

Homework H27 Solution

1. Problem 8.5 in the book. [Hint: Remember that CH_3 is planar. Considering it to be in the x-y plane, only $2s$, $2p_x$ and $2p_y$ participate in hybridization (and not $2p_z$, which is orthogonal to the plane.)]

Solution: The carbon atom in the methyl radical has the electronic configuration of $1s^2 2s^2 2p^2$. Considering the molecular plane to be the x-y plane, the $2s$ orbital undergoes hybridization with $2p_x$ and $2p_y$ orbitals, since the $2p_z$ orbital is out of plane and orthogonal wavefunctions have by definition zero overlap.

The 3 atomic orbitals $2s$, $2p_x$ and $2p_y$ on the same atom (carbon) undergo linear combination to form 3 hybrid sp^2 orbitals, each of which is singly occupied. Next, these 3 hybrid orbitals overlap with the 3 $1s$ orbitals on H's, to form the 3 sigma bonds.

The unpaired electron occupies the pure (unhybridized) p_z orbital.

2. Problem 8.6 in the book.

Solution:

The first sp^3 hybrid orbitals of C is given as (p. 162 of the text),

$$\phi_1 = \frac{1}{2}(\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z})$$
$$\int |\phi_1|^2 d\tau = \frac{1}{4} \int (\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z})^2 d\tau$$

Since the atomic orbitals are already orthonormal, the cross terms in the integral vanish, and we get,

$$\int |\phi_1|^2 d\tau = \frac{1}{4} \left[\int \psi_{2s}^2 d\tau + \int \psi_{2p_x}^2 d\tau + \int \psi_{2p_y}^2 d\tau + \int \psi_{2p_z}^2 d\tau \right]$$
$$= 1$$

Similarly, it can be shown the rest 3 orbitals are normalized as well. Note that the ϕ_1 orbital is a lobe pointing diagonally between the x, y and z axes in the positive direction, as shown in Figure 8.20. Think of it geometrically: by adding $p_x+p_y+p_z$, you get a p orbital pointing between the x, y and z axes. Then when you add $2s$, it adds up in the positive direction and cancels in the negative direction. Just like the sp hybrid did from $s \pm p$ in class. The orbitals ϕ_{2-4} do the same, just in the other three directions of a tetrahedron. The sp^3 basis functions are NOT eigenstates of the carbon atom Hamiltonian (because the $2s$ orbital is NOT degenerate with the p orbitals), but experience has shown that they are good basis functions for C atom bonding. Hence such localized basis functions are in use in calculations. Of course, one can get the same result by just using the s and p orbitals as functions and diagonalizing, but the sp^3 hybrids already point more-or-less in the right direction before diagonalizing, and allow a local description of bonding, whereas s and p do not.