M. 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 the calculation of the mean values or the matrix elements of some important operators. We will need this in the Hartree–Fock method, as well as in other important methods of quantum chemistry.

Only the final results of the derivations presented in this Appendix are the most important.

Antisymmetrization operator

The antisymmetrization operator is defined as

$$\hat{A} = \frac{1}{N!} \sum_{P} (-1)^p \hat{P}, \tag{M.1}$$

where $\hat{P}$ represents the permutation operator of N objects (in our case – electrons), 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 transpositions (i.e. exchanges) of two elements.

The operator $\hat{A}$ has some nice features. The most important 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.[1] This means that $\hat{A}$ represents a sort of magic wand: whatever it touches it makes antisymmetric or causes it disappear! The antisymmetrizer is also idempotent, i.e. 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:

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

Of course $\hat{P}\hat{P}'$ represents a permutation opera tor,[2] which is then multiplied by its own parity $(-1)^{p+p'}$ and there is a sum over such permutations at a given fixed $\hat{P}'$.

[1] 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, σ).

[2] The permutations form the permutation group.

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 "Grup-*

Independently of what $\hat{P}'$ is *we obtain the same result*[3] $N!$ 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 therefore conserves the scalar product. This means that for the two vectors ψ_1 and ψ_2 of the Hilbert space we obtain[4]

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

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

$$(N!)^{-1} \sum_{P^{-1}} (-1)^p \big\langle \hat{P}^{-1}\psi_1(1,2,\ldots,N) \big| \psi_2(1,2,\ldots,N) \big\rangle.$$

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: $\langle \psi_1 | \hat{A}\psi_2 \rangle = \langle \hat{A}\psi_1 | \psi_2 \rangle$, or[5]

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

Slater–Condon rules

The Slater–Condon rules serve to express the matrix elements involving the Slater determinants (which represent many-electron wave functions):

penpest": the pest of 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".

[3] 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 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. independently of $\hat{P}'$.

[4] 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 ψ_1 and $\hat{P}\psi_1$ are the same (similarly with ψ_2), and that the angle between the vectors is also conserved. If $\hat{P}$ is acting on ψ_2 alone, and ψ_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 (ψ_2) has been transformed (which means the rotation of a unit vector in the Hilbert space). *The same angle* would be obtained, if its partner ψ_1 were transformed in the *opposite* direction, i.e. when the operation $\hat{P}^{-1}\psi_1$ has been performed. Hence from the equality of the angles we have $\langle \psi_1 | \hat{P}\psi_2 \rangle = \langle \hat{P}^{-1}\psi_1 | \psi_2 \rangle$.

[5] $\hat{A}^\dagger$ 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 the present book) among the self-adjoint ($\hat{A}^\dagger = \hat{A}$) and Hermitian operators in mathematical physics (they differ by definition of their domains).

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

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 the 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 Slater determinants, because they are built of *one-electron* "bricks" ϕ_i called the spinorbitals (we assume them orthonormal) and because any Slater determinant is *automatically* antisymmetric with respect to the exchange of the coordinates of any two electrons (shown as arguments of ϕ_i's), 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 in consequence, having $\Psi = 0$ everywhere.[6]

Using Slater determinants gives quantum chemists a kind of comfort, since all the integrals which 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 WILL WE 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; the same pertains to $\hat{g}$.

The future meaning of the $\hat{F}$ and $\hat{G}$ operators is quite 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 $\hat{g}(i,j) = \frac{1}{r_{ij}}$.

WHAT ARE THE SLATER–CONDON RULES 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 $\hat{g}$ calculated with orthonormal spinorbitals ϕ_i*.

[6] Which is a kind of catastrophe in theory: because our system *is somewhere* and can be found there with a certain non-zero probability.

The operators $\hat{F}$ and $\hat{G}$ are invariant with respect to any permutation of the electrons (Chapter 2). In other words, the formulae for $\hat{F}$ and $\hat{G}$ do not change before and after any relabelling 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 below

All the proofs given below are based on the same simple trick. First, the integral under consideration is transformed into the sum of the following 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 the case $\hat{X} = \hat{h}(i)$ we obtain a product of one-electron integrals

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

  Since the spinorbitals are orthonormal, only one term will survive, the one which has $(n_1, n_2, \ldots, n_{i-1}, n_{i+1}, \ldots, n_N) = (1, 2, \ldots, i-1, i+1, \ldots, N)$. All the overlap integrals which 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 in this integral also we have to have $n_i = i$, because of the overlap integrals which force the matching of the indices mentioned above.
- In the case $\hat{X} = \hat{g}(i,j)$ we make the same transformations, but the rule for survival of the integrals pertains to the *two*-electron integral which involves the coordinates of the electrons i and j (not one-electron as before). Note that this time we will have some *pairs* of integrals which are going to survive, because the exchange of indices $ij \to ji$ also makes an integral survive.

I Slater–Condon rule

If ψ represents a normalized Slater determinant, then

$$\overline{F} = \langle\psi|\hat{F}|\psi\rangle = \sum_{i=1}^{N}\langle i|\hat{h}|i\rangle, \tag{M.5}$$

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

where

$$\langle i|\hat{h}|r\rangle \equiv \sum_{\sigma_1}\int \phi_i^*(1)\hat{h}(1)\phi_r(1)\,\mathrm{d}V_1, \tag{M.7}$$

$$\langle ij|kl\rangle \equiv \sum_{\sigma_1}\sum_{\sigma_2}\iint \phi_i^*(1)\phi_j^*(2)g(1,2)\phi_k(1)\phi_l(2)\,\mathrm{d}V_1\,\mathrm{d}V_2, \tag{M.8}$$

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

***Proof*: Operator $\hat{F}$.**

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

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

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

because what gives the non-zero 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 at integration. As a result we have:

$$\overline{F} = \langle\phi_1|\hat{h}|\phi_1\rangle + \langle\phi_2|\hat{h}|\phi_2\rangle + \cdots + \langle\phi_N|\hat{h}|\phi_N\rangle = \sum_i h_{ii}, \tag{M.9}$$

which is what we wanted to show.

Operator $\hat{G}$. Now let us consider the expression for $\overline{G}$

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

where once again $N!$ comes from the normalization of ψ. Taking (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

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

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 electrons $3, 4, \ldots, N$ will survive which 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 $2, 3, \ldots, N$) will make them

zero. This is why the first term will give rise to only *two* permutations which result in non-zero integrals: in the first two positions we will have $\phi_1(1)\phi_2(2)$, and in the other $\phi_1(2)\phi_2(1)$. Of course, they will differ by sign, and this is why we have the minus sign in the second surviving integral. Similar reasoning may be followed for the term with $\hat{g}(1,3)$, as well as for the other terms.

Thus, we have shown that

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

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

A special case: double occupation

The integrals in the expressions for $\overline{F}$ 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 the spin coordinates. The double occupation case is the most popular and the most important, when every orbital is used to form two spinorbitals[7]

$$\begin{aligned}
\phi_1(1) &= \varphi_1(1)\alpha(1),\\
\phi_2(1) &= \varphi_1(1)\beta(1),\\
\phi_3(1) &= \varphi_2(1)\alpha(1),\\
\phi_4(1) &= \varphi_2(1)\beta(1),\\
&\cdots
\end{aligned} \tag{M.12}$$

or

$$\begin{aligned}
\phi_{2i-1}(1) &= \varphi_i(1)\alpha(1),\\
\phi_{2i}(1) &= \varphi_i(1)\beta(1),
\end{aligned} \tag{M.13}$$

$i = 1, 2, \ldots, N/2$.

Thus, the one electron spinorbitals which represent the building blocks of the Slater determinant, are products of a spatial function (orbital φ), and one of the two simple functions of the spin coordinate σ (α or β functions, cf. p. 28).

[7] The functions below are written as if they were dependent on the coordinates of electron number 1. The reason is that we want to stress that they all are *one-electron functions.* Electron 1 serves here as an example (and when needed may be replaced by the 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 σ_1 if it corresponds to a spin function.

The first Slater–Condon rule (M.9) may be transformed as follows (for definition of the integrals see p. 334)

$$\overline{F} = \sum_{i=1}^{N} \langle i|\hat{h}|i\rangle = \sum_{i=1}^{\mathrm{MO}} \sum_{\sigma} \langle i\sigma|\hat{h}|i\sigma\rangle = 2\sum_{i}^{\mathrm{MO}} \big(i|\hat{h}|i\big) \equiv 2\sum_{i}^{\mathrm{MO}} h_{ii} \tag{M.14}$$

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

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

$$\overline{G} = \mathrm{I} - \mathrm{II}. \tag{M.15}$$

The first part reads as

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

where $i\sigma_i, \ldots$ etc. stands for the spinorbital composed of the orbital φ_i and a spin function that depends on σ_i. For any pair of values of σ_i, σ_j, the integral yields the same value (at a given pair of i, j) and therefore (cf. p. 334),

$$\mathrm{I} = \frac{1}{2} \sum_{i}^{\mathrm{MO}} \sum_{j}^{\mathrm{MO}} 4(ij|ij) = 2 \sum_{i}^{\mathrm{MO}} \sum_{j}^{\mathrm{MO}} (ij|ij).$$

The fate of part II will be a little different:

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

because this time the summation over σ_i and σ_j gives a non-zero result in half 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 non-zero (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, the electrons in the integral have the order 1 2 1 2). Finally the double occupation leads to

$$\overline{G} = \sum_{i,j}^{\mathrm{MO}} \big[2(ij|ij) - (ij|ji)\big]. \tag{M.16}$$

II Slater–Condon rule

Suppose 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 ψ_1 and ψ_2 differ only in that spinorbital ϕ_i in ψ_1 has been replaced by ϕ_i' (*orthogonal to all other spinorbitals*) in ψ_2. Then the Slater–Condon rule states that

$$F_{12} = \langle i|\hat{h}|i'\rangle, \tag{M.17}$$

$$G_{12} = \sum_{j=1} \big(\langle ij|i'j\rangle - \langle ij|ji'\rangle\big). \tag{M.18}$$

***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

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

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

Note first that the only integral to survive should involve ϕ_i and ϕ_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 which 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 ϕ_1, while ϕ_i' will therefore be *without* $\hat{h}$. When integrating over the electronic coordinates we obtain the product of one-electron integrals (for subsequent electrons), and in this product we always pinpoint the *overlap* integral of ϕ_i' multiplied by one of the spinorbitals $\phi_1, \phi_2, \ldots, \phi_N$. This integral (and therefore the whole product) is equal to 0, because ϕ_i' is orthogonal to *all* the spinorbitals. Identical reasoning can be given for $\hat{h}(2), \hat{h}(3), \ldots$, but not for $\hat{h}(i)$, and we obtain:

$$F_{12} = \sum_P (-1)^p\langle\phi_1\phi_2\cdots\phi_i\cdots\phi_N|\hat{P}\big[\phi_1\phi_2\cdots\hat{h}(i)\phi_i'\cdots\phi_N\big]\rangle.$$

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 to zero. Thus, finally we prove that

$$F_{12} = \langle i|h|i'\rangle. \tag{M.19}$$

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

$$\begin{aligned} G_{12} &= N!\langle\hat{A}(\phi_1\phi_2\cdots\phi_N)|\hat{A}\hat{G}|\phi_1\cdots\phi_i'\cdots\phi_N\rangle\rangle \\ &= N!\langle\hat{A}(\phi_1\phi_2\cdots\phi_N)|\{\big[\hat{g}(1,2)|\phi_1\cdots\phi_i'\cdots\phi_N\rangle\big] \end{aligned}$$

$$
\begin{aligned}
&+\left[\hat{g}(1,3)\left|\phi_1\cdots\phi_i'\cdots\phi_N\right\rangle\right]+\cdots\Big\}\Big\rangle \\
&=\frac{1}{2}{\sum_{k,l}}'\sum_P(-1)^p\left\langle\hat{P}(\phi_1\cdots\phi_i\cdots\phi_N)\left|\hat{g}(k,l)\right|\phi_1\cdots\phi_i'\cdots\phi_N\right\rangle.
\end{aligned}
$$

The number of g terms is equal to the number of interelectronic interactions. The prime in the summation $k,l=1,2,\ldots,N$ 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 is to be excluded),

$$
\begin{aligned}
G_{12}&=\frac{1}{2}{\sum_{l}}'\sum_P(-1)^p\left\langle\hat{P}(\phi_1\cdots\phi_i\cdots\phi_N)\left|\hat{g}(i,l)\right|\phi_1\cdots\phi_i'\cdots\phi_N\right\rangle \\
&\quad+\frac{1}{2}{\sum_{k}}'\sum_P(-1)^p\left\langle\hat{P}(\phi_1\cdots\phi_i\cdots\phi_N)\left|\hat{g}(k,i)\right|\phi_1\cdots\phi_i'\cdots\phi_N\right\rangle \\
&=\frac{1}{2}{\sum_{l}}'\left[\left\langle\phi_i\phi_l\left|\phi_i'\phi_l\right\rangle-\left\langle\phi_i\phi_l\left|\phi_l\phi_i'\right\rangle\right.\right]+\frac{1}{2}{\sum_{k}}'\left[\left\langle\phi_i\phi_k\left|\phi_i'\phi_k\right\rangle-\left\langle\phi_i\phi_k\left|\phi_k\phi_i'\right\rangle\right.\right] \right. \\
&=\sum_j{}'\left[\left\langle\phi_i\phi_j\left|\phi_i'\phi_j\right\rangle-\left\langle\phi_i\phi_j\left|\phi_j\phi_i'\right\rangle\right.\right],
\end{aligned}
$$

because only those two-electron integrals will survive which involve both ϕ_i *and* ϕ_i', and the 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, for the sake of simplicity leaving only the indices for the spinorbitals, we obtain

$$
G_{12}=\sum_{j(\neq i)}\left[\left\langle ij\left|i'j\right\rangle-\left\langle ij\right|ji'\right\rangle\right] \tag{M.20}
$$

and after adding $0=\langle ii|i'i\rangle-\langle ii|ii'\rangle$ we have[8]

$$
G_{12}=\sum_j\left\{\left\langle ij\left|i'j\right\rangle-\left\langle ij\right|ji'\right\rangle\right\}. \tag{M.21}
$$

This is our result.

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

III Slater–Condon rule

If ψ_1 and ψ_2 differ by two spinorbitals, say, in ψ_1 are ϕ_i and ϕ_s, and in ψ_2 we have ϕ'_i and ϕ'_s (normalized and orthogonal to themselves and to all other spinorbitals), i.e. ϕ'_i replaces ϕ_i while ϕ'_s replaces ϕ_s (all other spinorbitals are of the same order), then

$$F_{12} = 0, \tag{M.22}$$

$$G_{12} = \langle is|i's'\rangle - \langle is|s'i'\rangle, \tag{M.23}$$

***Proof*: Operator $\hat{F}$.**

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

where the spinorbitals in ψ_2 have been additionally labelled by primes (to stress that they *may* differ from those of ψ_1). In each term there will be $N-1$ overlap integrals between spinorbitals and one integral involving $\hat{h}$. Therefore, there will *always* be at least one overlap integral involving *different* spinorbitals. This will produce zero.

Operator $\hat{G}$. There will be something surviving in G_{12}. Using the previous arguments, we have

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

Note that $N!$ cancels $1/N!$ from the antisymmetrizer, and in the ket we have all possible permutations. A term to survive, it 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

$$G_{12} = \langle is|i's'\rangle - \langle is|s'i'\rangle. \tag{M.24}$$

IV Slater–Condon rule

Using the above technique it is easy to show that if the Slater determinants ψ_1 and ψ_2 differ by *more than two* (orthogonal) spinorbitals, the matrix elements $F_{12} = 0$

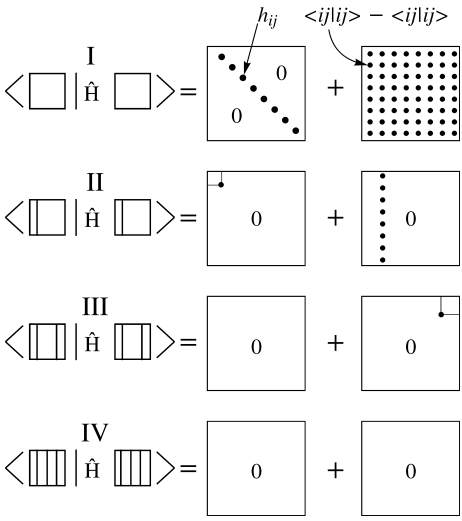

Fig. M.1. Four Slater–Condon rules (I, II, III, IV) for easy remembering. On the left side we see pictorial representations of matrix elements of the total Hamiltonian $\hat{H}$. The squares inside the brackets represent the Slater determinants. Vertical lines in bra stand for those spinorbitals, which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

and $G_{12} = 0$. This happens because operators $\hat{F}$ and $\hat{G}$ represent the sum of, at most, two-electron operators, which will involve at most four spinorbitals and there will always be an extra overlap integral over the orthogonal spinorbitals.[9]

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

[9] If the operators were more than two-particle, the result would be different.