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MODIFIED LEWIS THEORY

PART 1. POLAR COVALENT BONDS AND HYPERVALENCY

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ABSTRACT: A modification to Lewis's theory of valency is proposed to make it more consistent with the results of quantum-mechanical calculations on molecules containing polar covalent bonds (e.g., ClF) and hypervalent atoms (e.g., SF₆). A distinction is drawn between the valence shell of an atom (VS) and the Lewis shell (LS). [*Chem. Educ. Res. Pract. Eur.*: 2001, 2, 67-72]

KEY WORDS: *Lewis theory; polar covalent bond; hypervalency; valence shell; Lewis shell*

INTRODUCTION

Lewis's theory of valence (Lewis, 1916, 1923) occupies a central place in chemistry. Although he devised the theory many years before the development of quantum-mechanical calculations on molecules, it has survived these developments remarkably well. Quantum chemists have been able to obtain similar structures to his for many types of molecule by analysing wave functions or electron densities (see, for example, Schmiedekamp et al., 1979; Foster & Weinhold, 1980; Bader et al., 1984; Mingos & Hawes, 1985; Silvi & Savin, 1994). However, his theory needs to be modified to make it consistent with the results for molecules containing polar covalent bonds and hypervalent atoms, as I discuss below.

Lewis postulated that electrons pair up in molecules, and wrote formulae like [Na]⁺[:H]⁻ for ionic compounds and H:H for covalent ones. These formulae may be taken as indicating where electron density is concentrated, and hence, on White's interpretation of electron density, where electrons spend most time (White, 1934). Thus the formula [Na]⁺[:H]⁻ indicates that the two valence electrons spend most time near H, the formula H:H that they spend most time near and between both H's. Within these constraints the two electrons keep as far apart as possible.

Lewis reckoned shared electrons as belonging to both atoms. Thus in H:H each hydrogen atom has two electrons in its valence shell, like the hydrogen atom in [Na]⁺[:H]⁻. This method of counting must be distinguished from that used to obtain charge numbers.

Consider a diatomic molecule AB. Let the electron density (ρ) be partitioned between core (c) and valence (v) electrons, and ρ^v between bonding (b) and nonbonding (nb) electrons. Let ρ^b be further partitioned between the two centres:

$$\rho^b = \rho_A^b + \rho_B^b \quad (1)$$

Integration gives

$$N^b = N_A^b + N_B^b \quad (2)$$

where N^b is the total number of bonding electrons and N_A^b is the number on A. The total number of valence electrons on A is then

$$N_A = N_A^b + N_A^{nb} \quad (3)$$

and the charge number of A is

$$z_A = z_A^c - N_A \quad (4)$$

where z^c is the charge number of the core. On Lewis's reckoning, however, the total number of valence electrons on A is given by

$$N_A^L = N^b + N_A^{nb} = N_A^b + N_B^b + N_A^{nb} \quad (5)$$

For example, for H_2 , $N_A^b = N_B^b = 1$ and $N_A^{nb} = 0$. Equations 3 and 4 give $N_A = 1$ and $z_A = 0$, whereas eq 5 gives $N_A^L = 2$. Similarly for a halogen molecule, $N_A^b = N_B^b = 1$ and $N_A^{nb} = 6$, whence $N_A = 7$ and $z_A = 0$, or $N_A^L = 8$.

Equation 3 gives the "effective" number of valence electrons round an atom, eq 5 the "gross" number. Lewis's thesis was that, in compounds of main-group elements, the gross number is almost always even, and usually corresponds to a closed shell (2 for the lightest elements, 8 for the others).

POLAR COVALENT BONDS

Lewis postulated that bonds vary in character between polar and nonpolar extremes. In bonds of intermediate polarity atoms share electrons unequally. He represented this as in $Cl:F$, with the colon representing the bonding electrons nearer the more electronegative atom (I have omitted lone pairs for simplicity). He seems to have intended this formula to show that, while each atom still has two bonding electrons and a closed shell, the fluorine atom has a greater share of the bonding electrons than the chlorine atom.

This ties in with eqs 1-5. If B is more electronegative than A, partition of ρ^b by one of the standard methods (see Meister & Schwarz, 1994) will give $N_B^b > N_A^b$ (eqs 1 and 2). Equations 3 and 4 then give $z_A > 0$ and $z_B < 0$. But eq 5 still gives the same values of N_A^L and N_B^L .

However, Cioslowski & Mixon (1993) have pointed out that, if bonds of this type are represented by a combination of ionic and covalent forms according to valence-bond theory, unequal sharing decreases the number of electrons in the valence shell of the more electropositive atom. For a molecule A-B, the ionic form (A^+B^-) will have a weight equal to the ionicity (i) and the covalent form (A:B) equal to $1 - i$. The gross numbers of bonding electrons round A and B are accordingly given by

$$N_A^{b(CM)} = i \cdot 0 + (1 - i) \cdot 2 = 2 - 2i \quad (6)$$

$$N_B^{b(\text{CM})} = i \cdot 2 + (1 - i) \cdot 2 = 2 \quad (7)$$

Thus in the case of ClF, for which $i \approx 0.3$ (Appendix), the total number of valence electrons on the chlorine atom is $8 - 2i$ or about 7.4, and on the fluorine 8. In other words, unequal sharing does not affect the fluorine atom, which has eight electrons in its valence shell over the whole range of polarities from F_2 to X^+F^- . But unequal sharing does affect the chlorine atom, depressing the number of electrons in its valence shell below eight, down to six in Cl^+Y^- . This analysis spoils the idea that atoms adopt closed shells in molecules.

How this problem arises can be seen by substituting into eqs 6 and 7 $N_A^b + N_B^b = 2$ and $N_B^b - N_A^b = 2i$, and adding N_A^{nb} or N_B^{nb} . This gives

$$N_A^{\text{CM}} = 2N_A^b + N_A^{nb} \quad (8)$$

$$N_B^{\text{CM}} = N_A^b + N_B^b + N_B^{nb} \quad (9)$$

Equation 9 is the same as eq 5, but eq 8 has $2N_A^b$ instead of $N_A^b + N_B^b$. In eq 5 N_B^b represents the number of bonding electrons on B shared with A; eq 8 limits this number to N_A^b , the number on A shared with B (producing the covalent component of the bond), the remainder on B ($N_B^b - N_A^b$) not being shared (producing the ionic component). In other words eq 8 takes account of the unequal sharing of the bonding electrons which eq 5 does not.

One way of resolving this problem is to insist, for the purposes of Lewis theory, that N_A be calculated by eq 5. However, this is unsatisfactory when the resulting value exceeds the capacity of the valence shell, as discussed in the next section. An alternative solution is to retain eq 5, and reformulate the terms in it. This can be done by partitioning ρ^b in eq 1 such that integration gives $N_A^{b*} + N_B^{b*}$ with $N_A^{b*} = N_B^{b*}$. Equation 5 then becomes

$$N_A^L = N_A^{b*} + N_B^{b*} + N_A^{nb} \quad (10)$$

This equation now holds whatever the polarity. The necessary partitioning is illustrated in Figure 1. P_1 represents a normal partitioning, P_2 the partitioning required to give $N_A^b = N_B^b$.

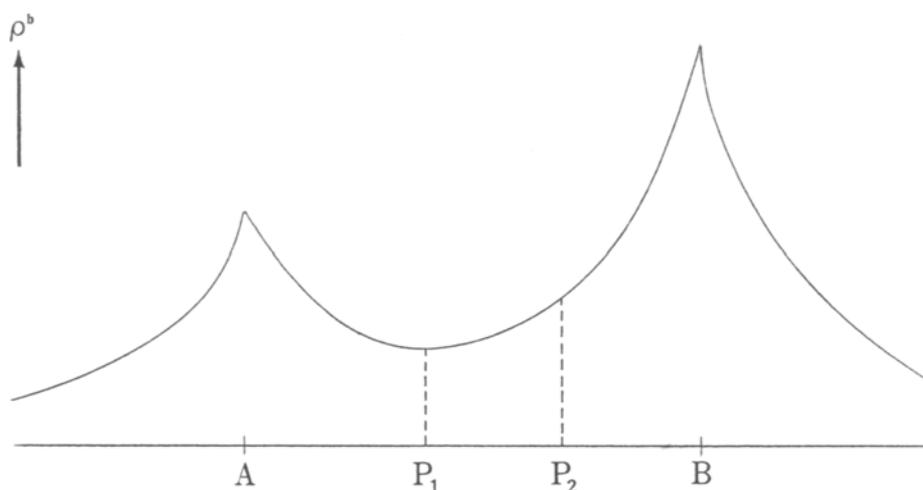


FIGURE 1. Partitioning bonding electron density in a molecule AB.

P_1 defines the valence shell (VS) of each atom, for which eqs 1-4 apply (and 6-9). P_2 defines the region for which eq 10 applies. I suggest that this be called the Lewis shell (LS). Lewis's thesis can now be restated: in compounds of main-group elements, the gross number of electrons in the Lewis shell of an atom is almost always even, and usually corresponds to a closed shell. Thus in the case of ClF, while the chlorine atom has about 7.4 electrons in its valence shell, it has 8 in its Lewis shell, as does the fluorine atom.

HYPervalENCY

Lewis suggested that in hypervalent molecules like PF_5 and SF_6 , the central atom has more than eight electrons in its valence shell (eight in a "primary" shell and the remainder in a "secondary" one). For example, he wrote the formula for SF_6 as $\text{S}(\text{:F})_6$ (I have again omitted lone pairs). However, quantum-mechanical calculations indicate that the central atom in hypervalent molecules never has more than eight electrons in its valence shell (Kutzelnigg, 1984; Reed & Weinhold, 1986; Reed & Schleyer, 1990; Cioslowski & Mixon, 1993). Participation of d orbitals in bonding does not exceed the level of polarization functions (Magnusson, 1990; Cooper et al., 1994).

The distinction between VS and LS helps us here. A central atom can have more than eight electrons in its Lewis shell provided that its valence shell contains no more than eight. This can occur in combination with more electronegative atoms, which take a greater share of the bonding electrons. Thus in SF_6 the sulfur atom can have twelve electrons in its Lewis shell provided that the polarity of the bonds exceeds $\text{S}^{1/3+}\text{F}^{1/3-}$ and of the molecule $(\text{S}^{2+})(\text{F}^{1/3-})_6$. The sulfur atom then has less than two-thirds of a share of the twelve electrons, i.e. fewer than eight electrons in its valence shell. Quantum-mechanical calculations indicate that this is the case, giving the polarity as about $(\text{S}^{3+})(\text{F}^{0.5-})_6$ (Appendix). Lewis's formula for SF_6 is therefore correct, provided that it is drawn with polar bonds: $\text{S}(\text{:F})_6$.

This conclusion can be extended to other hypervalent species. These are characterized by having highly electronegative atoms or radicals around the central atom. The high polarities ensure that the capacity of the valence shell is not exceeded (Table 1).

TABLE 1: Charge number of central atom in hypervalent species, and gross number of electrons in the valence shell and Lewis shell.*

Species	Charge Number	Number in VS	Number in LS
PF_5	~+3	~4	10
SF_4	~+2	~6	10
SF_6	~+3	~6	12
ClF_4^+	~+2	~8	10
AlF_6^{3-}	~+2	~2	12
SiF_6^{2-}	~+2	~4	12
PF_6^-	~+3	~4	12
SO_2	~+2	~6	8
SO_3	~+3	~6	8
PO_4^{3-}	~+3	~4	8
SO_4^{2-}	~+3	~6	8
ClO_4^-	~+3	~8	8

* Sources: see Appendix

Lewis's formulae for hypervalent species containing oxygen atoms do not involve expansion of the valence shell. For example, he wrote the formula for the sulfate ion as $[\text{S}(\text{O})_4]^{2-}$. Equal sharing of the bond pairs corresponds to a polarity of $\text{S}^{2+}(\text{O}^-)_4$; calculations give about $\text{S}^{3+}(\text{O}^{5/4-})_4$ (Table 1). Formulae involving expansion of the valence shell, e.g., $(\text{O}::)_2\text{S}(\text{O}^-)_2$, are incorrect (Suidan et al., 1995).

Note that restriction of the valence shell to an octet does not affect the valency of the central atom. It limits the covalency to 4, but this can be made up with electrovalency. Thus in $\text{S}^{3+}(\text{F}^{1/2-})_6$ the covalency is 3, the electrovalency is 3, a total of 6 (Nelson, 1997). Likewise in $\text{S}^{3+}(\text{O}^{5/4-})_4$ the covalency is 3, the electrovalency 3, total 6.

Distinguishing between VS and LS resolves the problems discussed by Gillespie & Robinson (1995) in interpreting the results of quantum-mechanical calculations on hypervalent molecules. A molecule like SF_6 can still be said to have twelve bonding electrons (cf. Bader et al., 1984). This means that valence-shell electron-pair repulsion theory (VSEPR), and its successor, valence-shell electron-pair domain theory (Gillespie, 1992; Gillespie & Robinson, 1996), still applies to such molecules, but with "valence shell" changed to "Lewis shell" (cf. Bader et al., 1988).

The above treatment can be extended to transition elements in relation to the 18-electron rule. There are some molecules in which a transition metal atom appears to have more than 18 valence electrons. For example, in $\text{W}(\text{CO})(\text{C}_2\text{H}_2)_3$ the tungsten atom appears to have 20. The above treatment shows that it is possible for a transition metal atom to have more than 18 electrons in LS provided that there are no more than 18 electrons in VS. For $\text{W}(\text{CO})(\text{C}_2\text{H}_2)_3$ this condition is met if the three C_2H_2 molecules contribute no more than 10 electrons to VS. Calculations show that this is the case (Albright et al., 1985). Another example is $(\eta^5\text{-C}_5\text{H}_5)_3\text{ZrCl}$ (see Strittmatter & Bursten, 1991). (I am grateful to Dr. Adam Bridgeman for drawing my attention to these molecules.)

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APPENDIX: SOURCES OF DATA

The charge on an atom in a molecule is not a precisely defined quantity (Mulliken, 1935), and the values obtained by different methods vary widely (Meister & Schwarz, 1994). I have adopted Weinhold's "natural" values (Reed, Weinstock & Weinhold, 1985) as being in about the middle of the range, and scaled other values to these. Thus in the text and Table 1 the value for SF_6 is from Reed & Weinhold (1986), and the values for the oxo-species are from Suidan et al. (1995). The remainder are scaled values, from Cioslowski & Mixon (1993) and Robinson et al. (1997).

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