

- (23) A. Hudson and G. R. Luckhurst, *Mol. Phys.*, **13**, 409 (1967).  
 (24) M. Plato, to be submitted for publication.  
 (25) J. H. Freed, *J. Chem. Phys.*, **43**, 2312 (1965).  
 (26) J. Brickmann and G. Kothe, *J. Chem. Phys.*, **59**, 2807 (1973).  
 (27) R. W. Kreilick, *Mol. Phys.*, **14**, 495 (1968); P. W. Kopf and R. W. Kreilick,

- J. Am. Chem. Soc.*, **91**, 6569 (1969).  
 (28) G. R. Luckhurst, *Mol. Phys.*, **11**, 205 (1966); K. Mukai, T. Kamata, T. Tamaki, and K. Ishizu, *Bull. Chem. Soc. Jpn.*, **49**, 3376 (1976).  
 (29) K. Scheffler and H. B. Stegmann, "Elektronenspinresonanz", Springer-Verlag, Berlin, 1970, p 339 ff, and references cited therein.

## Perturbation Theory, 3-Orbital-4-Electron and 4-Orbital-4-Electron Bonding, and the Inductive Effect in Tetrahedral Compounds

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**Abstract:** The 3-center-3-orbital-4-electron (3c-3o-4e) and 3-center-4-orbital-4-electron (3c-4o-4e) bonding in the linear molecules (fragments) L'-E-L have been considered by first-order perturbation theory (E is a transition metal M or main group element A atom). The difference in ligand orbital energies  $\delta\alpha' = \alpha(L') - \alpha(L)$  was taken as a perturbation when in the initial symmetric L-E-L molecule a ligand L was substituted by a ligand L'. It was shown that in the 4o-4e case the s (or  $sd_\sigma$ ) and p contribution to changes in the E-L bond overlap population,  $\delta N(E-L)/\delta\alpha'$ , are always of the opposite signs, the s (or  $sd_\sigma$ ) one negative and the p one positive. As the former contribution is usually larger in absolute value than the latter one, for  $\delta\alpha' > 0$  (L' is a better donor than L) the E-L bond will be weakened as compared with that in the initial symmetric L-E-L species. This result was generalized for 4o-4e bonding embracing any number of centers (ligands) which makes it applicable to many complexes, and in particular to tetrahedral  $AL_{4-k}L'_k$  and planar trigonal  $AL_{3-k}L'_k$ . It was proved that the first-order effects in  $AL_{m-k}L'_k$  are additive, which explains the nature and main regularities of the inductive effect and the mutual influence of ligands (MIL) in compounds in question. In particular, the dependence of the A-L bond strength on the number and the electronegativity of L' as well as Bent's rules concerning the central atom rehybridization has been represented in explicit form. It was shown that in the orbitally deficient 3o-4e case there is only a negative contribution to the E-L bond overlap population, so that for a better donor L' the E-L bond will always be weakened and much more than in the 4o-4e case. This weakening must take place regardless of the nature of the central atom orbital (s, p, or d) or the type of bonding ( $\sigma$  or  $\pi$ ). This result was also generalized for many-center cases, which is especially important for some hypervalent complexes of the  $AL_m$  type ( $m = 5-7$ ). The nodal structures of the canonical MOs for all these cases were obtained permitting a visual explanation of the MIL and, in particular, the trans influence. The results obtained agree with the experimental and computational data and permit a number of predictions to be made.

### Introduction

One of the most important questions in which a chemist is interested is how the E-L bonds are changed in substituted derivatives  $EL_{m-k}L'_k$  as compared with the initial compound  $EL_m$ . From this point of view it is useful to divide all the polyhedra  $EL_m$  into two groups depending on whether or not all the ligands L are geometrically equivalent with respect to the substituent L'. The first group includes, for instance, the linear L'-E-L, planar trigonal  $EL_2L'$ , and tetrahedral  $EL_3L'$  molecules; the second includes, for instance, square  $EL_3L'$ , trigonal bipyramidal  $EL_4L'$ , octahedral  $EL_5L'$ , and pentagonal bipyramidal  $EL_6L'$  compounds. In the course of our work to develop the perturbation MIL theory for all types of polyhedra<sup>2,3</sup> we found that the first group is not only simpler to consider but can be combined on the basis of 4o-4e bonding. On the other hand, we found that the orbitally deficient 3o-4e bonding represents the universal basis for a great variety of hypervalent molecules, from  $XeF_2$  to  $IF_7$ .

It should be added that the linear molecules L'-E-L have been theoretically studied mainly for the symmetric case  $L' = L^4$  but until now there has been no analytical consideration of the unsymmetrical case  $L' \neq L$  (see the last section of this work). Besides the linear case, it is even more interesting to consider general properties of the 4o-4e and 3o-4e bonding to establish those which do not depend on the number of centers (ligands). This can shed light on the nature of the trans influence in coordination compounds  $EL_{m-1}L'$  where the largest changes (as compared with  $EL_m$ ) take place within the linear

fragment L'-E-L.<sup>5</sup> Finally, as the effects of substitution in polyhedra of the first group (due to their isotropy) can be reduced to manifestations of the inductive effect, especially well studied for tetrahedral molecules  $AL_{4-k}L'_k$ , we can understand its nature along the same lines.

### Formulation of the Objective

The purpose of the present work is to develop the first-order perturbation theory of the 4o-4e and 3o-4e bonding for any number of centers and on this basis to consider the effects of substitution (the inductive effect) in linear, planar trigonal, and tetrahedral molecules, as well as possible applications of this theory to some polyhedra of the second group (the comprehensive perturbation MIL theory of these polyhedra will be given in the subsequent paper<sup>3</sup>).

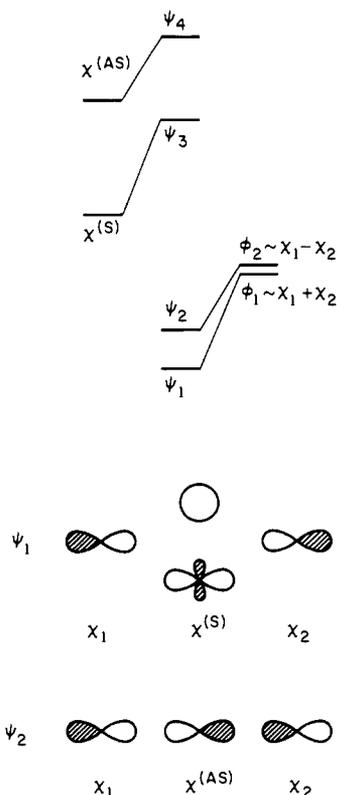
As a perturbation we shall use the difference in ligand orbital energies, i.e., diagonal matrix elements (Coulomb integrals).

$$\langle \chi_{L'} | H | \chi_{L'} \rangle - \langle \chi_L | H | \chi_L \rangle = \delta\alpha' \quad (1)$$

Our criterion for the E-L bond strength is the overlap population  $N(E-L)$  in the form

$$N(E-L) = \sum_i^{\text{occ}} \sum_m c_{im} c_{iL} S_{mL} \quad (2)$$

Here  $c_{im}$  and  $c_{iL}$  stand for the coefficients in the canonical MOs,  $\psi_i$ .



**Figure 1.** The 4o-4e case: the formation of the  $\psi_1$  and  $\psi_2$   $\sigma$  MOs and MO diagram. See explanations in the text.

$$\psi_i = \sum_m c_{im} \chi_m + \sum_L c_{iL} \chi_L \quad (3)$$

belonging to a given irreducible representation. The  $\psi_i$  are constituted of the relevant AOs  $\chi_m$  of the central atom E and ligand orbitals  $\chi_L$  (one per ligand), with overlap integrals  $S_{mL} = \langle \chi_m | \chi_L \rangle$ . All the perturbation formulas may be found in ref 3.

It should be noted that we neglect the perturbations in resonance integrals  $\delta\beta'$  as these are distinctly smaller than  $\delta\alpha'$  ( $\delta\beta' \approx S\delta\alpha'$ ). By similar reasoning we also neglect overlap integrals in the normalizing conditions, though we use these integrals in the criterion of the bond overlap population (cf. ref 2). Finally, it should be mentioned that the perturbation MO theory widely used in organic chemistry<sup>10</sup> has been developed only for  $\pi$  electron conjugated systems where every atom has only one valence orbital.

## Results and Discussion

**4o-4e Bonding. Three-Center Case.** Let us begin with a three-atom linear molecule  $L_{(1)}-E-L_{(2)}$  where equivalent  $E-L_{(1)}$  and  $E-L_{(2)}$  bonds are ordinary two-center two-electron  $\sigma$  bonds. In terms of canonical MOs this means that the central atom E has two valence orbitals,  $\chi^{(S)}$  and  $\chi^{(AS)}$ , which interact with the symmetric  $\varphi_1 \sim \chi_1 + \chi_2$  and antisymmetric  $\varphi_2 \sim \chi_1 - \chi_2$  group ligand orbitals, respectively.<sup>4b</sup> Neglecting all overlap integrals, we obtain the following orthonormalized ( $a^2 + b^2 = e^2 + f^2 = 1$ ) MOs (Figure 1):

$$\psi_1 = a\chi^{(S)} + b \frac{1}{\sqrt{2}} (\chi_1 + \chi_2) \quad (4)$$

$$\psi_2 = e\chi^{(AS)} + f \frac{1}{\sqrt{2}} (\chi_1 - \chi_2) \quad (5)$$

$$\psi_3 = b\chi^{(S)} - a \frac{1}{\sqrt{2}} (\chi_1 + \chi_2) \quad (6)$$

$$\psi_4 = f\chi^{(AS)} - e \frac{1}{\sqrt{2}} (\chi_1 - \chi_2) \quad (7)$$

where the two lower MOs  $\psi_1$  and  $\psi_2$  are filled,  $\chi^{(AS)}$  is an orbital of the  $p_\sigma$  type, and  $\chi^{(S)}$  may be some hybrid orbital of the  $sd_\sigma$  type.<sup>11</sup>

If we replace the ligand  $L_{(1)}$  by  $L'$ , we shall obtain the MOs

$$\psi_i' = a_i' \chi^{(S)} + e_i' \chi^{(AS)} + b_i' \chi_1' + f_i' \chi_2, \quad i = 1, 2, 3, 4 \quad (8.i)$$

where the coefficients  $a_i', e_i', \dots$ , are defined by some variation procedure. The MOs (8.i) cannot be reduced to the MOs (4)-(7) owing to the orthonormalization constraints. Actually, if we form the orthonormal combinations

$$\varphi_1 = \mu \chi_1' + \nu \chi_2 \quad (9)$$

$$\varphi_2 = \nu \chi_1' - \mu \chi_2 \quad (10)$$

then the orthogonalization requirement

$$\langle \varphi_1 | \chi^{(AS)} \rangle = 0 \quad (11)$$

results in

$$\frac{\mu}{\nu} = \frac{\langle -\chi_2 | \chi^{(AS)} \rangle}{\langle \chi_1' | \chi^{(AS)} \rangle} \equiv \frac{S_{(AS)}}{S'_{(AS)}} \quad (12)$$

but the orthogonalization requirement

$$\langle \varphi_2 | \chi^{(S)} \rangle = 0 \quad (13)$$

gives

$$\frac{\mu}{\nu} = \frac{\langle \chi_1' | \chi^{(S)} \rangle}{\langle \chi_2 | \chi^{(S)} \rangle} \equiv \frac{S'_{(S)}}{S_{(S)}} \quad (14)$$

Comparing (12) with (14), we see that they can be compatible only if  $L' = L$ . For  $L' \neq L$  where  $\chi_1'$  overlaps better than  $\chi_2$  ( $S' > S$ ) the  $\chi^{(S)}$  contribution will decrease the overlap population  $N(E-L)$  but the  $\chi^{(AS)}$  contribution will increase  $N(E-L)$ . This point is important for the further discussion.

Let us try to simulate the MO set (8.i) by perturbation of the initial MO set (4)-(7). To first order we obtain for changes in the overlap population

$$\frac{\delta N(E-L)}{\delta \alpha'} = -\frac{ab}{2\sqrt{2}} \left[ \left( \frac{f^2}{E_{23}} - \frac{e^2}{E_{14}} \right) - \frac{b^2 - a^2}{E_{13}} \right] S_{(S)} + \frac{ef}{2\sqrt{2}} \left[ \frac{f^2 - e^2}{E_{24}} - \left( \frac{b^2}{E_{14}} - \frac{a^2}{E_{23}} \right) \right] S_{(AS)} \quad (15)$$

From (4)-(7), (A1)-(A12) (see Appendix I), and Figure 1 we obtain the following relationships:

$$f^2 - e^2 > 0, \quad f^2 - e^2 > b^2 - a^2 \geq 0, \quad ef < ab, \quad |ef(f^2 - e^2)| \approx |ab(b^2 - a^2)| \quad (16)$$

$$E_{14} > E_{13} > E_{23}, \quad E_{14} > E_{24} > E_{23} \quad (17)$$

From the inequalities (16)-(17) we immediately obtain

$$\frac{f^2}{E_{23}} - \frac{e^2}{E_{14}} > \frac{f^2 - e^2}{E_{23}} > \frac{f^2 - e^2}{E_{13}} > \frac{b^2 - a^2}{E_{13}} \quad (18)$$

$$\frac{f^2 - e^2}{E_{24}} > \frac{f^2 - e^2}{E_{14}} > \frac{b^2 - a^2}{E_{14}} > \frac{b^2}{E_{14}} - \frac{a^2}{E_{23}} \quad (19)$$

so that we can conclude that  $\chi^{(S)}$  and  $\chi^{(AS)}$  contributions to  $\delta N(E-L)/\delta \alpha'$  (15) are of opposite sign, the  $\chi^{(S)}$  one negative but the  $\chi^{(AS)}$  one positive. Further, from (16)-(17) we have

$$\frac{f^2}{E_{23}} - \frac{e^2}{E_{14}} > \frac{f^2 - e^2}{E_{23}} > \frac{f^2 - e^2}{E_{24}} \quad (20)$$

$$\frac{b^2}{E_{14}} - \frac{a^2}{E_{23}} < \frac{b^2 - a^2}{E_{14}} < \frac{b^2 - a^2}{E_{13}} \quad (21)$$

so that the expression (in square brackets) before  $S_{(S)}$  can be, in principle, either larger or smaller than that before  $S_{(AS)}$ . But, taking into account that the main term in (15) is  $-f^2/E_{23}$

( $f^2$  is the largest coefficient and  $E_{23}$  is the smallest excitation energy which for  $EL_2 D_{\infty h}$  compounds corresponds to the  $\sigma_u \rightarrow 2\sigma_g^*$  transition), we found that typically<sup>14</sup>

$$\left(\frac{f^2}{E_{23}} - \frac{e^2}{E_{14}}\right) - \frac{b^2 - a^2}{E_{13}} > \frac{f^2 - e^2}{E_{24}} - \left(\frac{b^2}{E_{14}} - \frac{a^2}{E_{23}}\right) \quad (22)$$

If we add a typical inequality<sup>15</sup>

$$S_{(S)} > S_{(AS)} \quad (23)$$

we come to the conclusion that the  $\chi^{(S)}$  contribution will usually be larger in absolute value than the  $\chi^{(AS)}$  one, so the E-L bond, as a rule (but not always!), is weakened as compared with L-E-L. It is obvious that if L' is a poorer donor ligand than L ( $\delta\alpha' < 0$ ) the E-L bond will be strengthened.

One can easily obtain the nodal structure of the MOs (8.i) perturbing the initial MO set (4)-(7). To first order the coefficients  $e_1'$  and  $a_2'$  will be

$$\frac{e_1'}{\delta\alpha'} = \frac{bef}{2} \left(\frac{1}{E_{14}} - \frac{1}{E_{12}}\right) < 0 \quad (24)$$

$$\frac{a_2'}{\delta\alpha'} = \frac{abf}{2} \left(\frac{1}{E_{12}} + \frac{1}{E_{23}}\right) > 0 \quad (25)$$

which for  $\delta\alpha > 0$  corresponds to the nodal structures

$$\psi_1' = \chi^{(S)} - \delta\chi^{(AS)} + \chi_1 + \chi_2 \quad (26)$$

$$\psi_2' = \delta\chi^{(S)} + \chi^{(AS)} + \chi_1 - \chi_2 \quad (27)$$

The admixture of  $\delta\chi^{(S)}$  results in a node between the E and L atoms (weakens the E-L bond), but the admixture of  $\delta\chi^{(AS)}$  reinforces the wave function between these atoms (strengthens the E-L bond).<sup>16</sup> We see again how the  $\chi^{(S)}$  and  $\chi^{(AS)}$  orbitals contribute in opposing directions to the E-L bond strength.

The results obtained are confirmed by much experimental data from which we have chosen only a few examples concerning some linear L'-Hg-L molecules (Table I).

As in the next section we shall discuss general properties of 4o-4e bonding, now we shall give only two consequences of our model.

(1) Along the series L'-E-L where E and L' (L) are given and L' is a better donor than L the weakening of the E-L bond (the strengthening of the E-L' bond) will be larger the more electronegative is L (electropositive is the ligand L').

This conclusion follows from (15) where the right-hand side is the same for any ligand L' as it is defined by the coefficients and energies of the unperturbed MOs of the parent L-E-L molecule (or for the influence of L on the parent L'-E-L' molecule). This model prediction is confirmed by the series of  $H_3C-Hg-X$  for  $X = Cl, Br$ , and  $I$  and  $R-Hg-Br$  for  $R = CH_3$  and  $C_6H_5$  (see Table I).

(2) In main group element and post-transition-metal  $d^{10}$  compounds a weakening of the E-L bond (L is a more electronegative ligand) will be less than that in transition metal  $d^x$  ( $0 \leq x < 10$ ) compounds. Moreover, for some L's which are close in electronegativity to L' there may even be some strengthening of the E-L bond.<sup>55</sup>

This conclusion follows from (15) and (22) because in main-group element and post-transition-metal  $d^{10}$  compounds the  $np$  contribution to bonding is comparable to the  $ns$  one (i.e.,  $f \simeq b$ ), while in transition metal complexes the  $np$  contribution is much less than the  $ns$  and  $(n-1)d$  ones (i.e.,  $f \gg b$ ). Thus, in the former case the difference between the  $\chi^{(S)}$  and  $\chi^{(AS)}$  contributions has to be smaller in absolute value than that in the latter case. Actually, as seen from Table I, such strong  $\sigma$  donors as  $CH_3$  and  $C_6H_5$  cause a rather small (if any) weakening of the Hg-L bonds as compared with that in transition metal complexes where this trans weakening proves to be several times greater.<sup>3,6-9</sup>

Certainly, the analysis of such fine effects as a possible

Table I. Bond Lengths in Some Linear Vapor L'-Hg-L Compounds

compd	distance, Å		method	ref
	Hg-L'	Hg-L		
$H_3C-Hg-CH_3$	2.083 (C)		ED	a
Cl-Hg-Cl		2.252 (Cl)	ED	b
		2.34 (Cl)	ED	c
		< 2.415 (Br)	X-ray <sup>d</sup>	e
Br-Hg-Br		2.44 (Br)	ED	c
		< 2.62 (I)	X-ray <sup>d</sup>	f
I-Hg-I		2.61 (I)	ED	c
$H_3C-Hg-Cl$	1.99 (C)	2.282 (Cl)	MW	g
$H_3C-Hg-Br$	2.074 (C)	2.406 (Br)	MW	g
$H_3C-Hg-I$	2.087 (C)	2.528 (I)	MW	h
$H_5C_6-Hg-Br$	2.069 (C)	2.437 (Br)	ED	i
$H_5C_6-Hg-C_6H_5$	2.093 (C)		ED	j

<sup>a</sup> K. Kashiwabara, S. Konaka, T. Iijima, and M. Kimura, *Bull. Chem. Soc. Jpn.*, **47**, 407 (1973). <sup>b</sup> K. Kashiwabara, S. Konaka, and M. Kimura, *ibid.*, **46**, 410 (1973). <sup>c</sup> A. H. Gregg, G. H. Hampson, G. I. Jankins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937). <sup>d</sup> The only experimental data on  $HgBr_2$  and  $HgI_2$  in the vapor phase <sup>c</sup> were obtained 40 years ago and can hardly be reliable. In particular, the new measurements on  $HgCl_2$  by the same method (ED) gave  $R(Hg-Cl) = 2.25 \text{ \AA}$  instead of  $2.34 \text{ \AA}$  found in the work in question. <sup>e</sup> Therefore we use the X-ray data on various compounds containing the linear fragments  $Br-Hg-Br^e$  and  $I-Hg-I^f$  where the Hg-L bonds must be lengthened as compared with those in isolated  $HgL_2$  molecules. <sup>f</sup> H. Leligny, M. Grey, and J. C. Monier, *Acta Crystallogr., Sect. B*, **28**, 2104 (1972). <sup>g</sup> G. A. Jeffrey and M. Vlasse, *Inorg. Chem.*, **6**, 396 (1967). <sup>h</sup> W. Gordy and J. Sheridan, *J. Chem. Phys.*, **22**, 92 (1954). <sup>i</sup> C. Feige and H. Hartmann, *Z. Naturforsch. A*, **22**, 1286 (1967). <sup>j</sup> L. V. Wilkov and M. G. Anashkin, *Zh. Strukt. Khim.*, **9**, 690 (1968). <sup>k</sup> L. V. Wilkov, M. G. Anashkin, and G. I. Mamaeva, *ibid.*, **9**, 372 (1973).

shortening of the E-L bond requires special computational studies as well as a careful review of the available experimental data including not only Hg, but other 2A and 2B elements. These studies, however, are beyond the scope of the present work.

**Many-Center Case.** The approach in question can be easily generalized for 4o-4e bonds embracing any number of centers (ligands) making it applicable to polyatomic molecules. Let us consider any 4o-4e  $L_{(1)}-A-L_{(2)}$  species where the central atom A has one s and one  $p_z$  valence orbitals, and  $L_{(1)}$  and  $L_{(2)}$  are atomic or quasi-atomic ligands with normalized  $\sigma$  orbitals  $\chi_1$  and  $\chi_2$ , respectively, which may be both monocenter and group ligand orbitals of identical ligands L. Here we shall consider the case when all the ligands L in  $L_{(2)}$  are geometrically equivalent to the substituent  $L'_{(1)}$  (entering the  $L_{(1)}$  position), so that the values of  $\delta N(A-L)/\delta\alpha'$  will be the same for all ligands L. Tetrahedral compounds  $AL_{4-k}L'_k$  will be the particular case we examine.

In order to obtain the previous 4o-4e scheme corresponding to Figure 1 we need the following four  $\sigma$  MOs:

$$\psi_1 = as + b(k\chi_1 + l\chi_2) \quad (4')$$

$$\psi_2 = ep_z + f(l\chi_1 - k\chi_2) \quad (5')$$

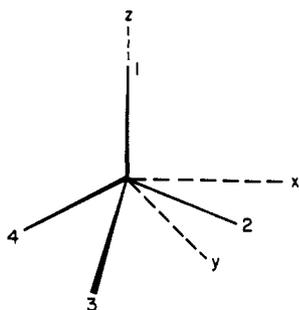
$$\psi_3 = bs - a(k\chi_1 + l\chi_2) \quad (6')$$

$$\psi_4 = fp_z - e(l\chi_1 - k\chi_2) \quad (7')$$

This is possible if we have the orthonormalized linear combinations

$$\varphi_1 = k\chi_1 + l\chi_2 \quad (28)$$

$$\varphi_2 = l\chi_1 - k\chi_2 \quad (29)$$



**Figure 2.** Enumeration of ligands and directions of the coordinate axes in  $C_{3v}$   $AL_3L'$  compounds ( $L'$  occupies the position 1 on the  $z$  axis;  $L_{(2)}$  is in the  $xz$  plane).

**Table II.** Assignments of Orbitals in  $C_{3v}$  Compounds  $AL_3L'$

irreducible representation	orbitals <sup>a,b</sup>		
	A	L	$L'$
$A_1$	s	$\frac{1}{\sqrt{3}}(\sigma_2 + \sigma_3 + \sigma_4)$	$\sigma_1$
	$p_z$		
$E$	$p_x$	$\frac{1}{\sqrt{6}}(2\sigma_2 - \sigma_3 - \sigma_4)$	
	$p_y$	$\frac{1}{\sqrt{2}}(\sigma_3 - \sigma_4)$	

<sup>a</sup> Enumeration of ligands and directions of the coordinate axes are given in Figure 2. <sup>b</sup> For the case of  $L = L'$  this representation of orbitals is quite equivalent to the usual one for  $AL_4 T_d$  compounds. <sup>c</sup> Using the orthonormalized combinations of the  $A_1$  symmetry  $\varphi_1 = (1/2)(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$  (28') and  $\varphi_2 = (1/2\sqrt{3})(3\sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)$  (29') which are orthogonal to the  $p_z$  and s orbital, respectively (see the text), we obtain the usual scheme of the  $AL_4 T_d$  MOs of the  $A_1$  and  $T_2$  symmetry with the group ligand integrals  $2S_s$  and  $(2/\sqrt{3})S_{p\sigma}$ , respectively. <sup>c,d</sup> The usual scheme of the  $AL_4 T_d$  MOs may be found, for instance, in C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory", W. A. Benjamin, New York, N.Y., 1964, pp 107-115. <sup>d</sup> For example,  $\langle p_z | \varphi_2 \rangle = (1/2\sqrt{3})(3 + 3 \cdot 1/3) S_{p\sigma} = (2/\sqrt{3}) S_{p\sigma}$ .

where

$$\langle \varphi_1 | p_z \rangle = 0 \quad (30)$$

$$\langle \varphi_2 | s \rangle = 0 \quad (31)$$

If we replace the ligand  $L_{(1)}$  by the ligand  $L'_{(1)}$ , we obtain to first order

$$\frac{\delta N(A-L)}{\delta \alpha'} = -abk^2l \left[ \left( \frac{f^2}{E_{23}} - \frac{e^2}{E_{14}} \right) - \frac{b^2 - a^2}{E_{13}} \right] \tilde{S}_s - eflk^2 \left[ \frac{f^2 - e^2}{E_{24}} - \left( \frac{b^2}{E_{14}} - \frac{a^2}{E_{23}} \right) \right] \tilde{S}_{p\sigma} \quad (32)$$

where  $\tilde{S}_s$  and  $\tilde{S}_{p\sigma}$  are the relevant overlap integrals. It is obvious that in the linear  $L'-A-L$  case (the  $z$  axis is directed toward the ligand  $L'$ ) we have

$$\chi_1 = \sigma_1, \quad \chi_2 = \sigma_2, \quad k = l = \frac{1}{\sqrt{2}} \\ \tilde{S}_s = \langle s | \sigma_2 \rangle = S_s, \quad \tilde{S}_{p\sigma} = \langle p_z | \sigma_2 \rangle = -S_{p\sigma} \quad (33)$$

for which (32) is identical with (15).

In tetrahedral complexes  $AL_4$  (Figure 2) we shall consider two cases,  $AL_3L'$  and  $ALL'_3$ , both of them corresponding to  $C_{3v}$  symmetry. The relevant orbital sets are given in Table II.

As seen from Table II, we again deal with the 4o-4e bonding as only the  $A_1$  representation includes the  $\sigma_1$  orbital. For  $L'-A-(L_3)$  we have (the  $z$  axis is directed toward the ligand  $L'$ )

$$\chi_1 = \sigma_1, \quad \chi_2 = \frac{1}{\sqrt{3}}(\sigma_2 + \sigma_3 + \sigma_4), \quad k = \frac{1}{2}, \quad l = \frac{\sqrt{3}}{2} \\ \tilde{S}_s = \left\langle s \left| \frac{1}{\sqrt{3}} \sigma_2 \right. \right\rangle = \frac{1}{\sqrt{3}} S_s, \\ \tilde{S}_{p\sigma} = \left\langle p_z \left| \frac{1}{\sqrt{3}} \sigma_2 \right. \right\rangle = -\frac{1}{3\sqrt{3}} S_{p\sigma} \quad (34)$$

for which (32) becomes

$$\frac{\delta N(A-L)}{\delta \alpha'} = -\frac{ab}{8} \left[ \left( \frac{f^2}{E_{23}} - \frac{e^2}{E_{14}} \right) - \frac{b^2 - a^2}{E_{13}} \right] S_s + \frac{ef}{8\sqrt{3}} \left[ \frac{f^2 - e^2}{E_{24}} - \left( \frac{b^2}{E_{14}} - \frac{a^2}{E_{23}} \right) \right] S_{p\sigma} \quad (35)$$

For  $(L'_3)-A-L$  we have (the  $z$  axis is directed toward the quasi-ligand  $L'_3$ )

$$\chi_1 = \frac{1}{\sqrt{3}}(\sigma_2 + \sigma_3 + \sigma_4), \quad \chi_2 = \sigma_1, \quad k = \frac{\sqrt{3}}{2}, \quad l = \frac{1}{2} \\ \tilde{S}_s = \langle s | \sigma_1 \rangle = S_s, \quad \tilde{S}_{p\sigma} = \langle p_z | \sigma_1 \rangle = -S_{p\sigma} \quad (36)$$

for which (32) becomes

$$\frac{\delta N(A-L)}{\delta \alpha'} = -\frac{3ab}{8} \left[ \left( \frac{f^2}{E_{23}} - \frac{e^2}{E_{14}} \right) - \frac{b^2 - a^2}{E_{13}} \right] S_s + \frac{\sqrt{3}ef}{8} \left[ \frac{f^2 - e^2}{E_{24}} - \left( \frac{b^2}{E_{14}} - \frac{a^2}{E_{23}} \right) \right] S_{p\sigma} \quad (37)$$

It is obvious that for both (34) and (36) we have the same linear combinations

$$\varphi_1 = \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \quad (28')$$

$$\varphi_2 = \frac{1}{2\sqrt{3}}(3\sigma_1 - \sigma_2 - \sigma_3 - \sigma_4) \quad (29')$$

The relationships (15), (35), and (37) are obtained as the special cases of the same general expression (32). Thus, their qualitative structure is quite similar, so that the previous conclusion concerning the opposing contributions of the s and p orbitals to  $\delta N(A-L)$  in the linear  $L'-A-L$  molecules with the typically prevailing s contribution (negative for  $\delta \alpha' > 0$ ) remains valid for the tetrahedral molecules  $L'-A-L_3$  and  $L-A-L'_3$ . But here there is a very important new point. The value of (37) is three times larger than that of (35). This not only demonstrates the additivity of the first-order perturbation effects (which is quite similar to that in the perturbation theory of  $\pi$  electron systems<sup>10</sup>), but gives a simple and reliable explanation of the nature of the inductive effect in saturated  $\sigma$ -bonded tetrahedral compounds of the  $AL_{4-k}L'_k$  type: typically a weakening of all the A-L bonds as more electropositive ligands  $L'$  ( $\delta \alpha' > 0$ ) enter the parent compound  $AL_4$  and a strengthening of these bonds for more electronegative ligands  $L'$  ( $\delta \alpha' < 0$ ).

It should be mentioned that in  $AL_{4-k}L'_k$  compounds, unlike linear  $L'-A-L$  ones, we sometimes have to take into account steric effects, especially for such small central atoms, like C, and bulky ligands, like Br or I.<sup>18</sup> Therefore some regularities of the inductive effect may be obscured, especially when the absolute values of changes are small and these values are obtained by different experimental methods. In particular, bond lengths in free molecules (the most reliable criterion of bond strength<sup>9</sup>) are obtained by electron diffraction and various spectroscopic (microwave, IR, Raman, etc.) methods.<sup>20</sup> All these different methods use different definitions of interatomic

**Table III.** Bond Lengths in Some Vapor Tetrahedral  $AL_{4-k}L'_k$  Compounds<sup>a</sup>

compd	method	distance, Å		ref
		A-L	A-L'	
CF <sub>4</sub>	ED	1.323 (F)		e
CF <sub>3</sub> H	MW	1.332 (F)	1.098 (H)	f
CF <sub>2</sub> H <sub>2</sub>	MW	1.357 (F)	1.093 (H)	g
CH <sub>3</sub> F	MW	1.382 (F)	1.095 (H)	h
CH <sub>4</sub>	IR		1.094 (H)	i
	Raman		1.094 (H)	j
CH <sub>3</sub> Cl	MW	1.785 (Cl)	1.090 (H)	k
CCl <sub>3</sub> H <sub>2</sub>	MW	1.772 (Cl)	1.082 (H)	l
CCl <sub>3</sub> H	MW	1.758 (Cl)	1.100 (H)	m
CCl <sub>4</sub>	ED	1.771 (Cl)		n
C(CH <sub>3</sub> ) <sub>4</sub>	ED		1.539 (C)	o
C(CH <sub>3</sub> ) <sub>3</sub> Cl	ED	1.828 (Cl)	1.532 (C)	p
Si(CH <sub>3</sub> ) <sub>4</sub>	ED		1.875 (C)	q
Si(CH <sub>3</sub> ) <sub>3</sub> Cl	MW	2.022 (Cl)	1.857 (C)	r
SiCl <sub>4</sub>	ED	2.019 (Cl)		s
Sn(CH <sub>3</sub> ) <sub>4</sub>	ED		2.144 (C)	t
Sn(CH <sub>3</sub> ) <sub>3</sub> Cl	ED	2.351 (Cl)	2.106 (C)	u
SnCl <sub>4</sub>	ED	2.281 (Cl)		

<sup>a</sup> Table contains the experimental data obtained by spectroscopic and electron diffraction methods. As different methods do not use identical definitions of interatomic distance parameters, the discussion of small differences ( $\sim 0.01$  Å) should be very cautious. <sup>b</sup> Nevertheless, the regularities which are of interest to us can be confirmed by a great number of examples (see, for instance, ref c and d) from which we have chosen only a few. The irregular changes in the C-H bond lengths may be explained by, first, their general insensitivity to substitution (see the text) and, second, the different accuracies of the experimental data (see above). <sup>b</sup> See, for instance, A. G. Robiette in ref 18a, Chapter 4. <sup>c</sup> Reference 19. <sup>d</sup> Reference 20. <sup>e</sup> C. G. Thornton, *Diss. Abstr.*, **14**, 604 (1954). <sup>f</sup> J. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952). <sup>g</sup> E. Hirota, T. Tanaka, A. Sakakibara, Y. Ohashi, and Y. Morino, *J. Mol. Spectrosc.*, **34**, 222 (1970). <sup>h</sup> J. L. Duncan, *J. Mol. Struct.*, **6**, 447 (1970). <sup>i</sup> D. R. J. Boyd and H. W. Thompson, *Trans. Faraday Soc.*, **49**, 1281 (1953). <sup>j</sup> M. A. Thomas and H. L. Welsh, *Can. J. Phys.*, **38**, 1291 (1960). <sup>k</sup> J. L. Duncan, D. C. McKean, P. D. Mallinson, and R. D. McCulloch, *J. Mol. Spectrosc.*, **46**, 232 (1973). <sup>l</sup> R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **20**, 1420 (1952). <sup>m</sup> M. Jen and D. R. Lide, *J. Chem. Phys.*, **36**, 2525 (1962). <sup>n</sup> J. Haase and W. Zeil, *Z. Phys. Chem. (Frankfurt am Main)*, **45**, 202 (1965). <sup>o</sup> B. Beagley, D. P. Brown, and J. J. Monaghan, *J. Mol. Struct.*, **4**, 233 (1969). <sup>p</sup> F. A. Momany, R. A. Bonham, and M. L. Druelinger, *J. Am. Chem. Soc.*, **85**, 3075 (1963). <sup>q</sup> B. Beagley, J. J. Monaghan, and T. G. Hewitt, *J. Mol. Struct.*, **8**, 401 (1971). <sup>r</sup> J. R. Durig, R. O. Carter, and Y. S. Li, *J. Mol. Spectrosc.*, **44**, 18 (1972). <sup>s</sup> R. D. Ryan and K. Hedberg, *J. Chem. Phys.*, **50**, 4986 (1969). <sup>t</sup> M. Nagashima, H. Fujii, and M. Kimura, *Bull. Chem. Soc. Jpn.*, **46**, 3708 (1973). <sup>u</sup> B. Beagley, K. McAloon, and J. M. Freeman, *Acta Crystallogr., Sect. B*, **33**, 444 (1974). <sup>v</sup> H. Fujii and M. Kimura, *Bull. Chem. Soc. Jpn.*, **43**, 1933 (1970).

distance parameters, not to mention the variation in accuracy of the concrete measurements within the same technique. In this connection the relationships (35) and (37) are of special importance. They prove the monotonic character of the inductive effect, and we can check our conclusions on  $ALL_3'$  compounds where the value of  $\delta N(A-L)/\delta\alpha'$  is largest and extrapolate the results to all other  $AL_{4-k}L'_k$  compounds. Further, from (35) and (37) we can explain substantially additive regularities of various manifestations of the inductive effect, for instance the shifts in binding energies of the central atom A and the ligands L as the number of substituents  $L'$  increases.<sup>21</sup>

Now we turn to some general consequences of our model with brief justifications and some experimental illustrations.

1. The central atom A must increase its s character and decrease its p character in the bond with the better donor ligand

$L'$  (with a poorer donor ligand L the reverse rehybridization will take place).

This conclusion immediately follows from the signs of the coefficients before  $S_s$  and  $S_{p\sigma}$  in the relationships (35), (37), and (15). Confirming figures may be found, for instance, in the ab initio calculations on  $CF_{4-k}H_k$ .<sup>22</sup> This model result easily explains the well-known semiempirical Walsh's<sup>23a</sup> and Bent's<sup>23b</sup> rules for the first- and second-row element compounds  $AL_{m-k}L'_k$  concerning concentration of central atom s character in orbitals directed toward electropositive substituents and of p character in orbitals directed toward electronegative substituent.

Relationships like (15), (35), and (37) easily explain numerous semiempirical correlations of E-L bond strength with Mössbauer isomer shifts  $\delta_E$  or nuclear spin coupling constant  $^1K(E-L)$ , both directly related to the s character of the E-L bond,<sup>24</sup> as well as the E-L bond polarity (in particular, an increased participation of the higher p orbital in the E-L bonding must increase the negative charge on L as is usually seen from shifts of the core binding energies<sup>21</sup>).

2. Along the series  $AL_{4-k}L'_k$ , where  $k = 0-4$ , the changes in  $\delta N(A-L)$  and  $\delta N(A-L')$  must be of monotonic character as  $k$  increases.

This conclusion again immediately follows from (35) and (37). Thus there is no need to consider separately the less symmetric and therefore more complicated case of  $AL_2L_2'$ . The A-L' bonds will change monotonically in the opposite direction as compared with the A-L bonds.

The bond lengths in the series  $CF_{4-k}H_k$  and  $CCl_{4-k}H_k$  (Table III) illustrate this second prediction. The insensitivity of the C-H bonds to substitution will be explained further on.

In our model the A-L bond lengthening along the series  $AL_{4-k}L'_k$ ,  $k = 0-3$  ( $\delta\alpha' > 0$ ), will be accompanied by an increase of the negative charge on the ligands L (a consequence of the above-mentioned rehybridization), but a decrease of the total positive charge on the central atom A (a consequence of a decrease in the number of L).<sup>14</sup> Therefore we can foresee, for instance, a monotonic decrease in Cls and FIs binding energies along the series  $CF_4$  to  $CH_3F$  (and  $CH_4$ ). Actually, this prediction is confirmed by experimental data and ab initio calculations.<sup>26</sup> Similarly, Cls binding energies decrease from  $CH_2Cl_2$  to  $CH_3Cl$  and  $CH_4$ .<sup>26</sup> A great number of other examples can be found in ref 21.

3. For the compound  $AL_{4-k}L'_k$ , where A, L, and  $k$  are given, the weakening of the A-L bonds for a better donor  $L'$  (the strengthening for a better acceptor  $L'$ ) will increase as the difference in electronegativity of L vs.  $L'$  increases.

This result strictly follows from (35) and (37), which are the same for any substituent  $L'$  as they are defined by the coefficients and excitation energies of the parent compound  $AL_4$  (cf. the similar result for the  $L'-E-L$  molecules). Many confirming examples can be found in ref 19 and 20.

It should be borne in mind that, if the ligands L and  $L'$  are very close in their electronegativities ( $\delta\alpha' \rightarrow 0$ ) and we take  $AL_3L'$  where  $\delta N(A-L)$  is the lesser, the effect in question may be so small as to be obscured by steric and other (usually "secondary") factors.<sup>18,27</sup>

4. For the compound  $AL_{4-k}L'_k$ , where A, L, and  $k$  are given, the weakening of the A-L' bond for a better donor L (the strengthening for a better acceptor L) will increase, as a rule, as the difference in electronegativity of L vs.  $L'$  increases.

The A-L' bond strength has to be compared with that in  $AL_4'$ , so that the relationships (35) and (37) should be related to  $AL_3'L$  and  $AL'L_3$ , respectively. In this case for different  $L'$  ( $L'$  is varied!) the right-hand part of (35) and (37) will be different. If we accept that the dominant factor is the  $f^2/E_{23}$  term ( $f^2$  is the largest coefficient and  $E_{23}$  is the smallest excitation energy which for  $AL_4 T_d$  compounds equals the energy

of the  $t_2 \rightarrow 2a_1^*$  transition), it can be shown<sup>14</sup> that this term, as a rule, increases as the energy of the ligand  $\sigma$  orbital decreases (increases in absolute value), i.e.,  $|\delta\alpha'|$  increases. Thus the value of  $\delta N(A-L')$  is the product of two multipliers, each increasing as the electronegativity of  $L'$  increases. This justifies the conclusion above which can be written as follows:

$$|\delta N(A-L')| > |\delta N(A-L'')| \text{ for } |\delta\alpha'| > |\delta\alpha''| \quad (38)$$

From here we can predict, for instance, that a weakening of the C-F bond in  $\text{CH}_3\text{F}$  will be more significant than that of the C-Cl bond in  $\text{CH}_3\text{Cl}$  (as compared with  $\text{CF}_4$  and  $\text{CCl}_4$ , respectively). This actually is the case (see Table III).

As the consequence of the above conclusion, we can foresee that for any pair  $\text{AL}_3\text{L}$  and  $\text{AL}_3\text{L}'$  where  $|\delta\alpha'|$  is the same, the value of  $|\delta N(A-L)|$  in  $\text{AL}_3\text{L}$  will be larger than  $|\delta N(A-L')|$  in  $\text{AL}_3\text{L}'$  if the  $\sigma$  orbital of L is lower than that of  $L'$  (L is more electronegative than  $L'$ ).

As an example we can take  $\text{CH}_3\text{F}$  and  $\text{CHF}_3$  where  $|\Delta R(\text{C-F})| \gg |\Delta R(\text{C-H})|$  (see Table III). This model result explains the insensitivity of the C-H bond to substitution. The same conclusion follows from ab initio calculations on the series  $\text{CF}_{4-k}\text{H}_k$ <sup>22</sup> where the total overlap populations in C-F bonds decrease by a factor of 3 from  $\text{CF}_4$  (0.316) to  $\text{CH}_3\text{F}$  (0.096), while there is only an 8% increase for C-H bonds from  $\text{CH}_4$  (0.751) to  $\text{CHF}_3$  (0.812).<sup>28</sup> It is worthwhile to add that simple arguments concerning the A-L' and A-L bond energies, e.g., a weaker bond is more sensitive to substitution, do not work here as the C-H bond energy is smaller than the C-F one (416 and 485  $\text{kJ mol}^{-1}$ , respectively<sup>29</sup>).

5. For the series of  $\text{AL}_{4-k}\text{L}'_k$  where L,  $L'$ , and  $k$  are given (A is varied) the values of  $\delta N(A-L)$  and  $\delta N(A-L')$  may change in both monotonic and nonmonotonic ways.

This conclusion follows again from (35) and (37) as long as any A set the relevant coefficients and energies (see Appendix I) may vary significantly and in a nonmonotonic way.<sup>14</sup> Consider the series  $\text{A}(\text{CH}_3)_3\text{Cl}$ ,  $\text{A} = \text{C}, \text{Si}, \text{Sn}$ , as an example. The strengthening of the A- $\text{CH}_3$  bonds is of monotonic character in the order  $\text{C} < \text{Si} < \text{Sn}$  but the weakening of the A-Cl bonds is not monotonic, namely,  $\text{C} > \text{Si} < \text{Sn}$  (see Table III). In a purely empirical manner these changes may be connected with the fact that the A-C bond energies decrease monotonically along the series  $\text{C} > \text{Si} > \text{Sn}$  but the A-Cl bond energies are changed nonmonotonically in the order  $\text{C} < \text{Si} > \text{Sn}$ .<sup>29</sup>

A summary of the results for tetrahedral compounds is given in Table IV.

**Planar Trigonal Compounds.** Our model can be also applied to planar trigonal compounds  $\text{AL}_3 D_{3h}$ . Indeed, under substitution  $\text{AL}_3 D_{3h} \rightarrow \text{AL}_2\text{L}' C_{2v}$  ( $L'$  occupies the position  $L_{(1)}$  on the  $x$  axis) we can again consider a perturbation of the 4o-4e bonding including the  $s, p_x, (1/\sqrt{3})(\sigma_1 + \sigma_2 + \sigma_3)$ , and  $(1/\sqrt{6})(2\sigma_1 - \sigma_2 - \sigma_3)$  orbitals.<sup>30</sup> So the results will be exactly the same as those for tetrahedral  $\text{AL}_{4-k}\text{L}'_k$  compounds. In particular we can predict additive monotonic changes of the first-order effects for both A-L and A-L' bonds along the series  $\text{AL}_{3-k}\text{L}'_k$ ,  $k = 0-3$  (Table IV). As the experimental data concerning the relevant A-L bond lengths are very poor,<sup>55</sup> the more convincing arguments are striking similarities of the substitution effects on various spectroscopic properties of  $\text{AL}_{4-k}\text{L}'_k$  and  $\text{AL}_{3-k}\text{L}'_k$  compounds, for instance, of binding energies<sup>21</sup> or spin coupling constants.<sup>31</sup> Let us stress, however, that the effects of substitution in pyramidal  $\text{AL}_{3-k}\text{L}'_k$  compounds may be quite different.<sup>25</sup> This is another illustration of the principal difference in manifestations of the substitution effects in main group element compounds  $\text{AL}_{m-k}\text{L}'_k$  depending on the oxidation state of the central atom.<sup>3,13</sup>

**3o-4e Bonding. Three-Center Case.** The simplest 3o-4e case corresponds to a three-atom linear molecule  $L_{(1)}-E-L_{(2)}$  with identical ligands L and four valence electrons when every atom has one valence orbital,  $\chi_1, \chi_E$ , and  $\chi_2$ , respectively.<sup>4a</sup> Thus the

**Table IV.** Changes in Properties of the Bonds in  $\text{AL}_{m-k}\text{L}'_k$  Compounds<sup>a</sup>

given	varied	property	character of changes
A, L, L'	k	$\delta N(A-L)$	always monotonic
		$\delta N(A-L')$	always monotonic
		% s(p) in A-L	always monotonic
		% p(s) in A-L'	always monotonic
A, k, L	L'	$\delta N(A-L)$	always monotonic
		$\delta N(A-L')$	typically monotonic
L, L', k	A	$\delta N(A-L)$	monotonic or nonmonotonic
		$\delta N(A-L')$	depending upon A, L, L'

<sup>a</sup>  $m = 2-4; k = 0-m$ .

relevant MOs can be obtained simply from the MO set (4)-(7) omitting one central atom orbital,  $\chi^{(S)}$  or  $\chi^{(AS)}$ , so that the corresponding pair of bonding and antibonding MOs,  $\psi_1, \psi_3$  or  $\psi_2, \psi_4$ , respectively, transforms into one nonbonding MO

$$a = 0, \quad b = 1, \quad \varphi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2) \quad (39)$$

or

$$e = 0, \quad f = 1, \quad \varphi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2) \quad (40)$$

Thus, using (40) as an example, we have, for instance,

$$\psi_1 = a\chi_E + b \frac{1}{\sqrt{2}}(\chi_1 + \chi_2) \quad (41)$$

$$\psi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2) \quad (42)$$

$$\psi_3 = b\chi_E - a \frac{1}{\sqrt{2}}(\chi_1 + \chi_2) \quad (43)$$

For (39) the similar set of MOs is obvious. The relevant interactions and MO diagrams are shown in Figure 3.

If we replace the ligand  $L_{(1)}$  by a better donor ligand  $L'$  we obtain from (41)-(43) to first order

$$\frac{\delta N(E-L)}{\delta\alpha'} = \frac{ab}{2\sqrt{2}} \left( \frac{b^2 - a^2}{E_{13}} - \frac{1}{E_{23}} \right) S_{(S)} \quad (44)$$

If we used (39) instead of (40), we would obtain substantially the same relationship (cf. Figure 3)

$$\frac{\delta N(E-L)}{\delta\alpha'} = \frac{ef}{2\sqrt{2}} \left( \frac{f^2 - e^2}{E_{13}} - \frac{1}{E_{23}} \right) S_{(AS)} \quad (45)$$

As

$$E_{13} > E_{23}, \quad b^2 - a^2 < 1, \quad f^2 - e^2 < 1 \quad (46)$$

we immediately conclude that

$$\frac{\delta N(E-L)}{\delta\alpha'} < 0 \quad (47)$$

Thus in the orbitally deficient 3o-4e case introduction of a better donor ligand  $L'$  must always lead to the weakening of the E-L bond (and vice versa for  $\delta\alpha' < 0$ ) regardless of the nature of the central atom orbital (s, p, or d) or the type of bonding ( $\sigma$  or  $\pi$ ). Moreover, the comparison of (44)-(45) with (15) or (35), (37) permits the prediction that the relative weakening of the E-L bond must be substantially larger for the 3o-4e case owing to lack of the opposing contributions.

In the linear 3o-4e molecule  $L'-E-L$  the MOs (41)-(43) will be modified into

$$\psi'_i = c_{iE}\chi_E + c_{i1}\chi_1 + c_{i2}\chi_2, \quad i = 1, 2, 3 \quad (48.i)$$

where the coefficients  $c_{ij}$  are defined by some variation procedure. To first order the coefficient  $c_{2E}$  will be

Table V. Bond Lengths in Some Linear 3o-4e Molecules

molecule L'-A-L	distance, Å		ref
	L'-A	A-L	
I-I-I	2.92 (av)	2.92 (av)	a
I-I-Br	2.78 (I)	2.91 (Br)	b
Cl-I-Br	2.91 (Cl)	2.51 (Br)	c
Cl-I-Cl	2.55 (Cl)	2.55 (Cl)	d
F-Xe-F	2.01 (F <sub>i</sub> )	2.01 (F <sub>t</sub> )	e
F-Xe-FXeF <sub>2</sub> <sup>f</sup>	1.90 (F <sub>i</sub> )	2.14 (F <sub>b</sub> )	g
F-Xe-FRuF <sub>3</sub> <sup>f</sup>	1.87 (F <sub>i</sub> )	2.18 (F <sub>b</sub> )	h
F-Xe-FSb <sub>2</sub> F <sub>10</sub> <sup>f</sup>	1.84 (F <sub>i</sub> )	2.35 (F <sub>b</sub> )	i
(etu)-Te(C <sub>6</sub> H <sub>5</sub> )-Cl <sup>j</sup>	2.521 (S)	2.849 (Cl)	k
(etu)-Te(C <sub>6</sub> H <sub>5</sub> )-Br <sup>j</sup>	2.523 (S)	2.969 (Br)	l
(etu)-Te(C <sub>6</sub> H <sub>5</sub> )-I <sup>j</sup>	2.614 (S)	3.003 (I)	m
(esu)-Te(C <sub>6</sub> H <sub>5</sub> )-I <sup>j</sup>	2.679 (Se)	3.095 (I)	m
(esu)-Te(C <sub>6</sub> H <sub>5</sub> )-Br <sup>j</sup>	2.616 (Se)	3.054 (Br)	k

<sup>a</sup> T. Migchelsen and A. Vos, *Acta Crystallogr.*, **23**, 796 (1967). <sup>b</sup> G. B. Carpenter, *ibid.*, **20**, 330 (1966). <sup>c</sup> T. Migchelsen and A. Vos, *ibid.*, **22**, 872 (1967). <sup>d</sup> G. J. Visser and A. Vos, *ibid.*, **17**, 1336 (1964). <sup>e</sup> H. A. Levy and P. A. Agron, *J. Am. Chem. Soc.*, **85**, 241 (1963). <sup>f</sup> In these three compounds the bridging F atom (F<sub>b</sub>) is a poorer donor ligand than the terminal F atom (F<sub>t</sub>) according to <sup>19</sup>F NMR and Fls binding energy shifts [see, for instance, discussion in E. M. Shustorovich, *Zh. Strukt. Khim.*, **15**, 977 (1974)]. <sup>g</sup> F. O. Sladky, P. A. Bulliner, B. Bartlett, B. G. DeBoer, and A. Zalkin, *Chem. Commun.*, 1048 (1968). <sup>h</sup> N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrel, and A. Zalkin, *Inorg. Chem.*, **12**, 1717 (1973). <sup>i</sup> V. M. McRae, R. D. Peakcock, and D. R. Russel, *Chem. Commun.*, 62 (1969). <sup>j</sup> In all these compounds the Te-C bond lengths are practically the same (2.11-2.12 Å) and the D-Te-X fragments are practically linear ( $\angle DTeX = 176-177^\circ$ ). <sup>k</sup> Reference 47c. <sup>l</sup> Reference 47a. <sup>m</sup> Reference 47d.

$$\frac{c_{2E}}{\delta\alpha'} = \frac{ab}{2} \left( \frac{1}{E_{12}} + \frac{1}{E_{23}} \right) \quad (49)$$

which for  $\delta\alpha' > 0$  is always positive, i.e., corresponds to the nodal structure

$$\psi_2' = \chi_E + \chi_1' - \chi_2 \quad (50)$$

where a node is located between the E and L atoms.<sup>32</sup> Thus the weakening of the E-L bond can be visually explained in terms of the nodal structure of the MO (48.2) as was suggested earlier<sup>9,33</sup> by purely qualitative arguments.

From (44)-(45) we can again conclude that, other conditions being equal,  $|\delta N(E-L)|$  will be the larger the bigger is the difference in electronegativity of L vs. L'. But we also see that the dominant factor in  $\delta N(E-L)$  is the energy  $E_{23}$  which in the 3o-4e case can be expressed as follows [cf. (A12) in Appendix I]:

$$E_{23} \approx \alpha_E - \alpha_L + \frac{\beta_{EL}^2}{\alpha_E - \alpha_L} \quad (51)$$

As in (51) we assume that  $\alpha_E - \alpha_L \gg |\beta_{EL}|$ ; the weakening of the E-L bond will be (for a given L') the more substantial the less is the difference  $\alpha_E - \alpha_L$ , i.e., the stronger a donor is L and the weaker a donor is E. This conclusion correlates with the fact that in 3o-4e bonds the ligands L must be more electronegative than the central atom E and the E-L bonds will be the weaker the smaller is the difference  $\alpha_E - \alpha_L$ .<sup>35</sup>

A direct experimental check of these conclusions may be easily made on linear molecules of the trihalide anion  $[L'-I-L]^-$  or xenon fluoride  $L'-Xe-F$  type.<sup>41</sup> Some examples collected in Table V confirm the above predictions.

Another possibility for checking the predictions concerning the 3o-4e bonds is to consider the quasi-square and quasi-octahedral complexes of main group elements A where A is not of the highest oxidation state (as was shown,<sup>13</sup> such an atom A forms substantially the 3o-4e bonds within the linear fragments L'-A-L). Actually, in the quasi-octahedral complexes

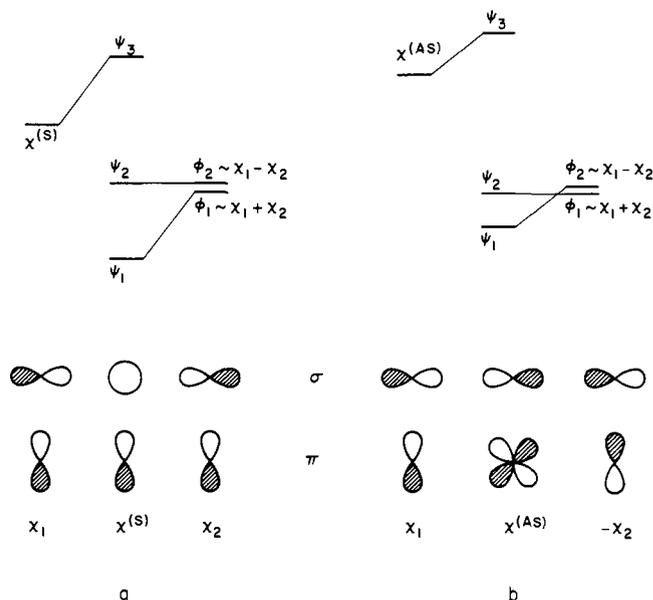


Figure 3. The 3o-4e case: the formation of the  $\psi_1$  MO ( $\sigma$  or  $\pi$ ) and the MO diagrams. (a) The  $\chi^{(S)}$  interaction. (b) The  $\chi^{(AS)}$  interaction. See explanations in the text.

of Sn(II), Sb(III), Te(IV), I(V), and Xe(VI)<sup>43,44</sup> or in the quasi-square complexes of Te(II)<sup>45</sup> the strongest (shortened) A-L' bond and the weakest (lengthened) A-L bond are always located trans to one another. Moreover, in these complexes the relevant A-L bonds are usually so weak that they are considered as "secondary" ones.<sup>43,46</sup>

Referring the reader to the relevant reviews,<sup>43-45</sup> let us discuss only a few examples. In *trans*-Te<sup>II</sup>(tu)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)Cl the lengthening of the Te-Cl bond equals 0.7 Å as compared with *cis*-Te<sup>II</sup>(tu)<sub>2</sub>Cl<sub>2</sub>.<sup>45</sup> Such a lengthening is very large even by comparison with typical transition metal cases<sup>6-9</sup> and especially with the  $(n-1)d^{10}$  R-M-X cases (see Table I) in complete agreement with our model predictions. Moreover, though divalent tellurium most often forms four-coordinated square-planar complexes, when a phenyl group is one of the ligands, the position opposite to the phenyl group is virtually vacant.<sup>45,47</sup>

A similar effect was found in quasi-octahedral *trans*-dibenzotellurophen diiodide C<sub>12</sub>H<sub>8</sub>Te<sup>VI</sup>I<sub>2</sub> where the Te...I distances in the linear C-Te...I fragments equal 3.70-3.72 Å, longer by 0.9 Å than the normal Te-I bond length but shorter by 0.7 Å than the length of the van der Waals Te-I contact.<sup>48</sup>

In various three-coordinated (C<sub>6</sub>H<sub>5</sub>)Te<sup>II</sup>(D)X complexes where D is a neutral donor molecule like thiourea (tu), ethylthiourea (etu), and ethyleneselenourea (esu), X = Cl, Br, I, the Te-C bond length remains practically the same<sup>45,47</sup> permitting the linear D-Te-X fragment to be considered as an independent moiety. Similar D-E-L fragments where L is some acido ligand may be found in many other complexes.

To discuss their structure we have, generally speaking, to modify our relationships (44)-(45) which have been obtained under a perturbation of the symmetric L'-E-L fragment (L' = L). This approach is a better starting approximation the closer in properties are the ligand L and L'. In the D-E-L case a better starting approximation may be to consider the perturbation of the normal 2o-2e E-L bond by the ligand L' = D having a lone pair. If the bonding  $\theta_1$  and antibonding  $\theta_3$  orbitals of the E-L bond have the forms

$$\theta_1 = k\chi_E + l\chi_L \quad (52)$$

$$\theta_3 = l\chi_E - k\chi_L \quad (53)$$

and the lone pair of the D ligand occupies the orbital  $\theta_2$

$$\theta_2 = \chi_D \quad (54)$$

we obtain the first order

$$N(E-D) = -\frac{\beta_{ED}S_{ED}l^2}{E_{23}} \sim \frac{S_{ED}^2l^2}{E_{23}} \quad (55)$$

where  $E_{23} = \epsilon(\theta_3) - \epsilon(\theta_2) > 0$ .

For given E and D [for given  $\beta_{ED}$  and  $\epsilon(\theta_2)$ ] an increase of donor ability of the ligand L decreases the coefficient  $l$  and increases (decreases in absolute value) the energy  $\epsilon(\theta_3)$ , i.e.,  $E_{23}$ . Thus both factors in (55) will combine to decrease  $N(A-D)$ . In fact, in the aforementioned D-Te<sup>II</sup>-X fragments the relative trans bond lengthening effect of halogens on a Te-S or a Te-Se bond is I > Br ~ Cl.<sup>47</sup>

We see from (47) that a strengthening of the E-L' bond must always cause a weakening of the E-L bond. This conclusion also holds for the D-E-L case in question because it follows from quite general properties of the MOs (48.i) (see Appendix II). Thus the stronger a donor is D the weaker must be a given Te-X bond. Actually the experimental data indicate the trans bond lengthening order  $tu \geq esu > etu$  for a Te-Br bond.<sup>47</sup> Examples of D-Te(C<sub>6</sub>H<sub>5</sub>)-X compounds are given in Table V.

We see that all the variety of the 3o-4e bonds can be considered on the same basis regardless of the nature of L', an acido ligand or a neutral donor molecule. The approach in question permits previously purely qualitative arguments<sup>36-40, 43-45</sup> to be combined and explained.

**Many-Center Case.** Our analysis of the 3o-4e case can be generalized for any number of centers (ligands) just as was the 4o-4e analysis. Let us again stress that the relationships (44)-(45) and the nodal structure (50) are of quite general character for any 3o-4e interaction where  $\chi_1'$  corresponds to a better donor orbital, whether  $\chi_1'$  is a one-center or many-center group ligand orbital. For example, for any bipyramidal main group complex  $AL_m$  ( $m = 5$  or  $7$ ), within the totally symmetric irreducible representation  $A_1$  there are three orbitals, namely,  $\sigma_{ax} = (1/\sqrt{2})(\sigma_1 + \sigma_2)$  and  $\sigma_{eq} = (1/\sqrt{m-2})(\sigma_3 + \sigma_4 + \dots + \sigma_m)$ .<sup>2</sup> So we can predict that the nodal structure of the MO  $2a_1$  will be

$$\psi_2^{(1)} = s + \sigma_{ax} - \sigma_{eq} \quad (56)$$

or

$$\psi_2^{(2)} = s - \sigma_{ax} + \sigma_{eq} \quad (57)$$

depending on which orbital,  $\sigma_{ax}$  or  $\sigma_{eq}$ , plays the role of the better donor. Certainly in unsubstituted complexes  $AL_m$  we cannot use  $\delta\alpha'$  (1) as a perturbation as  $\delta\alpha' = 0$  by definition. But considering interligand interactions as a perturbation<sup>2</sup> we find that  $\psi_2^{(1)}$  (56) must correspond to pentagonal  $AL_7 D_{5h}$  complexes, but  $\psi_2^{(2)}$  (57) to trigonal  $AL_5 D_{3h}$  complexes. This again agrees with the results of direct quantitative calculations and correlates with the fact that axial bonds are stronger and less polar in  $AL_7 D_{5h}$  but weaker and more polar in  $AL_5 D_{3h}$  complexes (see general discussion in ref 2).

Further, we can predict that upon going from  $AL_5 D_{3h}$  to  $AL_2L_3' D_{3h}$ , with better donor ligands L' occupying equatorial positions, the axial bonds A-L must be substantially weakened from the increased contribution of the MO  $\psi_2^{(2)}$  (57). This prediction entirely agrees with experiment (for example, in  $PF_2(CH_3)_3$  the P-F bonds are much longer, by 0.11 Å, than those in  $PF_5$ <sup>49</sup>) and the calculations.<sup>50</sup>

Another important example of the generalized 3o-4e case takes place as one goes from an octahedron  $AL_6 (O_h)$  to a tetragonal bipyramid  $AL_4L_2' (D_{4h})$ . Here again three orbitals

belong to the same irreducible representation  $A_{1g}$ , namely,  $s$ ,  $\sigma_{ax} = (1/\sqrt{2})(\chi_1' + \chi_2')$ , and  $\sigma_{eq} = 1/2(\chi_3 + \chi_4 + \chi_5 + \chi_6)$ .<sup>2</sup> In this case our approach can be applied directly. Let us clarify that we use the normalized MO  $\sigma_{ax}$ , so that the coefficient before  $\delta\alpha'$  in the relevant perturbation relationships will equal 1 as in the simplest monosubstituted case  $EL_{m-1}L'$ . If L' is a stronger donor, the MO  $\psi_2^{(1)}$  (56) will be formed weakening the equatorial A-L bonds. If L' is a weaker donor, the MO  $\psi_2^{(2)}$  (57) will be formed and the equatorial bonds A-L will be strengthened. These conclusions which strictly follow from the relationship (47) confirm our previous "hand-waving" arguments<sup>13</sup> and will be extensively used in a subsequent paper<sup>3</sup> to explain and predict various structural regularities.

**Comparison with Other Approaches.** We would like to compare our approach to the 3o-3e and 4o-4e cases with the approaches by other authors to the same problems. Certainly there is nothing new in our consideration of the symmetric L-E-L molecules (fragments).<sup>4,36,37</sup> The ginger is in our analytical treatment of the substituted L'-E-L moieties.

For instance, Walsh's<sup>23a</sup> and Bent's<sup>23b</sup> rules (concerning orbital rehybridization in the main group elements of the first and second rows in substituted tetrahedral  $AL_{4-k}L'_k$  compounds) represent "an attempt to review in non-mathematical terms a self-consistent interpretation of experimental data".<sup>23b</sup> Certainly the various 3o-4e and 4o-4e cases have been considered both purely qualitatively<sup>52</sup> and purely computationally.<sup>53</sup> To our knowledge, however, until now there was no analytical solution of interrelations between E-L' and E-L bond strength excepting the possible extrapolation of the PMO theory of  $\pi$ -electron systems<sup>10</sup> on the 3c-3o-4e case and the Zink approach<sup>34a</sup> to the 3c-3o-4e case.

Zink's approach was to do a direct analysis of the relevant third-order determinant for the 3o-4e case to determine that the nodal structure of  $\psi_2'$  (shown in eq 57) always occurs for a stronger donor ligand L' (W in Zink's designation).<sup>34a</sup> There are two limitations to Zink's approach, however. The first is that only the nonbonding  $\psi_2$  orbital has been analyzed while actually the major contribution to bond strengths is given by the bonding orbital,  $\psi_1'$  (48.1). The contributions of both  $\psi_1'$  and  $\psi_2'$  must be considered for conclusions about E-L and E-L' bond strengths to be certain.

The second limitation is that a direct analysis of the fourth-order determinant for the 4o-4e case is impossible, so Zink<sup>34b</sup> has considered this case from a purely computational viewpoint. We would like to emphasize that in our approach all the necessary relationships for a complete analysis of the 3o-4e and 4o-4e problems are developed explicitly. Zink included excited states in his studies,<sup>34</sup> so we also wish to point out that it is a straightforward matter to extend our analysis to excited states.<sup>51</sup>

## Conclusion

The main conclusion of the present research is that in any 4o-4e case there always exist two opposing contributions to the E-L bond overlap population, the s (or sd) one negative and the p one positive for a better donor substituent L', while in any 3o-4e case there always exists only a negative contribution (and vice versa for a better acceptor L'). This fact eventually determines the effects of substitution in linear  $ELL'$ , planar trigonal  $AL_{3-k}L'_k$ , and tetrahedral  $AL_{4-k}L'_k$  compounds, in particular many regularities of the inductive effect. In general this fact is of great importance for the effects of substitution in all coordination compounds  $EL_{m-k}L'_k$ .<sup>3</sup>

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### Appendix I

Below we shall give some expressions which are useful for analyzing  $\delta N(E-L')$  and  $\delta N(E-L)$ .

For any pair of MOs, bonding  $\psi$  and antibonding  $\psi^*$ , which have the forms

$$\psi = C_a\chi_a + C_b\chi_b \quad (A1)$$

$$\psi^* = C_b\chi_a - C_a\chi_b \quad (A2)$$

where

$$\alpha_b < \alpha_a < 0, \beta_{ab} < 0, C_b > C_a > 0, C_b^2 + C_a^2 = 1 \quad (A3)$$

and

$$\zeta = \frac{\alpha_b - \alpha_a}{\beta_{ab}} > 0 \quad (A4)$$

there exist the following relationships for the coefficients  $C_a$  and  $C_b$ :

$$\frac{C_a}{C_b} = \frac{\sqrt{\zeta^2 + 4} - \zeta}{2} \quad (A5)$$

$$C_b^2 = \frac{1}{2} \left( 1 + \frac{\zeta}{\sqrt{\zeta^2 + 4}} \right) \quad (A6)$$

$$C_b^2 - C_a^2 = \frac{\zeta}{\sqrt{\zeta^2 + 4}} \quad (A7)$$

$$C_a C_b = \frac{1}{\sqrt{\zeta^2 + 4}} \quad (A8)$$

$$C_a C_b (C_b^2 - C_a^2) = \frac{\zeta}{\zeta^2 + 4} \quad (A9)$$

As  $\zeta$  increases, the relationships (A6) and (A7) monotonically increase and (A8) decreases, so that (A9) at first increases and then decreases. All these changes are shown in Figure 4.

If  $\zeta > 1$ , the energies  $\epsilon(\psi)$  and  $\epsilon(\psi^*)$  will be approximately equal to

$$\epsilon(\psi) \simeq \alpha_b - \frac{\beta_{ab}^2}{\alpha_a - \alpha_b} \quad (A10)$$

$$\epsilon(\psi^*) \simeq \alpha_a + \frac{\beta_{ab}^2}{\alpha_a - \alpha_b} \quad (A11)$$

so that

$$\epsilon(\psi^*) - \epsilon(\psi) \simeq \alpha_a - \alpha_b + \frac{2\beta_{ab}^2}{\alpha_a - \alpha_b} \quad (A12)$$

### Appendix II

For the basis set (58)-(60) the MO (48.3) will be

$$\psi_3' = |C_3E|X_E - |C_3D|X_D - |C_3L|X_L \quad (A13)$$

So, using the general relationship

$$\sum_i^{\text{occ}} C_{iE} C_{iD(L)} = \sum_j^{\text{unocc}} C_{jE} C_{jD(L)} \quad (A14)$$

we obtain for the overlap populations

$$N(E-D) = |C_3E C_3D| S_{ED} \quad (A15)$$

$$N(E-L) = |C_3E C_3L| S_{EL} \quad (A16)$$

As (A13) is normalized, an increase of  $|C_3D|$  and  $N(E-D)$  must decrease  $N(E-L)$  via a decrease of  $|C_3E|$  and  $|C_3L|$ .

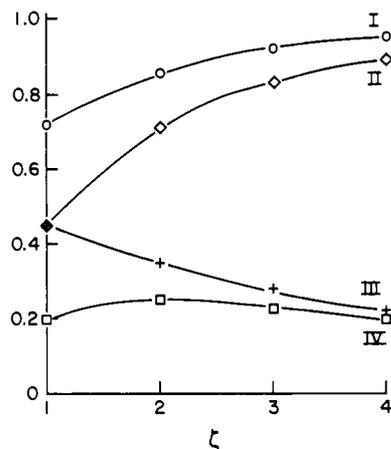


Figure 4. Dependence on  $\zeta$ :  $C_b^2$  (I),  $C_b^2 - C_a^2$  (II),  $C_a C_b$  (III), and  $C_a C_b (C_b^2 - C_a^2)$  (IV).

### References and Notes

- Formerly of the N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Moscow B-71, 117071, U.S.S.R.
- E. Shustorovich, *Inorg. Chem.*, **17**, 2648 (1978).
- E. Shustorovich, *J. Am. Chem. Soc.*, in press.
- The LCAO MO theoretical treatment of bonding in linear three-atom molecules L-E-L may be found in many textbooks on quantum chemistry, for instance, (a) the 3c-3o-4e bonding: F. A. Cotton, "Chemical Applications of Group Theory", 2nd ed., Interscience, New York, N.Y., 1971, pp 170-178; (b) the 3c-4o-4e bonding: H. B. Gray, "Electrons and Chemical Bonding", W. A. Benjamin, New York, N.Y., 1965, Chapter 3.
- See, for instance, the recent reviews<sup>8-9</sup> and references cited therein.
- T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
- F. R. Hartley, *Chem. Soc. Rev.*, **2**, 163 (1973).
- K. B. Yatzimirsky, *Pure Appl. Chem.*, **38**, 341 (1974).
- (a) E. M. Shustorovich, M. A. Poray-Koshits, and Yu. A. Buslaev, *Coord. Chem. Rev.*, **17**, 1 (1975); (b) E. M. Shustorovich, *Koord. Khim.*, **1**, 740 (1975); (c) *Ibid.*, **2**, 435 (1976).
- M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, N.Y., 1975.
- This hybrid orbital will be  $\chi^{(8)} = \lambda s + \delta d_\sigma$  where the normalized coefficients  $\lambda$  and  $\delta$  ( $\lambda^2 + \delta^2 = 1$ ) can be found from the orthogonalization requirement  $\langle \delta s - \lambda d_\sigma | \chi_1 \rangle = 0$  which corresponds to  $\lambda/\delta = \langle s | \chi_1 \rangle / \langle d_\sigma | \chi_1 \rangle$  [cf. the relationships (9)-(12) in the text].
- The inequality  $b^2 - a^2 > 0$  is typical for transition metals, but  $b^2 - a^2 < 0$  for most main group elements.<sup>13</sup>
- (a) E. M. Shustorovich and Yu. A. Buslaev, *Koord. Khim.*, **1**, 1020 (1975); (b) *Inorg. Chem.*, **15**, 1142 (1976).
- E. M. Shustorovich, unpublished results.
- The inequality (23) is typical but not universal as it depends on the nature of E and L. See, for instance, S. P. McGlynn, L. G. Vanquickenborn, M. Kinoshita, and D. G. Carroll, "Introduction to Applied Quantum Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1972, pp 54-55, 116-117, 128.
- The nodal structure of  $\psi_2'$  (27) is exactly the same as was suggested by us earlier<sup>9,17</sup> on the basis of purely qualitative arguments, but the nodal structure of  $\psi_1'$  (26) differs from the suggested one<sup>9,17</sup> by the sign of the coefficient  $e_1'$ . This is one of the illustrations of the efficiency of the present approach as compared with previous "hand-waving" arguments.
- E. M. Shustorovich, *Zh. Strukt. Khim.*, **15**, 123 (1974).
- See, for instance, B. Beagley in ref 19a, Chapter 2.
- "Molecular Structure by Diffraction Methods", The Chemical Society, Burlington House, London: (a) Vol. 1, 1973; (b) Vol. 2, 1974; (c) Vol. 3, 1975; (d) Vol. 4, 1976.
- Landolt-Börnstein, "New Series," K.-H. Hellwege, Ed., Group II, "Atomic and Molecular Physics", Vol. 7, "Structural Data of Free Polyatomic Molecules", Springer-Verlag, West Berlin, 1976.
- (a) K. Siegbahn, C. Nordling, G. Johansson, J. Heden, P. F. Heden, K. Hamrin, U. Gellius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969; (b) D. A. Shirley, Ed., "Electron Spectroscopy", North-Holland Publishing Co., Amsterdam, 1972; (c) W. L. Jolly, *Coord. Chem. Rev.*, **13**, 45 (1974).
- C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, **53**, 2196 (1970).
- (a) A. D. Walsh, *Discuss. Faraday Soc.*, **2**, 18 (1947); (b) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).
- For instance, the similar perturbation approach proved to be effective to develop the theory of reduced spin coupling constants  $^1K(E-L)$  in various substituted compounds  $EL_m - kL_k$ <sup>25</sup> where L has a valence  $ns$  orbital (H, CR<sub>3</sub>, SiR<sub>3</sub>, PR<sub>3</sub>, etc.)<sup>25a</sup> or a lone  $ns^2$  pair (F, etc.)<sup>25b</sup> in very encouraging agreement with experiment.
- (a) E. Shustorovich, *Mol. Phys.*, submitted for publication; (b) E. Shustorovich and P. A. Dobosh, *Ibid.*, submitted for publication.
- See references and discussion in D. B. Adams and D. T. Clark, *Theor. Chim.*

- Acta*, **31**, 171, (1973).
- (27) Sometimes these "secondary" factors become more important than the "primary" electronic ones. See, for instance, the discussion in C. J. Marsden and L. S. Bartell, *Inorg. Chem.*, **15**, 3004 (1976); L. S. Bartell, F. B. Clippard, and E. J. Jacob, *ibid.*, **15**, 3009 (1976).
- (28) (a) True, this trend in overlap populations of the C-F is also connected with the antibonding contributions of the C-F  $\pi$  bonds,<sup>22</sup> a factor not entering in the explicit form in our model. This illustrates difficulties of a direct use of sophisticated calculations for checking any model using another (usually simpler) formalism. See the discussion of this aspect in ref 2 and 9c. (b) The CNDO/2 calculations on the  $CF_{4-k}H_k$  series (D. P. Brown, cited in ref 18, p 95) do not agree with the ab initio ones<sup>22</sup> in the C-F bond population trend.
- (29) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, N.Y., 1972, p 310.
- (30) See, for instance, ref 4a, p 219.
- (31) For a detailed discussion see ref 25.
- (32) This conclusion is valid for both  $\sigma$  and  $\pi$  bonding. Numerous examples of such  $\pi$  bonding can be found in the linear  $L'-M-L$  fragments of  $ML_m-kL'_k$  complexes where the  $d_{\pi}$  metal orbitals do not interact with the  $\sigma$  ligand orbitals, say  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$  orbitals in quasi-octahedral complexes  $ML_6-kL'_k$  (cf. Figure 3b),<sup>9,33,34</sup>
- (33) (a) E. M. Shustorovich, Yu. A. Buslaev, and Yu. V. Kokunov, *Zh. Strukt. Khim.*, **13**, 111 (1972); (b) E. M. Shustorovich, M. A. Poray-Koshits, T. S. Khodasheva, and Yu. A. Buslaev, *ibid.*, **14**, 706 (1973).
- (34) (a) J. I. Zink, *J. Am. Chem. Soc.*, **94**, 8039 (1972); (b) *ibid.*, **96**, 4464 (1974).
- (35) This fact is a keystone of the  $3o-3c-4e$  model itself.<sup>4a,9b,36-40</sup>
- (36) (a) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951); (b) G. C. Pimentel and R. D. Spratley, *J. Am. Chem. Soc.*, **85**, 826 (1963).
- (37) (a) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951); (b) R. E. Rundle, *ibid.*, **85**, 112 (1963); (c) *Rec. Chem. Prog.*, **23**, 195 (1962).
- (38) E. E. Havinga and E. H. Wibenga, *Recl. Trav. Chim. Pays-Bas*, **78**, 724 (1959).
- (39) H. H. Hyman, Ed., "Noble-Gas Compounds", University of Chicago Press, Chicago, Ill., 1963, Chapter 9.
- (40) Reference 29, pp 109-111.
- (41) Some strong hydrogen bonds  $X-H\cdots Y$  may be included here as well, but usually weak asymmetric bonds  $X-H\cdots Y$  are not the object of the  $3o-4c$  model (see discussion in ref 42).
- (42) P. A. Kollmann in "Applications of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press, New York, N.Y., 1977, Chapter 3.
- (43) N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, **15**, 1 (1972).
- (44) I. D. Brown, *J. Solid State Chem.*, **11**, 214 (1974).
- (45) O. Foss, *Pure Appl. Chem.*, **24**, 31 (1970).
- (46) J.-S. Lee, D. D. Titus, and R. F. Ziolo, *J. Chem. Soc., Chem. Commun.*, 501 (1976).
- (47) (a) O. Vikane, *Acta Chem. Scand., Ser. A*, **29**, 738 (1975); (b) S. Hauge and O. Vikane, *ibid.*, **29**, 755 (1975); (c) O. Vikane, *ibid.*, **29**, 763 (1975); (d) *ibid.*, **29**, 787 (1975).
- (48) J. D. McCullough, *Inorg. Chem.*, **14**, 1142 (1975).
- (49) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965).
- (50) (a) EHM and CNDO/2: J. M. Howell, *J. Am. Chem. Soc.*, **97**, 3930 (1975). (b) Ab initio: F. Keil and W. Kutzelnigg, *ibid.*, **97**, 3623 (1975), and references cited therein.
- (51) E. M. Shustorovich, to be submitted for publication.
- (52) See, for instance, ref 36-39, 43-45.
- (53) For example, a great number of the relevant molecules have been calculated by ab initio methods,<sup>54</sup> not to mention the countless semiempirical calculations like those in ref 38 and 39.
- (54) W. G. Richards, T. E. H. Walker, L. Farnell, and P. R. Scott, "Bibliography of *ab initio* Molecular Wave Functions. Supplement for 1970-1973", Clarendon Press, Oxford, 1974.
- (55) In linear  $ALL'$  and planar trigonal  $AL_3-kL'_k$  compounds where A has vacant valence  $p_{\pi}$  orbitals, the A-L bonds may even be strengthened by a better  $\sigma$  donor  $L'$  owing to donor-acceptor  $\pi_L \rightarrow \pi_A$  interactions if  $L'$  is not a  $\pi$  donor (such as H or  $CH_3$ ) but L is a good  $\pi$  donor (such as I or Br).

## Generalized Berlin Diagram for Polyatomic Molecules

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**Abstract:** The region-functional concept of electron density, which was first presented by Berlin for diatomic molecules (Berlin diagram), is explicitly generalized for polyatomic molecules on the basis of the electrostatic Hellmann-Feynman theorem. For a given internal coordinate (process), the space around the molecule is separable into accelerating (A) and resisting (R) regions (generalized Berlin diagram). The electron density in the A region accelerates the process, while the density in the R region resists it. The generalized Berlin diagram thus gives an explicit regional definition useful for the density-guiding rule for nuclear-rearrangement processes. The generalized Berlin diagrams are illustrated for the three internal modes of  $H_2O$  and are superposed on the density difference maps. They are shown to give a basis for clarifying the density origin of the geometry and vibration.

### Introduction

In recent years, the force and density approaches based on the electrostatic Hellmann-Feynman (H-F) theorem<sup>1</sup> have received much attention in molecular quantum chemistry.<sup>2</sup> The primary advantage of the force concept lies in its simplicity and visually compared with those of the energetics. Furthermore, the H-F forces are directly connected with the electron density of a system, so that the forces along the process are mainly governed by the behavior of the electron density along the process.<sup>3,4</sup> From this point of view, we have given previously a density-guiding rule for nuclear-rearrangement processes, based on intuition for the region-functional roles of the electron density along the process.<sup>4</sup>

In 1951, Berlin considered the region-functional role of the electron density for diatomic molecules.<sup>5</sup> He divided the molecular space into binding and antibinding regions. Namely, the electron density in the binding region gives a force which binds the two nuclei, while the density in the antibinding region

gives a force which separated the nuclei. At the equilibrium internuclear distance, the binding force just balances with the sum of the antibinding force and the nuclear repulsion. For diatomic molecules, Bader et al.<sup>6a</sup> and others<sup>6b</sup> have studied the nature of chemical bonds using the Berlin diagram superposed on the electron density and density difference maps.

For polyatomic molecules, Bader<sup>7a</sup> and Johnson<sup>8</sup> have "synthesized" generalized Berlin diagrams by superposing the diatomic Berlin diagrams for the bonds included in a molecule. Bader and Preston<sup>7b</sup> have also considered a different superposition. Though they have obtained some intuitive results from such diagrams, their method seems to be less general. Indeed, it would be difficult to get a region-functional diagram for a bending mode, a twisting mode, etc. from such a simple modification of the diatomic Berlin diagram.

A purpose of this paper is to generalize unambiguously Berlin's region-functional concept of electron density to any internal coordinates of polyatomic molecules. We will use the center-of-mass-of-the-nuclei (CMN) coordinates, instead of the geometric-center-of-the-nuclei (GCN) coordinates used

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