

Orbital Alignments*

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1 Introduction

In discussions of twisted ethylene derivatives, Figure 1, and similar discussions concerning Woodward Hoffman rules¹ the $\cos \chi$ (χ is the twist angle) dependence rule of the overlap integral between adjacent, but relatively canted, p-type orbitals is usually taken for granted. Since semi-empirical methods and most hand-waving arguments in quantum chemistry are dominated by reference to overlap and its changes, it seems worthwhile to rigorously explain why the $\cos \chi$ rule exists. As a side benefit, the computation of the overlap between orbitals which do not share a common origin helps to clarify issues concerning orthogonality in a molecular setting which are normally ignored.

2 LCAO-MOs

The Linear Combination of Atomic Orbitals forming Molecular Orbitals concept is central to most discussions of bonding in small molecules. The H_2^+ case, the case most widely used for introductory work, is used here. The two nuclei and one electron case can be handled “exactly” (although not in closed form); the charges on the two nuclei are equal in homonuclear molecules ions, and otherwise they are heteronuclear.

We assume that a one electron π -molecular orbital is given by a linear combination of 2 p-orbitals located on different nuclei. By convention, the

*12h2:orbalign

¹David, C. W., J. Chem. Ed., 1999, 76, 999-1001

z-axis is chosen, Figure 2, such that the nuclei lie at $(0,0,R/2)$ and $(0,0,-R/2)$. This means that if the p-orbitals which are being “combined” are p_x orbitals, then we have for the LCAO-MO form:

$$\Psi_{LCAO-MO} = c_1\psi_{2p_x}^A + c_2\psi_{2p_x}^B = c_1xe^{-\sqrt{x^2+y^2+(z-R/2)^2}/2} + c_2xe^{-\sqrt{x^2+y^2+(z+R/2)^2}/2} \quad (1)$$

where, in the homonuclear case under consideration $c_1 = c_2$ which we can take to be one (i.e., un-normalized total wave function). Our $\Psi_{LCAO-MO}$ is formed from two parallel p-orbitals, one located above the other. The question addressed herein consists of what happens when one of the orbitals is twisted about the bond axis relative to the other?

2.1 Coördinate Systems

The un-natural (from the point of view of most textbooks) notation used in specifying the p-orbitals in Equation 1 is deliberate, focusing attention on two aspects of wave function notation which are normally not emphasized:

1. Every text book writes p-orbitals either in spherical polar coördinates i.e.,

$$r \sin \theta \cos \phi e^{-r/2}$$

or in mixed notation, i.e.,

$$xe^{-r/2}$$

which means that one rarely sees orbitals written out when their “centers” are not at the origin. It is important to stress this “un-natural” notation when dealing with molecules, since otherwise, the θ 's and ϕ 's become confused with the spherical polar coördinates which are normally used for origin centered orbitals.

2. The LCAO-MO wave functions of molecules represents electronic wave functions which are parametrically dependent on nuclear coördinates, i.e., they are not “origin centered”.

2.2 Twisted Orbitals

We choose a twist angle χ for one of the two p-orbitals (say the “upper” one at $(0,0,R/2)$), and write that orbital now as the proper linear combination

$$\psi_{twisted} = \cos \chi \psi_{2p_x}^A + \sin \chi \psi_{2p_y}^A = \cos \chi \left(xe^{-\sqrt{x^2+y^2+(z-R/2)^2}/2} \right) + \sin \chi \left(ye^{-\sqrt{x^2+y^2+(z-R/2)^2}/2} \right)$$

which emphasizes the fact that one is twisting the orbital, not the coordinate system ². $\psi_{twisted}$ is itself an LCAO of p_x and p_y orbitals and is, in fact, also

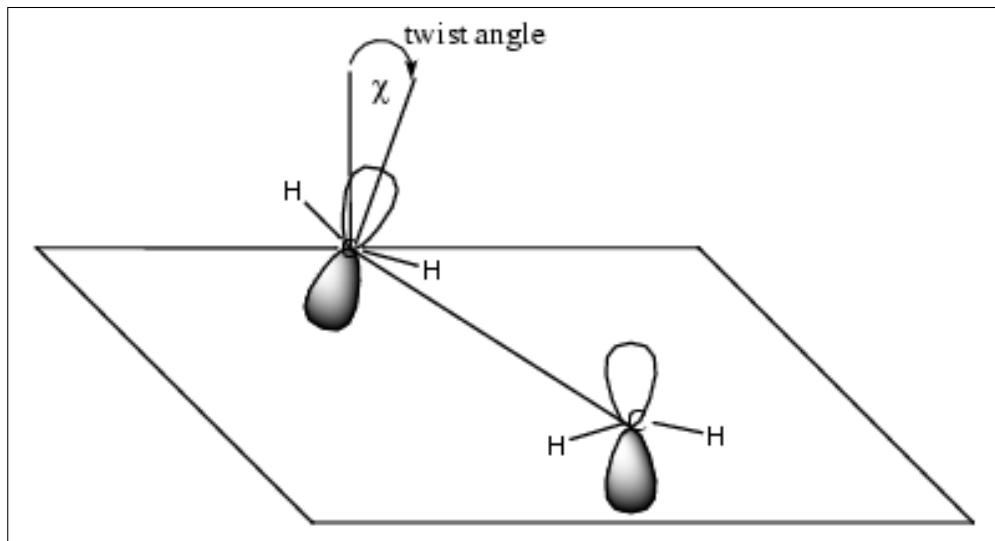


Figure 1: Twisted Ethylene, showing the p-orbitals canted relative to each other.

a p orbital.

The overlap between the two orbitals, one twisted (on A), the other not (on B), is given by

$$\int (\cos \chi \psi_{2p_x}^A + \sin \chi \psi_{2p_y}^A) \psi_{2p_x}^B = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left\{ \cos \chi \left(x e^{-\sqrt{x^2+y^2+(z-R/2)^2}/2} \right) x e^{-\sqrt{x^2+y^2+(z+R/2)^2}/2} + \sin \chi \left(y e^{-\sqrt{x^2+y^2+(z-R/2)^2}/2} \right) x e^{-\sqrt{x^2+y^2+(z+R/2)^2}/2} \right\}$$

The second integral ($\sin \chi$ related) vanishes, leaving the $\cos \chi$ dependence sought:

$$S_{p-p}(\chi) = \cos \chi S_{p-p}(\chi = 0)$$

²see, for example, Albright, T. A., Burdett, J. K. and Myung-Hwan, W., "Orbital Interactions in Chemistry", John Wiley & Sons, New York, pages 7-9 and page 77.

i.e.,

$$S_{p-p}(\chi) = \cos \chi \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left(x e^{-\sqrt{x^2+y^2+(z-R/2)^2/2}} \right) x e^{-\sqrt{x^2+y^2+(z+R/2)^2/2}} \quad (2)$$

Note that $\chi = 0$ makes the overlap maximum and positive, while at $\chi = \pi$ we have the opposite, i.e, the overlap is minimum and negative.

2.3 Evaluating the Resultant Integral

It is a straight forward task to evaluate the integral (Equation 2) if one converts to elliptical coordinates (λ, μ, ϕ) ³. In mixed coordinate notation, one has

$$S_{p-p}(\chi = 0) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left\{ x e^{-r_A/2} x e^{-r_B/2} \right\} \quad (3)$$

in un-normalized form. Since $\lambda \equiv \frac{r_A+r_B}{R}$, and $\mu \equiv \frac{r_A-r_B}{R}$ one obtains $r_A = \frac{R}{2}(\lambda + \mu)$ and $r_B = \frac{R}{2}(\lambda - \mu)$, while ϕ is the same as in spherical polar coordinates. Further, one has

$$z = \frac{R\lambda\mu}{2}$$

$$x = \frac{R}{2} \cos \phi \sqrt{(\lambda^2 - 1)(1 - \mu^2)}$$

and

$$y = \frac{R}{2} \sin \phi \sqrt{(\lambda^2 - 1)(1 - \mu^2)}$$

The volume element in this coordinate system is $dV = dx dy dz = \frac{R^3}{8}(\lambda^2 - \mu^2) d\lambda d\mu d\phi$ and the limits of integration required to cover all space are $\lambda = 1 \rightarrow \infty$ $\mu = 1 \rightarrow -1$ and, of course, $\phi = 0 \rightarrow 2\pi$.

Our integral, Equation 3, becomes

$$\int_1^{\infty} d\lambda \int_1^{-1} d\mu \int_0^{2\pi} d\phi \left(\left(\frac{R}{2} \cos \phi \sqrt{(\lambda^2 - 1)(1 - \mu^2)} \right)^2 e^{-\frac{R}{2}(\frac{\lambda+\mu}{2})} e^{-\frac{R}{2}(\frac{\lambda-\mu}{2})} \frac{R^3}{8} (\lambda^2 - \mu^2) \right)$$

³David, C. W., J. Chem. Ed., 1982, 59, 299-289, and see http://www.sp.uconn.edu/~ch351vc/cgi-bin/main_menu.pl here one of the readings discusses Elliptical Coordinates.

which becomes, finally,

$$S_{p-p}(\chi = 0) = \frac{4\pi}{15} e^{-R/2} (R^3 + 12R^2 + 60R + 120)$$

Similarly, Slater type orbital overlaps are available in the literature ⁴.

2.4 Relatively twisted $d_\pi - p_\pi$ bonds

In $d_\pi - p_\pi$ bonding, see Figure 3, the twisting of one orbital relative to the other is not quite so obviously related to the $\cos \chi$ rule. We have (for the untwisted case) an LCAO orbital resembling

$$\psi_{d_\pi-p_\pi} = x(z - R/2)e^{-\sqrt{x^2+y^2+(z-R/2)^2}/3} + (6 - r_B)xe^{-\sqrt{x^2+y^2+(z+R/2)^2}/3}$$

if the $3d_{xz}$ orbital is on atom A and the $3p_x$ orbital is on atom B.

Twisting the p orbital (centered on nucleus B), we obtain for the overlap integral

$$S_{d_\pi-p_\pi}(\chi) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left(x(z - R/2)e^{-\sqrt{x^2+y^2+(z-R/2)^2}/3} \right) \times \\ \left(\cos \chi \left[(6 - r_B)xe^{-\sqrt{x^2+y^2+(z+R/2)^2}/3} \right] + \sin \chi \left[(6 - r_B)ye^{-\sqrt{x^2+y^2+(z+R/2)^2}/3} \right] \right)$$

Again, the $\sin \chi$ contribution vanishes since p_y^B is orthogonal to d_{xz}^A . We are left with a non-trivial, but do-able, integral which again is easier when evaluated in elliptical coördinates than in Cartesian coördinates. Rewriting, we have (in mixed notation)

$$S_{d_\pi-p_\pi}(\chi) = \cos \chi \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left[(x^2(z - R/2)(6 - r_B)) e^{-r_A/3} e^{-r_B/3} \right] \quad (4)$$

In elliptical coördinates this becomes

$$S_{d_\pi-p_\pi}(\chi = 0) = \int_1^{\infty} d\lambda \int_1^{-1} d\mu \int_0^{2\pi} d\phi \frac{R^3}{8} (\lambda^2 - \mu^2) \\ \left(\left(\frac{R}{2} \cos \phi \sqrt{(\lambda^2 - 1)(1 - \mu^2)} \right)^2 \left(\frac{R\lambda\mu}{2} \right) \left(6 - \frac{R}{2}(\lambda - \mu) \right) e^{-\frac{R}{3}(\frac{\lambda+\mu}{2})} e^{-\frac{R}{3}(\frac{\lambda-\mu}{2})} \right)$$

which becomes, finally,

$$S_{d_\pi-p_\pi}(\chi = 0) = \frac{3\pi}{140} e^{-R/3} R (R^4 + 30R^3 + 405R^2 + 2835R + 8505)$$

⁴Mulliken, R. S., Rieke, C. A., Orloff, D., and Orloff, H., J. Chem. Phys., 1949, 17, 1248.

3 Conclusions

Students of elementary quantum chemistry are usually unable to understand the relationship between nuclear coordinates and electronic wavefunctions. Since LCAO-MO wave functions are used almost exclusively at this level, it makes sense to stress the manner in which atomic orbitals are translated from their origin centered forms in the H-atom and similar atomic situations to nuclei centered contributors in molecular situations.

Clarifying the “origin dependence” of atomic orbital contributors to molecular orbitals is also enhanced by actually evaluating overlap integrals, showing how the coordinate systems influence our ability to carry out such integrals, and reducing student’s dependence on spherical polar coordinate representations of atomic orbitals.

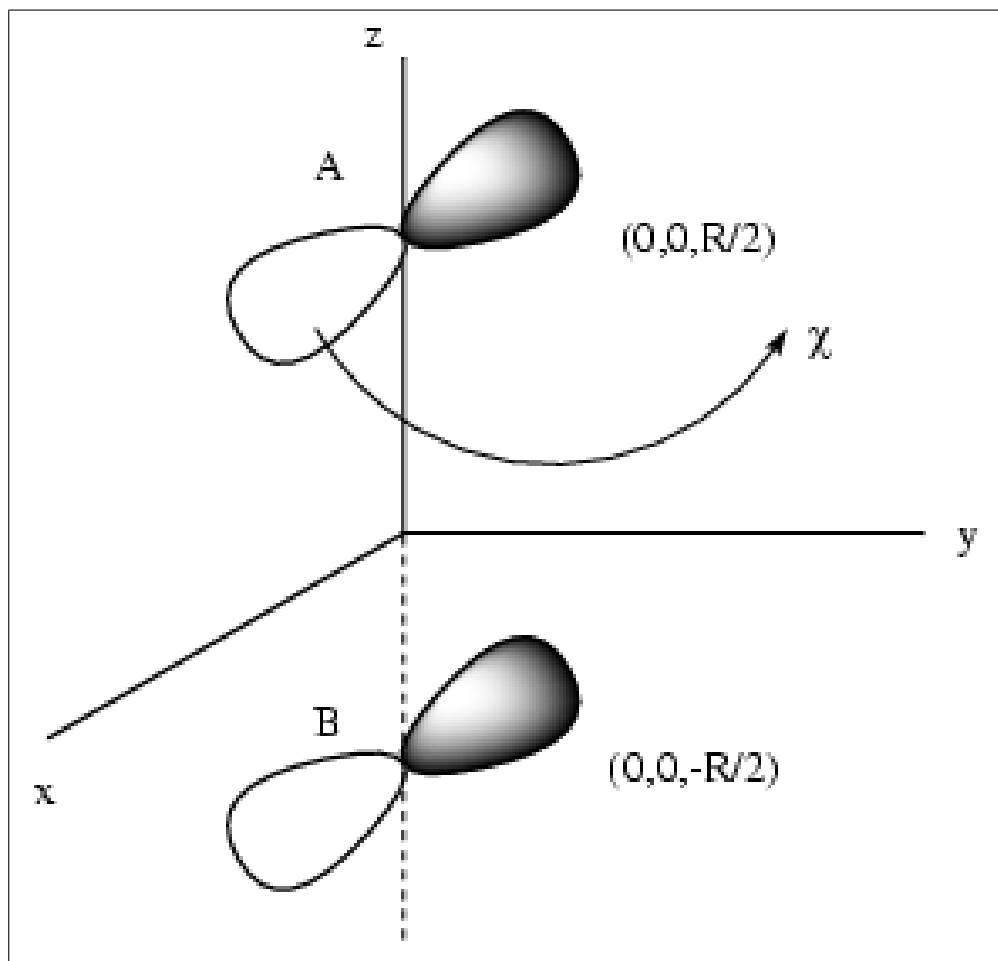


Figure 2: Two p_x orbitals canted relative to each other

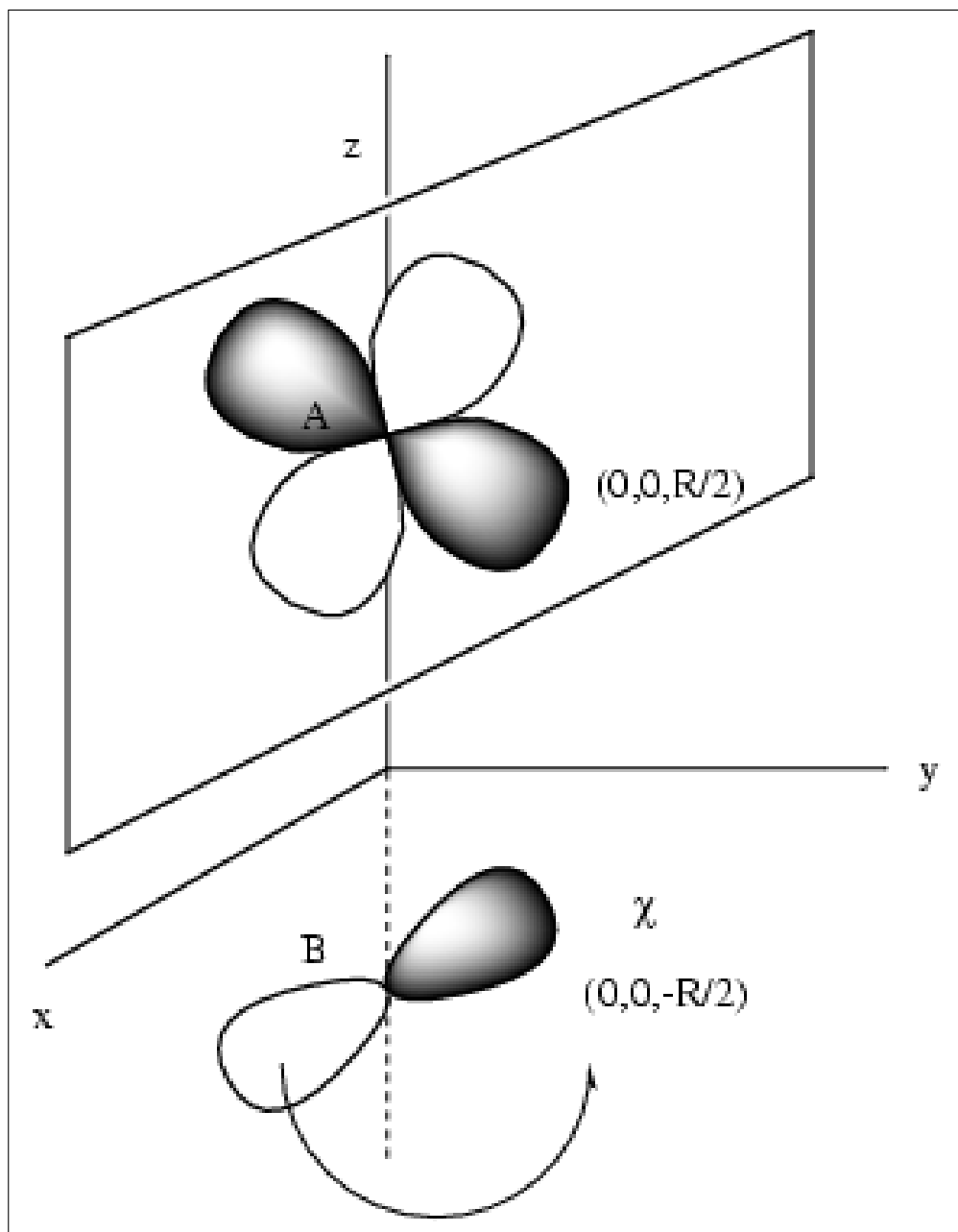


Figure 3: $3p_x$ and $3p_{xz}$ orbitals canted relative to each other