

0.1 Hybrid Orbitals

This morning, we learned about the Coulomb degeneracy and discovered that

$$E_{kl} = \frac{-E_I}{(k+l)^2}$$

Due to this dependency, we replaced the set of quantum numbers $\{k, l, m\}$ with $\{n, l, m\}$ where $n = k + l \geq 1$, and $l = 0, 1, \dots, n - 1$. In Hydrogen, this means

$$E_{2S} = E_{2P}$$

Because these states are degenerate, the eigenstates of the Hamiltonian can be linear combinations of these states. This turns out to be critical for bonding models. For example,

$$\varphi_{n,1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} R_{n1}(r) \sin(\theta) e^{\pm i\varphi}$$

$$\varphi_{n10} = \sqrt{\frac{3}{4\pi}} R_{n1}(r) \cos(\theta)$$

We can make linear combinations

$$\varphi_{nP_x} = -\frac{1}{\sqrt{2}} [\varphi_{n,1,+1} - \varphi_{n,1,-1}] = \sqrt{\frac{3}{4\pi}} R_{n1}(r) \frac{x}{r}$$

$$\varphi_{nP_y} = \frac{i}{\sqrt{2}} [\varphi_{n,1,+1} + \varphi_{n,1,-1}] = \sqrt{\frac{3}{4\pi}} R_{n1}(r) \frac{y}{r}$$

and

$$\varphi_{nP_z} = \sqrt{\frac{3}{4\pi}} R_{n1}(r) \frac{z}{r}$$

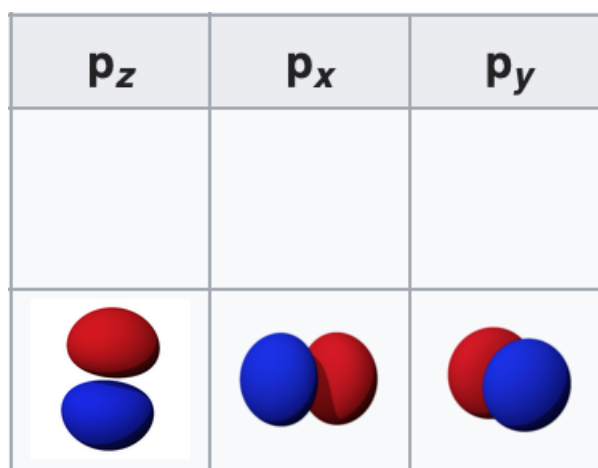
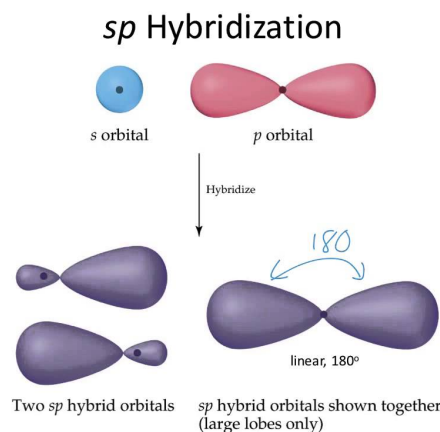


Figure 0.1.1: Plots of the wave functions $\varphi_{nP_{x/y/z}}$

Suppose we constructed a linear combination of the φ_{P_z} and φ_S wave functions. We call the resulting functions “hybrid orbitals”.

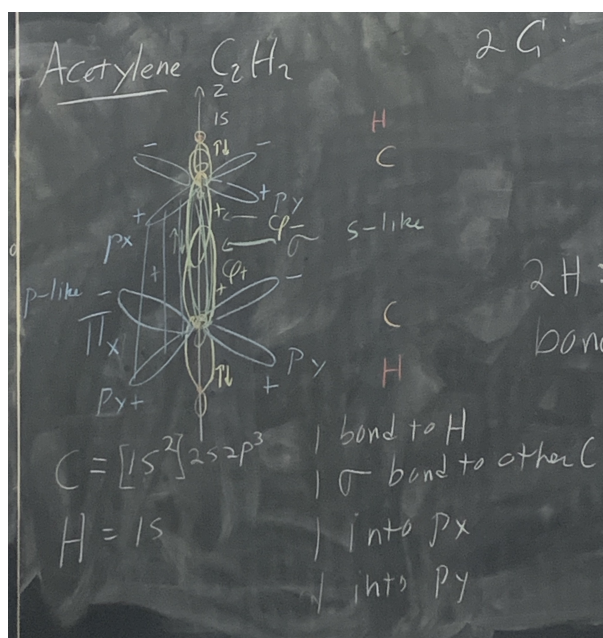
We can use these hybrid orbitals to understand interatomic bonding in real atoms and real molecules.

**Figure 0.1.2:** sp hybrid orbitals**Example.** Acetylene (C_2H_2)

The carbon atoms will have the following electron configuration: $[1s^2]2s2p^3$ where the innermost electron is tightly bound and does not interact. On the other hand, hydrogen has the configuration $1s$. If we call $\varphi_{\pm} = \varphi_{P_z} \pm \varphi_S$, then we see that the overlapping wave functions between the carbon atoms is an s -like bond which we call a σ bond. Similar bonds will exist between the carbon and hydrogen atoms. Each of these bonds will contain one spin-up and one spin-down electron. Additionally, the P_x and P_y orbitals from the carbon atoms can hybridize in planes to form Π_x and Π_y orbitals, which are p -like orbitals since rotation around the z -axis will result in a change in the sign of the wave function.

In conclusion, the $C-H$ bonds are single bonds, whereas the bonds between the carbon atoms are triple bonds ($C \equiv C$), made up of two Π bonds and a σ bond.

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**Figure 0.1.3:** The bonding structure of Acetylene

The sp^2 -hybrids can be described by the wave functions

$$\varphi_{SP_x P_y} = \frac{1}{\sqrt{3}}\varphi_S + \sqrt{\frac{2}{3}}\varphi_{P_x}$$

$$\varphi''_{SP_xP_y} = \frac{1}{\sqrt{3}}\varphi_S + \frac{1}{\sqrt{6}}\varphi_{P_x} + \frac{1}{\sqrt{2}}\varphi_{P_y}$$

$$\varphi'''_{SP_xP_y} = \frac{1}{\sqrt{3}}\varphi_S + \frac{1}{\sqrt{6}}\varphi_{P_x} - \frac{1}{\sqrt{2}}\varphi_{P_y}$$

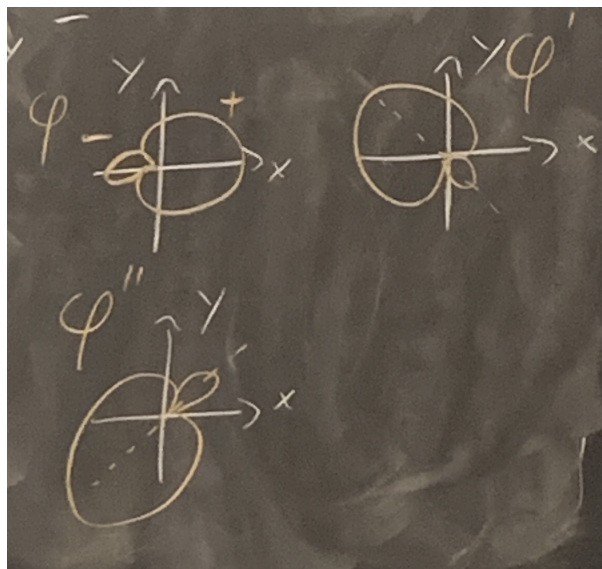


Figure 0.1.4: The SP^2 Hybrids

Example. Ethylene (C_2H_4) has SP^2 hybrid orbitals which bond to the hydrogen atoms (the primed orbitals) and to each other (the unprimed orbital). There will also be a P_z orbital which can bond in a Π bond, creating the double bond between the carbon atoms. \diamond