

1261. Size of *d*-Orbitals and Valence-state Promotion Energies in Sulphur

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d-Orbital size and promotion energies for various spectroscopic and valence states are estimated. It is found that in $V_6(sp^3d^2)$ the mean radius of $3d$ -orbitals is nearly the same as that previously derived by an electrostatic treatment¹ and differs significantly from that of 3I and 7F spectroscopic states.² The promotion energies for the processes $s^2p^4 \rightarrow s^2p^3d$ and $s^2p^4 \rightarrow sp^3d^2$ are estimated to be >7.3 and >31.3 eV, respectively. Thus, *d*-orbital contraction by ligands must occur to make them effective in bonding. Moreover *d*-orbital participation in bivalent sulphur compounds is likely to be negligible.

AN assessment of the size of *d*-orbitals in sulphur is of great importance in discussing physical and chemical properties, not only of compounds where sulphur is bonded to more than two ligands, but also of ground, reactional, and excited states of sulphides.

The effect of ligands on $3d$ - as well on $3s$ - and $3p$ -orbitals has been previously investigated theoretically by employing an electrostatic approach:¹ for the free atom in the electron configuration sp^3d^2 the mean radius of $3d$ -orbitals was found to be 5.74 a.u., a value that does not differ much from that derived from the Slater rule. More recently Cruickshank, Webster, and Mayers² computed SCF functions for sulphur in various spectroscopic states arising from electron configurations sp^3d^2 and s^2p^3d : for the former they concluded that, although the promotion-energy estimate previously made¹ is essentially correct, the radial maxima of *d*-functions are "well within the bonding region," and thus it does not seem necessary to invoke ligand perturbation to make *d*-function useful in bonding.

For the configuration s^2p^3d the mean radius of the *d*-orbital was found to be very much the same as that estimated from the Slater rule, and thus too large for bonding.

However, Cruickshank, Webster, and Mayers imply in their calculations that the size of *d*-orbitals is nearly the same for the various spectroscopic states, so that the values obtained for the 7F and 3I states are supposed to hold also for the valence state, which is the one involved in molecule formation. This inference is unlikely to be correct, as the following qualitative considerations indicate. By expressing the total energy of an atomic state *A* as a sum of the electrostatic energy ϵ and of the exchange energy τ , when the *d*-orbitals are represented by a one-parameter (K_d) function, the corresponding variational condition may be written as in equation (1):

$$\epsilon/\partial K_d = -\partial\tau/\partial K_d \quad (1)$$

the remaining parameters having their optimum values. Thus, in the range of interest of K_d , if the right-hand side of equation (1) is not very steep, as expected in the case under

¹ D. P. Craig and C. Zauli, *Gazzetta*, 1960, **90**, 1700; *J. Chem. Phys.*, 1962, **37**, 601, 609.

² D. W. Cruickshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, 1964, **40**, 3733.

consideration, then the magnitude of the left-hand side will become critical for the determination of the optimum value of the K_d parameters and thus of the mean radius ($r_m^d = 1.8522/K_d \text{ \AA}$), as is clearly indicated by the difference in the latter parameter obtained² for the 7F and 3I states. Since for the valence state, which possesses a random spin distribution, the exchange term appearing in equation (1) is smaller than in the case of 7F and 3I , only a moderate increase from the K_d value minimising the electrostatic energy is expected. This means that the size of the *d*-functions in the valence configuration sp^3d^2 will be still too large for efficient bonding, so that *d*-orbital contraction must still occur in molecule formation.

In order to test quantitatively these considerations, previous calculations¹ based on an electrostatic treatment are now extended by including exchange among orbitals in the valence shell to a variety of sulphur states, including valence states. At the same time, the comparison with SCF data allows an assessment to be made of the sensitivity of the calculations on the analytical wave-functions employed and on the neglect of intra-atomic exchange. This represents a test of the validity of the conclusions previously reached concerning ligand perturbation.¹

The calculations also afford a more accurate evaluation of promotion energies of the various valence states which are of great interest in the discussion and interpretation of chemical and physical properties of compounds containing sulphur, where *d*-orbital participation is often invoked. The results of the calculations are collected in Table 1, where the mean radii r_m^d of *d*-orbitals are given, together with those derived from SCF calculations.²

TABLE 1

Energy, exponential factors, K_i , and mean radii, r_m^d , of *d*-orbitals for various sulphur states

State and configuration	Energy ^a (a.u.)	K_s	K_p	K_d	r_m^d (Å)
${}^3P(s^2p^4)$	-9.58	2.19 [1.91] ^b	1.75	—	—
${}^1D(s^2p^4)$	-9.53	2.19 [1.91] ^b	1.74	—	—
$V_2[s^2p_x^2p_+p_-]$	-9.56	2.19	1.74	—	—
$V_2[s^2p_x^2p_zp_y]$	-9.57	2.19	1.74	—	—
$V_3[s^2p^3d]$	-9.57	2.19	1.74	0.05	~35
${}^5D(s^2p^3d)$	-9.35	2.24	1.88	0.39	4.74 (4.00) ²
$V_4[s^2p_0p_+p_-d_0]$	-9.29	2.24	1.87	0.33	5.61
$V_4[s^2p_xp_yp_zd_{xz}]$	-9.30	2.24	1.87	0.33	5.61
${}^7F(s^2p^3d^2)$	-8.78	2.47	1.96	1.06	1.75 (1.88) ²
${}^3I(s^2p^3d^2)$	-8.48	2.39	1.94	0.79	2.34 (2.28) ^c
$V_6[s^2p_0p_+p_-d_+d_+]$	-8.40	2.35	1.95	0.69	2.68
$V_6[s^2p_xp_yp_zd_x^2d_y^2-d_z^2]$	-8.42	2.35	1.95	0.68	2.72
$E(s^2p^3d^2)$ ^e	-8.12	2.25	1.91	0.61	3.04
${}^4S(s^2p^3)$	-9.29	2.24 [2.06] ^b	1.88	—	—

^a Energy of valence shell electrons. ^b For 3P , 1D , and 4S the average orbital exponent for *s* and *p* functions does not differ significantly from the value reported in ref. 3, given in square brackets. ^c Cruickshank, Webster, and Mayers in ref. 2 given as 2.88: misprint. ^d Cruickshank, Webster, and Mayers refer to a 1I term: since they mention a single determinantal wave-function, it must be a 3I term. ^e Electrostatic energy from ref. 1.

The various promotion and excitation energies of interest are collected in Table 2, which shows that the agreement between calculated promotion and excitation energies with experimental values or with SCF results is reasonably good: moreover the data compare favourably also with values computed with wave-functions including explicitly inner-shell electrons.^{3*} This gives a feeling that the computed promotion energies $V_2[s^2p^4] \rightarrow V_4[s^2p^3d]$ and $V_2[s^2p^4] \rightarrow V_6[s^2p^3d^2]$ are of the right order of magnitude, although they probably represent lower limits for the following reasons. The computed excitation energy ${}^3P \rightarrow {}^5D$ is lower than the experimental value: this, in the context of variational calculations, means that the excited state (5D) is more accurately described

* Radial functions of orbitals with equal *n* but different *l* were, however, not differential.

³ P. Palmieri and C. Zauli, *Boll. sci. Fac. Chim. ind. Bologna*, 1963, **21**, 189.

TABLE 2

Calculated and experimental promotion and excitation energies			
Process		ΔE computed (ev)	ΔE experimental (ev)
$^3P \longrightarrow ^1D$	1.52 [1.63] ³	1.13
$^3P \longrightarrow ^5D$	6.48 [7.21] ²	8.38
$^3P \longrightarrow ^7F$	21.93 [24.48] ²	—
$^3P \longrightarrow ^3I$	30.99 [35.36] ²	—
$^3P \longrightarrow ^4S(s^2p^3)^+$	8.03 [7.6] ²	10.36
$^3P \longrightarrow V_2[s^2p^4]$	0.38	0.31*
$V_2[s^2p^4] \longrightarrow V_4[s^2p^3d]$	7.35	—
$V_2[s^2p^4] \longrightarrow V_6[s^2p^3d^2]$	31.34	—
$V_2[s^2p^4] \longrightarrow V_3[s^2p^4d]^-$	~0.03	—

* From spectroscopic states.

than the ground state (3P). Since for the 5D -term (configuration s^2p^3d) the $3d$ -electron orbital is practically non-penetrating, this fits with the observation that the s^2p^3 configuration in 4S is more accurately described than the s^2p^4 ,^{3*} as the computed ionisation potential (8.03 ev) $^3P(s^2p^4) \longrightarrow ^4S(s^2p^3)^+$, lower than the experimental value (10.36 ev), shows. Moreover, the difference between computed and experimental energies for the processes $^3P(s^2p^4) \longrightarrow ^5D(s^2p^3d)$ and $^3P(s^2p^4) \longrightarrow ^4S(s^2p^3)^+$ are roughly the same. Consequently, the computed energy for $V_4[s^2p^3d]$ must be a lower limit. The same situation is to be expected for the configuration sp^3d^2 and thus the computed promotion energy $V_2[s^2p^4] \longrightarrow V_6[sp^3d^2]$ is likely to be also a lower limit.

As far as d -orbital dimensions are concerned, for the 5D term the r_m^d value is a little bigger than that given by SCF calculation: however, the mean radius in this region is a very critical function of K_d . For 7F and 3I , the r_m^d values are practically the same as those given by SCF calculations. This indicates that the crude wave-functions used in the present (and previous¹) work are sufficiently correct to reliably reproduce orbital dimension.

The mean radius found for $3d$ -orbitals in $V_6[sp^3d^2]$ (valence state) is much bigger than that of 7F and 3I : this indicates that the assumption of Cruickshank, Webster, and Mayers,² as previously discussed, is not justified for the configuration sp^3d^2 . The present value ($r_m^d = 2.72 \text{ \AA}$) is not very far from that ($r_m^d = 3.04 \text{ \AA}$), reported previously,¹ by neglecting intra-atomic exchange. Thus, d -orbital contraction by ligands must be effective, if these orbitals are to take part efficiently in bonding together with $3s$ and $3p$ -orbitals: for these valence orbitals the mean radii are in fact $r_m^s = 0.83 \text{ \AA}$, $r_m^p = 0.97 \text{ \AA}$. It is of interest to notice that d -orbitals in the valence configurations s^2p^3d and sp^3d^2 differ quite considerably in size, as predicted with reasonable accuracy by the Slater rule.

From the results in Tables 1 and 2, some conclusions can also be drawn on the possibility of sulphur valence-shell expansion involving d_n -orbitals in aromatic sulphides. This process can essentially occur in two ways: (i) by promoting one electron from a p - to a d_n -function, which corresponds to a Rydberg transition; and (ii) by accepting charge in the vacant d_n -function. One can see (Table 2) that the promotion energy for the process $V_2[s^2p^4] \longrightarrow V_4[s^2p^3d]$ is $>170 \text{ kcal./mol.}$, while the electron affinity of a d -orbital, expressed by $V_3[s^2p^4d]^- - V_2[s^2p^4]$ is practically zero. Moreover, for the configuration s^2p^3d , $r_m^d = 5.6 \text{ \AA}$, while in s^2p^4d the mean radius of the d -functions is very large: both values greatly exceed the C-S bond distance. Thus, taking in account also ligand perturbation, which in any case is not very significant for sulphides,¹ the results on the whole indicate that it is unlikely that a significant participation of d_n -orbitals will occur in ground, reactional, and first few electronically excited states of aromatic sulphides.⁴

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* No doubt because when the electrons occupy different p -orbitals, as in $^4S(s^2p^3)^+$, the correlation energy is small.

⁴ See, e.g., A. Mangini, "The Valence State of Sulphur in Organic Compounds," in N. Kharasch, "Organic Sulphur Compounds," Symposium Publications Division, Pergamon Press, Oxford, vol. IV.