APPENDIX U

Second Quantization

When we work with a basis set composed of the Slater determinants, we are usually confronted with a large number of matrix elements involving one- and two-electron operators. The Slater-Condon rules (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5) are expressing these matrix elements by the one and two-electron integrals. However, we may introduce an even easier tool called the *second quantization*, which is equivalent to the Slater-Condon rules.

Vacuum State

In the second quantization formalism, we introduce for the system under study a reference state that is a Slater determinant (usually the Hartree-Fock wave function) composed of N orthonormal spinorbitals, with N being the number of electrons. This function will be denoted by Φ_0 or, in a more detailed way, as $\Phi^N\left(n_1, n_2, \ldots, n_\infty\right)$. The last notation means that we are dealing with a normalized N electron Slater determinant, and in the parentheses we give the occupancy list ($n_i = 0, 1$) for the infinite number of the orthonormal spinorbitals considered in the basis set and listed one by one in the parentheses. 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 Φ_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, along with other occupancies, *including those corresponding to the number of electrons that differs from N*.

Creation and Annihilation of Electron

Let us make 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 the

[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 $\Phi^2(001000\ldots)$ does not make sense because the number of digits "1" has to equal 2, etc.

[2] The domain of the operators represents the space spanned by the Slater determinant's build of spinorbitals. Richard Feynman in one of his books says jokingly that he could not understand the very sense of the operators.

Ideas of Quantum Chemistry, Second Edition. http://dx.doi.org/10.1016/B978-0-444-59436-5.00041-6

spinorbital k and the annihilation operator $\hat{k}$ of an electron leaving the spinorbital k (just disappearing):

Creation and Annihilation Operators

$$\hat{k}^\dagger \Phi^N(\dots n_k \dots) = \theta_k(1-n_k)\Phi^{N+1}(\dots 1_k, \dots)$$
$$\hat{k}\Phi^N(\dots n_k \dots) = \theta_k n_k \Phi^{N-1}(\dots 0_k, \dots),$$
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., it is not present in the Slater determinant. The factors $\left(1-n_k\right)$ and n_k ensure an important property of these operators; namely, that

any attempt of *creation* of the electron on an already *occupied spinorbital* gives zero, and similarly, any attempt of *annihilation of 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

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

If we annihilate or create an electron, then what about the system's electroneutrality? Happily enough, these operators will always act in pairs: creator-annihilator.

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

$$\theta_k \left\langle \hat{k}^\# \Phi_b | \Phi_a \right\rangle = \theta_k \left\langle \hat{k}^\dagger \Phi_b | \Phi_a \right\rangle \text{ or } \hat{k}^\# = \hat{k}^\dagger,$$

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*:** $(k, l) = (0, 0)$
$[\hat{k}^\dagger, \hat{l}]_+ \Phi^N(\ldots 0_k \ldots 0_l \ldots) = [\hat{k}^\dagger \hat{l} + \hat{l}\hat{k}^\dagger]\Phi^N(\ldots 0_k \ldots 0_l \ldots) = \hat{k}^\dagger \hat{l}\Phi^N(\ldots 0_k \ldots 0_l \ldots) + \hat{l}\hat{k}^\dagger \Phi^N(\ldots 0_k \ldots 0_l \ldots) = 0 + \hat{l}\theta_k \Phi^{N+1}(\ldots 1_k \ldots 0_l \ldots) = \theta_k \hat{l}\Phi^{N+1}(\ldots 1_k \ldots 0_l \ldots) = \theta_k \delta_{kl} \theta_k \Phi^N(\ldots 0_k \ldots) = \delta_{kl}\Phi^N(\ldots 0_k \ldots)$. So far, so good.

***Case*:** $(k, l) = (0, 1)$
$[\hat{k}^\dagger, \hat{l}]_+ \Phi^N(\ldots 0_k \ldots 1_l \ldots) = [\hat{k}^\dagger \hat{l} + \hat{l}\hat{k}^\dagger]\Phi^N(\ldots 0_k \ldots 1_l \ldots) = \hat{k}^\dagger \hat{l}\Phi^N(\ldots 0_k \ldots 1_l \ldots) + \hat{l}\hat{k}^\dagger \Phi^N(\ldots 0_k \ldots 1_l \ldots) = \theta_k \theta_l \Phi^N(\ldots 1_k \ldots 0_l \ldots) - \theta_k \theta_l \Phi^N(\ldots 1_k \ldots 0_l \ldots) = \delta_{kl}\Phi^N(\ldots 0_k \ldots 1_l \ldots)$. This is what we have expected.[5]

***Case*:** $(k, l) = (1, 0)$
$[\hat{k}^\dagger, \hat{l}]_+ \Phi^N(\ldots 1_k \ldots 0_l \ldots) = [\hat{k}^\dagger \hat{l} + \hat{l}\hat{k}^\dagger]\Phi^N(\ldots 1_k \ldots 0_l \ldots) = \hat{k}^\dagger \hat{l}\Phi^N(\ldots 1_k \ldots 0_l \ldots) + \hat{l}\hat{k}^\dagger \Phi^N(\ldots 1_k \ldots 0_l \ldots) = \big(0 + 0\big)\, \Phi^N(\ldots 1_k \ldots 0_l \ldots) = \delta_{kl}\Phi^N(\ldots 1_k \ldots 0_l \ldots)$.

***Case*:** $(k, l) = (1, 1)$
$[\hat{k}^\dagger, \hat{l}]_+ \Phi^N(\ldots 1_k \ldots 1_l \ldots) = [\hat{k}^\dagger \hat{l} + \hat{l}\hat{k}^\dagger]\Phi^N(\ldots 1_k \ldots 1_l \ldots) = \hat{k}^\dagger \hat{l}\Phi^N(\ldots 1_k \ldots 1_l \ldots) + \hat{l}\hat{k}^\dagger \Phi^N(\ldots 1_k \ldots 1_l \ldots) = \hat{k}^\dagger \hat{l}\Phi^N(\ldots 1_k \ldots 1_l \ldots) + 0 = \theta_k^2 \delta_{kl}\Phi^N(\ldots 1_k \ldots 1_l \ldots) = \delta_{kl}\Phi^N(\ldots 1_k \ldots 1_l \ldots)$.

Operators in the Second Quantization

The creation and annihilation operators may be used to represent the one- and two-electron operators. The resulting matrix elements with Slater determinants[6] *correspond exactly to the Slater-Condon rules* (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5, p. e107).

One-Electron Operators

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

[4] The above formulas are valid under the common assumption that the spinorbitals are orthonormal. If this assumption is not true, then 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.

[5] What decided is the change of sign (due to θ_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, though. The second ones can act only on the Slater determinants or their combinations, while the first ones have a larger domain. Since we are only going to work with the creation and annihilation operators in those methods that use Slater determinants (CI, MC SCF, etc.), then the difference is irrelevant.

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

I Slater-Condon rule says (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5), that for the Slater determinant ψ build of the spinorbitals ϕ_i, the matrix element $\left\langle \psi | \hat{F} \psi \right\rangle = \sum_i h_{ii}$, where $h_{ij} = \left\langle \phi_i | \hat{h} \phi_j \right\rangle$.

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 $\left\langle \psi | \hat{F} \psi \right\rangle$. We have

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

This is a correct result.

What about the II Slater-Condon rule (the Slater determinants ψ_1 and ψ_2 differ by a single spinorbital: the spinorbital i in ψ_1 is replaced by the spinorbital i' in ψ_2)? We have

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

The Slater determinants that differ by one spinorbital produce the overlap integral equal to zero[8]; therefore $\left\langle \psi_1 | \hat{F} \psi_2 \right\rangle = h_{ii'}$. 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 $\hat{G}$ takes the following form:

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

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

[8] It is evident that if in this situation the Slater determinants ψ_1 and ψ_2 differed by more than a single spinorbital, then we would get zero (by the III and IV Slater-Condon rules).

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

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

because the overlap integral $\left\langle\hat{i}\hat{j}\psi|\hat{k}\hat{l}\psi\right\rangle$ of the two Slater determinants $\hat{i}\hat{j}\psi$ and $\hat{k}\hat{l}\psi$ is nonzero in the two cases only: either if $i=k$, $j=l$, or $i=l$, $j=k$ (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 ψ_1 we have the spinorbital i' in ψ_2)

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

where the summation index I has been introduced in order so it doesn't get mixed up with the spinorbital i. In the overlap integral $\left\langle\hat{I}\hat{j}\psi_1|\hat{k}\hat{l}\psi_2\right\rangle$, the sets of the spinorbitals in the Slater determinant $\hat{I}\hat{j}\psi_1$ and in the Slater determinant $\hat{k}\hat{l}\psi_2$ have to be *identical*; otherwise, the integral will equal zero. However, already in ψ_1 and ψ_2, we have a difference of one spinorbital. Thus, first of all, we have to get rid of just these spinorbitals (i and i')! For the integral to survive,[9] we have to satisfy at least one of the following conditions:

- $I=i$ 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 when taking into account the above cases in Eq. (U.1), we obtain

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

[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 in the two sums the coordinates of the electrons 1 and 2 have been exchanged, and as it has been noticed that the overlap integrals $\langle \hat{i}\hat{j}\psi_1|\hat{i}'\hat{j}\psi_2\rangle = \left\langle \hat{k}\hat{i}\psi_1|\hat{k}\hat{i}'\psi_2 \right\rangle = 1$, because the Slater determinants $\hat{i}\psi_1$ and $\hat{i}'\psi_2$ are identical. Also, from the anticommutation rules $\left\langle \hat{l}\hat{i}\psi_1|\hat{i}'\hat{l}\psi_2 \right\rangle = \langle \hat{i}\hat{j}\psi_1|\hat{j}\hat{i}'\psi_2\rangle = -1$. Thus, the II Slater-Condon rule has been correctly reproduced:

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

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 for us the space spanned by the Slater determinants; i.e., all the integrals involving Slater determinants can be easily transformed into the one- and two-electron integrals involving spinorbitals.