Perturbation Theory and "Quasi-Lone Pairs" in Main Group Angular and Trigonal Pyramidal Compounds

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Abstract: An analytical LCAO MO perturbation approach has been developed for treating the electronic structure and some properties of octet angular AL_2 and trigonal pyramidal AL_3 compounds where the main group atom A is not of highest oxidation state, A(NHOS), and has a "quasi-lone pair", (QLP). The formation of a QLP has been considered as an orthogonalization problem for the three-orbital four-electron (3o-4e) valence interactions within the A_1 irreducible representation of the AL_m compounds in question. The criteria of a QLP such as localization, sp^q hybridization, and bonding character have been discussed. It has been shown that the chemically and sterically active QLPs always correspond to the $2a_1$ MOs with the nodal structure resulting in s antibonding and p bonding contributions to the A–L bond strengths. For this reason the QLPs may be bonding, nonbonding, or antibonding depending on the relative values of the opposing s and p contributions so that changes of the initial AL_m molecular properties under coordination $L_mA \rightarrow X$ may be different depending on A, L, and the properties themselves. It has been shown that by the proper sp orthogonalization the electronic structure of the mentioned A(NHOS) molecules can be reduced to the 4o-4e bonding which is typical for linear AL_2 and trigonal planar AL_3 molecules where A is of the highest oxidation state, A(HOS), and which has been considered earlier. The energy orders, composition, and nodal structures of the LCAO MOs as well as the effects of substitution of L by L′ on the A–L bond strengths (lengths) have been presented in explicit form and agree with the known experimental and computational data. The developed model permits the fundamental regularities of the electronic structures and properties of the octet AL_2 and AL_3 molecules to be explained and predicted.

Introduction

The "lone pair" represents one of the most fundamental and widely used concepts in chemistry, being invoked to explain a variety of phenomena, for example, the donor ability of Lewis bases such as PR_3 compounds or the shapes of AL_m molecules, where A is not of the highest oxidation state, A(NHOS), through the VSEPR theory.[1] Clearly, then, it is important to realize that the nature of a lone pair is as dependent upon the molecule holding it as are the molecular bonds. Let us define a *pure* lone pair in a compound EL_m as an occupied MO formed from AOs on either the central atom E or ligands L, *only*. Such pure lone pairs, e.g., the oxygen p_π lone pair in water ($1b_1^2$), arise only as a consequence of symmetry and for the most part chemists deal with "quasi"-lone pairs (QLPs), i.e., MOs made up *predominantly* of orbitals located on the central atom or ligands.

Unlike pure lone pairs which are, *by definition*, nonbonding MOs and usually nonhybridized atomic orbitals (p_π or d_π in the A(NHOS) or transition metal Md^n cases, respectively), the QLPs may be of any bonding and hybrid character. Numerous misunderstandings appear in the chemical literature arising from a failure to consider the detailed orbital characteristics of QLPs in particular molecules.[2-4] Hall[2] has recently pointed out flaws in the VSEPR theory[1] based on incorrect assertions about QLPs. Hall's calculations on H_2O[2b] show that "the driving force for the formation of these hybrids is . . . the system's desire to keep the lower energy 2s orbital as fully occupied as possible, i.e., as a lone pair." This conclusion is hardly compatible with the common assumption that in the valence MO configuration of H_2O C_{2v} $1a_1^2 1b_2^2 2a_1^2 1b_1^2$ the highest a_1 orbital, $2a_1$, corresponds to the QLP.[3] Indeed, according to generalized valence bond calculations on H_2O,[5] $1a_1$ is about 82% oxygen 2s. Similarly, ab initio LCAO MO calculations[6] show $1a_1$ practically nonbonding but $2a_1$ almost as strongly bonding as $1b_2$ (the overlap populations are 0.034, 0.202, and 0.331, respectively[6]). The experimental data,[7] especially the vibrational structures of the photoelectron spectra,[7,8] confirm these conclusions. At the same time in F_2O the lowest a_1 valence orbital is strongly bonding (the overlap population is 0.202[6]). The composition, bonding, and directional properties of the a_1 QLPs in various octet AL_3 compounds where there are no pure lone pairs at all are even more complicated (see below).

Current qualitative models assuming the same QLP pattern for a given polyhedron AL_m, either the pure s or some hybrid sp^q orbital,[1,2,9,10] fail to embrace this variety and can lead chemists astray. Quantitative, ab initio LCAO MO and more sophisticated,[4] calculations, on the other hand, do not provide a generalizable set of rules for QLP structure and, in particular, provide no model for predicting substituent effects as we move away from AL_m compounds. Recently we have developed an analytical perturbation LCAO MO approach[11-14] for treating substituent effects on bond lengths (strengths)[11,12] and spin coupling constants[13,14] for the most common geometries such as linear, trigonal planar, tetrahedral,[11,13,14] square, octahedral,[12,14] etc. In this and another[15] papers a similar perturbation treatment of QLPs will be presented which we hope will provide a convenient and consistent model for various QLP effects.

Results and Discussion

Composition and Nodal Structures of the A_1 Valence Orbitals. Table I presents examples of QLPs from several parts of the periodic table and under several symmetries. The common feature of all this variety is that within each A_1 representation there are *three* delocalized valence orbitals

$$\psi_i(ia_1) = c_{i1}\chi_1 + c_{i2}\chi_2 + c_{i3}\chi_3,\ i = 1, 2, 3 \qquad (1)$$

where the lowest MOs ψ_1 and ψ_2 are occupied but ψ_3 is vacant. It is obvious that ψ_1 has *no* nodes, ψ_3 has *two* nodes, and ψ_2 has *one* node, but the problem is to locate this node. The three-orbital, four-electron (3o-4e) problem has been discussed in detail elsewhere[11] but we want to consider its peculiarities for octet AL_2 and AL_3 molecules.

The general (3×3) determinant (1) can be represented as a perturbation of some reduced $(2 \times 2) + (1 \times 1)$ determinantal form. In particular, in our consideration of QLPs we

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Table I. Some Examples of Quasi-Lone Pairs

compd	symmetry	irreducible representation	interacting orbitals		lone pair[a]	
			E	L	orbital	location
H_2O	C_{2v}	A_1	s p_z	$\sigma^{(+)} = (1/\sqrt{2})(\sigma_1 + \sigma_1)$	$\nu s - \mu p_z$	central atom
NH_3	C_{3v}	A_1	s p_z	$\sigma^{(+)} = (1/\sqrt{3})(\sigma_1 + \sigma_2 + \sigma_3)$	$\nu s - \mu p_z$	central atom
$PtCl_4^{2-}$	D_{4h}	A_{1g}	s d_{z^2}	$\sigma^{(+)} = \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$	$\mu s + \nu d_{z^2}$	central atom
PF_5	D_{3h}	A_1	s	$\sigma_{ax}^{(+)} = (1/\sqrt{2})(\sigma_1 + \sigma_2)$ $\sigma_{eq}^{(+)} = (1/\sqrt{3})(\sigma_3 + \sigma_4 + \sigma_5)$	$\sqrt{3/10}(\sigma_1 + \sigma_2) - \sqrt{2/15}(\sigma_3 + \sigma_4 + \sigma_5)$	ligands
IF_7	D_{5h}	A_1	s	$\sigma_{ax}^{(+)} = (1/\sqrt{2})(\sigma_1 + \sigma_2)$ $\sigma_{eq}^{(+)} = (1/\sqrt{5})(\sigma_3 + \sigma_4 + \ldots + \sigma_7)$	$\sqrt{5/14}(\sigma_1 + \sigma_2) - \sqrt{2/35}(\sigma_3 + \sigma_4 + \ldots + \sigma_7)$	ligands

[a] See explanations in the text.

would like to separate the (3 × 3) determinant into a (2 × 2) part which produces a bonding and antibonding pair and a (1 × 1) part representing the pure lone pair (remember that only for symmetry determined lone pairs does this breakup occur naturally). In carrying out the (3 × 3) → (2 × 2) + (1 × 1) reduction, one can start with any reasonable guess about the nature of the lone pair and correct for deficiencies by allowing the (2 × 2) and (1 × 1) determinants to interact via perturbation theory. What we want to demonstrate, however, is that a particular choice for the form of the lone pair will allow us to neglect the (2 × 2) + (1 × 1) interaction yet still retain a rigorous enough model for examining the effects of lone pairs on substituent effects (bond lengths, spin coupling constants, and so on).

Before presenting our general solution, let us first consider two extremes for lone pairs in octet AL_2 and AL_3 molecules. In the first extreme the p_A and $\sigma^{(+)}$ orbitals (see Table I) are close in energy and lie much higher than the s_A one. In the second extreme the s_A and $\sigma^{(+)}$ orbitals are close in energy and lie much lower than the p_A one. The former is represented by H_2O where both experiment[7,8] and ab initio calculations[2b,5,6,17,18] show the QLP to be $1a_1$ and predominantly $2s^2$. The latter is a more idealized case because along the series O → Te and N → Sb the ns_A-np_A energy splittings rapidly decrease, the s_A orbital energies increasing (decreasing in absolute value) much faster than the p_A ones.[25a] For P, which will be of special interest in this and another[15] paper, the 3s-3p splittings is ca. 6 eV.[8,19,20] Nevertheless, PF_3 as well as many other PR_3 and AL_3 compounds are close to the second extreme where the QLP should be $2a_1$ and mainly of p character, which agrees with both experiment[7,8,19,26] and ab initio calculations.[16,18-20,26,27]

In the first case we can start with

$$\psi_3 = f p_z - e\sigma^{(+)} \tag{2}$$

$$\psi_2 = e p_z + f\sigma^{(+)} \tag{3}$$

$$\psi_1 = s \tag{4}$$

$$\epsilon_1(\psi_1) < \epsilon_2(\psi_2) < \epsilon_3(\psi_3) \tag{5}$$

and consider the interaction of $\psi_1 = s$ with ψ_2 and ψ_3 as a perturbation. In the second case we can start with

$$\psi_3 = b s - a\sigma^{(+)} \tag{6}$$

$$\psi_2 = p_z \tag{7}$$

$$\psi_1 = a s + b\sigma^{(+)} \tag{8}$$

$$|\epsilon_2 - \epsilon_3| \ll |\epsilon_2 - \epsilon_1|, a \simeq b \tag{9}$$

and consider the interaction of $\psi_2 = p_z$ with ψ_1 and ψ_3 as a perturbation. Introducing for AL_m the relevant parameters

$$\sqrt{m}x_i^{(s)} = \frac{(s|H|\sigma^{(+)})}{\epsilon_1 - \epsilon_i} > 0, i = 2, 3 \tag{10}$$

$$\sqrt{m}x_i^{(p)} = \left|\frac{(p_z|H|\sigma^{(+)})}{\epsilon_2 - \epsilon_i}\right| > 0, i = 1, 3 \tag{11}$$

we obtain, to first order,

$$\psi_3' = f p_z - e\sigma^{(+)} + \sqrt{m}e x_3^{(s)} s \tag{2'}$$

$$\psi_2' = e p_z + f\sigma^{(+)} - \sqrt{m}f x_2^{(s)} s \tag{3'}$$

$$\psi_1' = s + \sqrt{m}[f^2 x_2^{(s)} + e^2 x_3^{(s)}]\sigma^{(+)} + \sqrt{m}ef[x_2^{(s)} - x_3^{(s)}]p_z \tag{4'}$$

and

$$\psi_3' = b s - a\sigma^{(+)} + \sqrt{m}a x_3^{(p)} p_z \tag{6'}$$

$$\psi_2' = p_z - \sqrt{m}ab[x_1^{(p)} + x_3^{(p)}]s + \sqrt{m}[a^2 x_3^{(p)} - b^2 x_2^{(p)}]\sigma^{(+)} \tag{7'}$$

$$\psi_1' = a s + b\sigma^{(+)} + \sqrt{m}b x_2^{(p)} p_z \tag{8'}$$

both sets possessing the same nodal structures

$$\psi_3' = s + p_z - \sigma^{(+)} \tag{12}$$

$$\psi_2' = -s + p_z + \sigma^{(+)} \tag{13}$$

$$\psi_1' = s + p_z + \sigma^{(+)} \tag{14}$$

i.e., ψ_1' has no nodes, ψ_3' has two nodes, and ψ_2' has one node which corresponds to p_z bonding and s antibonding, in complete agreement with the ab initio calculations on H_2O,[17] NH_3,[21] and other molecules[18] (see below).

From (4′) we can anticipate that in the QLP $1a_1$ the admixture of $\sigma^{(+)}$ should be larger than that of p_z, again in agreement with the ab initio calculations on H_2O.[6,17,18] It is obvious that the lower is s_A the smaller is the difference $x_2^{(s)} - x_3^{(s)} > 0$, so that in the limit

$$x_2^{(s)} = x_3^{(s)} = x_s \tag{15}$$

the lowest $1a_1$ level will not contain the p admixture at all, namely[22]

$$\psi_1' = s + \sqrt{m}x_s\sigma^{(+)} \tag{16}$$

Table II. Changes in Some P-L Bond Lengths (Å) and LPL Valence Angles (deg) on Coordination $L_3P \rightarrow X$

compd	method	ΔR^a	$\Delta\phi^a$	ref	compd	method	ΔR^a	$\Delta\phi^a$	ref
PF_3	ED	(1.570)	(97.8)	*b*	$P(CH_3)_3$	ED	(1.846)	(98.6)	*g*
F_3PO	ED	−0.05	3.5	*c*	$(CH_3)_3PO$	ED	−0.04	7.4	*h*
$F_3P{\cdot}BH_3$	MW	−0.03	2.0	*d*	*cis*-$[(CH_3)_3P]_2PtCl_2$	X-ray	0.02	4.0	*i*
$F_3P{\cdot}B(BF_2)_3$	X-ray	−0.06	3.9	*e*	PPh_3	X-ray	(1.828)	(103.0)	*j*
$(F_3P)_4Pt$	ED	−0.02	1.1	*f*	$(PPh_3)_2Ni(C_2H_4)$	X-ray	0.01	−0.5	*k*
$(F_3P)_4Ni$	ED	−0.01	0.6	*f*	$(PPh_3)_3RuCl_2$	X-ray	0.02	−1.4	*l*

[a] $\Delta R(\phi) = R(\phi)_{L_3PX,av} - R(\phi)_{PL_3}$. The values of $R(\phi)_{PL_3}$ are given in parentheses. [b] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969). [c] T. Moritani, K. Kichitsu, and Y. Morino, *ibid.*, **10**, 344 (1971). [d] R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, **46**, 357 (1967). [e] B. G. DeBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 836 (1969). [f] J. Marriott, J. A. Salthouse, M. J. Ware, and J. M. Freeman, *Chem. Commun.*, 595 (1970). [g] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960). [h] H. K. Wang, *Acta Chem. Scand.*, **19**, 879 (1965). [i] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967). [j] J. J. Daly, *J. Chem. Soc.*, 3799 (1964). [k] B.-T. Cheng, C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Acta Crystallogr., Sect. B*, **27**, 1904 (1971). [l] S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

Indeed, already for H_2S the $SL_{l,\eta}$ spectrum shows practically no sulfur 3p contribution to the $\psi_1(1a_1)$ level.[24]

On the other hand, from (7′) we can anticipate that in the QLP $2a_1$ the admixture of $\sigma^{(+)}$ will be smaller than that of s, so that the QLP $2a_1$ should be a strongly localized p_z or hybrid s-p_z orbital, in complete agreement with experiment[8,25,26] and ab initio calculations,[18] specifically on PL_3 compounds.[16,19,20,26,27] One can show[28] that PF_3 or PCl_3 should have more s character in the QLP $2a_1$ than will PH_3 or $P(CH_3)_3$, again in agreement with the ab initio calculations on these molecules[16,20,27] (see also eq 17′-24). The simplest way of thinking about it is as follows. Let us consider the perturbation of $\sigma_L{}^{(+)}$ by an interaction with the $\underline{\text{lower}}$ s_A and the $\underline{\text{higher}}$ p_A. In such a typical case $\psi(2a_1) = \sigma^{(+)} - c_s s + c_p p$, where $c_s > 0$, $c_p > 0$, therefore $\psi(2a_1)$ has the same nodal structure as (13). If $\sigma^{(+)}$ is closer in energy to p_A (the PH_3 case), then $c_p > c_s$. If, however, $\sigma^{(+)}$ is closer to s_A (the PF_3 case), then $c_s > c_p$.

Because the nodal structures (12)-(14) hold for both extreme cases we can consider them as a general pattern for any octet AL_2 or AL_3 molecules.[25] Certainly, the most important result is the nodal structure (13) showing p_z bonding and s antibonding. A number of consequences result. First, the total s contribution from the occupied MOs $1a_1$ (14) and $2a_1$ (13) to the A-L bonding should be substantially canceled. As the other contributions to the A-L bond ($1b_2$ in AL_2 C_{2v} or le in AL_3 C_{3v}) are of pure p character, the A-L bonds, as a whole, should be mostly of p and only marginally of s character. This result is confirmed by all quantitative calculations on various octet AL_2[2,5,6,17,18] and AL_3[16,18-21,26,27] compounds and naturally combines the molecular orbital[2,9b] and Pauling's valence bond[9a] descriptions.

Second, we can anticipate *different* changes in molecular geometries of the QLP AL_m compounds under their coordination depending on A and L. The various PL_3 compounds are a good example. In the PF_3 case where in the $2a_1$ QLP the *antibonding* s_A-σ_L interaction prevails (cf. also ref 16 and 19) the P-F bonds should typically be *shortened* (strengthened) in $F_3P \rightarrow X$ vs. PF_3. On the other hand, in the PR_3 cases, R = CH_3 or Ph, where in the $2a_1$ QLP the *bonding* p_A-σ_L interaction prevails (cf. also ref 16 and 19) the P-C bonds should typically be *lengthened* (weakened) or, at least, remain unchanged in $R_3P \rightarrow X$ vs. PR_3. This prediction (which eventually follows from the relative energies of σ_L and s_A and p_A[28], see above) is confirmed by experiment as seen from Table II.

Two comments to Table II might be useful. First, the π back-bonding to the PL_3 ligands (on the antibonding 2e MO[16,19,26,27]) should *weaken* the P-L bonds. This weakening must be biggest for PF_3 but, as seen from Table II, it is obviously of secondary importance as compared with the σ donor-acceptor bonding [cf. PF_3 vs. $F_3P{\cdot}BR_3$ vs. $(F_3P)_4M$]. Thus, the observed weakening of the P-C bonds is definitely caused by the σ donor-acceptor rather than π back-bonding interactions. These conclusions agree with the photoelectron spectra[8,26b,f] and computations.[16,19,26,29] Second, the observed dependence ΔR vs. $\Delta\phi$ can be understood in terms of all the current qualitative theories,[1,9,10] with the only exception *cis*$[(CH_3)_3P]_2PtCl_2$ vs. $P(CH_3)_3$. These theories assume the same bonding pattern for coordination $L_3A \rightarrow X$ regardless of A and L, however, and therefore cannot explain the differences between the PF_3 and PR_3 cases. In particular, the VSEPR theory[1] is good for the former but not for the latter. A comprehensive analysis of the above problems (including peculiarities of L_3P^VO and L_3P^VS compounds) will be given elsewhere.[30]

Finally, the relationships (2′)-(8′) permit some seeming contradictions concerning the nature of QLPs to be resolved. Remember that a pure lone pair of the central atom such as $1b_1{}^2$ in H_2O will be, by definition, localized, unhybridized (pure p_π), and nonbonding. A QLP of the central atom should be, by definition, predominantly localized on this atom but the QLP's hybridization and bonding character are not well defined. We saw that the most localized a_1 orbital is $1a_1$ in H_2O but $2a_1$ in PL_3 so that in octet AL_2 and AL_3 molecules both $1a_1$ and $2a_1$ can, in principle, be considered as QLPs though they have quite different hybrid, nodal, and bonding properties (even within the PL_3 series). A chemist is interested, however, in the chemically and sterically *active* QLPs which should, first, have a low ionization potential (IP), and second, be of directional character. Obviously, both conditions lead to $2a_1$. Let us clarify that the $s - p_z$ ($2a_1$) will concentrate the QLP electron density *out* of the AL_m space while the $s + p_z$ ($1a_1$) will concentrate it *in* the AL_m space, as shown in Figures 1c,f and 1b,e, respectively. Further if a pure lone pair is always nonbonding due to perfect localization, a QLP $2a_1$ (13) may be bonding, nonbonding, or antibonding depending on the relative values of the opposing s and p contributions. For this last reason the $2a_1$ (13) can prove to be substantially nonbonding but strongly delocalized, i.e., not a QLP at all. The composition and nodal structure of the $2a_1$ can result in different changes of the initial AL_m molecular properties under coordination $L_mA \rightarrow X$ depending on A, on L (cf. Table II), and on the properties themselves. For instance, the changes in total and s contributions to the A-L bonds, which determine the changes in bond lengths and spin coupling constants, respectively, may be similar or different[11-15,30] (see below).

While comparing the Lewis basicity of various AL_2 and AL_3 molecules we have to bear in mind the very delicate balance between IP and localization and directional properties of the $2a_1$ QLP. Typically, if we gain in the first we lose in the second and vice versa. Therefore, there are not, and cannot be, simple interrelations between IP and the Lewis basicity of the octet AL_2 and AL_3 molecules. For instance, the donor ability of many bulky phosphorus ligands are determined by steric rather than electronic factors.[31] Additional complications are caused by the nature of the Lewis acids such as H^+, BL_3, transition metal fragments ML_n, etc. We will consider the above problems in detail elsewhere.[30]

The QLP as a Solution of the Diagonalization Problem. As we start to consider the general model, remember that a pure lone pair exists *if* and *only if* we have two identical orbitals, say, $\chi_1 = \chi_3$ [see (1)] in three-atom compounds such as XeF_2 or H_2CCHCH_2 (σ or π three-center 3o-4e bonding, respectively). In all χ_j are different, at best a QLP can be formed which will be closer to a pure lone pair the closer χ_1 will be to χ_3. The procedure we will follow will be to form two orthonormalized linear combinations, ϕ_1 and ϕ_2, of the orbitals χ_1 and χ_3

$$\phi_1 = \mu\chi_1 + \nu\chi_3 \tag{17}$$

$$\phi_2 = \nu\chi_1 - \mu\chi_3 \tag{18}$$

such that

$$(\phi_2|\chi_2\rangle = 0 \tag{19}$$

Here,

$$\mu^2 + \nu^2 = 1 \tag{20}$$

$$\frac{\mu}{\nu} = \frac{(\chi_1|\chi_2\rangle}{(\chi_3|\chi_2\rangle} \tag{21}$$

To emphasize again what was stated at the beginning of the paragraph, although ϕ_2 is orthogonal to χ_2, the interaction between the two orbitals, $(\phi_2|H|\chi_2\rangle$, will not equal zero unless χ_1 and χ_3 are identical, in which case ϕ_2 is a pure lone pair.

In transition-metal complexes ML_m ns and $(n - 1)$d orbitals are close in energy (and overlapping) so that the sd_{z^2} metal hybrid lone pairs, $\mu s + \nu d_{z^2}$ in d^8 ML_4D_{4h}[12] or $\nu s - \mu d_{z^2}$ in $ML_2D_{\infty h}$[11] (see Table I) are rather good approximations. Similarly, the group ligand orbitals, σ_{ax} and σ_{eq}, in trigonal AL_5D_{3h} are pentagonal AL_7D_{5h} bipyramidal complexes are almost degenerate,[32] so the relevant ligand lone pairs (see Table I) are very close to reality.[12,32] Thus, the metal ns(n − 1)d hybridization or ligand orbital combinations within a given irreducible representation are usually well justified.

Obviously, for main group sp hybridization, where the ns_A–np_A splitting is large, the QLP character of ϕ_2 requires special examination. Let us consider in detail the octet AL_2 and AL_3 cases (groups 6 and 5). For AL_2 and AL_3 we have the MOs (1′) which are obtained from (1)

$$\psi_i(ia_1) = c_{is}s + c_{i\sigma}\sigma^{(+)} + c_{ip}p_z \tag{1′}$$

for $\chi_1 = s$, $\chi_3 = p_z$, and $\chi_2 = \sigma^{(+)} = (1/\sqrt{2})(\sigma_1 + \sigma_2)$ or $(1/\sqrt{3})(\sigma_1 + \sigma_2 + \sigma_3)$ (see Table I). The (2 × 2) determinant will involve $\phi_1 = \mu s + \nu p_z$ and $\sigma^{(+)}$ combining to form a bonding $\psi_1(1a_1)$ and antibonding $\psi_3(3a_1)$ while $\phi_2 = \nu s - \mu p_z$ becomes the nonbonding MO $\psi_{\bar{1}}(2a_1)$.

$$\phi_1 = \mu s + \nu p_z \tag{17′}$$

$$\phi_2 = \nu s - \mu p_z \tag{18′}$$

$$\left\langle\phi_2 \middle| \frac{1}{\sqrt{2}}(\sigma_1 + \sigma_2)\right\rangle = 0 \quad \text{or} \left\langle\phi_2 \middle| \frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3)\right\rangle = 0 \tag{19′}$$

$$\frac{\mu}{\nu} = \frac{(p_z|\sigma_1\rangle}{(s|\sigma_1\rangle} = \cos\theta_1 \frac{S_{p\sigma}}{S_s} \tag{21′}$$

where the angles θ_1 for AL_m are shown in Figures 1a,d. For AL_2

$$\psi_1 = a(\mu s + \nu p_z) + b\frac{1}{\sqrt{2}}(\sigma_1 + \sigma_2) \tag{22}$$

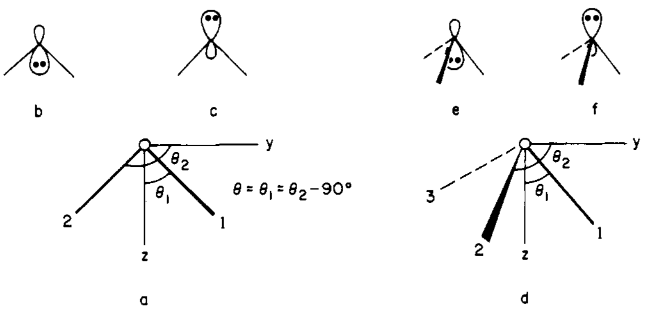

Figure 1. Geometry, enumeration of ligands, and directions of the coordinate axes and $(s + p_z)$ and $(s - p_z)$ hybrid orbitals for angular AL_2 [(a), (b), (c)] and trigonal pyramidal AL_3 [(d), (e), (f)] compounds.

$$\psi_{\bar{1}} = \phi_2 = \nu s - \mu p_z \tag{23}$$

$$\psi_3 = b(\mu s + \nu p_z) - a\frac{1}{\sqrt{2}}(\sigma_1 + \sigma_2) \tag{24}$$

$$a^2 + b^2 = 1 \tag{25}$$

For AL_3

$$\psi_1 = a(\mu s + \nu p_z) + b\frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3) \tag{26}$$

$$\psi_3 = b(\mu s + \nu p_z) - a\frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3) \tag{27}$$

To complete the σ MO model we need to add in the orbitals of the other irreducible representations, p_y and $\sigma^{(-)} = (1/\sqrt{2})(\sigma_1 - \sigma_2)$ for B_2 in AL_2C_{2v} or p_y and $\sigma^{(-)} = (1/\sqrt{6})(2\sigma_1 - \sigma_2 - \sigma_3)$ for E in AL_3C_{3v},[33] where two electrons will occupy the bonding MOs ψ_2 (28) and (30) leaving the antibonding ψ_4 (29) and (31) vacant

$$\psi_2(1b_2) = ep_y + f\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2) \tag{28}$$

$$\psi_4(2b_2) = fp_y - e\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2) \tag{29}$$

or

$$\psi_2(1e) = ep_y + f\frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \tag{30}$$

$$\psi_4(2e) = fp_y - e\frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \tag{31}$$

$$e^2 + f^2 = 1 \tag{32}$$

Verification of the Model. From the general relationship[34]

$$\sum_i^{\text{occ}} c_{i\chi}c_{iL} = -\sum_j^{\text{unocc}} c_{j\chi}c_{jL} \tag{33}$$

and from the fact that the unoccupied antibonding MOs ψ_3 [relationships (12), (24), and (27)] always have the same nodal structure (two nodes) we can conclude that the set (22)–(27) will be good enough to reproduce both s and p contributions to the A–L bond overlap (bond strength). In other words, although $\psi_{\bar{1}}$ does not contribute at all, ψ_1 is sufficiently complete and flexible due to the variable coefficients a, b, μ and ν. Furthermore, not only $\psi_1(1a_1)$ and $\psi_3(3a_1)$ but also $\psi_{\bar{1}}(2a_1)$ have the correct nodal structures [cf. (12)–(14)].

Remember two discussed aspects of the QLP problem, localization and hybridization. If some ψ'_i (1′) can be considered as the central atom QLP, then the condition of QLP localization will be $c_{i\sigma}^2 \ll c_{is}^2 + c_{ip}^2$. With respect to hybridization, if $c_{is} \gg c_{ip}$ or $c_{is} \ll c_{ip}$, one can talk about *predominantly* lone ns^2 or np^2 pair, respectively. Within the set (22)–(27) this QLP hybridization can be expressed in terms of the coefficients a,

b, μ and ν. Though μ and ν can formally be found from the orthonormalization conditions (20)–(21), their values will eventually depend on the s_A–p_A energy splitting and the relative energies of $\sigma^{(+)}$ vs. s_A and p_A. Thus, along the series H_2O–TeF_2 or NH_3–SbF_3 we will encounter a variety of the extreme and intermediate cases[30] (see above).

As a test of the model we can consider the ordering of energy levels in AL_m molecules in question. From (22)–(32) we obtain the electronic configurations $\psi_1{}^2(1a_1)\psi_2{}^2(1b_2)\psi_{\bar{1}}{}^2(2a_1)\psi_{\bar{2}}{}^2(1b_1)$ for AL_2 and $\psi_1{}^2(1a_1)\psi_2{}^4(1e)\psi_{\bar{1}}{}^2(2a_1)$ for AL_3, in complete agreement with the photoelectron spectra[7,8,19,25,26] and quantitative computations[6,17–21,26,27] on these molecules. Moreover, we can foresee the above discussed peculiarities of the MO compositions, for instance, that in H_2O $\psi_1(1a_1)$ is mainly of s character ($\mu > \nu$, $a > b$) or that in AL_3, A = N, P, As, Sb, the HOMOs $2a_1$[25] are substantially of p character,[8,19,26] as for $\psi_{\bar{1}}$ (23) we have again $\mu > \nu$. Let us clarify that in our model, because of the nonbonding character of $\psi_{\bar{1}}$, the main difference between the discussed extreme cases, the H_2O and PF_3 ones, is in the a and b coefficients, namely, $a \gg b$ and $a \simeq b$, respectively.

Application to Substituent Effects on Bond Lengths. Now we are ready to attack substitution effects on bond lengths in the AL_m compounds in question. From (22)–(32) we see that the substitution of $L_{(1)}$ by L′ will perturb *four* orbitals (ψ_1, ψ_2, ψ_3, and ψ_4) with *four* electrons and, to first-order perturbation theory, can be reduced to the 4o–4e case considered earlier.[11] Introducing again the difference in the ligand σ orbital energies, $\delta\alpha'$ (34), as a perturbation

$$\delta\alpha' = \langle\sigma_{L'}|H|\sigma_{L'}\rangle - \langle\sigma_L|H|\sigma_L\rangle \qquad (34)$$

we obtain for the change in bond overlap population, N(A–L), in angular ALL′ (see Figure 1a)

$$\frac{\delta N(\text{A–L})}{\delta\alpha'} = -\frac{ab\mu}{2\sqrt{2}}\left[\left(\frac{f^2}{E_{23}} - \frac{e^2}{E_{14}}\right) - \frac{b^2 - a^2}{E_{13}}\right] S_s - \frac{ab\nu\cos\theta}{2\sqrt{2}}\left[\left(\frac{f^2}{E_{23}} - \frac{e^2}{E_{14}}\right) - \frac{b^2 - a^2}{E_{13}}\right] S_{p\sigma} + \frac{ef\sin\theta}{2\sqrt{2}}\left[\frac{f^2 - e^2}{E_{24}} - \left(\frac{b^2}{E_{14}} - \frac{a^2}{E_{23}}\right)\right] S_{p\sigma} \qquad (35)$$

where $S_s = \langle s|\sigma_1\rangle$, $S_{p\sigma} = \langle p_z|\sigma_1\rangle/\cos\theta = \langle p_y|\sigma_1\rangle/\sin\theta$

$$E_{ij} = \epsilon_j(\psi_j) - \epsilon_i(\psi_i) > 0 \qquad (36)$$

For trigonal pyramidal AL_2L' we have (see Figure 1d)

$$\frac{\delta N(\text{A–L})}{\delta\alpha'} = -\frac{ab\mu}{3\sqrt{3}}\left[\left(\frac{f^2}{E_{23}} - \frac{e^2}{E_{14}}\right) - \frac{b^2 - a^2}{E_{13}}\right] S_s - \frac{ab\nu\cos\theta_1}{3\sqrt{3}}\left[\left(\frac{f^2}{E_{23}} - \frac{e^2}{E_{14}}\right) - \frac{b^2 - a^2}{E_{13}}\right] S_{p\sigma} - \frac{2ef\cos\theta_2}{3\sqrt{6}}\left[\frac{f^2 - e^2}{E_{24}} - \left(\frac{b^2}{E_{14}} - \frac{a^2}{E_{23}}\right)\right] S_{p\sigma} \qquad (37)$$

which is similar to (35).

The expressions in square brackets in (35) and (37) are exactly the same as those found earlier for linear ALL′ and trigonal planar AL_2L' where A is of the highest oxidation state, A(HOS) [cf. the relationships (15), (35), and (37) in ref 11]. In the A(HOS) case we *always* have[11]

$$\frac{\delta N(\text{A–L})}{\delta\alpha'} = -C_sS_s + C_{p\sigma}S_{p\sigma},\ C_s > 0,\ C_{p\sigma} > 0 \qquad (38)$$

where the negative s contribution is typically (but not always!) larger in absolute value than the positive p contribution. Remember that in the A(HOS) cases there is only one p contribution.[11]

In the present A(NHOS) cases the analysis of the s and p contributions, their signs and relative values, is more complicated. The fact is that the A(HOS) atoms are rather electropositive beginning elements such as Hg, Be, B, etc. but the A(NHOS) atoms are rather electronegative ending elements such as O, N, etc. In both cases we have[11]

$$E_{14} > E_{13} > E_{23},\ E_{14} > E_{24} > E_{23} \qquad (39)$$

However, if in the A(HOS) case we always have[34]

$$f > e,\ f^2 - e^2 > b^2 - a^2 \gtrless 0,\ ef < ab \qquad (40)$$

(from (39)–(40) one can easily obtain (38)[11]); in the A(NHOS) case the corresponding interrelations among the coefficients a, b, e, and f will depend on the nature of A and L.

For the most electronegative ligands L, for instance, in PF_3, we typically have the same relationships (40), but for the most electropositive L and most electronegative A, for instance, in H_2O, NH_3, and PH_3, we typically have

$$f \leq e,\ b \ll a,\ a^2 - b^2 \gg e^2 - f^2 \gtrless 0,\ ef > ab \qquad (41)$$

One can show,[28] however, that the relationships (40) and (41) usually result in the same signs of the square bracket expressions in (35) and (37) so that we have two *opposite* p contributions, negative from p_z and positive from p_y.[35] Because the latter is typically bigger in absolute value[28] the expression (38) remains typically valid for the A(NHOS) cases in question, too. Thus, we come to the conclusion that for a better donor substituent L′ ($\delta\alpha' > 0$) the s contribution to N(A–L) will be *negative* but the p one will be *positive* (and vice versa for a better acceptor L′), justifying, analytically, Bent's rules[10] for these A(NHOS) compounds in the same way as for the A(HOS) compounds.[11] The relative values of both the s and p contributions in the A(NHOS) cases will be smaller because the s one is multiplied by $\mu < 1$ and the p one has opposing p_z and p_y terms.

We have found[11] that in planar trigonal and tetrahedral compounds $AL_{m-k}L_k'$, m = 3 or 4, $k = 0 - m$, changes in the s, p, and total contributions to $\delta N(\text{A–L})/\delta\alpha'$ should be monotonic (additive, to first order) as k increases. Obviously, the same holds for trigonal pyramidal compounds $AL_{3-k}L_k'$. Two examples of the bond-length changes confirming our model conclusions are the O–F bond length increase from 1.405 to 1.442 Å[36] from OF_2 to HOF and the P–F bond lengths along the series PF_2L', L′ = F, NH_2, PF_2, PH_2, and H (1.570, 1.581, 1.587, 1.587, and 1.582, respectively[36]). Other examples can be found in recent reviews.[36,37]

Conclusion

The perturbation model gives a qualitative picture of various aspects of the electronic structures of octet AL_2 and AL_3 molecules which is simple, more general, and more reliable than any current qualitative model. We have developed a simple orthogonalization scheme that allows us to consider lone pairs in the perturbation manner and applied the model to bond-length changes upon substitution. It was shown that in many cases A(NHOS)L_m compounds will behave the same under substitution as do A(HOS)L_m compounds, in following Bent's rules, for example. An equally important conclusion, however, is that substituent effects in A(NHOS)L_m compounds depend upon the details of the s and p hybridization on A so that we can anticipate more varied substitution effects.[30] The regularities of spin coupling constants in some A(NHOS)$L_{m-k}L_k'$ compounds, interpreted on the basis of our model in another paper,[15] will provide a good example of such variety.

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