# U. SECOND QUANTIZATION

When we work with a basis set composed of Slater determinants we are usually confronted with a large number of matrix elements involving one- and two-electron operators. The Slater–Condon rules (Appendix M) are doing the job to express these matrix elements by the one-electron and two-electron integrals. However, we may introduce an even easier tool called second quantization, which is equivalent to the Slater–Condon rules.

### The vacuum state

In the second quantization formalism we introduce a reference state for the system under study, which is a Slater determinant (usually the Hartree–Fock wave function) composed of $N$ orthonormal spinorbitals, where $N$ is the number of electrons. This function will be denoted in short by $\Phi_0$ or in a more detailed way by $\Phi^N(n_1, n_2, \ldots, n_\infty)$. The latter notation means that we have to do with a normalized $N$ electron Slater determinant, and in parenthesis we give the occupancy list ($n_i = 0, 1$) for the infinite number of orthonormal spinorbitals considered in the basis set and listed one by one in the parenthesis. This simply means that some spinorbitals are present in the determinant (they have $n_i = 1$), while others are absent[1] ($n_i = 0$). Hence, $\sum_i n_i = N$. The reference state is often called the *vacuum state*. The subscript 0 in $\Phi_0$ means that we are going to consider a single-determinant approximation to the *ground state*. Besides the reference state, some normalized Slater determinants of the excited states will be considered, with other occupancies, *including those corresponding to the number of electrons which differs from N*.

### The creation and annihilation of electrons

Let us make quite a strange move, and consider operators that change the number of electrons in the system. To this end, let us define the creation operator[2] $\hat{k}^\dagger$ of the electron going to occupy spinorbital $k$ and the annihilation operator $\hat{k}$ of an electron leaving spinorbital $k$:

[1] For example, the symbol $\Phi^2(001000100000\ldots)$ means a normalized Slater determinant of dimension 2, containing the spinorbitals 3 and 7. The symbol $\Phi^2(001000\ldots)$ is a nonsense, because the number of "ones" has to be equal to 2, etc.

[2] The domain of the operators represents the space spanned by the Slater determinants built of spinorbitals.

Richard Feynman, in one of his books, says jokingly that he could not understand the very sense of the operators. If we annihilate or create an electron, then what about the system's electroneutrality? Happily enough, these operators will always act in creator–annihilator pairs.

CREATION AND ANNIHILATION OPERATORS

$$\hat{k}^\dagger \Phi^N(\ldots n_k \ldots) = \theta_k (1 - n_k) \Phi^{N+1}(\ldots 1_k, \ldots),$$
$$\hat{k} \Phi^N(\ldots n_k \ldots) = \theta_k n_k \Phi^{N-1}(\ldots 0_k, \ldots),$$

where $\theta_k = (-1)^{\Sigma_{j<k} n_j}$.

The symbol $1_k$ means that the spinorbital $k$ is present in the Slater determinant, while $0_k$ means that this spinorbital is empty, i.e. is not present in the Slater determinant. The factors $(1 - n_k)$ and $n_k$ ensure an important property of these operators, namely that

any attempt at *creating* an electron on an already *occupied spinorbital* gives zero, similarly any attempt at *annihilating an empty spinorbital* also gives zero.

It can be easily shown,[3] that (as the symbol suggests) $\hat{k}^\dagger$ is simply the adjoint operator with respect to $\hat{k}$.

The above operators have the following properties that make them equivalent to the Slater–Condon rules:

ANTICOMMUTATION RULES

$$\left[\hat{k}, \hat{l}\right]_+ = 0,$$
$$\left[\hat{k}^\dagger, \hat{l}^\dagger\right]_+ = 0,$$
$$\left[\hat{k}^\dagger, \hat{l}\right]_+ = \delta_{kl},$$

anticommutator

where the symbol $[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$ is called the *anticommutator*.[4] It is simpler than the Slater–Condon rules, isn't it? Let us check the rule $[\hat{k}^\dagger, \hat{l}]_+ = \delta_{kl}$. We have to check how it works for all possible occupancies of the spinorbitals $k$ and $l$, $(n_k, n_l)$: $(0,0)$, $(0,1)$, $(1,0)$ and $(1,1)$.

***Case:*** $(n_k, n_l) = (0,0)$

$$\left[\hat{k}^\dagger, \hat{l}\right]_+ \Phi^N(\ldots 0_k \ldots 0_l \ldots) = \left[\hat{k}^\dagger \hat{l} + \hat{l}\hat{k}^\dagger\right] \Phi^N(\ldots 0_k \ldots 0_l \ldots)$$
$$= \hat{k}^\dagger \hat{l} \Phi^N(\ldots 0_k \ldots 0_l \ldots) + \hat{l}\hat{k}^\dagger \Phi^N(\ldots 0_k \ldots 0_l \ldots)$$

[3] *Proof.* Let us take two Slater determinants $\Phi_a = \Phi^{N+1}(\ldots 1_k \ldots)$ and $\Phi_b = \Phi^N(\ldots 0_k \ldots)$, in both of them the occupancies of all other spinorbitals are identical. Let us write the normalization condition for $\Phi_b$ in the following way: $1 = \langle \Phi_b | \theta_k \hat{k} \Phi_a \rangle = \theta_k \langle \Phi_b | \hat{k} \Phi_a \rangle = \theta_k \langle \hat{k}^\# \Phi_b | \Phi_a \rangle$, where as $\hat{k}^\#$ has been denoted the operator adjoint to $\hat{k}$, $\theta_k$ appeared in order to compensate for ($\theta_k^2 = 1$) the $\theta_k$ produced by the annihilator. On the other hand, from the normalization condition of $\Phi_a$ we see that $1 = \langle \Phi_a | \Phi_a \rangle = \theta_k \langle \hat{k}^\dagger \Phi_b | \Phi_a \rangle$. Hence, $\theta_k \langle \hat{k}^\# \Phi_b | \Phi_a \rangle = \theta_k \langle \hat{k}^\dagger \Phi_b | \Phi_a \rangle$ or $\hat{k}^\# = \hat{k}^\dagger$, This is what we wanted to show.

[4] The above formulae are valid under the (common) assumption that the spinorbitals are orthonormal. If this assumption is not true, only the last anticommutator changes to the form $[\hat{k}^\dagger, \hat{l}]_+ = S_{kl}$, where $S_{kl}$ stands for the overlap integral of spinorbitals $k$ and $l$.

$$
\begin{aligned}
&= 0 + \hat{l}\theta_k \Phi^{N+1}(\ldots 1_k \ldots 0_l \ldots) \\
&= \theta_k \hat{l} \Phi^{N+1}(\ldots 1_k \ldots 0_l \ldots) \\
&= \theta_k \delta_{kl} \theta_k \Phi^N(\ldots 0_k \ldots) \\
&= \delta_{kl} \Phi^N(\ldots 0_k \ldots).
\end{aligned}
$$

So far so good.

***Case:*** $(n_k, n_l) = (0, 1)$

$$
\begin{aligned}
\left[\hat{k}^\dagger, \hat{l}\right]_+ \Phi^N(\ldots 0_k \ldots 1_l \ldots) &= \left[\hat{k}^\dagger \hat{l} + \hat{l}\hat{k}^\dagger\right] \Phi^N(\ldots 0_k \ldots 1_l \ldots) \\
&= \hat{k}^\dagger \hat{l} \Phi^N(\ldots 0_k \ldots 1_l \ldots) + \hat{l}\hat{k}^\dagger \Phi^N(\ldots 0_k \ldots 1_l \ldots) \\
&= \theta_k \theta_l \Phi^N(\ldots 1_k \ldots 0_l \ldots) - \theta_k \theta_l \Phi^N(\ldots 1_k \ldots 0_l \ldots) \\
&= \delta_{kl} \Phi^N(\ldots 0_k \ldots 1_l \ldots).
\end{aligned}
$$

This is what we expected.[5]

***Case:*** $(n_k, n_l) = (1, 0)$

$$
\begin{aligned}
\left[\hat{k}^\dagger, \hat{l}\right]_+ \Phi^N(\ldots 1_k \ldots 0_l \ldots) &= \left[\hat{k}^\dagger \hat{l} + \hat{l}\hat{k}^\dagger\right] \Phi^N(\ldots 1_k \ldots 0_l \ldots) \\
&= \hat{k}^\dagger \hat{l} \Phi^N(\ldots 1_k \ldots 0_l \ldots) + \hat{l}\hat{k}^\dagger \Phi^N(\ldots 1_k \ldots 0_l \ldots) \\
&= (0 + 0) \Phi^N(\ldots 1_k \ldots 0_l \ldots) \\
&= \delta_{kl} \Phi^N(\ldots 1_k \ldots 0_l \ldots).
\end{aligned}
$$

This is OK.

***Case:*** $(n_k, n_l) = (1, 1)$

$$
\begin{aligned}
\left[\hat{k}^\dagger, \hat{l}\right]_+ \Phi^N(\ldots 1_k \ldots 1_l \ldots) &= \left[\hat{k}^\dagger \hat{l} + \hat{l}\hat{k}^\dagger\right] \Phi^N(\ldots 1_k \ldots 1_l \ldots) \\
&= \hat{k}^\dagger \hat{l} \Phi^N(\ldots 1_k \ldots 1_l \ldots) + \hat{l}\hat{k}^\dagger \Phi^N(\ldots 1_k \ldots 1_l \ldots) \\
&= \hat{k}^\dagger \hat{l} \Phi^N(\ldots 1_k \ldots 1_l \ldots) + 0 \\
&= \theta_k^2 \delta_{kl} \Phi^N(\ldots 1_k \ldots 1_l \ldots) \\
&= \delta_{kl} \Phi^N(\ldots 1_k \ldots).
\end{aligned}
$$

The formula has been proved.

### Operators in the second quantization

Creation and annihilation operators may be used to represent one- and two-electron operators.[6] The resulting matrix elements with Slater determinants *correspond exactly to the Slater–Condon rules* (see Appendix M, p. 986).

[5] What decided is the change of sign (due to $\theta_k$) when the order of the operators has changed.

[6] The original operator and its representation in the language of the second quantization are not identical in practical applications. The second ones can act only on the Slater determinants or their combinations. Since we are going to work with the creation and annihilation operators in only those methods which use Slater determinants (CI, MC SCF, etc.), the difference is irrelevant.

### One-electron operators

The operator $\hat{F} = \sum_i \hat{h}(i)$ is the sum of the one-electron operators[7] $\hat{h}(i)$ acting on functions of the coordinates of electron $i$.

The I Slater–Condon rule says (see Appendix M), that for the Slater determinant $\psi$ built of the spinorbitals $\phi_i$, the matrix element $\langle\psi|\hat{F}\psi\rangle = \sum_i h_{ii}$, where $h_{ij} = \langle\phi_i|\hat{h}\phi_j\rangle$.

In the second quantization

$$\hat{F} = \sum_{ij}^{\infty} h_{ij}\hat{i}^\dagger\hat{j}.$$

Interestingly, the summation extends to infinity, and therefore the operator is independent of the number of electrons in the system.

Let us check whether the formula is correct. Let us insert $\hat{F} = \sum_{ij} h_{ij}\hat{i}^\dagger\hat{j}$ into $\langle\psi|\hat{F}\psi\rangle$. We have

$$\langle\psi|\hat{F}\psi\rangle = \left\langle\psi\middle|\sum_{ij} h_{ij}\hat{i}^\dagger\hat{j}\psi\right\rangle = \sum_{ij} h_{ij}\langle\psi|\hat{i}^\dagger\hat{j}\psi\rangle = \sum_{ij} h_{ij}\delta_{ij} = \sum_i h_{ii}.$$

This is correct.

What about the II Slater–Condon rule (the Slater determinants $\psi_1$ and $\psi_2$ differ by a single spinorbital: the spinorbital $i$ in $\psi_1$ is replaced by the spinorbital $i'$ in $\psi_2$)? We have

$$\langle\psi_1|\hat{F}\psi_2\rangle = \sum_{ij} h_{ij}\langle\psi_1|\hat{i}^\dagger\hat{j}\psi_2\rangle.$$

The Slater determinants that differ by one spinorbital produce an overlap integral equal to zero,[8] therefore $\langle\psi_1|\hat{F}\psi_2\rangle = h_{ii'}$. Thus, the operator in the form $\hat{F} = \sum_{ij} h_{ij}\hat{i}^\dagger\hat{j}$ ensures equivalence with all the Slater–Condon rules.

### Two-electron operators

Similarly, we may use the creation and annihilation operators to represent the two-electron operators $\hat{G} = \frac{1}{2}\sum'_{ij}\hat{g}(i,j)$. In most cases $\hat{g}(i,j) = \frac{1}{r_{ij}}$ and $\hat{G}$ has the form:

$$\hat{G} = \frac{1}{2}\sum_{ij}{}' \frac{1}{r_{ij}} = \frac{1}{2}\sum_{ijkl}^{\infty}\langle ij|kl\rangle\hat{j}^\dagger\hat{i}^\dagger\hat{k}\hat{l}.$$

[7] Most often this will be the kinetic energy operator, the nuclear attraction operator, the interaction with the external field or the multipole moment.

[8] It is evident, that if in this situation the Slater determinants $\psi_1$ and $\psi_2$ differed by more than a single spinorbital, we would get zero (III and IV Slater–Condon rule).

Here also the summation extends to infinity and the operator is independent of the number of electrons in the system.

The proof of the I Slater–Condon rule relies on the following chain of equalities

$$\begin{aligned}\langle\psi|\hat{G}\psi\rangle &= \frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\langle\psi|\hat{\jmath}^{\dagger}\hat{\imath}^{\dagger}\hat{k}\hat{l}\psi\rangle = \frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\langle\hat{\imath}\hat{\jmath}\psi|\hat{k}\hat{l}\psi\rangle \\ &= \frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle(\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk}) = \frac{1}{2}\sum_{ij}\big(\langle ij|ij\rangle - \langle ij|ji\rangle\big),\end{aligned}$$

because the overlap integral $\langle\hat{\imath}\hat{\jmath}\psi|\hat{k}\hat{l}\psi\rangle$ of the two Slater determinants $\hat{\imath}\hat{\jmath}\psi$ and $\hat{k}\hat{l}\psi$ is non-zero in the two cases only: either if $i=k$, $j=l$ or if $i=l$, $j=k$ (then the sign has to change). This is what we get from the Slater–Condon rules.

For the II Slater–Condon rule we have (instead of the spinorbital $i$ in $\psi_1$ we have the spinorbital $i'$ in $\psi_2$):

$$\langle\psi_1|\hat{G}\psi_2\rangle = \frac{1}{2}\sum_{Ijkl}\langle Ij|kl\rangle\langle\psi_1|\hat{\jmath}^{\dagger}\hat{I}^{\dagger}\hat{k}\hat{l}\psi_2\rangle = \frac{1}{2}\sum_{Ijkl}\langle Ij|kl\rangle\langle\hat{I}\hat{\jmath}\psi_1|\hat{k}\hat{l}\psi_2\rangle, \tag{U.1}$$

where the summation index $I$ has been introduced in order not to mix with spinorbital $i$. In the overlap integral $\langle\hat{I}\hat{\jmath}\psi_1|\hat{k}\hat{l}\psi_2\rangle$ the sets of the spinorbitals in the Slater determinant $\hat{I}\hat{\jmath}\psi_1$ and in the Slater determinant $\hat{k}\hat{l}\psi_2$ have to be *identical*, otherwise the integral will equal zero. However, in $\psi_1$ and $\psi_2$ we already have a difference of one spinorbital. Thus, first we have to get rid of these spinorbitals ($i$ and $i'$). For the integral to survive[9] we have to have at least one of the following conditions satisfied:

- $I=i$ and $k=i'$ (and then $j=l$),
- $j=i$ and $k=i'$ (and then $I=l$),
- $I=i$ and $l=i'$ (and then $j=k$),
- $j=i$ and $l=i'$ (and then $I=k$).

This means that, taking into account the above cases in eq. (U.1), we obtain

$$\begin{aligned}\langle\psi_1|\hat{G}\psi_2\rangle &= \frac{1}{2}\sum_{j}\langle ij|i'j\rangle\langle\hat{\imath}\hat{\jmath}\psi_1|\hat{\imath}'\hat{\jmath}\psi_2\rangle + \frac{1}{2}\sum_{l}\langle li|i'l\rangle\langle\hat{l}\hat{\imath}\psi_1|\hat{\imath}'\hat{l}\psi_2\rangle \\ &\quad + \frac{1}{2}\sum_{j}\langle ij|ji'\rangle\langle\hat{\imath}\hat{\jmath}\psi_1|\hat{\jmath}\hat{\imath}'\psi_2\rangle + \frac{1}{2}\sum_{k}\langle ki|ki'\rangle\langle\hat{k}\hat{\imath}\psi_1|\hat{k}\hat{\imath}'\psi_2\rangle \\ &= \frac{1}{2}\sum_{j}\langle ij|i'j\rangle - \frac{1}{2}\sum_{l}\langle li|i'l\rangle - \frac{1}{2}\sum_{j}\langle ij|ji'\rangle + \frac{1}{2}\sum_{k}\langle ki|ki'\rangle \\ &= \frac{1}{2}\sum_{j}\langle ij|i'j\rangle - \frac{1}{2}\sum_{j}\langle ji|i'j\rangle - \frac{1}{2}\sum_{j}\langle ij|ji'\rangle + \frac{1}{2}\sum_{j}\langle ji|ji'\rangle\end{aligned}$$

[9] This is a necessary, but not a sufficient condition.

$$= \frac{1}{2}\sum_j \langle ij|i'j\rangle - \frac{1}{2}\sum_j \langle ij|ji'\rangle - \frac{1}{2}\sum_j \langle ij|ji'\rangle + \frac{1}{2}\sum_j \langle ij|i'j\rangle$$
$$= \sum_j \langle ij|i'j\rangle - \sum_j \langle ij|ji'\rangle,$$

where the coordinates of electrons 1 and 2 have been exchanged in the two sums. Notice that the overlap integrals

$$\langle \hat{i}\hat{j}\psi_1|\hat{i}'\hat{j}\psi_2\rangle = \langle \hat{k}\hat{i}\psi_1|\hat{k}\hat{i}'\psi_2\rangle = 1,$$

because the Slater determinants $\hat{i}\psi_1$ and $\hat{i}'\psi_2$ are identical. Also, from the anti-commutation rules

$$\langle \hat{l}\hat{i}\psi_1|\hat{i}'\hat{l}\psi_2\rangle = \langle \hat{i}\hat{j}\psi_1|\hat{j}\hat{i}'\psi_2\rangle = -1.$$

Thus the II Slater–Condon rule has been correctly reproduced:

$$\langle \psi_1|\hat{G}\psi_2\rangle = \sum_j \left[\langle ij|i'j\rangle - \langle ij|ji'\rangle\right].$$

We may conclude that the definition of the creation and annihilation operators and the simple anticommutation relations are equivalent to the Slater–Condon rules. This opens up the space spanned by the Slater determinants for us, i.e. all the integrals involving Slater determinants can be easily transformed into one- and two-electron integrals involving spinorbitals.