation of operators, which can lead to confusion with the notation normally used for wave functions.

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 sea 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 the ground state vector; that is, the *holes* created in the Fermi sea by annihilation operators and the *particles* created above the Fermi level by creation operators. 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 with positive charge e (a *quasi-particle*), and a neutral pair formed by an electron and a hole interacting by electrostatic attraction is sometimes called an *exciton*. The Fermi sea can be considered as a new vacuum with no particles (above the Fermi level) and no holes (below the Fermi level).

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 post-Hartree-Fock methods.

7 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 de 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)).