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Convenient Formulas for Evaluation of the Hybridized Valence States Involving the $s-p$ Hybrid Orbitals and Their Applications to the Atoms and the Ions of Carbon, Nitrogen, and Oxygen

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Formulas to calculate the energies of the hybridized valence states are given. The formulas cover any of the hybridized valence states, so far as the valence orbitals involved are $s-p$ hybrids, and are useful in the sense that they give essentially the same results as those obtained with the modified Öpik method [1] quickly. The prescriptions and the numerical data for the actual evaluation of the hybridized valence-state energies are also given with particular reference to the atoms and the ions of carbon, nitrogen, and oxygen. In Appendix, addenda and corrigenda of the previous paper [1] are given.

Key words: Hybridized valence state energy formulas

1. Introduction

In a previous paper [1], it has been pointed out that off-diagonal terms, corresponding to interactions among multiplets of the same symmetry arising from different configurations participating in the hybridized valence state, must also be considered in addition to the diagonal terms considered in Öpik's method for evaluation of the hybridized valence-state energies [2], in order that Moffitt's [3] philosophy of defining the valence state be preserved even for the hybridized valence states. This modified Öpik method however is too complicated to be used. Therefore, formulas useful for the evaluation of the energies of hybridized valence states in the sense that they give essentially the same results as those obtained with the modified Öpik method quickly have been derived, although we have confined ourselves to those valence states which involve s–p hybrid AO's only. It is the purpose of the present paper to present such formulas and to give the prescriptions for the actual evaluation of the hybridized valence-state energies of the atoms and the ions of carbon, nitrogen, and oxygen.

2. Derivation of Formulas

Since we are confining ourselves to valence states involving s–p hybrid orbitals only, the atomic orbitals containing valence electrons may be expressed as

$$t_i = c_{si}s + c_{xi}x + c_{yi}y + c_{zi}z \quad (i = 1, 2, 3, 4) \tag{1}$$

without loss of generality. In Eq. (1), s, x, y, and z represent the s, p_x, p_y, and the p_z AO, respectively, while c_{si}, c_{xi}, c_{yi}, and c_{zi} are numerical coefficients subject to the orthonormalization conditions of t_i's. The formulas to be presented are then as follows:

$$E(t_1, V_1) - c_{s1}^2\, E(s, V_1) - (1 - c_{s1}^2)\, E(x, V_1) = 0\,, \tag{2}$$

$$\begin{aligned} &E(t_1 t_2, V_2) - (c_{s1}^2 + c_{s2}^2)\, E(sx, V_2) - (1 - c_{s1}^2 - c_{s2}^2)\, E(xy, V_2) \\ &\quad = (1/2)\, c_{s1}^2 c_{s2}^2 Q\,, \end{aligned} \tag{3}$$

$$E(t_1^2, V_0) - c_{s1}^2\, E(s^2, V_0) - (1 - c_{s1}^2)\, E(x^2, V_0) = c_{s1}^2 (c_{s1}^2 - 1)\, Q\,, \tag{4}$$

$$\begin{aligned} &E(t_1 t_2 t_3, V_3) - (1 - c_{s4}^2)\, E(sxy, V_3) - c_{s4}^2\, E(xyz, V_3) \\ &\quad = (1/2)\,(c_{s1}^2 c_{s2}^2 + c_{s1}^2 c_{s3}^2 + c_{s2}^2 c_{s3}^2)\, Q\,, \end{aligned} \tag{5}$$

$$\begin{aligned} &E(t_1^2 t_2, V_1) - (2c_{s1}^2 + c_{s2}^2 - 1)\, E(s^2 x, V_1) \\ &\quad - (2 - 2c_{s1}^2 - c_{s2}^2)\, E(sx^2, V_1) \\ &\quad = (c_{s1}^4 + c_{s1}^2 c_{s2}^2 - 2c_{s1}^2 - c_{s2}^2 + 1)\, Q \\ &\quad - 5(c_{s1}^2 + c_{s2}^2 - 1)\, R\,, \end{aligned} \tag{6}$$

$$E(t_1 t_2 t_3 t_4, V_4) - E(sxyz, V_4) = (1/4)\left(1 - \sum_{i=1}^{4} c_{si}^4\right) Q\,, \tag{7}$$

$$\begin{aligned} &E(t_1^2 t_2 t_3, V_2) - (c_{s1}^2 - c_{s4}^2)\, E(s^2 xy, V_2) - (1 - c_{s1}^2 + c_{s4}^2)\, E(sx^2 y, V_2) \\ &\quad = [c_{s4}^2 - c_{s1}^2 c_{s4}^2 + (1/2)\, c_{s2}^2 c_{s3}^2]\, Q + 5c_{s4}^2 R\,, \end{aligned} \tag{8}$$

$$\begin{aligned} &E(t_1^2 t_2^2, V_0) - (c_{s1}^2 + c_{s2}^2)\, E(s^2 x^2, V_0) - (1 - c_{s1}^2 - c_{s2}^2)\, E(x^2 y^2, V_0) \\ &\quad = (c_{s1}^2 + c_{s2}^2)(c_{s1}^2 + c_{s2}^2 - 1)\, Q\,, \end{aligned} \tag{9}$$

$$\begin{aligned} &E(t_1^2 t_2 t_3 t_4, V_3) - c_{s1}^2\, E(s^2 xyz, V_3) - (1 - c_{s1}^2)\, E(sx^2 yz, V_3) \\ &\quad = (1/2)\,(c_{s2}^2 c_{s3}^2 + c_{s2}^2 c_{s4}^2 + c_{s3}^2 c_{s4}^2)\, Q\,, \end{aligned} \tag{10}$$

$$\begin{aligned} &E(t_1^2 t_2^2 t_3, V_1) - (c_{s1}^2 + c_{s2}^2 - c_{s4}^2)\, E(s^2 x^2 y, V_1) \\ &\quad - (1 - c_{s1}^2 - c_{s2}^2 + c_{s4}^2)\, E(sx^2 y^2, V_1) \\ &\quad = c_{s4}^2 (1 - c_{s1}^2 - c_{s2}^2)\, Q + 5c_{s4}^2 R\,, \end{aligned} \tag{11}$$

$$\begin{aligned} &E(t_1^2 t_2^2 t_3 t_4, V_2) - (1 - c_{s3}^2 - c_{s4}^2)\, E(s^2 x^2 yz, V_2) \\ &\quad - (c_{s3}^2 + c_{s4}^2)\, E(sx^2 y^2 z, V_2) = (1/2) c_{s3}^2 c_{s4}^2 Q\,, \end{aligned} \tag{12}$$

$$\begin{aligned} &E(t_1^2 t_2^2 t_3^2, V_0) - (1 - c_{s4}^2)\, E(s^2 x^2 y^2, V_0) \\ &\quad - c_{s4}^2\, E(x^2 y^2 z^2, V_0) = c_{s4}^2 (c_{s4}^2 - 1)\, Q\,, \end{aligned} \tag{13}$$

$$E(t_1^2 t_2^2 t_3^2 t_4, V_1) - (1 - c_{s4}^2)\, E(s^2 x^2 y^2 z, V_1) - c_{s4}^2\, E(sx^2 y^2 z^2, V_1) = 0\,. \tag{14}$$

In Eqs. (2)–(14), Q and R are the following combinations of the usual electron repulsion integrals:

$$\begin{aligned} Q &= (ss|ss) + (xx|xx) - 2(ss|xx) - 4(sx|sx)\,, \\ R &= (sx|sx) - (xy|xy)\,. \end{aligned} \tag{15}$$

The idea underlying our formulas is to express the energy of a hybridized valence state with reference to an appropriate weighted mean of energies of a pair of unhybridized valence states, in such a way that the core energies which are difficult to estimate do not appear in the formulas. The choice of the weights and the reference unhybridized valence states is, however, not unique. Our choice is based on the requirements that the resulting formula is as compact as possible and that the reliable values of the reference unhybridized valence-state energies are easily available.

Formulas (2)–(14) may be proved in the following ways:

(i) Write the energy expressions of the hybridized valence states in terms of the one- and the two-electron integrals over hybrid AO's.

(ii) Expand these integrals in terms of integrals over unhybridized AO's, using Eq. (1). The energy expressions of the hybridized valence states in terms of integrals over unhybridized AO's will then be obtained.

(iii) Write the energy expressions of the unhybridized valence states appearing in the left-hand sides of Eqs. (2)–(14) in terms of integrals over unhybridized AO's.

(iv) Make the expressions of the left-hand sides of Eqs. (2)–(14), using the valence-state energy expressions obtained in (ii) and (iii) above. Equations (2)–(14) will then be obtained by using assumptions for the one- and the two-electron integrals, which are best described with reference to some examples. Let us take Eq. (10) as an example. If one looks at the expressions of the quantities

$$E(t_1^2 t_2 t_3 t_4, V_3)\,, \tag{16}$$

$$E(s^2 xyz, V_3)\,, \tag{17}$$

$$E(sx^2 yz, V_3)\,, \tag{18}$$

obtained in (ii) and (iii) above, one will find that integrals such as H_{ss} (one-electron core integral over s AO) and $(ss|zz)$ appear in the expressions of all of (16)–(18). We assume that the value of a given one of such integrals in (16) is equal to the weighted mean of the values of that integrals in (17) and (18) with weights c_{s1}^2 and $(1-c_{s1}^2)$, respectively. The second of our assumptions is concerned with those integrals which appear in not all of (16)–(18); we assume that the value of a given one of such integrals is independent of the electron configuration.

Equations (2)–(14) can also be obtained by using the modified Öpik method [1] for the hybridized valence states and Moffitt's method [3] for the unhybridized valence states, if the orbital approximation and the set of assumptions on the equalities among the integrals mentioned in the preceding paragraph are adopted for the difference between the hybridized valence-state energy and the weighted mean of the energies of the pair of the unhybridized valence states, given as the left-hand side of each of Eqs. (2)–(14). It is to be noted that Eqs. (7), (8), and (10) have already been derived by the present author [4] for special cases where $c_{s4} = 0$.

3. Numerical Evaluation

To evaluate the energies of hybridized valence states with Eqs. (2)–(14), those of unhybridized valence states must be determined first. These values are preferably determined directly from the observed term values as described by Moffitt [3]. Although Pritchard and Skinner [5] have already given such results, we have determined the energies of all the unhybridized valence states belonging to the configurations of $1s^2\,2s^m\,2p^n$ ($m = 0, 1, 2$; $n = 0, 1, \ldots 6$) for the neutral atoms, the singly-negative ions, and the singly- and the doubly-positive ions of carbon, nitrogen, and oxygen with Moffitt's procedure. The results are given in Table 1. The observed term values have been taken from Moore's table [6] by averaging out the fine structure, each component of a particular term being given a weight of $2J + 1$. When no observed term values are available, the values obtained by extrapolation along isoelectronic series, have been used. In doing extrapolations, quadratic functions of atomic number have been used for most cases, but linear function had to be used for $1s^2\,2p^5\;{}^2P$ for lack of data, while cubic functions have been used for $1s^2\,2p^6\;{}^1S$, $1s^2\,2s^2\,2p^5\;{}^2P$, and $1s^2\,2s^2\,2p^4\;{}^3P$, because term values extrapolated for the negative ions using quadratic functions have turned out to be higher than those of the neutral atoms for these isoelectronic series; one would expect that the term value of a given term should decrease with decreasing (positive) ionic charge along isoelectronic series. For the $1s^2\,2p^4$ configuration, reliable term values are available only for O^{2+}, so that no inter- or extrapolation is possible for this isoelectronic series. The energies of the valence states of C and N^+ belonging to this configuration have therefore been determined from the semiempirical values of the average energy E_{av} of the configuration and of $F^2(2p, 2p)$ given by Anno and Teruya [7].

Another data necessary for using Eqs. (2)–(14) are the values of the quantities Q and R defined by Eqs. (15). The values of $(xy|xy)$ and $(sx|sx)$ may be evaluated from $F^2(2p, 2p)$ and $G^1(2s, 2p)$, respectively, since it holds that

$$(xy|xy) = (3/25)\,F^2(pp)\,, \tag{19}$$

$$(sx|sx) = (1/3)\,G^1(sp)\,. \tag{20}$$

The Q value on the other hand may be evaluated from the energy change ΔE of the reaction

$$2\mathrm{A}(sxy^m z^n) \rightarrow \mathrm{A}(s^2 y^m z^n) + \mathrm{A}(x^2 y^m z^n) \tag{21}$$

and the $(sx|sx)$ value determined by Eq. (20), since it can be shown that

$$\Delta E = (ss|ss) + (xx|xx) - 2(ss|xx) + (sx|sx) \tag{22}$$

Table 1. Energies of valence states of atoms and ions of carbon, nitrogen, and oxygen as calculated with Moffitt's method (eV)[a]

Valence state	Energy		Valence state	Energy	
sx, V_2	C^{2+}	8.0392	x^2y^2, V_0	C	20.7225[b]
xy, V_2	C^{2+}	17.2946		N^+	30.0113[b]
x^2, V_0	C^{2+}	19.5939		O^{2+}	38.8301
s^2x, V_1	C^+	0.0053	s^2xyz, V_3	C^-	(0.7243)
$(=s^2p, {}^2P)$	N^{2+}	0.0144		N	1.1915
sxy, V_3	C^+	8.4172		O^+	1.6619
	N^{2+}	11.2025	s^2x^2y, V_1	C^-	(1.8063)
sx^2, V_1	C^+	10.1780		N	2.9787
	N^{2+}	13.7599		O^+	4.1696
xyz, V_3	C^+	18.1258	sx^2yz, V_3	C^-	(9.1461)
	N^{2+}	24.1612		N	(14.1669)
x^2y, V_1	C^+	19.7816		O^+	19.1647
	N^{2+}	26.8635	sx^2y^2, V_1	C^-	(10.2282)
s^2xy, V_2	C	0.3187		N	(16.0406)
	N^+	0.4828		O^+	21.8010
	O^{2+}	0.6474	x^2y^2z, V_1	C^-	(18.7542)
s^2x^2, V_0	C	1.7367	$(=p^5, {}^2P)$	N	(29.0878)
	N^+	2.6160		O^+	(39.4215)
	O^{2+}	3.4590	s^2x^2yz, V_2	N^-	(0.3398)
$sxyz, V_4$	C	8.2605		O	0.4989
	N^+	11.9532	$s^2x^2y^2, V_0$	N^-	(1.8503)
	O^{2+}	15.3933		O	2.7072
sx^2y, V_2	C	9.8502	sx^2y^2z, V_2	N^-	(12.4735)
	N^+	14.1812		O	17.6229
	O^{2+}	18.3555	$x^2y^2z^2, V_0$	N^-	(24.2436)
x^2yz, V_2	C	18.8124[b]	$(=p^6, {}^1S)$	O	(36.2761)
	N^+	27.1765[b]	$s^2x^2y^2z, V_1$	O^-	(0.0061)
	O^{2+}	35.6297	$(=s^2p^5, {}^2P)$		
			$sx^2y^2z^2, V_1$	O^-	(14.9792)
			$(=sp^6, {}^2S)$		

[a] The valence state energies given are referred to the ground states of the respective atoms or ions. The observed term values necessary for the evaluation of the valence-state energies have been taken from Moore [6] by averaging out the fine structure, each component of a particular term being given a weight of $2J+1$. If no observed term value is available, the value obtained by extrapolation along isoelectronic series has been used. The valence-state energies based on such extrapolated term values are enclosed in parentheses. See Section 3 of text for detail.

[b] For isoelectronic series atoms with $1s^2\,2p^4$ configuration, reliable term values are available only for O^{2+}, so that no inter- or extrapolation is possible for this isoelectronic series. The energies of the valence states of C and N^+ belonging to this configuration have therefore been determined from the semiempirical values of the average energy E_{av} of the configuration and of $F^2(2p, 2p)$. As for $F^2(2p, 2p)$ for this purpose, "corrected values" given in Table 2 of Ref. [7] have been used, while the E_{av} values have been obtained by the same method as described in footnote f to Table 1 of Ref. [7], except in that a quadratic function has been used for extrapolation.

for Reaction (21) within the usual orbital approximation. In either sides of Reaction (21), the two atoms concerned are supposed to be separated infinitely from each other. Moreover, the spins of electrons belonging to different orbitals of a given atom are supposed to be random. This means that the atoms are in valence states, although the valency number, which depends upon the *m* and the *n* values, is not shown. Thus, the ΔE of Reaction (21) may easily be evaluated with the data of Table 1 if A is the atom or an ion of C, N, or O. It is to be noted that the Anno-Teruya values [7] of F^2 and G^1 have to be used for Eqs. (19) and (20), because some of the data of Table 1 are based on these values[1].

Although we have described all the prescriptions and the data necessary for the application of our formulas derived in Section 2, a numerical example should facilitate the understanding of our prescriptions. For this purpose, a neutral nitrogen atom in its valence state $tr_1^2\, tr_2\, tr_3\, z,\ V_3$, where tr_1, tr_2, and tr_3 are three equivalent sp^2 hybrid AO's lying in the xy plane, will be considered, because this is the example adopted in a previous publication [1]. Now, if one would look at Table 1, remembering that x, y, and z are equivalent with each other, it should not be difficult to find that Eq. (21) as applied to the present example is

$$\mathrm{N}(sxy^2z,\, V_3) \rightarrow \mathrm{N}(s^2y^2z,\, V_1) + \mathrm{N}(x^2y^2z,\, V_1)\,.$$

Therefore, it is rather straightforward to obtain 9.2099 eV as the energy of this valence state above the ground state of the nitrogen atom from Eq. (10), by using the data of Table 1 and the $G^1(2s, 2p)$ value taken from Table 3 of Ref. [7], since $c_{s1}^2 = c_{s2}^2 = c_{s3}^2 = 1/3$ and $c_{s4}^2 = 0$ in the present example. The value obtained for the same quantity with the modified Öpik method [1], by using the data which are used previously [1] and are the same as those used in the present work, is 9.2097 eV. This is very close to 9.2099 eV obtained above.

Appendix

Addenda and Corrigenda for Previous Work [1]

Since a valence state is an eigenstate neither of L^2, S^2, L_z, nor of S_z in general cases, more than one component of a given multiplet may be involved in an expansion of a valence-state wavefunction Φ_V. This fact has been disregarded in Ref. [1]. Therefore, Eqs. (1) and (2) of Ref. [1] must now be written as

$$\tilde{\Phi}_V = \sum_{r=1}^{N} \sum_{i=1}^{f_r} c_{r,i} \tilde{\psi}_{r,i} \tag{A.1}$$

$$\Phi_V = \sum_{r=1}^{N} \sum_{i=1}^{f_r} c_{r,i} \psi_{r,i} \tag{A.2}$$

respectively, where $\psi_{r,i}$ is the wavefunction of the i^{th} component of the r^{th} multiplet, which is supposed to be in an f_r-fold degeneracy if the spin-orbit

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[1] As for the $G^1(2s, 2p)$ value, it is inevitable to use that of the sp^n configurations, since the semi-empirical value of this parameter can be determined only for such type of configurations. As for the $F^2(2p, 2p)$ value, it would be logical to use an appropriate weighted mean of values determined for different configurations of a given atom (or ion) if available. For example, the $F^2(2p, 2p)$ value to be used for the calculation of the R value of Eq. (8), through Eqs. (15) and (19), would be the weighted mean of its values determined for the s^2p^2 and the sp^3 configurations with weights $c_{s1}^2 - c_{s4}^2$ and $1 - c_{s1}^2 + c_{s4}^2$, respectively.

interaction is neglected and $c_{r,i}$ is the expansion coefficient, the order notations being the same as those used in Ref. [1]. As a consequence, we have

$$\Phi_V = \sum_{\substack{r=1\\ r\neq s,t}}^{N} \sum_{i=1}^{f_r} c_{r,i}\psi_{r,i} + \sum_{i=1}^{f_s} c_{s,i}\psi'_{s,i} + \sum_{i=1}^{f_t} c_{t,i}\psi'_{t,i} \tag{A.3}$$

instead of Eq. (7) of Ref. [1] and similarly for Eqs. (4) and (6) of Ref. [1]. As in Ref. [1] s and t refer to the multiplets of the same symmetry by definition and $\psi'_{s,i}$ and $\psi'_{t,i}$ must correspond to the same M_L and the same M_S values in order that they interact to each other. Therefore, it holds that

$$f_s = f_t \equiv f \tag{A.4}$$

and that

$$\begin{aligned} E_V = {} & \sum_{\substack{r=1\\ r\neq s,t}}^{N} \sum_{i=1}^{f_r} |c_{r,i}|^2 \langle\psi_{r,i}|\mathscr{H}|\psi_{r,i}\rangle \\ & + \sum_{i=1}^{f} |c_{s,i}|^2 \langle\psi'_{s,i}|\mathscr{H}|\psi'_{s,i}\rangle + \sum_{i=1}^{f} |c_{t,i}|^2 \langle\psi'_{t,i}|\mathscr{H}|\psi'_{t,i}\rangle \\ & + \sum_{i=1}^{f} (c^*_{s,i}c_{t,i} + c_{s,i}c^*_{t,i}) \langle\psi'_{s,i}|\mathscr{H}|\psi'_{t,i}\rangle . \end{aligned} \tag{A.5}$$

If the spin-orbit interaction is neglected, the matrix elements involved in Eq. (A.5) are independent of i, so that this equation may be reduced to

$$\begin{aligned} E_V = {} & \sum_{\substack{r=1\\ r\neq s,t}}^{N} \left(\sum_{i=1}^{f_r} |c_{r,i}|^2\right) \langle\psi_r|\mathscr{H}|\psi_r\rangle \\ & + \left(\sum_{i=1}^{f} |c_{s,i}|^2\right) \langle\psi'_s|\mathscr{H}|\psi'_s\rangle + \left(\sum_{i=1}^{f} |c_{t,i}|^2\right) \langle\psi'_t|\mathscr{H}|\psi'_t\rangle \\ & + \left[\sum_{i=1}^{f} (c^*_{s,i}c_{t,i} + c_{s,i}c^*_{t,i})\right] \langle\psi'_s|\mathscr{H}|\psi'_t\rangle , \end{aligned} \tag{A.6}$$

which shows that the following replacements are necessary in Eq. (8) of Ref. [1]:

$$\left.\begin{aligned} |c_r|^2 &\to \sum_{i=1}^{f_r} |c_{r,i}|^2 \\ |c_s|^2 &\to \sum_{i=1}^{f} |c_{s,i}|^2 \\ |c_t|^2 &\to \sum_{i=1}^{f} |c_{t,i}|^2 \\ c^*_s c_t + c^*_t c_s &\to \sum_{i=1}^{f} (c^*_{s,i}c_{t,i} + c_{s,i}c^*_{t,i}) \end{aligned}\right\} . \tag{A.7}$$

This set of replacements is also necessary in Eqs. (3), (5), (13), (15), and (17) of Ref. [1]. Fortunately, however, the conclusions of Ref. [1], including the numerical value of $E_V(\mathrm{I}) - E_V(\mathrm{II})$ (see Eq. (26) of Ref. [1]), are unchanged with this modification. This is due to the fact that the set of replacements is necessary in Eqs. (13) and (15) of Ref. [1] at the same time.

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