

SLATER DETERMINANTS

11.1 Matrix Elements—General

In Section 8.4 we saw that multielectron wave functions $\psi(\lambda_1, \lambda_2, \dots, \lambda_N)$ must be antisymmetric with respect to an interchange of the (space and spin) coordinates of any two electrons. Antisymmetry can be ensured by expressing the wave function in terms of Slater determinants as in (8.4-13). To facilitate the calculation of various physical quantities, we shall need expressions for matrix elements of operators when the wave functions are written in determinantal form.

Consider a two-electron system and let

$$\Psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_j(\lambda_1) & \psi_k(\lambda_1) \\ \psi_j(\lambda_2) & \psi_k(\lambda_2) \end{vmatrix}, \quad (11.1-1)$$

$$\Psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_j(\lambda_1) & \psi_i(\lambda_1) \\ \psi_j(\lambda_2) & \psi_i(\lambda_2) \end{vmatrix}, \quad (11.1-2)$$

$$\Psi_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_i(\lambda_1) & \psi_m(\lambda_1) \\ \psi_i(\lambda_2) & \psi_m(\lambda_2) \end{vmatrix}. \quad (11.1-3)$$

In $\psi_k(\lambda_i)$, k is a label that identifies a particular spin orbital, i.e., a one-electron function that depends on both space and spin coordinates; the index i is an electron label. The notation may be shortened by writing

$$\psi_k(\lambda_i) \equiv \psi_k(i). \quad (11.1-4)$$

It will also be assumed that for any two spin orbitals such as ψ_k and ψ_l

$$\langle \psi_k(i) | \psi_l(i) \rangle = \delta_{kl}. \quad (11.1-5)$$

This has the immediate consequence that

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad (11.1-6)$$

where Ψ_i and Ψ_j are any of the determinantal functions (11.1-1)–(11.1-3).

Let us now suppose that we have a sum of one-electron operators

$$F = f_1 + f_2$$

where f_1 and f_2 have the same functional dependence but f_1 operates only on the spin orbital occupied by electron 1, namely $\psi(\lambda_1)$, and f_2 operates only on $\psi(\lambda_2)$. Since variables of integration are dummy variables we may write

$$\langle \psi_k(1) | f_1 | \psi_l(1) \rangle = \langle \psi_k(2) | f_2 | \psi_l(2) \rangle = \langle \psi_k | f | \psi_l \rangle. \quad (11.1-7)$$

Therefore, in view of the orthonormality relation (11.1-5),

$$\langle \Psi_1 | F | \Psi_1 \rangle = \langle \psi_j | f | \psi_j \rangle + \langle \psi_k | f | \psi_k \rangle \quad (11.1-8)$$

with analogous expressions for $\langle \Psi_2 | F | \Psi_2 \rangle$ and $\langle \Psi_3 | F | \Psi_3 \rangle$. For the off-diagonal elements

$$\langle \Psi_1 | F | \Psi_2 \rangle = \langle \psi_k | f | \psi_i \rangle, \quad (11.1-9a)$$

$$\langle \Psi_1 | F | \Psi_3 \rangle = 0, \quad (11.1-9b)$$

$$\langle \Psi_2 | F | \Psi_3 \rangle = -\langle \psi_j | f | \psi_m \rangle. \quad (11.1-9c)$$

A two-electron operator g_{12} operates on both $\psi(\lambda_1)$ and $\psi(\lambda_2)$, as, for example, in the case of the electronic Coulomb repulsion operator e^2/r_{12} . For a typical diagonal element

$$\langle \Psi_1 | g_{12} | \Psi_1 \rangle = \langle \psi_j(1)\psi_k(2) | g_{12} | \psi_j(1)\psi_k(2) \rangle - \langle \psi_j(1)\psi_k(2) | g_{12} | \psi_k(1)\psi_j(2) \rangle, \quad (11.1-10)$$

and for off-diagonal elements

$$\langle \Psi_1 | g_{12} | \Psi_2 \rangle = \langle \psi_j(1)\psi_k(2) | g_{12} | \psi_j(1)\psi_i(2) \rangle - \langle \psi_j(1)\psi_k(2) | g_{12} | \psi_i(1)\psi_j(2) \rangle, \quad (11.1-11a)$$

$$\langle \Psi_1 | g_{12} | \Psi_3 \rangle = \langle \psi_j(1)\psi_k(2) | g_{12} | \psi_i(1)\psi_m(2) \rangle - \langle \psi_j(1)\psi_k(2) | g_{12} | \psi_m(1)\psi_i(2) \rangle, \quad (11.1-11b)$$

$$\langle \Psi_2 | g_{12} | \Psi_3 \rangle = -\langle \psi_j(1)\psi_i(2) | g_{12} | \psi_m(1)\psi_i(2) \rangle + \langle \psi_j(1)\psi_i(2) | g_{12} | \psi_i(1)\psi_m(2) \rangle. \quad (11.1-11c)$$

These results for the special case of the Slater determinants (11.1-1)–(11.1-3) may be generalized to determinants of arbitrary dimension. Thus, let

$$A = \frac{1}{\sqrt{N!}} \begin{vmatrix} a_1(1) & a_2(1) & \cdots & a_N(1) \\ a_1(2) & a_2(2) & \cdots & a_N(2) \\ \vdots & \vdots & \cdots & \vdots \\ a_1(N) & a_2(N) & \cdots & a_N(N) \end{vmatrix}, \quad (11.1-12)$$

$$B = \frac{1}{\sqrt{N!}} \begin{vmatrix} b_1(1) & b_2(1) & \cdots & b_N(1) \\ b_1(2) & b_2(2) & \cdots & b_N(2) \\ \vdots & \vdots & \cdots & \vdots \\ b_1(N) & b_2(N) & \cdots & b_N(N) \end{vmatrix}, \quad (11.1-13)$$

$$F = \sum_{i=1}^N f_i, \quad (11.1-14)$$

$$G = \sum_{i < j} g_{ij} = \frac{1}{2} \sum_{i \neq j} g_{ij}, \quad (11.1-15)$$

in which $a_k(i), b_k(i)$ are spin orbitals; f_i and g_{ij} are one- and two-electron operators, respectively.

We must also take note of the order in which the orbitals appear in (11.1-12) and (11.1-13) because an interchange of two columns (or rows) will change the sign of the determinantal wave function. As previously written the order is

$$A: a_1, a_2, \dots, a_k, a_{k+1}, \dots, a_l, a_{l+1}, \dots, a_N,$$

$$B: b_1, b_2, \dots, b_k, b_{k+1}, \dots, b_l, b_{l+1}, \dots, b_N.$$

For the diagonal matrix element of F ,

$$\langle A|F|A \rangle = \sum_{k=1}^N \langle a_k|f|a_k \rangle \quad (11.1-16)$$

in which the argument of a_k and the subscript on f have been omitted, as they will be henceforth, since they are arbitrary (see, for example, (11.1-7)). The matrix element $\langle B|F|B \rangle$ has the same form with respect to the b orbitals. For an off-diagonal matrix element

$$\langle A|F|B \rangle = 0 \quad (11.1-17)$$

if A and B differ by more than one pair of orbitals, and

$$\langle A|F|B \rangle = \pm \langle a_k|f|b_l \rangle \quad (11.1-18)$$

if $a_k \neq b_l$, but the rest of the orbitals in B are the same as those in A . The plus sign occurs when an even number of interchanges are required to move

the b_l orbital into the k th position or, in other words, when the parity of the permutation is even; the minus sign appears as a result of an odd-parity permutation. Examples of (11.1-18) are provided by (11.1-9a) and (11.1-9c). It may also be remarked that for one-electron operators such as (11.1-14), simple product functions, and determinantal functions give the same matrix elements.

The diagonal matrix elements of G are

$$\begin{aligned} \langle A|G|A \rangle &= \sum_{k < l} [\langle a_k(1)a_l(2)|g_{12}|a_k(1)a_l(2) \rangle \\ &\quad - \langle a_k(1)a_l(2)|g_{12}|a_l(1)a_k(2) \rangle] \end{aligned} \quad (11.1-19)$$

and for off-diagonal elements we have the cases:

- (1) If A and B differ by more than two pairs of spin orbitals,

$$\langle A|G|B \rangle = 0. \quad (11.1-20)$$

- (2) If A and B differ by two pairs of orbitals, i.e., a_k, a_l in A are not the same as b_m, b_n in B but all other orbitals in A are the same as orbitals in B ,

$$\begin{aligned} \langle A|G|B \rangle &= \pm [\langle a_k(1)a_l(2)|g_{12}|b_m(1)b_n(2) \rangle \\ &\quad - \langle a_k(1)a_l(2)|g_{12}|b_n(1)b_m(2) \rangle]. \end{aligned} \quad (11.1-21)$$

- (3) If A and B differ by one pair of orbitals, e.g., $a_k \neq b_l$,

$$\begin{aligned} \langle A|G|B \rangle &= \pm \sum_{i \neq k} [\langle a_k(1)a_i(2)|g_{12}|b_l(1)a_i(2) \rangle \\ &\quad - \langle a_k(1)a_i(2)|g_{12}|a_i(1)b_l(2) \rangle]. \end{aligned} \quad (11.1-22)$$

The same rule as in (11.1-18) applies to the \pm signs in (11.1-21) and (11.1-22). Examples of diagonal and off-diagonal elements are given by (11.1-10) and (11.1-11).

It will now be assumed that the general spin orbital $a(\lambda_i)$ consists of a product of a spatial function $\varphi_a(\mathbf{r}_i)$ and a spin function $\xi_i^a(m_s)$. The latter is always either an α or a β spin function depending on whether m_s is $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus

$$a(\lambda_i) = \varphi_a(\mathbf{r}_i)\xi_i^a(m_s) \quad \text{or} \quad a(i) = \varphi_a(i)\xi_i^a(m_s). \quad (11.1-23)$$

Therefore

$$\langle a|f|b \rangle = \langle \varphi_a|f|\varphi_b \rangle \langle \xi^a(m_s)|\xi^b(m_s) \rangle = \langle \varphi_a|f|\varphi_b \rangle \delta(m_s^a, m_s^b) \quad (11.1-24)$$

in which the orthonormality of the spin functions has been inserted.

If $a, b, c,$ and d are spin orbitals of form (11.1-23), the general matrix element of a two-electron operator becomes

$$\begin{aligned} \langle a(1)b(2)|g_{12}|c(1)d(2)\rangle &= \langle \varphi_a(1)\varphi_b(2)|g_{12}|\varphi_c(1)\varphi_d(2)\rangle \\ &\times \langle \xi_1^a(m_s)|\xi_1^c(m_s)\rangle \langle \xi_2^b(m_s)|\xi_2^d(m_s)\rangle \\ &= \langle \varphi_a(1)\varphi_b(2)|g_{12}|\varphi_c(1)\varphi_d(2)\rangle \delta(m_s^a, m_s^c) \delta(m_s^b, m_s^d). \end{aligned} \quad (11.1-25)$$

11.2 Matrix Elements—Special Cases

We shall now specialize the discussion in two ways. It will be assumed that the spin-orbital $a(i)$ in (11.1-23) is given by

$$a(i) = R_{nl}^a(r_i) Y_{lm}^a(\Omega_i) \xi_i^a(m_s) = \frac{1}{r_i} P_{nl}^a(r_i) Y_{lm}^a(\Omega_i) \xi_i^a(m_s), \quad (11.2-1)$$

that is, the spatial part of $a(i)$ is a product of a radial function and a spherical harmonic; and that

$$g_{12} = e^2/r_{12} \quad (11.2-2)$$

in which $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between electrons 1 and 2. With these assumptions, integrals of the type that occur in (11.1-24) and (11.1-25) can be given a more explicit form.

As a first step, e^2/r_{12} is expanded in spherical harmonics as in (1.2-22):

$$\frac{e^2}{r_{12}} = 4\pi e^2 \sum_{k=0}^{\infty} \sum_{m=-k}^k \frac{1}{2k+1} \frac{r_{<}^k}{r_{>}^{k+1}} Y_{km}^*(\Omega_1) Y_{km}(\Omega_2). \quad (11.2-3)$$

Then

$$\begin{aligned} \langle a(1)b(2)|g_{12}|c(1)d(2)\rangle &= \left\langle a(1)b(2) \left| \frac{e^2}{r_{12}} \right| c(1)d(2) \right\rangle \\ &= \left\langle \frac{1}{r_1} P_{n_1}^a(r_1) Y_{l_1 m_1}^a(\Omega_1) \frac{1}{r_2} P_{n_2}^b(r_2) Y_{l_2 m_2}^b(\Omega_2) \left| \frac{e^2}{r_{12}} \right| \frac{1}{r_1} P_{n_1}^c(r_1) Y_{l_1 m_1}^c(\Omega_1) \right. \\ &\quad \left. \times \frac{1}{r_2} P_{n_2}^d(r_2) Y_{l_2 m_2}^d(\Omega_2) \right\rangle \delta(m_s^a, m_s^c) \delta(m_s^b, m_s^d). \end{aligned} \quad (11.2-4)$$

When e^2/r_{12} is replaced by (11.2-3), the radial part of (11.2-4) is a sum over quantities such as

$$R^k(abcd) \equiv e^2 \int_0^{\infty} \int_0^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} P_{n_1}^a(r_1) P_{n_2}^b(r_2) P_{n_1}^c(r_1) P_{n_2}^d(r_2) dr_1 dr_2. \quad (11.2-5)$$

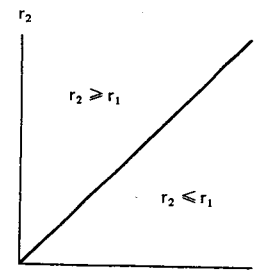


FIG. 11.1 Regions of integration for Eq. (11.2-7).

Integrals of this type may now be evaluated: Let

$$I = \int_0^{\infty} \int_0^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} f(r_1) g(r_2) dr_1 dr_2 \quad (11.2-6)$$

where it is understood that $r_{<}$ means the smaller of the quantities r_1 and r_2 while $r_{>}$ means the greater of the two. If the integration space is subdivided into two regions as shown in Fig. 11.1, then

$$I = \int_0^{\infty} dr_1 \int_0^{r_1} \frac{r_2^k}{r_1^{k+1}} f(r_1) g(r_2) dr_2 + \int_0^{\infty} dr_2 \int_0^{r_2} \frac{r_1^k}{r_2^{k+1}} f(r_1) g(r_2) dr_1. \quad (11.2-7)$$

In order to perform the radial integration we require the radial wave functions which, for a multielectron atom, necessitate rather elaborate computations (see Chapter 19).

The angular integrals in (11.2-4) are of the form

$$\frac{4\pi}{2k+1} \langle Y_{l_1 m_1}^a(\Omega_1) | Y_{km}^*(\Omega_1) | Y_{l_1 m_1}^c(\Omega_1) \rangle \langle Y_{l_2 m_2}^b(\Omega_2) | Y_{km}(\Omega_2) | Y_{l_2 m_2}^d(\Omega_2) \rangle.$$

These are readily evaluated by means of the general formula (1.2-29), namely:

$$\begin{aligned} \langle l' m' | Y_{LM} | l m \rangle &= (-1)^{m'} \sqrt{\frac{(2l'+1)(2L+1)(2l+1)}{4\pi}} \\ &\quad \times \begin{pmatrix} l' & L & l \\ -m' & M & m \end{pmatrix} \begin{pmatrix} l' & L & l \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (11.2-8)$$

which is nonvanishing only when

$$-m' + M + m = 0, \quad l' + L + l \text{ is even}, \quad \Delta(l' L l). \quad (11.2-9)$$

It is customary to define a quantity $c^k(lm, l'm')$ as

$$\begin{aligned} c^k(lm, l'm') &= \sqrt{\frac{4\pi}{2k+1}} \langle Y_{lm} | Y_{k m-m'} | Y_{l'm'} \rangle \\ &= (-1)^{\overline{m-m'}} c^k(l'm', lm). \end{aligned} \quad (11.2-10)$$

These integrals have been evaluated for special cases and are tabulated in Table 11.1. Remembering that $Y_{km}^* = (-1)^m Y_{k-m}$ and adopting the notation in which m_i^a, m_i^b, \dots are the projection quantum numbers associated with $Y_{lm_i}^a, Y_{lm_i}^b, \dots$, we have, from (11.2-9), the conditions on the projection quantum numbers:

$$-m_i^a - m + m_i^c = 0, \quad -m_i^b + m + m_i^d = 0,$$

$$\text{or} \quad m_i^a + m_i^b = m_i^c + m_i^d. \quad (11.2-11)$$

TABLE 11.1

$c^k(lm, l'm')$ for s, p, and d Electrons^{a,b}

	m	m'	k				
			0	1	2	3	4
ss	0	0	1	0	0	0	0
sp	0	±1	0	$-\sqrt{\frac{3}{5}}$	0	0	0
	0	0	0	$\sqrt{\frac{3}{5}}$	0	0	0
pp	±1	±1	1	0	$-\sqrt{\frac{15}{25}}$	0	0
	±1	0	0	0	$\sqrt{\frac{30}{25}}$	0	0
	±1	∓1	0	0	$-\sqrt{\frac{30}{25}}$	0	0
sd	0	0	1	0	$\sqrt{\frac{30}{25}}$	0	0
	0	±2	0	0	$\sqrt{\frac{15}{25}}$	0	0
	0	±1	0	0	$-\sqrt{\frac{30}{25}}$	0	0
pd	0	0	0	0	$\sqrt{\frac{30}{25}}$	0	0
	±1	±2	0	$-\sqrt{\frac{30}{45}}$	0	$\sqrt{\frac{30}{245}}$	0
	±1	±1	0	$\sqrt{\frac{30}{45}}$	0	$-\sqrt{\frac{30}{245}}$	0
	±1	0	0	$-\sqrt{\frac{30}{45}}$	0	$\sqrt{\frac{150}{245}}$	0
	±1	∓1	0	0	0	$-\sqrt{\frac{30}{245}}$	0
	±1	∓2	0	0	0	$\sqrt{\frac{45}{245}}$	0
	0	±2	0	0	0	$\sqrt{\frac{15}{245}}$	0
dd	0	±1	0	$-\sqrt{\frac{30}{45}}$	0	$-\sqrt{\frac{30}{245}}$	0
	0	0	0	$\sqrt{\frac{30}{45}}$	0	$\sqrt{\frac{270}{245}}$	0
	±2	±2	1	0	$-\sqrt{\frac{30}{49}}$	0	$\sqrt{\frac{14}{441}}$
	±2	±1	0	0	$\sqrt{\frac{30}{49}}$	0	$-\sqrt{\frac{5}{441}}$
	±2	0	0	0	$-\sqrt{\frac{30}{49}}$	0	$\sqrt{\frac{15}{441}}$
	±2	∓1	0	0	0	0	$-\sqrt{\frac{35}{441}}$
	±2	∓2	0	0	0	0	$\sqrt{\frac{70}{441}}$
	±1	±1	1	0	$\sqrt{\frac{1}{49}}$	0	$-\sqrt{\frac{16}{441}}$
±1	0	0	0	$\sqrt{\frac{1}{49}}$	0	$\sqrt{\frac{30}{441}}$	
±1	∓1	0	0	$-\sqrt{\frac{30}{49}}$	0	$-\sqrt{\frac{40}{441}}$	
0	0	1	0	$\sqrt{\frac{30}{49}}$	0	$\sqrt{\frac{36}{441}}$	

^a Slater (1960).

^b Where two ± signs appear, the two upper or the two lower signs are taken together.

Combining (11.2-3)–(11.2-5), (11.2-10), and (11.2-11),

$$\begin{aligned} & \left\langle a(1)b(2) \left| \frac{e^2}{r_{12}} \right| c(1)d(2) \right\rangle \\ &= \delta(m_s^a, m_s^c) \delta(m_s^b, m_s^d) \delta(m_i^a + m_i^b, m_i^c + m_i^d) \\ & \times \sum_{k=0}^{\infty} c^k(l^a m_i^a, l^c m_i^c) c^k(l^d m_i^d, l^b m_i^b) R^k(abcd). \end{aligned} \quad (11.2-12)$$

A special case of (11.2-12) is one in which

$$a = c, \quad b = d. \quad (11.2-13)$$

The resulting integral $J(a, b)$ is known as a Coulomb or direct integral and is given by

$$J(a, b) = \left\langle a(1)b(2) \left| \frac{e^2}{r_{12}} \right| a(1)b(2) \right\rangle \quad (11.2-14a)$$

$$= \left\langle \varphi_a(1)\varphi_b(2) \left| \frac{e^2}{r_{12}} \right| \varphi_a(1)\varphi_b(2) \right\rangle \quad (11.2-14b)$$

$$= \sum_{k=0}^{\infty} \frac{c^k(l^a m_i^a, l^a m_i^a) c^k(l^b m_i^b, l^b m_i^b) R^k(abab)}{\alpha^k F^k} \quad (11.2-14c)$$

or defining

$$\begin{aligned} a^k(l^a m_i^a, l^b m_i^b) &\equiv c^k(l^a m_i^a, l^a m_i^a) c^k(l^b m_i^b, l^b m_i^b) \\ &= \frac{4\pi}{2k+1} \langle l^a m_i^a | Y_{k0} | l^a m_i^a \rangle \langle l^b m_i^b | Y_{k0} | l^b m_i^b \rangle, \end{aligned} \quad (11.2-15)$$

$$\begin{aligned} F^k(n^a l^a, n^b l^b) &= R^k(abab), \\ &= e^2 \int_0^{\infty} \int_0^{\infty} \frac{r_1^k}{r_{12}^{k+1}} [P_{nl}^a(r_1)]^2 [P_{nl}^b(r_2)]^2 dr_1 dr_2. \end{aligned} \quad (11.2-16)$$

we have

$$J(a, b) = \sum_{k=0}^{\infty} a^k F^k = J(b, a). \quad (11.2-17)$$

Numerical values of $a^k(lm, l'm') = a^k(l'm', lm)$ are tabulated in Table 11.2.

A second special case occurs when

$$a = d, \quad b = c.$$

TABLE 11.2

 $a^k(l^a, l^b)$ for s, p, and d Electrons^{a, b}

	m	m	k		
			0	2	4
ss	0	0	1	0	0
sp	0	±1	1	0	0
	0	0	1	0	0
pp	±1	±1	1	1/25	0
	±1	0	1	-3/25	0
	0	0	1	3/25	0
sd	0	±2	1	0	0
	0	±1	1	0	0
	0	0	1	0	0
pd	±1	±2	1	3/35	0
	±1	±1	1	-1/35	0
	±1	0	1	-3/35	0
	0	±2	1	-3/35	0
	0	±1	1	3/35	0
	0	0	1	3/35	0
dd	±2	±2	1	1/49	1/441
	±2	±1	1	-3/49	-4/441
	±2	0	1	-3/49	9/441
	±1	±1	1	3/49	19/441
	±1	0	1	3/49	-24/441
	0	0	1	3/49	36/441

^a Slater (1960). ^b Where two ± signs appear, they can be combined in any of the four possible ways.

This produces another integral $K(a, b)$ known as an exchange integral:

$$K(a, b) = \left\langle a(1)b(2) \left| \frac{e^2}{r_{12}} \right| b(1)a(2) \right\rangle \quad (11.2-18a)$$

$$= \delta(m_s^a, m_s^b) \left\langle \varphi_a(1)\varphi_b(2) \left| \frac{e^2}{r_{12}} \right| \varphi_b(1)\varphi_a(2) \right\rangle \quad (11.2-18b)$$

$$= \delta(m_s^a, m_s^b) \sum_{k=0}^{\infty} c^k(l^a m_l^a, l^b m_l^b) c^k(l^a m_l^a, l^b m_l^b) R^k(abba). \quad (11.2-18c)$$

We define $b^k(l^a m_l^a, l^b m_l^b) \equiv [c^k(l^a m_l^a, l^b m_l^b)]^2$ (11.2-19)

$$G^k(n^a l^a, n^b l^b) = R^k(abba),$$

$$= e^2 \int_0^{\infty} \int_0^{\infty} \frac{r_1^k}{r_1^{k+1}} P_{n_l}^a(r_1) P_{n_l}^b(r_2) P_{n_l}^b(r_1) P_{n_l}^a(r_2) dr_1 dr_2. \quad (11.2-20)$$

Then

$$K(a, b) = \delta(m_s^a, m_s^b) \sum_{k=0}^{\infty} b^k G^k = K(b, a). \quad (11.2-21)$$

The radial integrals F^k and G^k are both positive and are known as Slater-Condon parameters. Often it is convenient to define related parameters as shown in Table 11.3.

TABLE 11.3

Slater-Condon and Racah Parameters

	Slater-Condon	Racah
s	$F_0 = F^0$	
p	$F_0 = F^0$ $F_2 = F^2/25$	
d	$F_0 = F^0$ $F_2 = F^2/49$ $F_4 = F^4/441$	$A = F_0 - 49F_4$ $B = F_2 - 5F_4$ $C = 35F_4$
f	$F_0 = F^0$ $F_2 = F^2/225$ $F_4 = F^4/1089$ $F_6 = F^6/184041$	

Two electrons with the same values of n and l are said to be *equivalent*. In that case the radial parts of the two wave functions are the same, i.e.,

$$P_{n_l}^a(r_i) = P_{n_l}^b(r_i)$$

or

$$n^a = n^b, \quad l^a = l^b$$

and the integrals in (11.2-16) and (11.2-20) become identical so that

$$F^k = G^k. \quad (11.2-22)$$

The integrals $J(a, b)$ and $K(a, b)$ may be expressed in terms of two operators J_b and K_b known as Coulomb or direct and exchange operators, respectively, where

$$\text{Coulomb } J_b(1)a(1) = \left[\int b^*(2) \frac{e^2}{r_{12}} b(2) d\tau_2 \right] a(1),$$

$$\text{Exchange } K_b(1)a(1) = \left[\int b^*(2) \frac{e^2}{r_{12}} a(2) d\tau_2 \right] b(1), \quad (11.2-23)$$

or, in terms of spatial orbitals alone,

$$J_b(1)\varphi_a(1) = \left[\int \varphi_b^*(2) \frac{e^2}{r_{12}} \varphi_b(2) dr_2 \right] \varphi_a(1),$$

$$K_b(1)\varphi_a(1) = \left[\delta(m_s^a, m_s^b) \int \varphi_b^*(2) \frac{e^2}{r_{12}} \varphi_a(2) dr_2 \right] \varphi_b(1). \quad (11.2-24)$$

The Coulomb and exchange integrals may now be written as

$$J(a, b) = \langle a(1) | J_b(1) | a(1) \rangle = \left\langle a(1)b(2) \left| \frac{e^2}{r_{12}} \right| a(1)b(2) \right\rangle, \quad (11.2-25)$$

$$K(a, b) = \langle a(1) | K_b(1) | a(1) \rangle = \left\langle a(1)b(2) \left| \frac{e^2}{r_{12}} \right| b(1)a(2) \right\rangle, \quad (11.2-26)$$

as in (11.2-14) and (11.2-18). It is also observed that if

$$G = \sum_{i < j} e^2/r_{ij},$$

it is possible to express (11.1-19) in the form

diagonal matrix
element

$$\langle A | G | A \rangle = \sum_{k < t} [J(k, t) - K(k, t)] \quad (11.2-27)$$

where A is a determinantal wave function such as (11.1-12).

Let us now consider the Hamiltonian

$$\mathcal{H} = \sum_i^N \mathcal{H}_0(i) + \sum_{i < j} e^2/r_{ij} \quad (11.2-28)$$

where

$$\mathcal{H}_0(i) = \frac{p_i^2}{2m} - \frac{Ze^2}{r_i}$$

and a wave function $\psi(\lambda_1, \lambda_2, \dots, \lambda_N)$ expressed in the form of a single Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\lambda_1) & \psi_2(\lambda_1) & \cdots & \psi_N(\lambda_1) \\ \psi_1(\lambda_2) & \psi_2(\lambda_2) & \cdots & \psi_N(\lambda_2) \\ \vdots & \vdots & \cdots & \vdots \\ \psi_1(\lambda_N) & \psi_2(\lambda_N) & \cdots & \psi_N(\lambda_N) \end{vmatrix} \quad (11.2-29)$$

in which $\psi_k(\lambda_i) \equiv \psi_k(i)$ is a spin orbital and

$$\langle \psi_k(i) | \psi_j(i) \rangle = \delta_{kj}.$$

We shall be interested in the total energy

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle$$

which may be written, with the aid of (11.1-16) and (11.1-19) as

$$E = \sum_{i=1}^N \langle \psi_i(1) | \mathcal{H}_0(1) | \psi_i(1) \rangle + \sum_{i < j} \left[\left\langle \psi_i(1)\psi_j(2) \left| \frac{e^2}{r_{12}} \right| \psi_i(1)\psi_j(2) \right\rangle - \left\langle \psi_i(1)\psi_j(2) \left| \frac{e^2}{r_{12}} \right| \psi_j(1)\psi_i(2) \right\rangle \right], \quad (11.2-30)$$

or, in terms of the spatial orbitals, using (11.1-24), (11.2-14), and (11.2-18),

$$E = \sum_i^N I_i + \sum_{i < j} \left[\left\langle \varphi_i(1)\varphi_j(2) \left| \frac{e^2}{r_{12}} \right| \varphi_i(1)\varphi_j(2) \right\rangle - \delta(m_s^i, m_s^j) \left\langle \varphi_i(1)\varphi_j(2) \left| \frac{e^2}{r_{12}} \right| \varphi_j(1)\varphi_i(2) \right\rangle \right] \quad (11.2-31)$$

where

$$I_i \equiv \langle \psi_i | \mathcal{H}_0 | \psi_i \rangle = \langle \varphi_i | \mathcal{H}_0 | \varphi_i \rangle. \quad (11.2-32)$$

An important special case is one in which the determinantal wave function represents a system of $2N$ electrons distributed among N spatial orbitals each of which is occupied by two electrons with opposite spin. Such a system is known as a *closed shell*. We consider a specific example. Let

$$\Psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \varphi_2(1)\alpha(1) & \varphi_2(1)\beta(1) \\ \varphi_1(2)\alpha(2) & \vdots & \vdots & \vdots \\ \varphi_1(3)\alpha(3) & \vdots & \vdots & \vdots \\ \varphi_1(4)\alpha(4) & \vdots & \vdots & \varphi_2(4)\beta(4) \end{vmatrix} \quad (11.2-33)$$

be the Slater determinant for a closed shell containing four electrons. To calculate the energy we may use (11.2-30) and (11.2-31) and for this purpose it is convenient to define

$$\psi_a = \overset{\textcircled{1}}{\varphi_1\alpha}, \quad \psi_b = \overset{\textcircled{2}}{\varphi_1\beta}, \quad \psi_c = \overset{\textcircled{3}}{\varphi_2\alpha}, \quad \psi_d = \overset{\textcircled{4}}{\varphi_2\beta}. \quad (11.2-34)$$

We then have

$$\langle \psi_a | \mathcal{H}_0 | \psi_a \rangle = \langle \psi_b | \mathcal{H}_0 | \psi_b \rangle = \langle \varphi_1 | \mathcal{H}_0 | \varphi_1 \rangle = I_1,$$

$$\langle \psi_c | \mathcal{H}_0 | \psi_c \rangle = \langle \psi_d | \mathcal{H}_0 | \psi_d \rangle = \langle \varphi_2 | \mathcal{H}_0 | \varphi_2 \rangle = I_2,$$

and the contribution to the energy from the one-electron integrals is

$$2(I_1 + I_2). \quad (11.2-35)$$

The six possible Coulomb integrals are

$$\left\langle \begin{array}{l} \psi_a(1)\psi_b(2) \\ \psi_a(1)\psi_c(2) \\ \psi_a(1)\psi_d(2) \\ \psi_b(1)\psi_c(2) \\ \psi_b(1)\psi_d(2) \\ \psi_c(1)\psi_d(2) \end{array} \left| \frac{e^2}{r_{12}} \right| \begin{array}{l} \psi_a(1)\psi_b(2) \\ \psi_a(1)\psi_c(2) \\ \psi_a(1)\psi_d(2) \\ \psi_b(1)\psi_c(2) \\ \psi_b(1)\psi_d(2) \\ \psi_c(1)\psi_d(2) \end{array} \right\rangle = \left\langle \begin{array}{l} \varphi_1(1)\varphi_1(2) \\ \varphi_1(1)\varphi_2(2) \\ \varphi_1(1)\varphi_2(2) \\ \varphi_1(1)\varphi_2(2) \\ \varphi_1(1)\varphi_2(2) \\ \varphi_2(1)\varphi_2(2) \end{array} \left| \frac{e^2}{r_{12}} \right| \begin{array}{l} \varphi_1(1)\varphi_1(2) \\ \varphi_1(1)\varphi_2(2) \\ \varphi_1(1)\varphi_2(2) \\ \varphi_1(1)\varphi_2(2) \\ \varphi_1(1)\varphi_2(2) \\ \varphi_2(1)\varphi_2(2) \end{array} \right\rangle = \begin{array}{l} J(1,1) \\ J(1,2) \\ J(1,2) \\ J(1,2) \\ J(1,2) \\ J(2,2) \end{array}$$

and their contribution to the energy is

$$J(1,1) + J(2,2) + 4J(1,2).$$

The orthogonality of the spin functions causes all but two of the six exchange integrals to vanish. The ones that remain are

$$\begin{aligned} \left\langle \psi_a(1)\psi_c(2) \left| \frac{e^2}{r_{12}} \right| \psi_c(1)\psi_a(2) \right\rangle &= \left\langle \psi_b(1)\psi_d(2) \left| \frac{e^2}{r_{12}} \right| \psi_d(1)\psi_b(2) \right\rangle \\ &= \left\langle \varphi_1(1)\varphi_2(2) \left| \frac{e^2}{r_{12}} \right| \varphi_2(1)\varphi_1(2) \right\rangle = K(1,2) \end{aligned}$$

with a contribution of $-2K(1,2)$ to the energy. The total energy is the sum of the contributions from the three kinds of integrals:

$$E = 2(I_1 + I_2) + J(1,1) + J(2,2) + 4J(1,2) - 2K(1,2).$$

It is a simple matter to extend this formalism to a system of $2N$ electrons in a closed shell configuration. The Slater determinant is

$$\Psi = \frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \cdots & \varphi_N(1)\alpha(1) & \varphi_N(1)\beta(1) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \varphi_1(2N)\alpha(2N) & \varphi_1(2N)\beta(2N) & \cdots & \varphi_N(2N)\alpha(2N) & \varphi_N(2N)\beta(2N) \end{vmatrix} \quad (11.2-36)$$

and the total energy may be written

$$\langle E = 2 \sum_{k=1}^N I_k + \sum_{k,l}^N [2J(k,l) - K(k,l)] \rangle \quad (11.2-37)$$

provided one sets

$$J(k,k) \stackrel{?}{=} K(k,k) = \left\langle \varphi_k(1)\varphi_k(2) \left| \frac{e^2}{r_{12}} \right| \varphi_k(1)\varphi_k(2) \right\rangle \quad (11.2-38)$$

The sums in (11.2-37) are taken over N spatial orbitals which correspond to $2N$ spin orbitals (or $2N$ electrons). It should also be noted that the relation $J(k,k) = K(k,k)$ is a necessary requirement for the validity of the energy expression (11.2-37) but is not true in general.

$$K(i,i) = 0$$