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On the Evaluation of the Energies of Hybridized Valence States

TOSINOBU ANNO

Laboratory of Chemistry, College of General Education,
Kyushu University, Ropponmatsu, Fukuoka, 810 Japan

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The method of evaluation of the valence-state energy from the observed term values, as proposed originally by Moffitt [1] for unhybridized valence state and extended by Öpik [3] to the hybridized one, is critically reviewed. It is shown for the hybridized valence states 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. Actual procedure of doing this is given. A numerical example given shows that the improvement of Öpik's method proposed here may be ignored in a crude theory but is worth considering in order that the accurate value of the valence-state energy be obtained.

Das Verfahren zur Berechnung der Energie von Valenzzuständen, wie es von Öpik für den Fall hybridizierter Orbitale erweitert wurde, wird bezüglich der Behandlung von Nichtdiagonalelementen kritisiert. Es wird gezeigt, daß solche Terme, die der Wechselwirkung von Multipletts gleicher Symmetrie, aber verschiedener Konfiguration entsprechen, nur bei verhältnismäßig groben Rechnungen vernachlässigt werden dürfen. Anhand eines Beispiels wird gezeigt, daß sie bei größeren Ansprüchen an die Genauigkeit eingeschlossen werden sollten.

1. Introduction

The concept of valence state has been often used in the literature. Conceptually, the valence state is defined as the state in which an atom is supposed to exist within a molecule. Moffitt [1] has presented an elegant way of defining the valence state. He has also given a way to calculate the valence state energy (VSE) and has presented a table of coefficients which give the VSE if they are multiplied by the term values and the products are summed up. Anno and Sakai [2] have shown that the most appropriate account can be taken of the effect of correlation energy upon the energy of the valence states defined by Moffitt, if the VSE is evaluated directly from the observed term values by using this table. However, Moffitt [1] and Anno and Sakai [2] have been concerned with the unhybridized valence states arising from the configurations of the $s^m p^n$ ($m = 0, 1, 2$; $n = 0, 1, \ldots, 6$) type only. As for the hybridized valence states, Öpik [3] has presented a similar table and Orloff and Sinanoğlu [4] have discussed such valence states with reference to the correlation energy. A characteristic feature of a hybridized valence state is that more than one spectroscopic state wave functions of the same symmetry but of different configurations may be found, if the wave function of the hybridized valence state is expanded into wave functions of various spectroscopic states. It seems to the present author that Öpik's treatments (which is followed by Orloff and Sinanoğlu) of such states of the same symmetry is not necessarily appropriate. It is the purpose of the present paper to describe how to improve Öpik's method.

2. Remarks on the Moffitt-Öpik Method

For practical purpose, Moffitt's method [1] of defining the valence state can be described in terms of the wave functions as follows:

(i) Construct the wave function of Molecule M in the valence-bond (VB) approximation.

(ii) Expand those parts of this wave function which correspond to a given atom A in terms of the wave functions of Atom A in its various spectroscopic states as expressed in orbital approximation.

(iii) Let the lengths of all the bonds starting from Atom A be infinite and drop out those parts of the wave function which do not correspond to Atom A. The resulting function $\tilde{\Phi}_V$ will be a linear combination of wave functions of Atom A in its various spectroscopic states as expressed in orbital approximation:

$$\tilde{\Phi}_V = \sum_{r=1}^{N} c_r \tilde{\psi}_r , \tag{1}$$

where $\tilde{\psi}_r$ is the wave function of the rth spectroscopic state of Atom A in orbital approximation and c_r is the coefficient.

(iv) Φ_V, which is obtained by replacing $\tilde{\varphi}_r$ in Eq. (1) with ψ_r, the *exact* wave function of the rth spectroscopic state of Atom A, is *defined* as the exact wave function of the valence state V of Atom A in Molecule M:

$$\Phi_V = \sum_{r=1}^{N} c_r \psi_r . \tag{2}$$

From this definition of the valence state, the "exact" energy E_V of Atom A in its valence state V can be obtained as

$$E_V = \langle \Phi_V | \mathscr{H} | \Phi_V \rangle = \sum_{r=1}^{N} |c_r|^2 \langle \psi_r | \mathscr{H} | \psi_r \rangle = \sum_{r=1}^{N} |c_r|^2 E_r , \tag{3}$$

where E_r is the exact energy of Atom A in its rth spectroscopic state and may be obtained as the observed spectroscopic term value T_r. It is to be noted that no cross term occurs in Eq. (3), because ψ_r is the eigenfunction of the total Hamiltonian $\mathscr{H}$ of Atom A by definition. Although original definition of Moffitt [1] covers unhybridized valence states only, Öpik [3] uses Eq. (2) for the definition of hybridized valence states as well. Orloff and Sinanoğlu's analysis [4] of the correlation energy of the carbon hybridized valence states is also based on Eq. (2). We shall show that this is not necessarily appropriate, by confining ourselves to those valence states which arise from the configurations of the $s^m p^n$ type for brevity.

As was mentioned in Introduction, a characteristic feature of a hybridized valence state is that more than one spectroscopic state wave functions of the same symmetry but belonging to different configurations may be found if the wave function of the hybridized valence state is expanded. For example, $(t_1^2 t_2 t_3 t_4)$ in Öpik's notation can be expanded in terms of the wave functions of spectroscopic states belonging to configurations s^2p^3, sp^4, and p^5. Of these spectroscopic states, two of ^2P are involved, one arising from s^2p^3 and the other from p^5. Let $\tilde{\psi}_s$ and $\tilde{\psi}_t$

be the wave functions, within the orbital approximations, of such a pair of states having the same symmetry. Eq. (1) in this case reads:

$$\tilde{\Phi}_V = \sum_{\substack{r=1\\ r\neq s,t}}^{N} c_r\tilde{\psi}_r + c_s\tilde{\psi}_s + c_t\tilde{\psi}_t\,. \tag{4}$$

It is to be noted that r extends, in Eq. (1), over only those states which belong to one configuration if V is unhybridized, but r may extend over more than one configuration in the case of a hybridized valence state, with which we are now concerned. Therefore, N in Eqs. (1), etc. is the number of spectroscopic states belonging to the configuration to which V belongs if V is unhybridized, but N is the total number of spectroscopic states belonging to several configurations if V is hybridized. Öpik evaluates the VSE in just the same way as in the case of unhybridized valence states:

$$E_V = \sum_{r=1}^{N} |c_r|^2\, T_r = \sum_{\substack{r=1\\ r\neq s,t}}^{N} |c_r|^2\, T_r + |c_s|^2\, T_s + |c_t|^2\, T_t\,. \tag{5}$$

This is tantamount to assume that

$$\Phi_V = \sum_{\substack{r=1\\ r\neq s,t}}^{N} c_r\psi_r + c_s\psi_s + c_t\psi_t\,. \tag{6}$$

Now, an important point we must remember is the fact that the concept of hybridization is based on the orbital approximation, in which the s^2p^n, sp^{n+1}, and the p^{n+2} configurations are regarded as independent configurations, whereas the interaction between s^2p^n and p^{n+2} ($n=3$ for the example quoted above) is incorporated in ψ_s and ψ_t. Therefore, the method adopted by Öpik is not consistent with the original method of Moffitt, since Moffitt's definition of the valence state is based on the orbital approximation as was mentioned before.

3. A Proposal of a Modification of Öpik's Method

To remove the inconsistency with Moffitt's method pointed out above for Öpik's method, Eq. (6) must be replaced by

$$\Phi_V = \sum_{\substack{r=1\\ r\neq s,t}}^{N} c_r\psi_r + c_s\psi'_s + c_t\psi'_t\,, \tag{7}$$

where ψ'_s and ψ'_t are "semi-exact" wave functions in which all but $\tilde{\psi}_s - \tilde{\psi}_t$ interactions are included. The exact value of VSE is then the expectation value of the Hamiltonian $\mathscr{H}$ with respect to Φ_V given by Eq. (7), not by Eq. (6):

$$\begin{aligned} E_V = \langle\Phi_V|\mathscr{H}|\Phi_V\rangle = \sum_{\substack{r=1\\ r\neq s,t}}^{N} |c_r|^2\langle\psi_r|\mathscr{H}|\psi_r\rangle + |c_s|^2\langle\psi'_s|\mathscr{H}|\psi'_s\rangle \\ + |c_t|^2\langle\psi'_t|\mathscr{H}|\psi'_t\rangle + (c_s^* c_t + c_t^* c_s)\langle\psi'_s|\mathscr{H}|\psi'_t\rangle\,. \end{aligned} \tag{8}$$

Of the various matrix elements appearing in the right-hand side of Eq. (8), $\langle\psi_r|\mathscr{H}|\psi_r\rangle$ $(r=1,2,\ldots,N; r\neq s,t)$ may be equated to the observed term value T_r. The other matrix elements may be obtained as follows.

Now, from the definitions of ψ_s, ψ_t, ψ'_s, and ψ'_t, it is obvious that

$$\left.\begin{aligned}\psi_s&=a_{11}\psi'_s+a_{12}\psi'_t\\ \psi_t&=a_{21}\psi'_s+a_{22}\psi'_t\end{aligned}\right\}, \tag{9}$$

where $a_{ij}\,(i,j=1,2)$ are numerical coefficients to be determined variationally, leading to the secular equation

$$\begin{vmatrix}\langle\psi'_s|\mathscr{H}|\psi'_s\rangle-E & \langle\psi'_s|\mathscr{H}|\psi'_t\rangle\\ \langle\psi'_t|\mathscr{H}|\psi'_s\rangle & \langle\psi'_t|\mathscr{H}|\psi'_t\rangle-E\end{vmatrix}=0. \tag{10}$$

The roots of this secular equation are equal to $\langle\psi_s|\mathscr{H}|\psi_s\rangle$ and $\langle\psi_t|\mathscr{H}|\psi_t\rangle$ which can now be equated to T_s and T_t, respectively. Therefore, $\langle\psi'_s|\mathscr{H}|\psi'_s\rangle$ and $\langle\psi'_t|\mathscr{H}|\psi'_t\rangle$ may be evaluated if the value of $\langle\psi'_s|\mathscr{H}|\psi'_t\rangle$ $[\equiv\langle\psi'_t|\mathscr{H}|\psi'_s\rangle]$ is known.

For the evaluation of $\langle\psi'_s|\mathscr{H}|\psi'_t\rangle$, we use an orbital approximation

$$\langle\psi'_s|\mathscr{H}|\psi'_t\rangle\approx\langle\tilde{\psi}_s|\mathscr{H}|\tilde{\psi}_t\rangle, \tag{11}$$

which is expected to be a good approximation for such an off-diagonal matrix element of fairly small magnitude. For hybridized valence states, which Öpik has dealt with, one member, say ψ_s, of a pair of wave functions which are of the same symmetry, always belongs to the configuration s^2p^n, if the other member, say ψ_t, of the same pair belongs to the configuration s^0p^{n+2} $(0\leqq n\leqq 4)$. In such cases, it can always be shown that $\langle\tilde{\psi}_s|\mathscr{H}|\tilde{\psi}_t\rangle$ has the following form:

$$\langle\tilde{\psi}_s|\mathscr{H}|\tilde{\psi}_t\rangle=f\,G^1(sp), \tag{12}$$

where f is a factor depending upon the valence state and the symmetry of ψ_s (and ψ_t) and $G^1(sp)$ is a Slater-Condon parameter. This factor can easily be calculated algebraically while $G^1(sp)$ is to be obtained from the Slater type treatment of the observed term values of the configuration sp^{n+1}. It is to be added that we use the $\langle\psi'_s|\mathscr{H}|\psi'_t\rangle$ value thus determined also in Eq. (8).

4. Discussions

We shall now discuss the difference in VSE's evaluated with Öpik's method (Eq. (5)) on the one hand and with our method (Eq. (8)) on the other. These VSE's will be distinguished by denoting them $E_V(I)$ and $E_V(II)$, respectively. There is no difference between Eqs. (5) and (8) as far as the first term in the right-hand side is concerned. Therefore,

$$\begin{aligned}E_V(I)-E_V(II)=&|c_s|^2\{\langle\psi_s|\mathscr{H}|\psi_s\rangle-\langle\psi'_s|\mathscr{H}|\psi'_s\rangle\}\\ &+|c_t|^2\{\langle\psi_t|\mathscr{H}|\psi_t\rangle-\langle\psi'_t|\mathscr{H}|\psi'_t\rangle\}\\ &-(c_s^*c_t+c_t^*c_s)\langle\psi'_s|\mathscr{H}|\psi'_t\rangle.\end{aligned} \tag{13}$$

As a numerical example, a valence state which is called $(t_1^2 t_2 t_3 t_4)$ by Öpik will be considered for the neutral nitrogen atom. As was mentioned in Section 2, the neglected term in Öpik's treatment is the interaction between $s^2p^3\,{}^2P$ and $p^5\,{}^2P$, which will be assigned to the sth and the tth "states", respectively, in our analysis. An algebraic calculation shows that

$$\langle\tilde{\psi}_s|\mathscr{H}|\tilde{\psi}_t\rangle = -(\sqrt{2}/3)\,G^1(sp)\,, \tag{14}$$

$$\left.\begin{aligned} |c_s|^2 &= (1/8)\,\{(1-\lambda_1)^2-\lambda_2^2-\lambda_3^2-\lambda_4^2\} \\ |c_t|^2 &= (1/4)\,\{(1-\lambda_1)^2-\lambda_2^2-\lambda_3^2-\lambda_4^2\} \\ c_s^*c_t+c_t^*c_s &= (1/2\sqrt{2})\,\{(1-\lambda_1)^2-\lambda_2^2-\lambda_3^2-\lambda_4^2\} \end{aligned}\right\}, \tag{15}$$

where λ_i is the amount of s character of $t_i\,(i=1,2,3,4)$ as defined by Öpik [3]. To be more realistic, let us take

$$\left.\begin{aligned} t_1 &= (1+\lambda^2)^{-\frac{1}{2}}(\lambda s+x) \\ t_2 &= [2(1+\lambda^2)^{-\frac{1}{2}}\,[s-\lambda x-(1+\lambda^2)^{\frac{1}{2}}y] \\ t_3 &= [2(1+\lambda^2)^{-\frac{1}{2}}\,[s-\lambda x+(1+\lambda^2)^{\frac{1}{2}}y] \\ t_4 &= z \end{aligned}\right\}, \tag{16}$$

where s, x, y, and z represent $2s, 2p_x, 2p_y$, and $2p_z$ AO, respectively, and λ is a parameter specifying the hybrid character of t_i's. It is to be noted that t_1, t_2, and t_3 in Eq. (16) becomes three equivalent sp^2 hybrid AO's lying in the xy plane for $\lambda=1/\sqrt{2}$ and $(t_1^2t_2t_3t_4)$ then becomes the valence state in which a nitrogen atom is expected to be found in the ground state of the nitrogen-containing heterocyclic molecules [5]. By expressing λ_i's involved in Eq. (15) in terms of λ of Eq. (16), it can be shown that

$$\left.\begin{aligned} |c_s|^2 &= 1/\{16(1+\lambda^2)^2\} \\ |c_t|^2 &= 1/\{8(1+\lambda^2)^2\} \\ c_s^*c_t+c_t^*c_s &= 1/\{4\sqrt{2}(1+\lambda^2)^2\} \end{aligned}\right\}. \tag{17}$$

For the numerical work, we use the following data [6, 7][1]:

$$G^1(sp) = 73111\ \mathrm{cm}^{-1}\,, \tag{18}$$

$$T(s^2p^3\,{}^2P) = 28840\ \mathrm{cm}^{-1}\,, \tag{19}$$

$$T(p^5\,{}^2P) = 234690\ \mathrm{cm}^{-1}\,. \tag{20}$$

The value of $\langle\psi_s'|\mathscr{H}|\psi_t'\rangle$ can be obtained immediately from Eqs. (11), (14), and (18):

$$\langle\psi_s'|\mathscr{H}|\psi_t'\rangle = -34465\ \mathrm{cm}^{-1}\,. \tag{21}$$

The values given in Eqs. (19) and (20) are supposed to be the expectation values of $\mathscr{H}$ with respect to the exact wave functions of the sth and the tth state and to

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[1] The $G^1(sp)$ value has been taken from [6]. The term values have been obtained from Moore's table [7] by averaging out fine structure, each component of a particular term being given a weight of $2J+1$. Since ${}^2P$ of $1s^2 2p^5$ is not given for N in Moore's table, its term value has been obtained by a linear extrapolation along isoelectronic series.

be the roots of the secular equation (10) as measured from the ground state of the nitrogen atom:

$$\langle \psi_s | \mathscr{H} | \psi_s \rangle = 28840 \text{ cm}^{-1}, \tag{22}$$

$$\langle \psi_t | \mathscr{H} | \psi_t \rangle = 234690 \text{ cm}^{-1}. \tag{23}$$

Therefore, $\langle \psi_s' | \mathscr{H} | \psi_s' \rangle$ and $\langle \psi_t' | \mathscr{H} | \psi_t' \rangle$ are obtained by the method described in Section 3, using (21), as

$$\langle \psi_s' | \mathscr{H} | \psi_s' \rangle = 34782 \text{ cm}^{-1}, \tag{24}$$

$$\langle \psi_t' | \mathscr{H} | \psi_t' \rangle = 228748 \text{ cm}^{-1}. \tag{25}$$

From Eqs. (13), (17), (21)–(25), $E_V(I) - E_V(II)$ is found to be

$$E_V(I) - E_V(II) = 2873 \text{ cm}^{-1} = 0.356 \text{ eV}, \tag{26}$$

for $\lambda = 1/\sqrt{2}$ (sp^2 hybridization). This value is rather small as compared with the one-center electron repulsion integral, which is obtained from the energy change in the course of electron-transfer reaction involving the atoms in their valence states [2, 8], and may be ignored in a crude theory. However, essential achievement of evaluation of the VSE directly from the observed term values is that one can expect a high degree of accuracy of evaluation and the difference shown by Eq. (26) is not negligible from this point of view. Therefore, it may safely be concluded that the improvement of Öpik's method suggested in the present paper is worth considering.

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Professor Dr. Tosinobu Anno
Laboratory of Chemistry
College of General Education
Kyushu University
Ropponmatsu, Fukuoka, 810 Japan