

# Slater-Condon Rules

The Slater determinants represent something like the “*daily bread*” of quantum chemists. Our goal is to learn how to use the Slater determinants when they are involved in calculation of the mean values or the matrix elements of some important operators. We will need that in the Hartree-Fock method, as well as in other important methods of quantum chemistry.

Most important are only the final results of the derivations presented in this appendix (p. e119).

## Antisymmetrization Operator

The antisymmetrization operator is defined as

$$\hat{A} = \frac{1}{N!} \sum_P (-1)^P \hat{P}, \quad (\text{M.1})$$

where  $\hat{P}$  represents a permutation operator of  $N$  objects (electrons, in our case), while  $(-1)^P$  stands for the parity of the permutation  $P$ , “*even*” (“*odd*”), if a given permutation  $P$  can be created from an even (odd) number  $p$  of the transpositions (i.e., exchanges) of two elements.

The operator  $\hat{A}$  has some nice features. The most important one is that when applied to *any* function, it produces either a function that is antisymmetric with respect to the permutations of  $N$  elements, or zero.<sup>1</sup> This means that  $\hat{A}$  represents a sort of magic wand: whatever it touches becomes antisymmetric or disappears! The antisymmetrizer is also idempotent; i.e., it does not change any function that is already antisymmetric, which means  $\hat{A}^2 = \hat{A}$ .

Let us check that  $\hat{A}$  is indeed idempotent. First, we obtain

$$\hat{A}^2 = (N!)^{-1} \sum_P (-1)^P \hat{P} (N!)^{-1} \sum_{P'} (-1)^{P'} \hat{P}' = (N!)^{-2} \sum_{PP'} (-1)^{P+P'} \hat{P} \hat{P}'. \quad (\text{M.2})$$

Of course,  $\hat{P} \hat{P}'$  represents a permutation operator,<sup>2</sup> which is then multiplied by its own parity  $(-1)^{P+P'}$ , and there is a sum over such permutations at a given fixed  $\hat{P}'$ . Independent of what

<sup>1</sup> In the near future, these elements will be identified with the electronic coordinates (one element will be represented by the space and spin coordinates of a single electron:  $x, y, z, \sigma$ ).

<sup>2</sup> The permutations form the permutation group.

Note this excerpt from “*Solid State and Molecular Theory*, Wiley, London (1975) by John Slater on the permutation group: “(...) It was at this point that Wigner, Hund, Heitler, and Weyl entered the picture, with their

$\hat{P}'$  is, we obtain the same result<sup>3</sup>  $N!$  times, and therefore  $\hat{A}^2 = (N!)^{-2} N! \sum_P (-1)^P \hat{P} = \hat{A}$ . This is what we wanted to show.

The operator  $\hat{A}$  is Hermitian. Since  $\hat{P}$  represents a (permutational) symmetry operator, it conserves the scalar product. This means that for the two vectors  $\psi_1$  and  $\psi_2$  of the Hilbert space, we obtain<sup>4</sup>

$$\begin{aligned} & \left\langle \psi_1(1, 2, \dots, N) | \hat{A} \psi_2(1, 2, \dots, N) \right\rangle \\ &= (N!)^{-1} \sum_P (-1)^P \left\langle \hat{P}^{-1} \psi_1(1, 2, \dots, N) | \psi_2(1, 2, \dots, N) \right\rangle. \end{aligned}$$

The summation over  $\hat{P}$  can be replaced by the summation over  $\hat{P}^{-1}$ :

$$(N!)^{-1} \sum_{P^{-1}} (-1)^P \left\langle \hat{P}^{-1} \psi_1(1, 2, \dots, N) | \psi_2(1, 2, \dots, N) \right\rangle.$$

Since the parity  $p$  of the permutation  $\hat{P}^{-1}$  is the same as that of  $\hat{P}$ , hence  $(N!)^{-1} \sum_{P^{-1}} (-1)^P \hat{P}^{-1} = \hat{A}$ , what shows that  $\hat{A}$  is Hermitian:  $\left\langle \psi_1 | \hat{A} \psi_2 \right\rangle = \left\langle \hat{A} \psi_1 | \psi_2 \right\rangle$ , or<sup>5</sup>

$$\hat{A}^\dagger = \hat{A}. \tag{M.3}$$

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*'Gruppenpest': the pest of the group theory, as certain disgruntled individuals who had never studied group theory in school described it. (...) The authors of the 'Gruppenpest' wrote papers, which were incomprehensible to those like me who had not studied group theory (...). The practical consequences appeared to be negligible, but everyone felt that to be in the mainstream of quantum mechanics, we had to learn about it. (...) It was a frustrating experience, worthy of the name of a pest.'*

<sup>3</sup> Of course,  $\hat{P} \hat{P}' = \hat{P}''$  has the parity  $(-1)^{p+p'}$ , because this is how such a permutation parity is to be calculated: first, we make  $p$  transpositions in order to get  $\hat{P}$ , and next, making  $p'$  transpositions, we obtain the permutation  $\hat{P} \hat{P}'$ . Note, that when keeping  $\hat{P}'$  fixed and taking  $\hat{P}$  from all possible permutations, we are running with  $\hat{P} \hat{P}'$  over all possible permutations as well. This is because the complete set of permutations is obtained independently of what the starting permutation looks like (i.e., independent of  $\hat{P}'$ ).

<sup>4</sup> The conservation of the scalar product  $\langle \psi_1 | \psi_2 \rangle = \langle \hat{P} \psi_1 | \hat{P} \psi_2 \rangle$  means that the lengths of the vectors  $\psi_1$  and  $\hat{P} \psi_1$  are the same (similarly with  $\psi_2$ ), and that the angle between the vectors is also conserved. If  $\hat{P}$  is acting on  $\psi_2$  alone and  $\psi_1$  does not change, the angle resulting from the scalar product  $\langle \psi_1 | \hat{P} \psi_2 \rangle$  is of course different because only one of the vectors ( $\psi_2$ ) has been transformed (which means a rotation of a unit vector in the Hilbert space). *The same angle* would be obtained if its partner  $\psi_1$  were transformed in the *opposite* direction; i.e., when the operation  $\hat{P}^{-1} \psi_1$  had been performed. Hence, from the equality of the angles, we have  $\langle \psi_1 | \hat{P} \psi_2 \rangle = \langle \hat{P}^{-1} \psi_1 | \psi_2 \rangle$ .

<sup>5</sup>  $\hat{A}^\dagger$  stands for the *adjoint* operator with respect to  $\hat{A}$ ; i.e., for arbitrary functions belonging to its domain, we have  $\langle \psi_1 | \hat{A} \psi_2 \rangle = \langle \hat{A}^\dagger \psi_1 | \psi_2 \rangle$ . There is a subtle difference (ignored in this book) among the self-adjoint ( $\hat{A}^\dagger = \hat{A}$ ) and Hermitian operators in mathematical physics (they differ by definition of their domains).

## Slater-Condon Rules

The Slater-Condon rules serve for expressing the matrix elements involving the Slater determinants (they are many-electron wave functions):

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(N) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_N(1) & \phi_N(2) & \cdots & \phi_N(N) \end{vmatrix}. \quad (\text{M.4})$$

The normalized Slater determinant has the form:  $\Psi = \sqrt{N!} \hat{A}(\phi_1 \phi_2 \cdots \phi_N)$ , where  $\phi_1 \phi_2 \cdots \phi_N$  represents a product  $\phi_1(1) \phi_2(2) \cdots \phi_N(N)$ , and therefore, the normalization constant before the determinant itself  $\det[\phi_1(1) \phi_2(2) \cdots \phi_N(N)]$  is equal to  $(N!)^{-1/2}$ .

Quantum chemists love the Slater determinants because they are built of the *one-electron "bricks"*  $\phi_i$  called *spinorbitals* (we assume them to be orthonormal) and because any Slater determinant is *automatically* antisymmetric with respect to exchange of the coordinates of any two electrons (shown as arguments of  $\phi_i$ ), the factor  $\frac{1}{\sqrt{N!}}$  ensures the normalization. At the same time, any Slater determinant automatically satisfies the Pauli exclusion principle, because any attempt to use the same spinorbitals results in two rows being equal, and as a consequence, in having  $\Psi = 0$  everywhere.<sup>6</sup>

Using the Slater determinants give quantum chemists some comfort since all the integrals that appear when calculating the matrix elements of the Hamiltonian are relatively simple. The most complicated ones contain the coordinates of two electrons.

### What Kind of Operators we will be Dealing with?

1. The sum of one-electron operators  $\hat{F} = \sum_i \hat{h}(i)$
2. The sum of two-electron operators  $\hat{G} = \sum_{i < j} \hat{g}(i, j)$

In both cases, the summation goes over all the electrons. Note that  $\hat{h}$  has the identical form independent of the particular electron; and the same pertains to  $\hat{g}$ .

The future meaning of the  $\hat{F}$  and  $\hat{G}$  operators is obvious; the first pertains to the non-interacting electrons (electronic kinetic energy with  $\hat{h}(i) = -\frac{1}{2} \Delta_i$  or the interaction of the electrons with the nuclei), the second operator deals with the electronic repulsion, with  $\hat{g}(i, j) = \frac{1}{r_{ij}}$ .

<sup>6</sup> This is a kind of catastrophe in theory: because our system *is somewhere* and can be found there with a certain nonzero probability.

### What the Slater-Condon Rules are all About?

The Slater-Condon rules show how to express the matrix elements of many-electron operators  $\hat{F}$  and  $\hat{G}$  with the Slater determinants by *the matrix elements of the operators  $\hat{h}$  and  $\hat{g}$  computed with the orthonormal spinorbitals  $\phi_i$* .

The operators  $\hat{F}$  and  $\hat{G}$  are invariant with respect to any permutation of the electrons (Chapter 2). In other words, the formulas for  $\hat{F}$  and  $\hat{G}$  do not change before and after any relabeling of the electrons. This means that any permutation operator commutes with  $\hat{F}$  and  $\hat{G}$ . Since  $\hat{A}$  is a linear combination of such commuting operators, then  $\hat{A}\hat{F} = \hat{F}\hat{A}$  and  $\hat{A}\hat{G} = \hat{G}\hat{A}$ .

### A Simple Trick Used in the Proofs

All the proofs given here are based on the same simple trick. First, the integral under consideration is transformed into a sum of the terms

$$\langle \phi_1(1)\phi_2(2) \cdots \phi_N(N) | \hat{A}\hat{X} | \phi_1(1)\phi_2(2) \cdots \phi_N(N) \rangle,$$

where  $\hat{X} = \hat{h}(i)$  or  $\hat{g}(i, j)$ . Then, we recall that  $\hat{A}$  is a linear combination of the permutation operators, and that in the integral  $\langle \phi_1(1)\phi_2(2) \cdots \phi_N(N) | \hat{X} | \phi_{n_1}(1)\phi_{n_2}(2) \cdots \phi_{n_N}(N) \rangle$ , only a few terms will survive.

- In case  $\hat{X} = \hat{h}(i)$ , we obtain a product of one-electron integrals:

$$\begin{aligned} & \langle \phi_1(1)\phi_2(2) \cdots \phi_N(N) | \hat{X} | \phi_{n_1}(1)\phi_{n_2}(2) \cdots \phi_{n_N}(N) \rangle \\ &= \langle \phi_1(1) | \phi_{n_1}(1) \rangle \langle \phi_2(2) | \phi_{n_2}(2) \rangle \cdots \langle \phi_i(i) | \hat{h}(i) | \phi_{n_i}(i) \rangle \cdots \langle \phi_N(N) | \phi_{n_N}(N) \rangle. \end{aligned}$$

Since the spinorbitals are orthonormal, then only one term will survive, the one that has  $(n_1, n_2, \dots, n_{i-1}, n_{i+1}, \dots, n_N) = (1, 2, \dots, i-1, i+1, \dots, N)$ . All the overlap integrals that appear there are equal to 1. Only one of the one-electron integrals will give something else:  $\langle \phi_i(i) | \hat{h}(i) | \phi_{n_i}(i) \rangle$ , but also in this integral, we have to have  $n_i = i$  because of the abovementioned overlap integrals that force the matching of the indices.

- If  $\hat{X} = \hat{g}(i, j)$ , we make the same transformations, but the rule for survival of the integrals pertains to the *two*-electron integral that involve the coordinates of the electrons  $i$  and  $j$  (not one-electron as before). Note that this time we will have some *pairs* of the integrals that are going to survive, because the exchange of the indices  $ij \rightarrow ji$  also makes an integral that survives.

## I Slater-Condon Rule

If  $\psi$  represents a normalized Slater determinant, then

$$\bar{F} = \langle \psi | \hat{F} | \psi \rangle = \sum_{i=1}^N \langle i | \hat{h} | i \rangle, \quad (\text{M.5})$$

$$\bar{G} = \langle \psi | \hat{G} | \psi \rangle = \frac{1}{2} \sum_{i,j} (\langle ij | ij \rangle - \langle ij | ji \rangle), \quad (\text{M.6})$$

where

$$\langle i | \hat{h} | r \rangle \equiv \sum_{\sigma_1} \int \phi_i^*(1) \hat{h}(1) \phi_r(1) dV_1 \quad (\text{M.7})$$

$$\langle ij | kl \rangle \equiv \sum_{\sigma_1} \sum_{\sigma_2} \iint \phi_i^*(1) \phi_j^*(2) g(1, 2) \phi_k(1) \phi_l(2) dV_1 dV_2, \quad (\text{M.8})$$

where the summation pertains to two spin coordinates (for electrons 1 and 2).

**Proof:**

**Operator  $\hat{F}$**

$$\bar{F} = \langle \psi | \hat{F} | \psi \rangle = N! \langle \hat{A}(\phi_1 \phi_2 \cdots \phi_N) | \hat{F} | \hat{A}(\phi_1 \phi_2 \cdots \phi_N) \rangle$$

Using  $\hat{A}\hat{F} = \hat{F}\hat{A}$ ,  $\hat{A}^\dagger = \hat{A}$  and  $\hat{A}^2 = \hat{A}$ , one gets

$$\begin{aligned} \bar{F} &= N! \langle \phi_1 \phi_2 \cdots \phi_N | \hat{A}[\hat{h}(1)\phi_1\phi_2\cdots\phi_N + \cdots (\phi_1\phi_2\cdots\hat{h}(N)\phi_N)] \rangle \\ &= \frac{N!}{N!} \langle \phi_1 \phi_2 \cdots \phi_N | \hat{1}[\hat{h}(1)\phi_1\phi_2\cdots\phi_N + \cdots (\phi_1\phi_2\cdots\hat{h}(N)\phi_N)] \rangle, \end{aligned}$$

because what gives a nonzero contribution from the antisymmetrizer  $\hat{A} = (N!)^{-1} (1 + \text{other permutations})$  is only the first term with the operator of multiplication by 1. Other terms disappear after any attempt of integration. As a result, we have

$$\bar{F} = \langle \phi_1 | \hat{h} | \phi_1 \rangle + \langle \phi_2 | \hat{h} | \phi_2 \rangle + \cdots + \langle \phi_N | \hat{h} | \phi_N \rangle = \sum_i h_{ii}, \quad (\text{M.9})$$

which we wanted to show.

**Operator  $\hat{G}$**

Now let us consider the expression for  $\bar{G}$ :

$$\bar{G} = N! \langle \hat{A}(\phi_1 \phi_2 \cdots \phi_N) | \hat{G} \hat{A} | \phi_1 \phi_2 \cdots \phi_N \rangle,$$

where once again  $N!$  comes from the normalization of  $\psi$ . Taking (similarly as above) into account that  $\hat{A}^\dagger = \hat{A}$ ,  $\hat{A}^2 = \hat{A}$ ,  $\hat{G}\hat{A} = \hat{A}\hat{G}$ , we get

$$\begin{aligned}\bar{G} &= N!(\langle\phi_1\phi_2\cdots\phi_N|\hat{A}[\hat{g}(1,2)\phi_1\phi_2\cdots\phi_N + \hat{g}(1,3)\phi_1\phi_2\cdots\phi_N + \cdots]\rangle \\ &= \langle\phi_1(1)\phi_2(2)|\hat{g}(1,2)|\phi_1(1)\phi_2(2)\rangle - \langle\phi_1(1)\phi_2(2)|\hat{g}(1,2)|\phi_2(1)\phi_1(2)\rangle \\ &\quad + \langle\phi_1(1)\phi_3(3)|\hat{g}(1,3)|\phi_1(1)\phi_3(3)\rangle \\ &\quad - \langle\phi_1(1)\phi_3(3)|\hat{g}(1,3)|\phi_3(1)\phi_1(3)\rangle + \cdots\end{aligned}\tag{M.10}$$

This transformation needs some explanation. The factor  $N!$  before the integral is annihilated by  $1/N!$  coming from the antisymmetrizer. The remainder of the antisymmetrizer permutes the electrons in the ket  $|\hat{g}(1,2)\phi_1\phi_2\cdots\phi_N + \hat{g}(1,3)\phi_1\phi_2\cdots\phi_N + \cdots\rangle$ . In the first term [with  $\hat{g}(1,2)$ ], the integrals with only those permutations of the electrons 3, 4,  $\dots$ ,  $N$  will survive that perfectly match the permutation  $\phi_1(1)\phi_2(2)\cdots\phi_N(N)$ , because otherwise the overlap integrals of the spinorbitals (over the coordinates of the electrons 2, 3,  $\dots$ ,  $N$ ) will make them zero. This is why the first term will give rise to only *two* permutations that result in nonzero integrals: we will have on the first two positions  $\phi_1(1)\phi_2(2)$ , and the other one will have  $\phi_1(2)\phi_2(1)$ . Of course, they will differ by sign, which is why we have the minus sign in the second surviving integral. A similar reasoning may be done for the term with  $\hat{g}(1,3)$ , as well as other terms.

Thus, we have shown that

$$\bar{G} = \sum_{i<j} (\langle ij|ij\rangle - \langle ij|ji\rangle) = \frac{1}{2} \sum_{i,j} (\langle ij|ij\rangle - \langle ij|ji\rangle),\tag{M.11}$$

where the factor  $\frac{1}{2}$  takes care of the fact that there is only  $\frac{N(N-1)}{2}$  interelectronic interactions  $g(i, j)$  (the upper triangle of the table  $N \times N$ ). There is no restriction in the summation over  $i, j = 1, 2, \dots, N$ , because any attempt of taking the “*illegal*” self-interaction (corresponding to  $i = j$ ) gives zero due to the identity of the Coulomb ( $\langle ij|ij\rangle$ ) and exchange ( $\langle ij|ji\rangle$ ) integrals. This is the formula that we wanted to prove.

### Special Case: Double Occupation

The integrals in the expressions for  $\bar{F}$  and  $G$  contain spinorbitals, and the integration goes over the electronic space-and-spin coordinates. When the spinorbitals are expressed by the orbitals and the spin functions, we may perform the summation over spin coordinates. The most popular and the most important is the double occupation case, when every orbital is used to form two spinorbitals<sup>7</sup>:

$$\phi_1(1) = \varphi_1(1)\alpha(1)$$

<sup>7</sup> The functions here are written as if they were dependent on the coordinates of electron 1. The reason is that we want to stress that they all are *one-electron functions*. The electron 1 serves here as an example (and when needed may be replaced by other electron). The symbol “1” means  $(x_1, y_1, z_1, \sigma_1)$  if it is an argument of a spinorbital,  $(x_1, y_1, z_1)$  if it corresponds to an orbital, and  $\sigma_1$  if it corresponds to a spin function.

$$\begin{aligned}\phi_2(1) &= \varphi_1(1)\beta(1) \\ \phi_3(1) &= \varphi_2(1)\alpha(1) \\ \phi_4(1) &= \varphi_2(1)\beta(1)\end{aligned}\tag{M.12}$$

$$\dots\tag{M.13}$$

or

$$\begin{aligned}\phi_{2i-1}(1) &= \varphi_i(1)\alpha(1) \\ \phi_{2i}(1) &= \varphi_i(1)\beta(1),\end{aligned}\tag{M.14}$$

where  $i = 1, 2, \dots, N/2$ .

Thus, the one electron spinorbitals that represent the building blocks of the Slater determinant are products of a spatial function (orbital  $\varphi$ ) and one of the two simple functions of the spin coordinate  $\sigma$  ( $\alpha$  or  $\beta$  functions, cf. p. 400).

The first Slater-Condon rule [Eq. (M.9)] may be transformed as follows (for the definition of the integrals, see p. 399):

$$\bar{F} = \sum_{i=1}^N \langle i | \hat{h} | i \rangle = \sum_{i=1}^{MO} \sum_{\sigma} \langle i\sigma | \hat{h} | i\sigma \rangle = 2 \sum_i^{MO} \langle i | \hat{h} | i \rangle \equiv 2 \sum_i^{MO} h_{ii},\tag{M.15}$$

where the summations denoted by MO go over the occupied *orbitals* (their number being  $N/2$ ), the factor 2 results from the summation over  $\sigma$ , which gives the same result for the two values of  $\sigma$  (because of the double occupation of the orbitals).

Let us make a similar operation with  $\bar{G}$ . The formula for  $\bar{G}$  is composed of two parts:

$$\bar{G} = \text{I} - \text{II}.\tag{M.16}$$

The first part reads as

$$\text{I} = \frac{1}{2} \sum_i^{MO} \sum_{\sigma_i} \sum_j^{MO} \sum_{\sigma_j} \langle i\sigma_i, j\sigma_j | i\sigma_i, j\sigma_j \rangle,$$

where  $i\sigma_i, \dots$  etc. stands for the spinorbital composed of the orbital  $\varphi_i$  and a spin function that depends on  $\sigma_i$ . For any pair of the values of  $\sigma_i, \sigma_j$ , the integral yields the same value (at a given pair of  $i, j$ ) and therefore (cf., p. 399)

$$\text{I} = \frac{1}{2} \sum_i^{MO} \sum_j^{MO} 4(ij | ij) = 2 \sum_i^{MO} \sum_j^{MO} (ij | ij).$$

The fate of part II will be a little different:

$$\text{II} = \frac{1}{2} \sum_i^{MO} \sum_{\sigma_i} \sum_j^{MO} \sum_{\sigma_j} \langle i\sigma_i, j\sigma_j | j\sigma_j, i\sigma_i \rangle = \frac{1}{2} \sum_i^{MO} \sum_j^{MO} 2(ij | ji) = \sum_i^{MO} \sum_j^{MO} (ij | ji),$$

because this time the summation over  $\sigma_i$  and  $\sigma_j$  gives the nonzero result in half of the cases when compared to the previous case. The pairs  $(\sigma_i, \sigma_j) = (\frac{1}{2}, \frac{1}{2}), (-\frac{1}{2}, -\frac{1}{2})$  give a nonzero (and the same) result, while  $(\frac{1}{2}, -\frac{1}{2}), (-\frac{1}{2}, \frac{1}{2})$  end up with zero (recall that by convention in the integral, the electrons have the order 1 2 1 2). Finally, the double occupation leads to

$$\bar{G} = \sum_{i,j}^{\text{MO}} [2(ij|ij) - (ij|ji)]. \quad (\text{M.17})$$

## II Slater-Condon Rule

Suppose that we are interested in two matrix elements:  $F_{12} \equiv \langle \psi_1 | \hat{F} | \psi_2 \rangle$  and  $G_{12} \equiv \langle \psi_1 | \hat{G} | \psi_2 \rangle$  and the two Slater determinants  $\psi_1$  and  $\psi_2$  differ only by that spinorbital  $\phi_i$  in  $\psi_1$  has been replaced by  $\phi'_i$  (orthogonal to all other spinorbitals) in  $\psi_2$ . Then the Slater-Condon rule states that

$$F_{12} = \langle i | \hat{h} | i' \rangle \quad (\text{M.18})$$

$$G_{12} = \sum_{j=1} \langle ij | i' j \rangle - \langle ij | j i' \rangle \quad (\text{M.19})$$

**Proof:**

**Operator  $\hat{F}$**

Using  $\hat{F}\hat{A} = \hat{A}\hat{F}$ ,  $\hat{A}^\dagger = \hat{A}$ , and  $\hat{A}^2 = \hat{A}$ , we obtain  $\hat{A}^\dagger \hat{F} \hat{A} = \hat{A} \hat{F} \hat{A} = \hat{A} \hat{A} \hat{F} = \hat{A} \hat{F}$ , and therefore

$$F_{12} = N! \langle \phi_1 \cdots \phi_i \cdots | \hat{A} \hat{F} | \phi_1, \dots, \phi'_i \dots \phi_N \rangle.$$

$$\begin{aligned} F_{12} &= N! \langle \phi_1 \phi_2 \cdots \phi_i \cdots \phi_N | \hat{A} \\ &\quad | [\hat{h}(1)\phi_1, \dots, \phi'_i \cdots \phi_N + \phi_1 \hat{h}(2)\phi_2 \cdots \phi'_i \cdots \phi_N + \cdots \phi_1, \dots, \phi'_i \cdots \hat{h}(N)\phi_N] \rangle \\ &= \sum_P (-1)^P \langle \phi_1 \phi_2 \cdots \phi_i \cdots \phi_N | \\ &\quad \hat{P} [\hat{h}(1)\phi_1, \dots, \phi'_i \cdots \phi_N + \phi_1 \hat{h}(2)\phi_2 \cdots \phi'_i \cdots \phi_N + \cdots \phi_1, \dots, \phi'_i \cdots \hat{h}(N)\phi_N] \rangle. \end{aligned}$$

Note first that the only integral to survive should involve  $\phi_i$  and  $\phi'_i$  in such a way that it leads to the one-electron integral  $\langle \phi_i | \hat{h} | \phi'_i \rangle$ . This however happens only if the  $i$ th term in the square bracket intervenes [that with  $\hat{h}(i)$ ]. Indeed, let us take an integral that is *not* like that ( $i \neq 1$ ):  $\langle \phi_1 \phi_2 \cdots \phi_i \cdots \phi_N | \hat{P} \hat{h}(1)\phi_1 \phi_2 \cdots \phi'_i \cdots \phi_N \rangle$ . Whatever permutation  $\hat{P}$  is,  $\hat{h}$  will always go with  $\phi_1$ , while  $\phi'_i$  will be therefore *without*  $\hat{h}$ . When integrating over the electronic coordinates, we



obtain a product of one-electron integrals (for subsequent electrons), and in this product, one always pinpoints the *overlap* integral of  $\phi'_i$  multiplied by one of the spinorbitals  $\phi_1, \phi_2, \dots, \phi_N$ . This integral (and therefore the whole product) is equal to 0 because  $\phi'_i$  is orthogonal to *all* the spinorbitals. An identical reasoning can be given for  $\hat{h}(2), \hat{h}(3), \dots$ , but not for  $\hat{h}(i)$ , and we obtain:  $F_{12} = \sum_P (-1)^P \langle \phi_1 \phi_2 \cdots \phi_i \cdots \phi_N | \hat{P} [\phi_1 \phi_2 \cdots \hat{h}(i) \phi'_i \cdots \phi_N] \rangle$ .

The only integral to survive is that which corresponds to  $\hat{P} = 1$ , because in other cases, the orthogonality of the spinorbitals will make the product of the one-electron integrals equal zero. Thus, finally, we prove that

$$F_{12} = \langle i | h | i' \rangle. \quad (\text{M.20})$$

### Operator $\hat{G}$

From  $\hat{A}^\dagger = \hat{A}$ ,  $\hat{A}\hat{G}\hat{A} = \hat{A}\hat{A}\hat{G} = \hat{A}\hat{G}$ , we obtain the following transformation:

$$\begin{aligned} G_{12} &= N! \langle \hat{A}(\phi_1 \phi_2 \cdots \phi_N) | \hat{A}\hat{G} | \phi_1, \dots, \phi'_i \cdots \phi_N \rangle \\ &= N! \langle \hat{A}(\phi_1 \phi_2 \cdots \phi_N) | \{ [\hat{g}(1, 2) | \phi_1, \dots, \phi'_i \cdots \phi_N] + [\hat{g}(1, 3) | \phi_1, \dots, \phi'_i \cdots \phi_N] + \cdots \} \rangle \\ &= \frac{1}{2} \sum'_{k,l} \sum_P (-1)^P \langle \hat{P}(\phi_1 \cdots \phi_i \cdots \phi_N) | \hat{g}(k, l) | \phi_1, \dots, \phi'_i \cdots \phi_N \rangle. \end{aligned}$$

The number of  $g$  terms is equal to the number of the interelectronic interactions. The prime in the summation  $k, l = 1, 2, \dots, N$  over interactions  $\hat{g}(k, l)$  means that  $k \neq l$  (we count the interactions twice, but the factor  $\frac{1}{2}$  takes care of that). Note that, due to the orthogonality of the spinorbitals, for a given  $\hat{g}(k, l)$ , the integrals are all zero if  $k \neq i$  and  $l \neq i$ . Thus, the integrals to survive have to have  $k = i$  or  $l = i$ . Therefore (prime in the summation means the summation index  $i$  to be excluded),

$$\begin{aligned} G_{12} &= \frac{1}{2} \sum'_l \sum_P (-1)^P \langle \hat{P}(\phi_1 \cdots \phi_i \cdots \phi_N) | \hat{g}(i, l) | \phi_1, \dots, \phi'_i \cdots \phi_N \rangle \\ &\quad + \frac{1}{2} \sum'_k \sum_P (-1)^P \langle \hat{P}(\phi_1 \cdots \phi_i \cdots \phi_N) | \hat{g}(k, i) | \phi_1, \dots, \phi'_i \cdots \phi_N \rangle \\ &= \frac{1}{2} \sum'_l [\langle \phi_i \phi_l | \phi'_i \phi_l \rangle - \langle \phi_i \phi_l | \phi_l \phi'_i \rangle] + \frac{1}{2} \sum'_k [\langle \phi_i \phi_k | \phi'_i \phi_k \rangle - \langle \phi_i \phi_k | \phi_k \phi'_i \rangle] \\ &= \sum'_j [\langle \phi_i \phi_j | \phi'_i \phi_j \rangle - \langle \phi_i \phi_j | \phi_j \phi'_i \rangle], \end{aligned}$$

because only those two-electron integrals will survive that involve both  $\phi_i$  and  $\phi'_i$ , and two other spinorbitals involved are bound to be identical (and have either the index  $k$  or  $l$  depending on whether  $l = i$  or  $k = i$ ). The difference in the square brackets results from two successful permutations  $\hat{P}$  in which we have the order  $i, j$  or  $j, i$  (in the last term). Finally, leaving for the

sake of simplicity only the indices for the spinorbitals, we obtain

$$G_{12} = \sum_{j(\neq i)} [\langle ij|i'j \rangle - \langle ij|ji' \rangle], \quad (\text{M.21})$$

and after adding  $0 = \langle ii|i'i \rangle - \langle ii|i'i \rangle$ , we have<sup>8</sup>

$$G_{12} = \sum_j \{ \langle ij|i'j \rangle - \langle ij|ji' \rangle \}. \quad (\text{M.22})$$

This is *what* had to be demonstrated.

### III Slater-Condon Rule

If  $\psi_1$  and  $\psi_2$  differ by two spinorbitals, say, in  $\psi_1$  are  $\phi_i$  and  $\phi_s$ , and in  $\psi_2$ , we have  $\phi'_i$  and  $\phi'_s$  (normalized and orthogonal to themselves and to all other spinorbitals)—i.e.,  $\phi'_i$  replaces  $\phi_i$  while  $\phi'_s$  replaces  $\phi_s$  (all other spinorbitals are in the same order)—then

$$F_{12} = 0 \quad (\text{M.23})$$

$$G_{12} = \langle is|i's' \rangle - \langle is|s'i' \rangle \quad (\text{M.24})$$

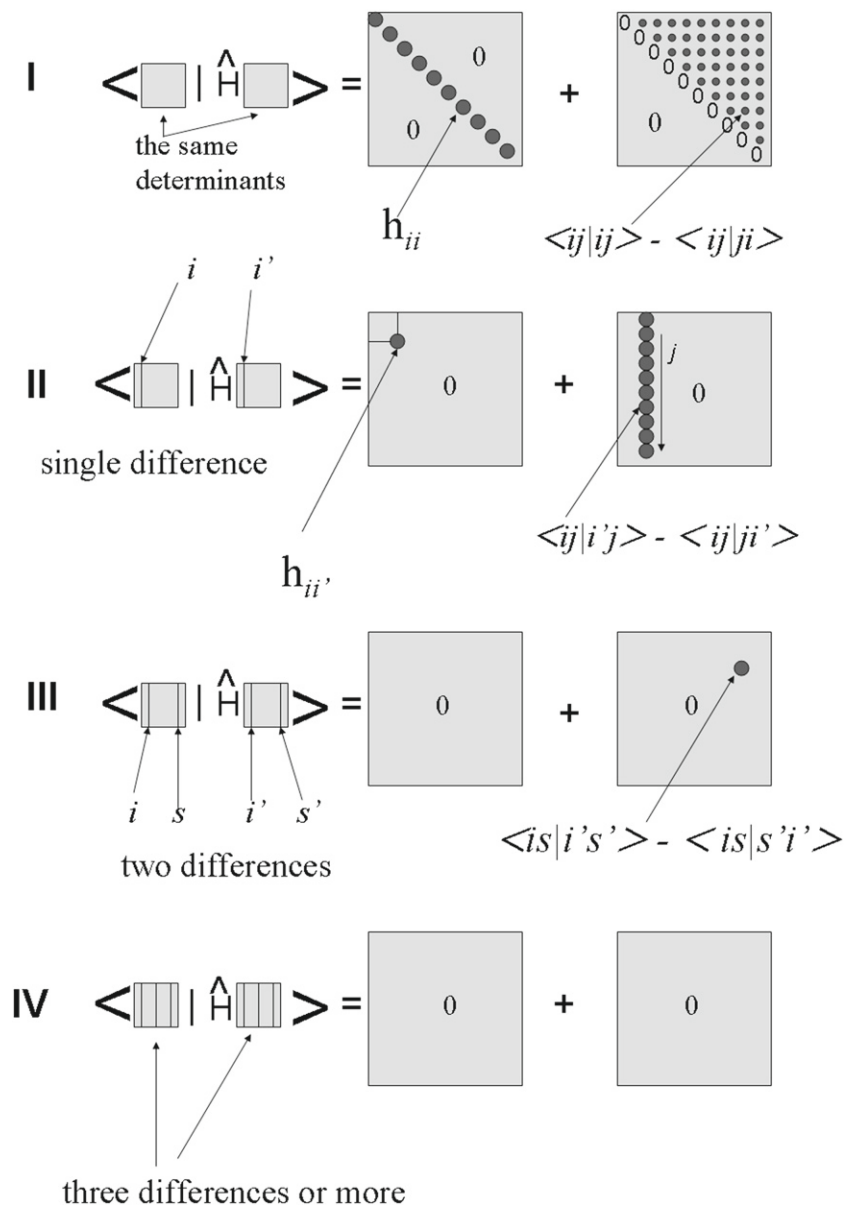
**Proof:**

**Operator  $\hat{F}$**

$$\begin{aligned} F_{12} &= N! \langle (\phi_1 \phi_2 \cdots \phi_N) | \hat{A} \hat{F} (\phi'_1 \phi'_2 \cdots \phi'_N) \rangle \\ &= N! \langle (\phi_1 \phi_2 \cdots \phi_N) | \hat{A} \{ (\hat{h}(1) \phi'_1 \phi'_2 \cdots \phi'_N) + (\phi'_1 \hat{h}(2) \phi'_2 \cdots \phi'_N) \\ &\quad + \cdots (\phi'_1 \phi'_2 \cdots \hat{h}(N) \phi'_N) \} \rangle \\ &= 0, \end{aligned}$$

where the spinorbitals in  $\psi_2$  have been labeled additionally by primes (to stress they *may* differ from those of  $\psi_1$ ). In each term, there will be  $N - 1$  overlap integrals between spinorbitals and one integral involving the  $\hat{h}$ . Therefore, there *always* will be at least one overlap integral involving *different* spinorbitals. This will produce zero.

<sup>8</sup> With this formula, we may forget that the integration has been carried out over the coordinates of the electrons  $i$  and  $j$ . It does not matter what is the symbol of the coordinate over which an integration is performed in a definite integral. When in the future we will have to declare which coordinates we are going to integrate over in  $\langle ij|i'j \rangle$ , then absolutely safely we can put any electrons, in the present book it will be electron 1 and electron 2.



**Fig. M.1.** Four Slater-Condon rules (I,II,III,IV) for easy reference. On the left side, we see pictorial representations of matrix elements of the total Hamiltonian  $\hat{H}$ . The squares inside the brackets represent the Slater determinants. Vertical lines in bra stand for those spinorbitals, which are different in bra and in ket functions. On the right side, we have two square matrices collecting the  $h_{ij}$  and  $\langle ij|ij \rangle - \langle ij|ji \rangle$  for  $i, j = 1, \dots, N$ . The gray circles in the matrices symbolize nonzero elements.

**Operator  $\hat{G}$** 

Something will survive in  $G_{12}$ . Using the previous arguments, we have

$$\begin{aligned}
 G_{12} &= N! \langle (\phi_1 \phi_2 \cdots \phi_N) | \hat{A} (g(1, 2) \phi'_1 \phi'_2 \cdots \phi'_N) + (g(1, 3) \phi'_1 \phi'_2 \cdots \phi'_N) + \cdots \rangle \\
 &= \langle \phi_1 \phi_2 | g(1, 2) | \phi'_1 \phi'_2 \rangle - \langle \phi_1 \phi_2 | g(1, 2) | \phi'_2 \phi'_1 \rangle \\
 &\quad + \langle \phi_1 \phi_3 | g(1, 3) | \phi'_1 \phi'_3 \rangle - \langle \phi_1 \phi_3 | g(1, 3) | \phi'_3 \phi'_1 \rangle + \cdots \\
 &= \langle \phi_1 \phi_2 | \phi'_1 \phi'_2 \rangle - \langle \phi_1 \phi_2 | \phi'_2 \phi'_1 \rangle \\
 &\quad + \langle \phi_1 \phi_3 | \phi'_1 \phi'_3 \rangle - \langle \phi_1 \phi_3 | \phi'_3 \phi'_1 \rangle \\
 &\quad + \cdots
 \end{aligned}$$

Note that  $N!$  cancels  $1/N!$  from the antisymmetrizer, and in the ket we have all possible permutations. The only term to survive has to engage all four spinorbitals:  $i, i', s, s'$ ; otherwise, the overlap integrals will kill it. Therefore, only two terms will survive and give

$$G_{12} = \langle is | i' s' \rangle - \langle is | s' i' \rangle. \quad (\text{M.25})$$

**IV Slater-Condon Rule**

Using the above technique, it is easy to show that if the Slater determinants  $\psi_1$  and  $\psi_2$  differ by *more than two* (orthogonal) spinorbitals, then  $F_{12} = 0$  and  $G_{12} = 0$ . This happens because the operators  $\hat{F}$  and  $\hat{G}$  represent a sum of at most two-electron operators, which will involve at most four spinorbitals and there will be always an extra overlap integral over orthogonal spinorbitals.<sup>9</sup>

The Slater-Condon rules are schematically depicted in Fig. M.1.

<sup>9</sup> If the operators were more than two-particle ones, then the result would be different.