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Triatomic Molecular Orbitals

Carl W. David
University of Connecticut, Carl.David@uconn.edu

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C. W. David
Department of Chemistry
University of Connecticut
Storrs, Connecticut 06269-3060
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I. SYNOPSIS

If elementary Quantum Chemistry stops at diatomic molecules, some students may be left with false impressions concerning how one builds polyatomic molecule's LCAO-MOs. This reading discusses building such molecular orbitals from atomic orbitals centered at different spatial coördinates.

II. INTRODUCTION

When we talk about diatomic molecules, there is no question in our minds where the contributing orbitals lie. One set of orbital lies centered on one nucleus and the other set lies on the other.

Now consider water. We wish to build up our understanding of the electronic structure of water from its constituents. For the protons, this is easy, we will build the protons with 1s orbitals attached. For the oxygen, this is also simple, since oxygen is $1s^2 2s^2 2p^4$.

The problem occurs when we start to put flesh on these words and symbols. To start with, let's locate the coördinates of the atoms, the nuclei. Although it might be convenient for some problems (concerning rotation) to locate our coördinate system on the center of mass, we choose instead to locate the origin of our coordinate system on the oxygen. The bond length of water's O-H bond is 0.9584Å, and the H-O-H bond angle is 104.5^o, which means that we can locate proton number one at

$$x_{H_1} = 0.9584 \cos\left(\frac{104.5}{2}\right) \tag{2.1}$$

$$y_{H_1} = 0.9584 \sin(52.25) \tag{2.2}$$

and the other proton, number 2, can be at

$$x_{H_2} = 0.9584 \cos(-52.25)$$
$$y_{H_2} = 0.9584 \sin(-52.25) \tag{2.3}$$

where we have guaranteed that the bond angle and bond lengths are *a priori* built in.

Now the 1s orbital on H_1 is

$$e^{-\alpha r_1}$$

in common parlance, which means

$$\psi_{H_1} = e^{-\alpha\sqrt{(x-0.9584\cos(52.25))^2 + (y-0.9584\sin(52.25))^2 + z^2}}$$

which guarantees that the proton's electron starts its existence in a proper orbital centered on the nucleus. Clearly, for the other proton's electron, we have

$$\psi_{H_2} = e^{-\alpha\sqrt{(x-0.9584\cos(-52.25))^2 + (y-0.9584\sin(-52.25))^2 + z^2}}$$

Of course, the orbitals of the oxygen are

$$\psi_{1s} = e^{-\beta r}$$

$$\psi_{2s} = (2 - r)e^{-\beta r/2}$$

$$\psi_{2p_x} = r\sin\vartheta\cos\varphi e^{-\beta r/2}$$

$$\psi_{2p_y} = r\sin\vartheta\sin\varphi e^{-\beta r/2}$$

$$\psi_{2p_z} = r\cos\vartheta e^{-\beta r/2}$$

where β is a constant which, for the naked H atom, is related to the Bohr radius, but here might be a potential variational parameter and $r = \sqrt{x^2 + y^2 + z^2}$. Figure 1 shows some of the various orbitals diagramatically.

Now, how do we build MO's? What linear combination of these orbitals are we going to use? "Aye, there's the rub! [1]".

Since the bond H-O-H bond angle is 104.5^o, and the tetrahedral angle is 109.471^o ($\cos^{-1}(-\frac{1}{3})$), one can see how tempting it is to hybridize the oxygen orbitals to tetrahedral <u>before</u> attempting an MO computation. On the other hand, the same bond angle is relatively close to 120°, which would imply that a choice of sp^2 hybridization would be only slightly less appropriate than the sp^3 hybridization associated with tetrahedrality.

How about

$$\psi_5 = c_1 1s_{H_1} + c_2 1s_{H_2} + c_3 2s_O + c_4 2p_{x_O} + c_5 2p_{y_O} \tag{2.4}$$

(based on no prior hybridization) versus

$$\psi_4^{sp^3\ based} = c_1 1s_{H_1} + c_2 1s_{H_2} + c_3 2sp_1^3 + c_4 2sp_2^3 + c_5 2sp_2^3$$

(based on prior sp^3 hybridization) versus

$$\psi_3^{sp^2\ based} = c_1 1s_{H_1} + c_2 1s_{H_2} + c_3 2sp_1^2 + c_4 2sp_2^2$$

(based on prior sp^2 hybridization)? And what about the spin?

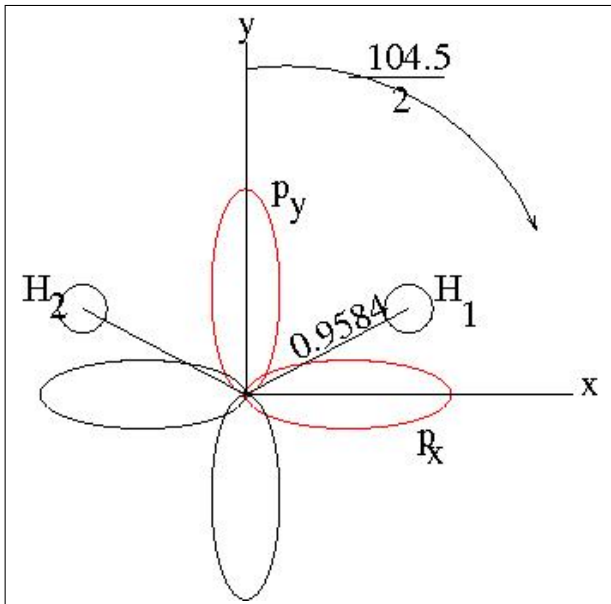FIG. 1: Looking down on a water molecule. The p_z orbital would have zero overlap with H atom's 1s orbital.

III. FERMIONS AND SPIN (1/2) PARTICLES IN SLATER TYPE ORBITALS

A. Hückel Systems Flashback

Ah Hah!

In the case of cyclopropene (or propene, linear for that matter), we had no trouble using an MO which looked like:

$$\psi_{LCAO-MO} = c_1\psi_1^z + c_2\psi_2^z + c_3\psi_3^z$$

where the subscripts referred to the nucleus upon which each of the contributing p orbitals were centered. We realized that there would turn out to be 3 related "eigen-

functions" $\psi_{LCAO-MO}^{(i)}$ with i being 1, 2, or 3. Then, we placed electrons into these resultant MO's with spins opposed. Thus, a wave function for this molecule might be (Equation 2.4):

$$\psi_{LCAO-MO}^{(1)}(1)\alpha(1)\psi_{LCAO-MO}^{(1)}(2)\beta(2)\psi_{LCAO-MO}^{(2)}(3)\alpha(3)$$

which was perfectly legal. But, of course, it wasn't an antisymmetric wave function, now, was it? To get it properly antisymmetrized, we had to write

$$\begin{vmatrix} \psi^{(1)}(1)\alpha(1) & \psi^{(1)}(1)\beta(1) & \psi^{(2)}(1)\alpha(1) \\ \psi^{(1)}(2)\alpha(2) & \psi^{(1)}(2)\beta(2) & \psi^{(2)}(2)\alpha(2) \\ \psi^{(1)}(3)\alpha(3) & \psi^{(1)}(3)\beta(3) & \psi^{(2)}(3)\alpha(3) \end{vmatrix}$$

which is a completely correct wave function (we left off the LCAO-MO subscripts for clarity sake). Figure 2 shows how the filling of the orbitals, assuming electrons are fermions, proceeds.
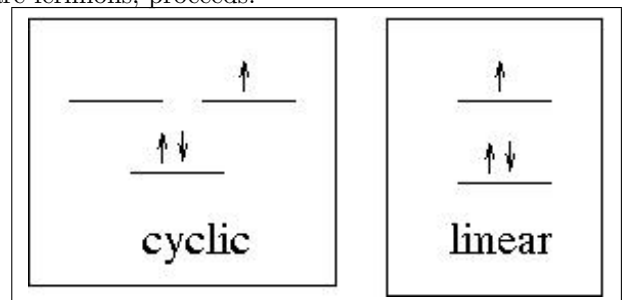

FIG. 2: Putting electrons into molecular orbitals as Fermions.

B. Returning to the Case of Water

In our (water) case, we could write assuming $\psi_5^{(i)}(j)\alpha(j)$ that the j'th electron is in the i'th molecular orbital based on ψ_5 (Equation 2.4), and using commas to delimit rows of the determinant,

$$\Psi = \left| \psi_5^{(1)}(1)\alpha(1), \psi_5^{(1)}(2)\beta(2), \psi_5^{(2)}(3)\alpha(3), \psi_5^{(2)}(4)\beta(4), \psi_5^{(3)}(5)\alpha(5), \psi_5^{(3)}(6)\beta(6), \psi_5^{(4)}(7)\alpha(7), \psi_5^{(4)}(8)\beta(8) \right|$$

as an appropriate synopsis of the complete Slater determinant for an electronic state (with suppressed core electrons) for water. Expanding the determinant would give

$$\Psi = \begin{vmatrix}
\psi_5^{(1)}(1)\alpha(1) & \psi_5^{(1)}(1)\beta(1) & \psi_5^{(2)}(1)\alpha(1) & \psi_5^{(2)}(1)\beta(1) & \psi_5^{(3)}(1)\alpha(1) & \psi_5^{(3)}(1)\beta(1) & \psi_5^{(4)}(1)\alpha(1) & \psi_5^{(4)}(1)\beta(1) \\
\psi_5^{(1)}(2)\alpha(2) & \psi_5^{(1)}(2)\beta(2) & \psi_5^{(2)}(2)\alpha(2) & \psi_5^{(2)}(2)\beta(2) & \psi_5^{(3)}(2)\alpha(2) & \psi_5^{(3)}(2)\beta(2) & \psi_5^{(4)}(2)\alpha(2) & \psi_5^{(4)}(2)\beta(2) \\
\psi_5^{(1)}(3)\alpha(3) & \psi_5^{(1)}(3)\beta(3) & \psi_5^{(2)}(3)\alpha(3) & \psi_5^{(2)}(3)\beta(3) & \psi_5^{(3)}(3)\alpha(3) & \psi_5^{(3)}(3)\beta(3) & \psi_5^{(4)}(3)\alpha(3) & \psi_5^{(4)}(3)\beta(3) \\
\psi_5^{(1)}(4)\alpha(4) & \psi_5^{(1)}(4)\beta(4) & \psi_5^{(2)}(4)\alpha(4) & \psi_5^{(2)}(4)\beta(4) & \psi_5^{(3)}(4)\alpha(4) & \psi_5^{(3)}(4)\beta(4) & \psi_5^{(4)}(4)\alpha(4) & \psi_5^{(4)}(4)\beta(4) \\
\psi_5^{(1)}(5)\alpha(5) & \psi_5^{(1)}(5)\beta(5) & \psi_5^{(2)}(5)\alpha(5) & \psi_5^{(2)}(5)\beta(5) & \psi_5^{(3)}(5)\alpha(5) & \psi_5^{(3)}(5)\beta(5) & \psi_5^{(4)}(5)\alpha(5) & \psi_5^{(4)}(5)\beta(5) \\
\psi_5^{(1)}(6)\alpha(6) & \psi_5^{(1)}(6)\beta(6) & \psi_5^{(2)}(6)\alpha(6) & \psi_5^{(2)}(6)\beta(6) & \psi_5^{(3)}(6)\alpha(6) & \psi_5^{(3)}(6)\beta(6) & \psi_5^{(4)}(6)\alpha(6) & \psi_5^{(4)}(6)\beta(6) \\
\psi_5^{(1)}(7)\alpha(7) & \psi_5^{(1)}(7)\beta(7) & \psi_5^{(2)}(7)\alpha(7) & \psi_5^{(2)}(7)\beta(7) & \psi_5^{(3)}(7)\alpha(7) & \psi_5^{(3)}(7)\beta(7) & \psi_5^{(4)}(7)\alpha(7) & \psi_5^{(4)}(7)\beta(7) \\
\psi_5^{(1)}(8)\alpha(8) & \psi_5^{(1)}(8)\beta(8) & \psi_5^{(2)}(8)\alpha(8) & \psi_5^{(2)}(8)\beta(8) & \psi_5^{(3)}(8)\alpha(8) & \psi_5^{(3)}(8)\beta(8) & \psi_5^{(4)}(8)\alpha(8) & \psi_5^{(4)}(8)\beta(8)
\end{vmatrix}$$

We are assuming 8 electrons (6 orbitals), 2 from H-atoms, and the $2 - 2s$ and $4 - 2p$ electrons, keeping the $2p_z$ electrons in their AO's (isolated, remote, aloof, safe). Equation 2.4 is being used as the Molecular Orbital basis. The Slater determinant is 8x8. Each contributor in the Slater determinant is itself an MO, a molecular orbital, containing contributions from both H-orbitals and the relevant O-orbitals.

Remember that the individual $\psi_5^{(i)}$ each have five constants in them.
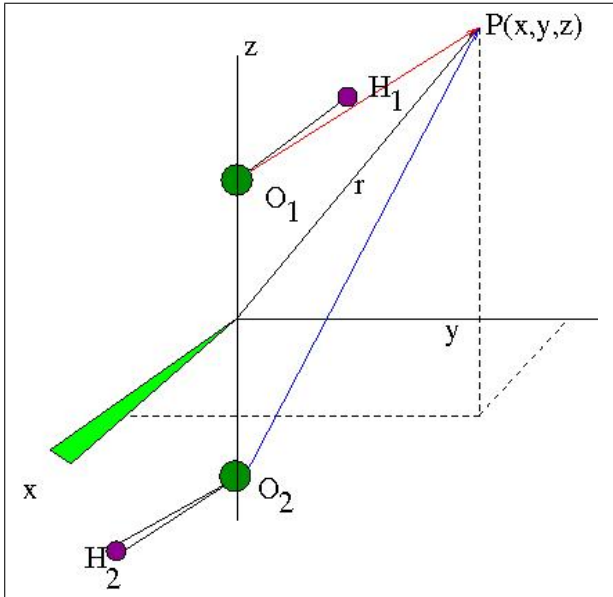
IV. HYDROGEN PEROXIDE

FIG. 3: H_2O_2; the relationship between the radius (from the origin) and the r values which are used for orbitals (normally, not here). For the point $P(x, y, z)$ there are four $\vec{r}$ corresponding to radii from O_1, O_2, H_1, and H_2. The radius from O_1 is shown in red, while that of O_2 is shown in blue.

To make sure that we understand what we are doing, let's consider hydrogen peroxide. This molecule H_2O_2 is not so simple. Placing one oxygen at 0,0,R/2 (where R is the O-O bond length) and the other at 0,0,-R/2 (just like the H_2^+ molecule), with each proton floating about near its oxygen, the contributing orbitals on the oxygens are no longer textbooky. They are not centered on the origin, so their functional form has to be adjusted to make them centered on where the nuclei actually are.

For orbitals for the oxygen at 0,0,R/2, call it O_1, we have that r is writable as

$$r = \sqrt{x^2 + y^2 + (z - R/2)^2}$$

so a $2s$-contributing orbital might be

$$(2 - \sqrt{x^2 + y^2 + (z - R/2)^2})e^{-\sqrt{x^2+y^2+(z-R/2)^2}/2}$$

Notice that the and values normally associated with orbitals in spherical polar coordinates need to be modified once we move nuclei off the origin. In this case, φ retains its meaning, but there is now a value associated with oxygen (call it 1) and another $_2$ associated with the other oxygen. Both of these angles refer to polar angles, but for the blue and red r vectors shown in Figure 3. A p_z orbital on O_1 might be

$$(z - R/2)e^{-\sqrt{x^2+y^2+(z-R/2)^2}}$$

while a p_x orbital on O_2 might be

$$xe^{-\sqrt{x^2+y^2+(z-R/2)^2}}$$

Lastly, a $1s$ orbital on H_1 might appear as

$$e^{\sqrt{(x-x_{H_1})^2+(y-y_{H_1})^2+\left(z-z_{H_1}\right)^2}}$$

i.e., centered on the H_1 nucleus, wherever it happens to be in space.

[1] W. Shakespeare, *Hamlet*, Act 3 Scene 4