

Interatomic Exchange and σ -Bonding of Outer 3d and 4s-Orbitals

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Received January 21, 1972

A valence bond treatment is applied to a diatomic model involving a σ -bond between an outer sulphur orbital $\varphi = 3d, 4s$ and a fluorine sp -hybrid. Interatomic exchange terms are included and the results discussed from the point of view of excited orbitals size and of hybridization in fluorine. In the case of 4s orbitals it is concluded that the electrostatic approach is fully adequate to discuss orbital size and energy. When states involving d_σ -orbitals are concerned, interatomic exchange terms with fluorine 2s orbital are very important, while those with 1s orbital are not of great relevance. For a reasonable amount of sp hybridization in fluorine the size of the d-function is strongly reduced from the free atom value.

Introduction

The main criticism made to a theoretical description of molecular valence states involving outer 3d and 4s-orbitals in sulphur or in other later second row elements based on an electrostatic approach inclusive of the potential field generated by ligands,^{1,3} concerns the neglect of all energy terms arising from interatomic exchange interactions. For states involving d_π -orbitals it was shown that these terms affect marginally the energy but contribute significantly to reduce the orbital size to values which are suitable for π -bonding.⁴ As far as states involving d_σ -orbitals are concerned, the results obtained with the electrostatic treatment were questioned on the basis of the relevance of the repulsive terms involving these excited orbitals and $1s^2$ pairs of ligands.^{5,6} In a previous investigation³ it was shown that the inclusion of these terms does not modify critically energy and size of d_σ -orbitals as obtained from the electrostatic treatment. An analysis of overlap integrals led to the inference that interatomic exchange terms involving 2s orbitals of ligands were more relevant in determining the degree of participation of d_σ -orbitals to molecular valence states, and the suggestion was made that sp hybridization in first row ligands plays an important role in the mechanism of orbital contraction and sta-

bilization.⁷ Similar conclusions were drawn by Mitchell⁸ from an investigation on systems SX_6 ($X = F, Cl, Br, H$) based on the perfect pairing approximation. According to his results, d_σ -orbital participation occurs when sp^2d^2 octahedral hybrids are considered. Non-orthogonality effects on molecular valence states involving 4s-orbitals have not yet been discussed from a quantitative point of view, although there are indications^{3,8,9} that 4s-orbitals could be involved as well as 3d-orbitals in a correct description of high covalencies in later second row elements. In view of this situation the present investigation is concerned with the analysis of the role of hybridization in the ligands and with a quantitative estimate of interatomic exchange terms involving 3d $_\sigma$ or 4s-orbitals and those of first row ligands. A diatomic system sulphur-fluorine, similar to the one previously employed for discussing the role of d_π -orbitals,⁴ is considered: in this model for σ bonding the two atoms are on the z internuclear axis, at a separation of 3 a.u. Only the excited orbital $\varphi (= 3d_\sigma, 4s)$ is explicitly considered on sulphur, the remaining electrons and the nucleus being represented by a potential inclusive of intravalence exchange terms simulating the configuration s^2p^3 . It was shown elsewhere that intrashell exchange terms are insensitive to changes in size of the orbital φ .⁴ Fluorine is assumed to be in valence state $1(1s^2h_1^2p_\pi^4h_2)$ where h_i are sp hybrids defined in equation (1)

$$\begin{aligned} h_1 &= \cos\theta(2s) - \sin\theta(2p_z) \\ h_2 &= \sin\theta(2s) + \cos\theta(2p_z) \end{aligned} \quad (1)$$

Orthonormal Slater-type orbitals on the same center are used. On the basis of previous results the following exponential factors for sulphur orbitals were adopted: $K_{1s} = 15.7$, $K_{2s} = 4.95$, $K_{2p} = 5.53$, $K_{3s} = 2.16$, and $K_{3p} = 1.6$. Those of fluorine were taken from ref. 11. An antisymmetrized Valence Bond singlet function is built out of φ and of fluorine orbitals and a complete energy expression derived where electrostatic and exchange terms involving φ and each fluorine orbital are separated (see Appendix).

The present results are fully equivalent to those obtained by using a function where s and p orbitals

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Table I. Total energy E_T , electrostatic energy E_e for the SF model and corresponding optimum values of exponential parameters K_φ and mean radii r_φ^m (Å). Energies in a.u. above that of S^+ and F at infinite separation. Fluorine valence state ($1s^2h^2, 2p^5h_2$), the optimum θ value being about 173° in every case.

	E_T	K_φ	r_φ^m	E_e	K_φ	r_φ^m
4s	-0.242	0.705	6.5	-0.246	0.75	6.1
$3d_{z^2}$	-0.176	0.26	7.0	-0.256	0.96	1.9
$3d_{z^2-x^2}$	-0.176	0.28	6.6	-0.220	0.85	2.2

or sulphur are explicitly considered with a random spin distribution and where interatomic exchange terms involving these orbitals are neglected.

Results and Discussion

The results of the calculations at the value of θ minimizing the energy (about 173° in every case) are presented in Table I for the three types of excited orbitals, $3d_{z^2}$, $3d_{z^2-x^2}$ and 4s (z internuclear axis), which can give σ -bonding.

The results obtained for the two types of d_σ -orbitals are similar, and in the following we shall refer only to $3d_{z^2}$. In the case of 4s-orbitals, the inclusion of interatomic exchange terms does not affect significantly the values of the parameters obtained from the simple electrostatic treatment, so that size and orbital energy are fixed by electrostatic interactions with the molecular environment. The same does not hold for d_σ -orbitals. In addition, the ability of excited orbitals φ to promote hybridization in fluorine is modest and the optimum θ value is mainly determined by the sp hybridization energy of fluorine that is rather large. Since the wavefunction adopted here predicts a rather unaccurate value of the promotion energy $s^2p^5 \rightarrow sp^6$ (0.98 a.u.) a test calculation was made with the experimental value (0.771 a.u.) substituted in the energy eq. A1, obtaining results substantially unchanged from those listed in Table I. The optimum value of the hybridization parameter is of little significance, since in the real case it will be chiefly determined by

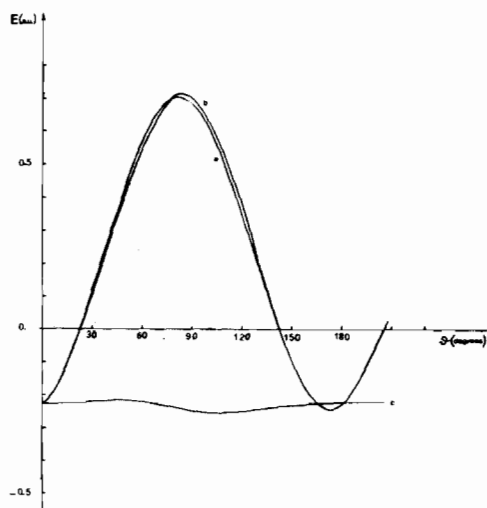


Figure 1. Energy minima (a.u.) in respect of K_φ versus θ : (a) total energy E_T , (b) electrostatic energy, (c) E_T minus sp -hybridization energy of fluorine.

interatomic exchange terms involving s and p orbitals of sulphur, here neglected. Consequently θ is not a variational parameter in our model, and in the following the θ -dependence of total energy, interatomic exchange terms and orbital size are discussed.

Figure 1 gives for the case $\varphi = 4s$ total energy E_T (curve a), electrostatic energy E_e (curve b) as functions of θ as well as E_T minus the sp hybridization energy of fluorine (curve c). It is clear that inclusion of interatomic exchange integrals does not modify appreciably the energy of the system for the whole range of θ while the hybridization energy is the most important term. In Figure 2, the mean radius of the

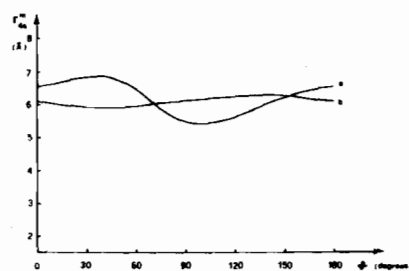


Figure 2. Optimum values of r_φ^m versus θ : (a) inclusive of interatomic exchange, (b) electrostatic treatment.

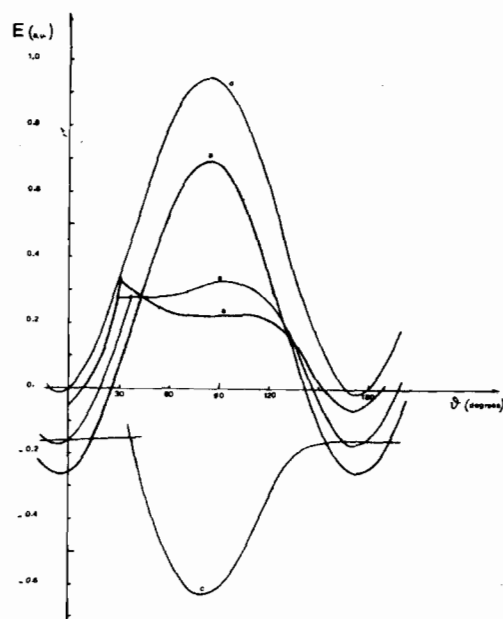


Figure 3. Energy minima in respect of K_{3d} versus θ : (a) total energy E_T , (b) electrostatic energy E_e , (c) E_T minus computed sp -hybridization energy of fluorine, (d) computed sp -hybridization energy, (e) computed with the empirical value of hybridization energy.

4s orbital r_{4s}^m is plotted against θ for both complete (curve *a*) and electrostatic (curve *b*) calculations. The two curves are rather similar, r_{4s}^m lying in the range 5-6 Å. Thus one can conclude that the electrostatic approach is adequate for discussing 4s-orbital participation to valence states of sulphur, and presumably, also Si, P, and Cl. For the case $\theta = 3d$, the corresponding curves are plotted in Figure 3. In addition the hybridization energy of fluorine (curve *d*) and E_T computed with the empirical *sp* promotion energy (curve *c*) are shown.

The importance of the hybridization term is seen to be relevant also for states involving *d*-orbitals, while that of interatomic exchange terms is fairly large for the whole range of θ . The inclusion of the latter contributions raises by 2-3 e.v. the energy curve of the electrostatic energy (*b*) for $-40^\circ \leq \theta \leq 40^\circ$ while it causes a strong stabilization for $50^\circ \leq \theta \leq 120^\circ$, i.e. when the fluorine bonding orbital is mainly 2s. Moreover this stabilization is not large enough to offset the hybridization energy, although the use of the empirical promotion energy improves somewhat the situation (curve *e*). The contributions $E_{\phi,\chi}$ due to interatomic exchange terms can be assigned to each fluorine orbital χ for the two limiting cases $\theta = 0^\circ$ and $\theta = 90^\circ$. This is done in Figures 4 and 5 respectively.

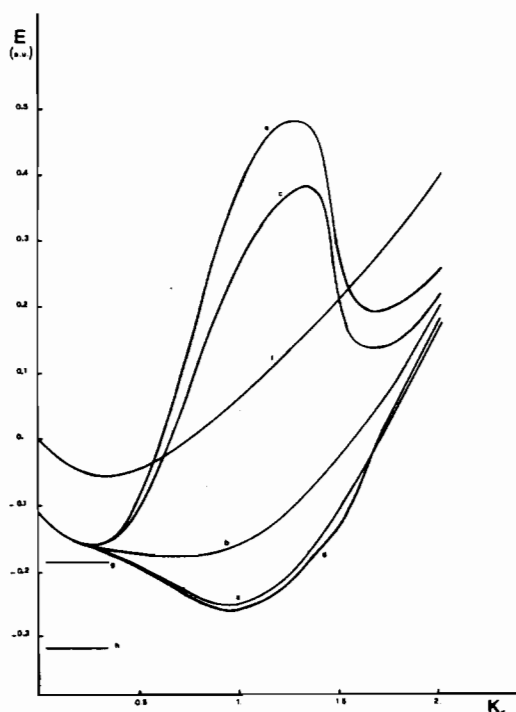


Figure 4. Energy of the system inclusive of exchange terms $E_{3d,\chi}$ at $\theta=0^\circ$: (a) E_e , (b) $E_e + E_{3d,1s}$, (c) $E_e + E_{3d,2s}$, (d) $E_e + E_{3d,2p_x}$, (e) E_T ; the contributions by $E_{3d,2p_{x,y}}$ are negligible; (f) atomic valence state $4[s^2p^3d] + F_e$, (g) energy of the SF system at infinite separation: S, $^3P(s^2p^3)$, F, $^2P(s^2p^3)$, (h) energy $S^+(s^2p^3) F^-(s^2p^6)$.

It is clear that the main contribution is given by $E_{3d,2s}$ (curves *c*) that for $\theta = 0^\circ$ is raising considerably the energy, especially in the range of K_d , corresponding to a size useful for σ -bonding while for $\theta = 90^\circ$ is is

strongly stabilizing in the same range of K_{3d} . $E_{3d,1s}$ although significant, is not paramount in determining the orbital size, as observed in a previous work.³ In fact, the essential features of curves *f* are reproduced by considering in eq. A1 $E_{3d,2s}$, and the following approximation can be suggested

$$E_T = E_e + \alpha S^2 E_{2s} \quad (1)$$

where S is the overlap integral $\langle 2s | 3d \rangle$, E_{2s} the energy of the 2s fluorine orbital and α a constant term, which for $\theta = 0^\circ$ is near unity (1.08) and for $\theta = 90^\circ$ is -1.26 . Eq. (1) reproduces eq. A1 with remarkable accuracy for $0 \leq K_d \leq 2.16$, and can find useful applications in semiempirical calculations.

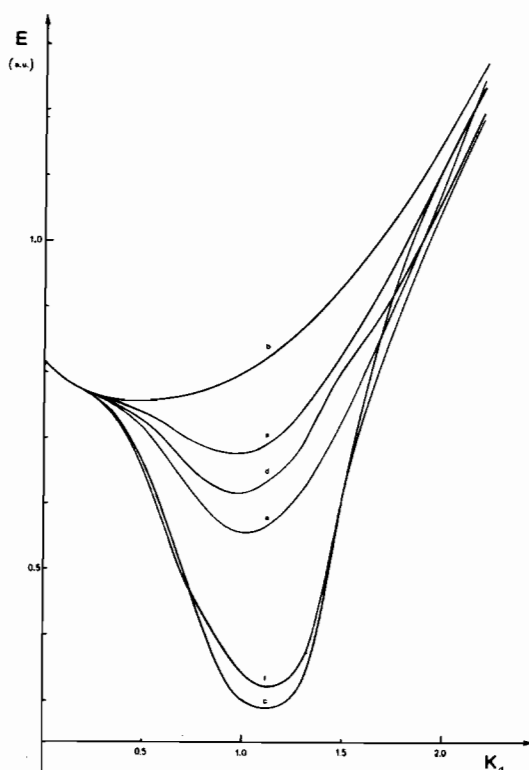


Figure 5. Energy of the system inclusive of exchange terms $E_{3d,\chi}$ at $\theta=90^\circ$: (a) E_e , (b) $E_e + E_{3d,1s}$, (c) $E_e + E_{3d,2s}$, (d) $E_e + E_{3d,2p_x}$, (e) $E_e + E_{3d,2p_x} + E_{3d,2p_y}$, (f) E_T .

In Figure 6 K_d is plotted against E_T for several values of θ . Each curve shows two minima, the first corresponding to a diffuse orbital is in our model the absolute minimum for low θ -values, while the second corresponds to compact functions with mean radius near to or below the S-F bonding distance, and it is favoured from the energy point of view for $\theta > 30^\circ$. The barrier between minima is located in a range of K_d corresponding approximately to the SF distance. Even if the present model does not allow one to reach conclusions on the energetics of d_σ -participation to molecular valence states, it is fairly obvious from Figure 5 that for reasonable degrees of *sp* hybridization in fluorine the size of the d_σ -orbital becomes suitable for efficient σ -bonding.

The main conclusions which can be drawn from the present work can be summarized as follows: i) the electrostatic approach is adequate for discussing 4s participation to molecular valence states; ii) hybridization in fluorine plays a fundamental role in determining d_{σ} -orbital size and energy. For values of θ , hybridization parameter, above 35° the size of d_{σ} -orbitals becomes compatible with efficient σ -bonding.

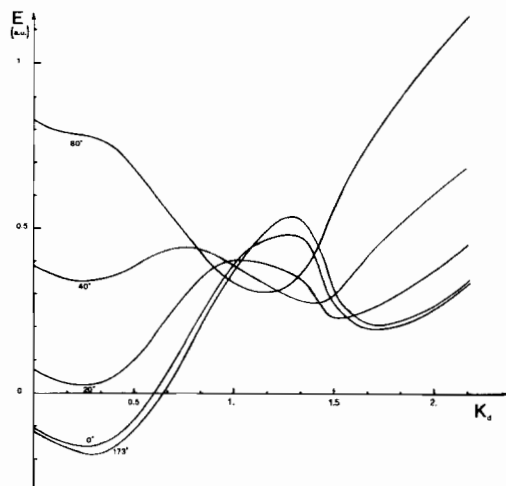


Figure 6. Total energy E_T versus K_d at various θ -values.

Since ligands like carbon are strongly hybridized, one can extrapolate the present results to suggest that carbon atoms are suitable to evoke higher covalencies in sulphur (presumably also in other later second row elements) involving d_{σ} -orbitals; iii) the most important interatomic term of energy is that involving sulphur $3d_{\sigma}$ and fluorine $2s$ orbitals.

Appendix

The energy of the sulphur-fluorine system can be written as follows:

$$E_T = E_F + E_{vs} + E_i(\theta) + [E_e(K_\sigma, \theta) + \sum_{\chi} E_{\varphi, \chi}(\theta, K_\varphi)] \cdot [1 + \sum_{\chi} S_{\chi}(\theta, K_\varphi)]^{-1} \quad (\text{A1})$$

Here E_F is the energy of a free fluorine atom in its ground state; E_{vs} is the energy of the charge distribution of fluorine in the electrostatic potential of sulphur, $E_i(\theta)$ accounts for changes in both E_F and E_{vs} due to sp -hybridization and is given by eq. A2

$$E_i(\theta) = 0.932 \sin^2 \theta + 0.227 \cos \theta \sin \theta \quad (\text{A2})$$

The other terms are $E_e(K_\sigma, \theta)$, bicentric electrostatic energy of the system, $E_{\varphi, \chi}(\theta, K_\varphi)$ the energy contribution due to exchange terms involving $\varphi = 3d, 4s$, and χ orbital of fluorine ($\chi = 1s, 2s, 2p_\pi, 2p_\sigma$), and S_{χ} the overlap integral $\langle \theta | \chi \rangle$.