

## Relation Between Electrons and Holes in Atomic Configurations\*†

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Shortley has shown that the energy expression of a state of an atomic configuration involving holes differs from the configuration involving electrons by an array of coefficients, which are characteristic for this configuration. General formulas are given for these coefficients for atomic configurations consisting of any combination of *s*, *p*, and *d* shells, and for a single *f* shell.

### I. REVIEW OF THE THEORY

THE energy *E* of a state of an atom with *N* electrons according to Slater's treatment, can be written as<sup>1</sup>

$$E = \sum_{i=1}^N I(n_i l_i) + \sum_{i=2}^N \sum_{j=1}^{i-1} \sum_{k=0}^{2(l_i, l_j) <} [a^k(l_i m_{i_i}, l_j m_{j_j}) F^k(n_i l_i, n_j l_j) - \delta(m_{i_i}, m_{j_j}) b^k(l_i m_{i_i}, l_j m_{j_j}) G^k(n_i l_i, n_j l_j)]. \quad (1)$$

The one-electron integral  $I(n_i l_i)$  is defined by

$$I(n_i l_i) = \int_0^\infty dr r^2 R(n_i l_i, r) (T + V) R(n_i l_i, r), \quad (2)$$

where *T* and *V* are, of course, the kinetic and potential energy operators, respectively, namely:

$$T = -(\hbar^2/2m)\nabla^2, \quad V = -Z/r, \quad (3)$$

and the  $R(nl, r)$  are the usual normalized radial functions. The two-electron integrals  $F^k(n_i l_i, n_j l_j)$  and  $G^k(n_i l_i, n_j l_j)$  are the so-called Slater integrals, namely,

$$F^k(n_i l_i, n_j l_j) = \int_0^\infty dr r^2 \int_0^\infty ds s^2 [R(n_i l_i, r) R(n_j l_j, s)]^2 \times U_k(r, s), \quad (4)$$

$$G^k(n_i l_i, n_j l_j) = \int_0^\infty dr r^2 \int_0^\infty ds s^2 R(n_i l_i, r) R(n_j l_j, s) \times R(n_i l_i, s) R(n_j l_j, r) U_k(r, s),$$

where

$$U_k(r, s) = [(\langle r, s \rangle)]^k / [(\langle r, s \rangle)]^{k+1}. \quad (5)$$

The Slater coefficients  $a^k$  and  $b^k$  are given by Condon and Shortley.<sup>2</sup>

The coefficients of the Slater integrals  $F^k$  and  $G^k$  for various states which arise from configurations involving *s*, *p*, and *d* shells have been tabulated by Jaffe and Hinze<sup>3</sup>; however, they did not evaluate these coefficients for any configuration with more than five *d* electrons.

Shortley<sup>4</sup> has shown that, aside from an array of coefficients common to the entire configuration, the energy of a state belonging to the configuration  $l^{4l+2-N} \times l'^{4l'+2-N'}$  is given by the same equation as that for the configuration  $l^N l'^{N'}$ , where *N* and *N'* are the numbers of electrons (occupation numbers) in the (*nl*) and (*n'l'*) shells, respectively.

Let us consider, for example, an atomic configuration consisting of closed shells plus several open shells, but *not more than one open shell for each symmetry species*. Then the energy of an atomic state of the above configuration can be written as

$$E = E_C + E_{CO} + E_O + W_S. \quad (6)$$

In this equation  $E_C$  represents the energy of closed shells only, and  $E_{CO}$  is the term arising from interactions of the closed shells with the open shells. The term  $E_O$  gives that part of open-shell-open-shell interaction which only involves the Slater integrals  $F^0$ , namely,

$$E_O = \sum_i \frac{1}{2} N_i (N_i - 1) F^0(n_i l_i, n_i l_i) + \sum_{ij} N_i N_j F^0(n_i l_i, n_j l_j), \quad (7)$$

where  $\sum_i$  represents the summation over all the open shells,  $\sum_{ij}$  stands for the summation over distinct pairs of open shells, and  $N_i$  and  $N_j$  are the occupation numbers of the (*n<sub>i</sub>l<sub>i</sub>*) and (*n<sub>j</sub>l<sub>j</sub>*) shells, respectively.

The last term in Eq. (6) is the only one which distinguishes different states within the configuration. It consists of Slater integrals  $F^k$  and  $G^k$ ,  $k \neq 0$ , with ap-

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<sup>1</sup> J. C. Slater, Phys. Rev. **34**, 1293 (1929).

<sup>2</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1951). The

Slater coefficients  $a^k$  and  $b^k$  are generally fractions, and because the denominators of the Slater coefficients are often rather large, it is common to use modified Slater integrals and coefficients defined by  $F_k = F^k/D_k$ ;  $G_k = G^k/D'_k$ ;  $a_k = a^k D_k$ ;  $b_k = b^k D'_k$ , where  $D_k$  and  $D'_k$  are the denominators of  $a^k$  and  $b^k$ , respectively, given by Condon and Shortley.

<sup>3</sup> H. H. Jaffe and J. A. Hinze, University of Cincinnati Research Foundation, Progress Report No. 4, April 1961 (unpublished).

<sup>4</sup> G. H. Shortley, Phys. Rev. **40**, 185 (1932).

appropriate coefficient  $f_s^k$  and  $g_s^k$ , namely,

$$W_S = \sum_{k \neq 0}^{2(l_i, l_j) <} [f_s^k(n_i l_i, n_j l_j) F^k(n_i l_i, n_j l_j) - g_s^k(n_i l_i, n_j l_j) G^k(n_i l_i, n_j l_j)]. \quad (8)$$

Next let us consider the configuration where electrons are replaced by holes in *open shells only*, and the closed-shell core is arbitrary. We shall denote the various quantities for this configuration by placing a bar over them; for example, the occupation numbers of the open shells are designated by  $\bar{N}_i, \bar{N}_j$ , etc.; whereas  $N_i, N_j$ , etc. represent the occupation numbers of open shells in the configuration involving electrons. These two configurations give rise to states of the same symmetry species; for instance,  $C(1s^2 2s^2 2p^2)$  and  $O(1s^2 2s^2 2p^4)$  give rise to  ${}^3P, {}^1D$  and  ${}^1S$  states.

The energy of the configuration involving holes is given by

$$\bar{E} = \bar{E}_C + \bar{E}_{CO} + \bar{E}_O + \bar{W}_S, \quad (9)$$

where the terms with bars placed over them arise from interactions similar to those of the corresponding terms in Eq. (6). The first three terms in Eq. (9) can be trivially obtained from the corresponding terms of Eq. (6); e.g., by substituting  $\bar{N}_i, \bar{N}_j$  and  $\bar{F}^0$  in Eq. (7), we get  $\bar{E}_O$ , where  $\bar{F}^k$  and  $\bar{G}^k$ , in general, are obtained from Eq. (4) by replacing  $R(nl, r)$  by  $\bar{R}(nl, r)$ .  $\bar{R}(nl, r)$  and  $R(nl, r)$  differ numerically as they belong to *two* different atomic configurations.

However, the term  $\bar{W}_S$ , like  $W_S$ , depends on the state only. If we now consider the *same state S* for the configuration of holes as for the configuration of electrons, then  $\bar{W}_S$  can be expressed by<sup>5</sup>

$$\bar{W}_S = \sum_{k \neq 0}^{2(l_i, l_j) <} \{ [f_s^k(n_i l_i, n_j l_j) + \Delta f^k] F^k(n_i l_i, n_j l_j) - [g_s^k(n_i l_i, n_j l_j) + \Delta g^k] G^k(n_i l_i, n_j l_j) \}, \quad (10)$$

where the coefficients  $f_s^k$  and  $g_s^k$  are those belonging to the state  $S$  of the system with *electrons* rather than holes, Eq. (8), and the  $\Delta f^k$  and  $\Delta g^k$  are *independent of the state S*.

<sup>5</sup> It should be pointed out that our notation from here on is slightly inconsistent, namely, in the following we write  $F^k$  and  $G^k$  for the Slater integrals for the system of holes rather than  $\bar{F}^k$  and  $\bar{G}^k$ . This simplifies the remaining formalism, which is only meant to yield the correct Slater coefficients for the holes. In any practical case, the  $F^k$  and  $G^k$  integrals have to be evaluated with *actual* occupied orbitals, and may even be considered to differ from state to state within the same system.

It is convenient to define  $\Delta W$  by<sup>6</sup>

$$\bar{W}_S = W_S + \Delta W, \quad (11)$$

so that

$$\Delta W = \sum_{k \neq 0}^{2(l_i, l_j) <} [\Delta f^k F^k(n_i l_i, n_j l_j) - \Delta g^k G^k(n_i l_i, n_j l_j)]. \quad (12)$$

The actual expression (12) for a specific case can be derived by evaluating (by standard techniques) the energies of *any two corresponding* states of the systems with electrons and holes, respectively. A very convenient state is the state of highest total angular momentum and highest multiplicity (in that order), since such a state can be represented by a single Slater determinant.

## II. RESULTS AND DISCUSSION

Our purpose was to obtain  $\Delta W$  for all possible combinations of the occupation numbers of  $s, p$ , and  $d$  shells, and for the configurations  $f^8, f^9, \dots, f^{13}$ . We checked our results, wherever possible, against those given by Hinze and Jaffe,<sup>7</sup> and obtained complete agreement. It was found that  $\Delta W$  could be expressed by two very simple formulas, namely,

$$\begin{aligned} \Delta W(sp^{6-m}d^{10-n}) = & (m-3)[(2/25)F^2(pp) + (1/3)G^1(sp) \\ & + (2/3)G^1(pd) + (3/7)G^3(pd)] \\ & + (n-5)[(2/7)F^2(dd) + (2/7)F^4(dd) \\ & + (1/5)G^2(sd) + (2/5)G^1(pd) \\ & + (9/35)G^3(pd)], \quad (13) \end{aligned}$$

$$\begin{aligned} \Delta W(f^{14-q}) = & (q-7)[(4/15)F^2(ff) + (2/11)F^4(ff) \\ & + (100/429)F^6(ff)], \quad (14) \end{aligned}$$

where  $1 \leq m \leq 3$ ,  $1 \leq n \leq 4$ , and  $1 \leq q \leq 6$ .

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<sup>6</sup> J. Hinze and H. H. Jaffe [J. Chem. Phys. **38**, 1834 (1963)] used the symbol  $W$  for the *difference* of the energy of the two systems, and expressed it in terms of the Slater coefficients and integrals as given in Ref. 2. In this difference they also absorbed the terms with  $F^0$ , Eq. (7). We use the symbol  $\Delta W$  for the difference, and omit the terms with  $F^0$  from this difference.

<sup>7</sup> See Ref. 6.