

## Dipole Moment of a Lone Pair

Electronic lone pairs play an important role in intermolecular interactions. In particular, a lone pair protruding in space toward its partner has a large dipole moment,<sup>1</sup> which may interact electrostatically with partner's multipole moments (see Appendix X available at [book-site.elsevier.com/978-0-444-59436-5](http://book-site.elsevier.com/978-0-444-59436-5), p. e169). 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:

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

with the normalized  $2s$  and  $2p_x$  atomic orbitals. The coefficient  $\lambda$  may change from  $-\infty$  to  $+\infty$ , giving a different degree of hybridization. Figure T.1 shows two series of the hybrids as a comparison: for the carbon and for the fluorine atoms. If  $\lambda = 0$ , then 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<sup>2</sup> as (with  $N = \frac{1}{\sqrt{1+\lambda^2}}$ )

$$\begin{aligned} \mu_x &= \langle h | -x | h \rangle = -N^2 [ \langle 2s | x | 2s \rangle + \lambda^2 \langle 2p_x | x | 2p_x \rangle + 2\lambda \langle 2s | x | 2p_x \rangle ], \\ \mu_y &= \mu_z = 0, \end{aligned}$$

where  $x$  stands for the  $x$  coordinate of the electron.

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

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

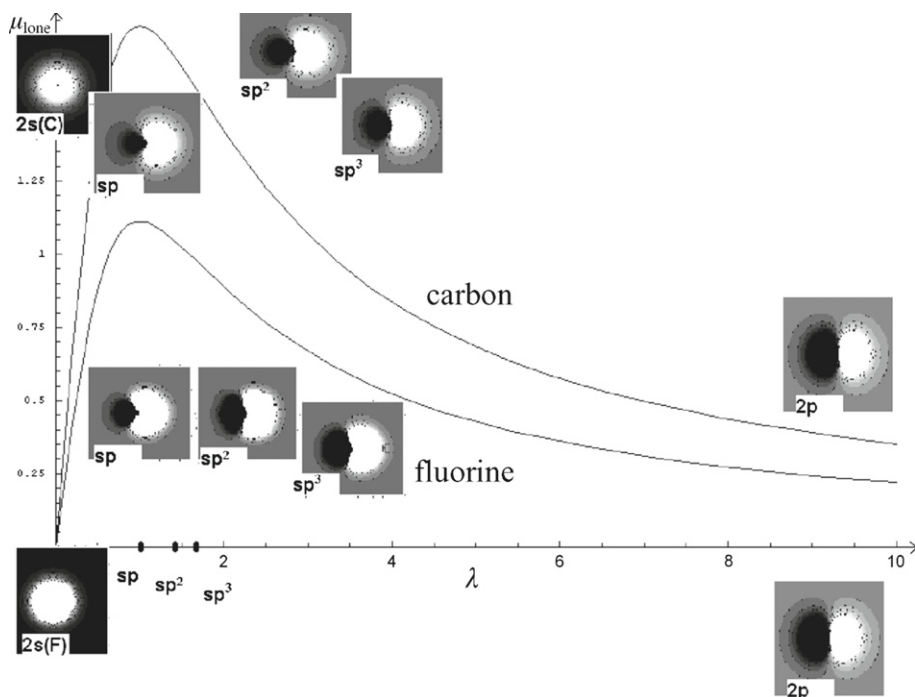
We will limit ourselves to  $\lambda \geq 0$ , which means that we are considering the hybrids protruding to the right side,<sup>4</sup> as in Fig. T.1, and since  $\langle 2s | x | 2p_x \rangle > 0$ , then  $\mu_x \leq 0$ . The negative sign stresses the fact that a negative electron is displaced to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

<sup>1</sup> This is calculated with respect to the nucleus; the term *large dipole moment* means here that the dipole moment vector is very long.

<sup>2</sup> Atomic units have been used throughout, so  $\mu$  is expressed in atomic units.

<sup>3</sup> Please recall that the orbital  $2p_x$  represents a spherically symmetric factor multiplied by  $x$ .

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



**Fig. T.1.** The length of the dipole moment vector (in a.u.) as a function of the mixing parameter  $\lambda$  for the carbon (upper-curve) and fluorine (lower-curve) atoms. The figure shows the shape of different hybrids  $h = \frac{1}{\sqrt{1+\lambda^2}}[(2s) + \lambda(2p_x)]$  that correspond to various combinations of the  $2s$  and  $2p_x$  carbon Slater orbitals (with the exponential factor  $\zeta = 1.625$ ) and the 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 the square windows of the size of 10 a.u. The fluorine orbitals are more compact due to the larger charge of the nucleus. A hybrid orbital that corresponds to  $\lambda < 0$  looks exactly as that with  $\lambda$ , 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  $2p$ . For the  $2s$  and  $2p$  atomic orbitals, let us take the Slater Type Orbitals (STOs):

$$\begin{aligned} 2s &= N' r \exp(-\zeta r), \\ 2p_x &= N'' x \exp(-\zeta r), \end{aligned}$$

where the exponential factor  $\zeta$  (the same for both orbitals) is calculated using simple rules for building the Slater orbitals; see p. 451.

Using the integral  $\int_0^\infty x^n \exp(-\alpha x) dx = n! \alpha^{-(n+1)}$ , in a four-minute calculation, 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 (“electron pair”) to the dipole moment is, therefore, equal to

$$\mu_{\text{lonc}} = 2\mu_x = -N^2 |\lambda| \langle 2s|x p_x \rangle = -2N^2 N' N'' (2\lambda) \int r x^2 \exp(-2\zeta r) dV$$

$$\begin{aligned}
&= -2N^2N'N''2\lambda \int r^3x^2 \exp(-2\zeta r) \sin\theta dr d\theta d\phi \\
&= -2N^2N'N''2\lambda \int_0^\infty dr r^5 \exp(-2\zeta r) \int_0^\pi \sin^3\theta d\theta \int_0^{2\pi} \cos^2\phi d\phi \\
&= -2N^2N'N''2\lambda \frac{5!}{(2\zeta)^6} \frac{4}{3}\pi \\
&= -\frac{4\lambda}{(1+\lambda^2)} \zeta^2 \sqrt{\frac{\zeta}{3\pi}} \zeta^2 \sqrt{\frac{\zeta}{\pi}} \frac{5!}{(2\zeta)^6} \frac{4}{3}\pi = -\frac{\lambda}{(1+\lambda^2)} \frac{10}{\zeta\sqrt{3}}.
\end{aligned}$$

$$\text{Dipole Moment of a Lone Pair: } \mu_{lone} = -\frac{\lambda}{(1+\lambda^2)} \frac{10}{\zeta\sqrt{3}}.$$

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 is also equal 0. It is interesting for which hybridization the length of the dipole moment is at its maximum, see Fig. T.1. We easily find  $\frac{\partial|\mu_{lone}|}{\partial\lambda} = \frac{10}{\zeta\sqrt{3}} \frac{(1+\lambda^2)-2\lambda^2}{(1+\lambda^2)^2} = 0$ , which gives  $\lambda = \pm 1$ , independent of  $\zeta$ .

Thus,

the maximum of the dipole moment is at the 1 : 1 mixing of  $2s$  and  $2p$  [i.e., for the digonal hybridization (for any element); see Table T.1].

The table shows that the dipole moment of a lone pair strongly depends on the chemical element,<sup>5</sup> and to a lesser extent on hybridization.

**Table T.1.** The length of dipole moments (a.u.) corresponding to doubly occupied hybrid atomic orbitals.

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

The orbital exponents of  $2s$  and  $2p$  STO's are identical and computed using the rules given by Slater:  $\zeta_C = 1.625$ ,  $\zeta_N = 1.95$ ,  $\zeta_O = 2.275$ ,  $\zeta_F = 2.60$ .

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

