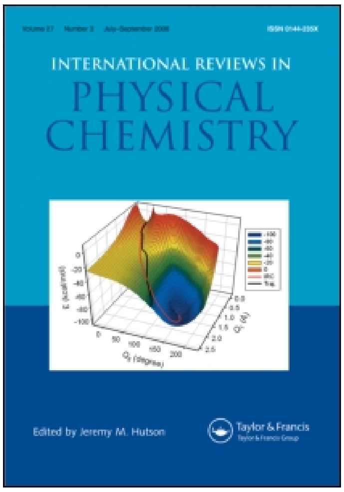

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d-Orbitals in molecular wavefunctions of main group molecules

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d-Orbitals in molecular wavefunctions of main group molecules

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Molecular wavefunctions calculated with basis sets supplemented with higher-order functions show a smooth increase in the degree of d-function involvement from a polarizing role in main group compounds of normal valency to a genuine valence-orbital role in hypervalent compounds; compounds of second-row elements, especially when bonded to electronegative elements, often use d-functions in a marginal valence role. d-Functions contribute to molecular wavefunctions predominantly in bonding; atomic population terms are very small. The absence of orthogonality constraints (the d-functions are nodeless) facilitates the use of dπ-functions to reduce excessive charge disparity built up in the σ-network. Although exponents may be no greater than those found for normal valency compounds, d-function supplementation is often indispensable for the description of the bonding in hypervalent compounds in many of which more than one set of gaussian d-functions may be needed.

1. Introduction

Interest in the involvement of d-orbitals in molecular bonding, aroused by Pauling in the 1930s and revived by Craig and others in the 1950s, is still strong. It has survived the actual demonstration of d-orbital utilization in bonding by all-electron calculations of molecular electronic structure and the fact that it has continued, with attendant controversy, is evidence for saying that d-orbitals in bonding are still not understood.

Hybridization of d-orbitals was the key to the puzzle of explaining how the electron pair concept of bonding could be applied to compounds like SF_6 and PF_5. The idea was strongly reinforced by the striking correlation between the geometrical structures discovered by experiment and the geometries appearing in the list of possible spd hybridizations. However, on second thought, it was clear that two-electron bonds could easily be described in hypervalent molecules without d-orbitals, in spite of the hybridization formulae (Mitchell 1969). Chemists also became sceptical about spd hybrid bonding when it was realized that shielding by inner electrons would make d-orbitals far too diffuse to be useful.

Exponents assigned to d-orbitals by Slater's rules in sulphur, for example, contrast strongly with those of the compact 3s and 3p orbitals (Craig *et al.* 1954). The radial maxima of the 3s- and 3p-orbitals are calculated to lie 80 pm from the nucleus, compared with 290 pm for the 3d-orbital; electron density in the latter then lies outside the attached atoms and no contribution to bonding can be contemplated.

d-Orbitals were rescued from this predicament by Craig (1954), who pointed out how strongly the diffuse orbitals of the central atom would be deformed by the potential field of arrays of atoms like fluorine or oxygen and proposed that the effective charge felt by the d-orbital could be raised to the point where mixing with s and p orbitals would be possible. The orbital modification theory was tested with a simple model (Craig and Magnusson 1956). Later work by Craig and Zauli (1962) relaxed the restrictions of the one-electron, point-charge model but the general conclusions were the same. What they did determine, however, was that the mechanism by which attached groups modified central atom orbitals was not primarily coulombic. Exchange terms in the hamiltonian provide a non-classical potential which is heavily responsible for the contraction of d-orbitals, leading to the label 'exchange potential'. This raises the expectation that d-orbital contraction will occur in bonds to atoms like carbon as well as with highly electronegative atoms like fluorine or oxygen.

The compatibility of d-orbitals with other valence shell orbitals was further urged after it was discovered how very differently d-orbitals behaved in different terms of a configuration and in different configurations (Coulson and Gianturco 1968, Cruickshank *et al.* 1964). Radial maxima calculated for a configuration average (say, for the terms of the sp^3d^2 configuration of sulphur) may be as much as 35 per cent lower than those calculated by applying Slater's rules to the same configuration (Craig and Thirunamachandran 1965, 1966, Chandler and Thirunamachandran 1967).

At this stage in the development of the d-bonding concept attention shifted to the results of all-electron calculations, now that non-empirical calculations were feasible. Early results produced conflicting claims about d-orbitals, a feature which the next fifteen years has done nothing to erase. On the one hand, calculations on hypervalent molecules received the expected reward of energy improvement when d-functions were added. One the other hand, energy improvements were obtained when they were not expected. It finally seemed that if accurate geometries and energies were to be had, then functions of higher angular quantum number were necessary for the description of all molecules (Hariharan and Pople 1973, Ahlrichs and Taylor 1981, Jankowski *et al.* 1985).

The conflict would be easily resolved if *functions* in gaussian basis sets and *orbitals* in molecular wavefunctions could be unequivocally distinguished. The ubiquity of the higher-order functions may be rationalized by noting that d-functions (and f- and g-functions) act to remove the deficiencies inherent in basis sets constrained to consist of s- and p-type functions only (Frisch *et al.* 1984). Since they allow much greater flexibility in the description of the electron distribution in the very complex internuclear regions of molecules, it is no surprise to find small contributions of d-functions even in molecules containing no atoms from beyond the first row. Because they are not needed to describe the density in the steep but less complex potential-well near the nuclei, the exponents are generally small.

In basis sets of elements of normal valency, nuclear-centred d-functions may be replaced by functions ('bond functions') centred at positions along the line of the bonds (Carlsen 1975, Breitenstein *et al.* 1983, Wright and Buenker 1984). Both show important effects on energies and on the topography of potential surfaces but neither can be regarded as genuine valence orbitals (Coulson 1969). Unfortunately however, there is no clear cut distinction between the way d-functions are utilized in hypervalent and normal-valency molecules; the optimum exponents are little different and the transition between the two in the effects of supplementation on energies and electron distributions is smooth. (See the table.) Changing attached atoms may have a bigger effect on d-functions in bonding than expanding the octet of the central atom.

The following population data are typical of results obtained on main group molecules. (Calculations at 3-21G basis level (Binkely *et al.* 1980, Gordon *et al.* 1982) with five d-functions added to the central atom basis.) The net atomic density at the central atom and, in parentheses, the overlap density in each bond is given separately for contributions by the s, p, and d functions in the valence shell. Within basis sets constructed on uniform procedures (like the Pople group's 3-21G, 4-31G, 6-31G sets)

Energy increments (Hartree) due to d-function supplementation of Dunning–Hay basis-set calculations of molecules containing second-row elements.†

Molecule	ΔE (1D)	ζ_d (1D)	ΔE (2D)
SiF_4	−0·093	0·58	−0·102
PF_3	−0·088	0·64	−0·099
H_2S	−0·024	0·70	−0·028
SF_2	−0·049	0·76	−0·059
SO_2	−0·139	0·71	−0·160
SF_4	−0·133	0·72	−0·156
ClF_3	−0·088	0·75	−0·101

† The d-functions were added to the Dunning–Hay (11s7p/6s4p) basis set for second-row atoms (Dunning and Hay 1977). The first-row atoms were represented by the Dunning–Hay (9s5p/4s2p) basis with an added d-function set (exponent 0·8) and hydrogen by the (4s/2s) set with an added set of p-functions (exponent 1.1).

the basis-set dependence of population indices of this kind is very small (Magnusson 1984c) but this is not true of all basis sets and it is easy to misjudge d-orbital involvement. The d-function occupations should be used with caution.

CH_4 $2s^{1\cdot16\ (0\cdot17)}$ $2p^{2\cdot19(0\cdot57)}$ $d^{0\cdot007(0\cdot02)}$

H_2S $3s^{1\cdot56(-0\cdot10)}$ $3p^{3\cdot06(0\cdot65)}$ $d^{0\cdot03(0\cdot04)}$

SO_2 $3s^{1\cdot68(-0\cdot27)}$ $3p^{1\cdot85(0\cdot72)}$ $d^{0\cdot17(0\cdot30)}$

The immediate conclusions from these data are that d-functions contribute to wavefunctions at three levels, and that the relative contribution of d-functions to intra-atomic terms in the molecular electron distribution is very much greater for d-functions than it is for s- and p-functions.

2. d-Functions in normal valency main group compounds

d-Functions in normal valency second-row compounds have been extensively studied (Magnusson 1984c, 1986) with the conclusion that the role of d-functions is intermediate between that of polarization functions and valence orbitals. A very high proportion of the total d-function density appears in the overlap density part of the distribution. By contrast, valence shell s-orbitals display close-to-maximal populations concentrated in the atomic parts of the distribution (except where topological constraints force sp-mixing in bonding) and p-orbitals, in spite of being responsible for the greater part of the bonding, still maintain large atomic densities (Magnusson 1984a).

Attached groups affect d-function participation in molecules of both first and second-row atoms. The following data (energy increments produced by supplementation of the central atom basis with five d-functions) attest the rising importance of d-functions when electronegative elements are attached. (Energies in Hartrees; 3-21G level calculations; exponents: $\zeta_d(N)=0\cdot8$, $\zeta_d(P)=0\cdot55$.)

NH_3 −0·016 H; NH_2CH_3 −0·018 H; NH_2F −0·038 H; NF_3 −0·053 H

PH_3 −0·050 H; PH_2CH_3 −0·047 H; PH_2F −0·069 H; PF_3 −0·111 H

Additional evidence for the predominantly bonding role of d-functions comes from the effect of supplementation on optimized bond distances, which are reduced, and on calculated stretching frequencies, which are increased (Pietro *et al.* 1982). The effects are even found in hydrogen-bonded species (Scheiner 1983).

The reduction in bond length produced by adding d-functions is substantial: for the substituted phosphine series PH_2X ($X = H, CH_3, NH_2, OH, F$) calculated at the split-valence 4-31G basis, the shortenings produced by adding 5d-functions rise steadily across the series from 2·3 pm to 6·9 pm. (Much larger shortenings are obtained in the optimized geometries at minimal basis set level, where the poorer quality of the s and p bases permits the effect of added d-functions to be exaggerated. As expected, the 'superposition effect' is most serious in molecules of electron-rich atoms such as N, O, and F, for the electrons of which the basis-set description is of lowest quality.) (Magnusson 1984 c).

The reasons for the increased effect of d-functions on calculated geometries, overlap densities, and energies in compounds containing the more electronegative elements are evident from analysis of electron distributions (Kwart and King 1977). In bonds to fluorine, for example, the d-functions are used in $d\pi$–$p\pi$ bonding (Hillier and Saunders 1970). The 4-31G level calculation of PH_2F with d-function supplementation produces a P–F bond-order of 0·231, of which one third is contributed by d-functions. Of that amount, 50 per cent comes from the π-bond. Nitrogen and oxygen are also π-donors, and similar bond shortenings in P–N and P–O bonds are similarly accounted for (Magnusson 1984 c). It is for this reason that $p\pi$-type functions must be included in the bonding region if bond functions are substituted for nuclear-centred d-functions in basis sets (Carlsen 1977 a, b).

In the NH_2-, OH-, and F-substituted phosphines $d\pi$–$p\pi$ overlap provides a route for transfer of electronic charge from substituent to phosphorus and helps to offset the polarity of σ-interaction; the charge disparity is reduced by 0·1–0·2*e* per bond by this means. Fairly strong $d\pi$–$p\pi$ bonding is also calculated to be present in what are formally single bonds in SiH_3X and PH_3X^+ compounds ($X = NH_2$, OH, F) and up to one-half of the π-type overlap density is due to the contribution of d-functions.

Differences in role provide an explanation for the differences in optimum d-function exponents found for molecules containing second-row elements. For three P(III) compounds calculated at supplemented 3-21G level the best d-function exponents are: PH_3, 0·42; $P(CH_3)_3$, 0·58; PF_3, 0·48. In PH_3 and PF_3 the d-functions are found mainly in high-lying molecular orbitals where small contributions mix in with the e-type 3p orbitals in P–X bonding. In $P(CH_3)_3$ this type of mixing is small but there is some utilization of the d_{z^2} function in the HOMO where it contributes to the shape of the lone pair (Magnusson 1984 b).

The involvement of d-functions in both σ- and π-bonding is partly facilitated by the fact that they are nodeless. Orthogonality to all other orbitals is maintained by virtue of their angular dependence, the radial form being unconstrained by orthogonality requirements. This is the second-row analogue of a concept applied to p-orbitals of first-row elements (Hirshfeld and Rzotkiewicz 1974). Because of the absence of orthogonality constraints on d-functions, $d\pi$–$p\pi$ overlap densities are independent of the highly conformationally-sensitive $p\pi$–$p\pi$ interactions and make almost no contribution to conformational energy differences (Magnusson 1986).

3. Hypervalent molecules

d-Function densities rise from the 0·1–0·4*e* range found for compounds of normal valency second-row elements to a range of 0·4–1·0*e* in hypervalent compounds. In most hypervalent compounds the effect of added d-functions is major and it is difficult to give even a qualitative account of the bonding without them. Nevertheless, the d-function contribution stops short of the level which formulae like sp^3d^2 or sp^3d would suggest. As in main group compounds of normal valency, the d-function contribution is concentrated in the overlap density part of the electron distribution.

Because of the concentration of the d-function contribution in the overlap parts of the electron distribution and because exponent-optimized d-functions are relatively diffuse, ordinary Mulliken population analysis underestimates the full involvement of the higher-order functions and projection operator techniques are necessary. The Roby scheme, in which 'shared populations' are estimated by projecting the d-functions from one centre on to the full set of contributing atomic orbitals from all centres, provides a more adequate estimate of the shared charge in the part of space covered by the rather diffuse d-functions (Roby 1974 a, b, Carlsen 1975, Cruickshank and Avramides 1982).

Although the nature of the attached groups has a major effect on d-function participation in bonding, the optimum d-function exponents are relatively little affected. Optimum exponents are surprisingly close to those obtained for compounds which do not expand the octet. Optimization results for a series of second-row compounds are given in the table. The data include entries for both one and two sets of d-functions added to the sp basis.

As might be expected, sets of s and p orbitals alone are often inadequate to describe the expanded valence shell of a second-row atom in a hypervalent molecule and major changes in the bonding pattern are produced when d-functions are omitted. Because of this, discrepancies between calculated (optimized) and experimental bond lengths are generally serious in hypervalent molecules, sometimes exceeding 50 pm (Pietro *et al.* 1982). The case of dimethyl sulphoxide is notorious (Mezey and Haas 1982), the added functions being necessary to produce the $S=O$ pattern, rather than the $S–O^-$ pattern obtained from unsupplemented basis sets. In consequence d-functions added to the small split-valence 3-21G basis reduce the optimized S–O bond length from 168 pm to 149 pm (experimental value 147·7 pm) (Pietro *et al.* 1982).

High-level calculations of molecules of both first and second-row elements frequently employ more than one set of gaussian d-functions and the addition of several higher-order function sets is said to be necessary for results of highest accuracy (Frisch *et al.* 1984). Strömberg *et al.* (1984) argue for the addition of as many as five sets of d-functions, basing their argument on the functions, some with exponents $\zeta \approx 8$, necessary to describe the d-orbital in certain excited states of second-row atoms. Without the d-orbital of the 'proper shape', incorrect bond distances for SO_2 were obtained with even quite extensive basis sets.

High-exponent d-functions are known to be important in determining correlation energies of molecules with second-row atoms (Pettersson *et al.* 1983) because of the need to calculate configurations like the $s^2p^2d^1$ configuration of S^+ which contains the ^4F state used by Strömberg *et al.* (1984), but ground-state calculations do not normally appear to require such measures. Calculation of the effects on energy of multi-d-function supplementation on a series of Si, P, S, and Cl compounds (Magnusson and Schaefer 1985) provides some support for the contention of Strömberg *et al.* A single set of five gaussian d-functions (exponent in the range 0·5–0·8) generally provides about 80 per cent of the energy improvement gained by adding five sets. A second set yields a further ~15 per cent. In each case, the additional function required a high exponent ($\zeta'' \approx 2{\cdot}0$). The results are consistent with the proposition that d-type valence orbitals are involved in the bonding and that a single set of gaussian functions is inadequate to describe their proper shape (Magnusson and Schaefer 1985).

d-Orbitals in bonding are like the Mafia; known to be involved but hard to apprehend. Small exponents and heavy concentration in bonding make population analysis controversial. Lack of angular dependence forestalls the use of conformational data to estimate involvement in bonding. The level of involvement in many compounds makes it difficult to distinguish the roles of genuine valence orbitals and functions added to remove deficiencies in gaussian basis sets. Nevertheless, the existence of a valence role for d-functions may be regarded as established and with reasonable progress made in d-orbital effects on structure, the way is open to define their influence on chemical reactivity.

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