T. THE DIPOLE MOMENT OF A LONE ELECTRON PAIR

The electronic lone pairs play an important role in intermolecular interactions. In particular, a lone pair protruding in space towards its partner has a large dipole moment,[1] which may interact electrostatically with its partner's multipole moments (see Appendix X, p. 1038). Let us see how the dipole moment depends on the atom to which it belongs and on the type of hybridization.

Suppose the electronic lone pair is described by the normalized hybrid

$$h = \frac{1}{\sqrt{1+\lambda^2}}\big[(2s) + \lambda(2p_x)\big],$$

with the normalized $2s$ and $2p_x$ atomic orbitals. The coefficient λ may change from $-\infty$ to $+\infty$ giving a different degree of hybridization. Fig. T.1 shows for comparison two series of the hybrids: for carbon and fluorine atoms. If $\lambda = 0$, we have the pure $2s$ orbital, if $\lambda = \pm\infty$ we obtain the pure $\pm 2p_x$ orbital.

The dipole moment of a single electron described by h is calculated[2] as ($N = \frac{1}{\sqrt{1+\lambda^2}}$):

$$\mu_x = \langle h|-x|h \rangle = -N^2\big[\langle 2s|x|2s \rangle + \lambda^2 \langle 2p_x|x|2p_x \rangle + 2\lambda \langle 2s|x|2p_x \rangle\big],$$

$$\mu_y = \mu_z = 0,$$

where x stands for the x coordinate of the electron.

The first two integrals equal zero, because the integrand represents an odd function[3] with respect to the reflection in the plane $x = 0$. As a result

$$\mu_x = -N^2 2\lambda \langle 2s|x|2p_x \rangle.$$

We will limit ourselves to $\lambda \geqslant 0$, which means we are considering hybrids protruding to the right-hand side[4] as in Fig. T.1, and since $\langle 2s|x|2p_x \rangle > 0$, then $\mu_x \leqslant 0$. The negative sign stresses the fact that a negative electron is displaced to the right-hand side (positive x).

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[1] Calculated with respect to the nucleus; a large dipole moment means here a large length of the dipole moment vector.

[2] Atomic units have been used throughout, and therefore μ is expressed in a.u.

[3] Please recall that the orbital $2p_x$ represents a spherically symmetric factor multiplied by x.

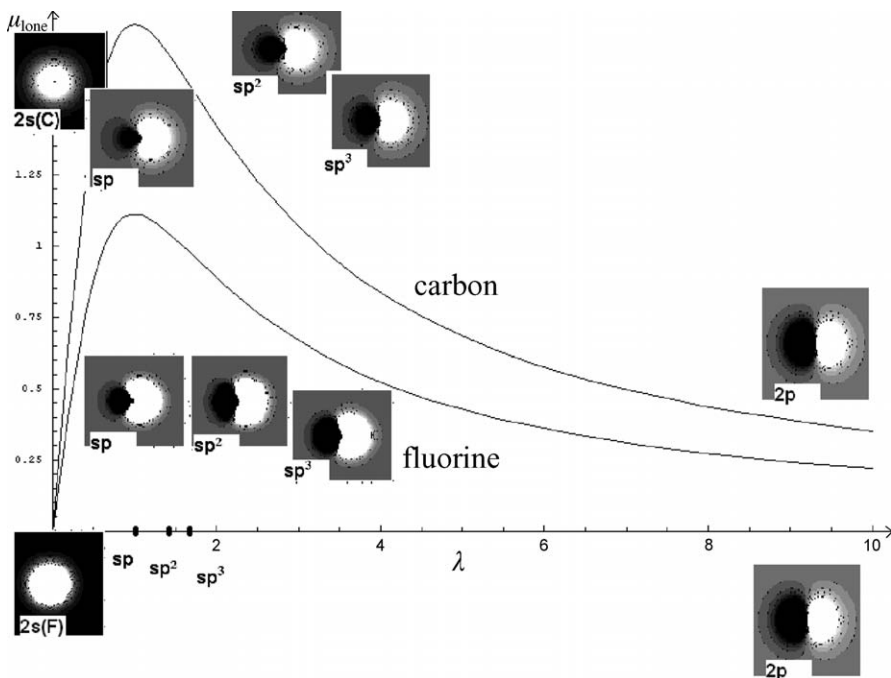[4] The hybrids with $\lambda < 0$ differ only by protruding to the left-hand side.

Fig. T.1. The length of the dipole moment vector μ_{lone} (in a.u.) as a function of the mixing parameter λ for carbon (upper curve) and fluorine (lower curve) atoms. The figure shows the shape of different hybrids $h = \frac{1}{\sqrt{1+\lambda^2}}[(2s) + \lambda(2p_x)]$ which correspond to various mixing of the $2s$ and $2p_x$ carbon Slater orbitals (with exponential factor $\zeta = 1.625$) and fluorine orbitals ($\zeta = 2.60$); from the left: $\lambda = 0$, $\lambda = 1$ (sp), $\lambda = 1.41$ (sp^2), $\lambda = 1.73$ (sp^3), $\lambda = 1000$. All the hybrids are shown in square windows of 10 a.u. The fluorine orbitals are more compact due to the larger charge of the nucleus. A hybrid orbital which corresponds to $\lambda < 0$ looks exactly like that with $\lambda' = -\lambda$, except it is reflected with respect to the yz plane. The maximum dipole moment corresponds to the sp hybridization.

To calculate $\langle 2s|x|2p_x\rangle$ *we need to specify the atomic orbitals* $2s$ *and* $2p$. As the $2s$ and $2p$ atomic orbitals, let us take Slater type orbitals:

$$2s = N'r\exp(-\zeta r),$$
$$2p_x = N''x\exp(-\zeta r),$$

where the exponential factor ζ (the same for both orbitals) is calculated using simple rules for building the Slater orbitals, see p. 355.

Using the integral

$$\int_0^\infty x^n \exp(-\alpha x)\,dx = n!\alpha^{-(n+1)},$$

we obtain the normalization constants $N' = \zeta^2\sqrt{\frac{\zeta}{3\pi}}$ and $N'' = \zeta^2\sqrt{\frac{\zeta}{\pi}}$. The contribution of two electrons ("lone electron pair") to the dipole moment is, therefore, equal to

$$\mu_{\text{lone}} = 2\mu_x = -N^2 |\lambda| (2s|xp_x) = -2N^2 N' N''(2\lambda) \int rx^2 \exp(-2\zeta r) \, dv$$

$$= -2N^2 N' N'' 2\lambda \int r^3 x^2 \exp(-2\zeta r) \sin \theta \, dr \, d\theta \, d\phi$$

$$= -2N^2 N' N'' 2\lambda \int_0^\infty dr \, r^5 \exp(-2\zeta r) \int_0^\pi \sin^3 \theta \, d\theta \int_0^{2\pi} \cos^2 \phi \, d\phi$$

$$= -2N^2 N' N'' 2\lambda \frac{5!}{(2\zeta)^6} \frac{4}{3} \pi = -\frac{4\lambda}{(1+\lambda^2)} \zeta^2 \sqrt{\frac{\zeta}{3\pi}} \zeta^2 \sqrt{\frac{\zeta}{\pi}} \frac{5!}{(2\zeta)^6} \frac{4}{3} \pi$$

$$= -\frac{\lambda}{1+\lambda^2} \frac{10}{\zeta \sqrt{3}}.$$

> THE DIPOLE MOMENT OF A LONE PAIR $\mu_{\text{lone}} = -\frac{\lambda}{1+\lambda^2} \frac{10}{\zeta\sqrt{3}}$.

The dipole moment at $\lambda = 0$, i.e. for the pure $2s$ orbital, is equal to 0, for $\lambda = \infty$, i.e. for the pure $2p_x$ orbital it is also equal 0. It is interesting to see for which hybridization the length of dipole moment has a maximum. We easily find

$$\frac{\partial |\mu_{\text{lone}}|}{\partial \lambda} = \frac{10}{\zeta \sqrt{3}} \frac{(1+\lambda^2) - 2\lambda^2}{(1+\lambda^2)} = 0,$$

which gives $\lambda = \pm 1$, independently of ζ.

Thus

> the maximum dipole moment is at the $1:1$ mixing of $2s$ and $2p$, i.e. for digonal hybridization (for any element), Fig. T.1.

From Table T.1 it is seen that the dipole moment of a lone pair strongly depends on the chemical element,[5] and to a lesser extent on hybridization.

Table T.1. The length of the dipole moments μ_{lone} (a.u.) corresponding to doubly occupied hybrid atomic orbitals. The orbital exponents of $2s$ and $2p$ STO's are identical and calculated using the rules given by Slater: $\zeta_C = 1.625$, $\zeta_N = 1.95$, $\zeta_O = 2.275$, $\zeta_F = 2.60$

Atom	Digonal $\lambda = 1$	Trigonal $\lambda = \sqrt{2}$	Tetrahedral $\lambda = \sqrt{3}$
C	1.776	1.675	1.538
N	1.480	1.396	1.282
O	1.269	1.196	1.099
F	1.110	1.047	0.962

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[5]From the practical point of view, it is probably most important to compare nitrogen and oxygen lone pairs. Thus, coordination of a cation by amines should correspond to a stronger interaction than that by hydroxyl groups.