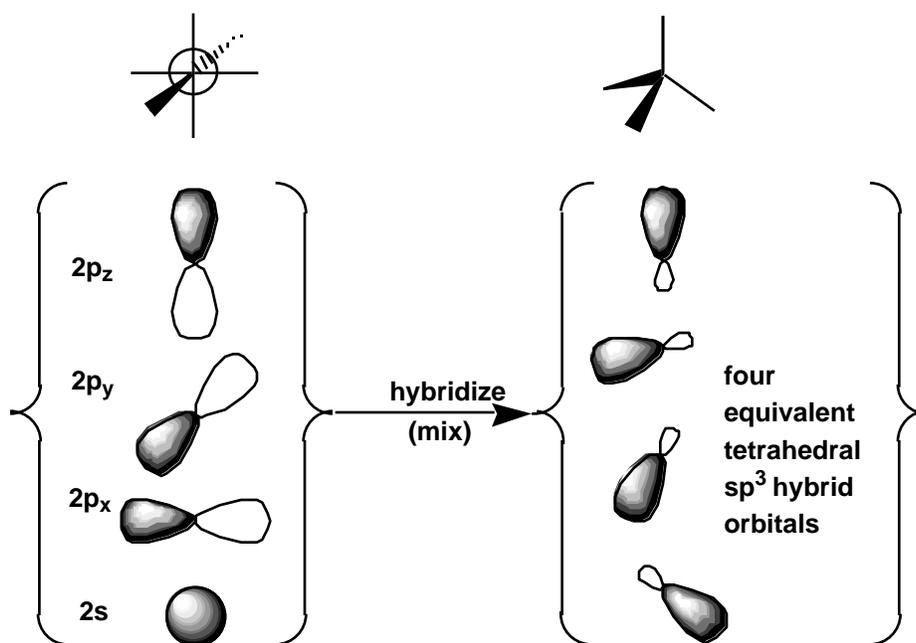


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We now are ready to develop a model that can describe the bonding in the hydrocarbon molecules we have already considered, starting with methane. Placed midway across the second row of the periodic table, carbon is not well positioned to form ionic bonds; instead, it is essentially always covalently bonded. The four C—H bonds of methane, each with a bond energy of about 99 kcal/mole, are qualitatively similar to the covalent bond in the hydrogen molecule. In the valence shell of elements in the second row we have seen that we have four orbitals with which to deal: a spherical 2s orbital, relatively close to the nucleus and not, in and of itself, very suitable for bonding; and three orthogonal 2p orbitals. On the other hand, we are confronted with the fact that there are four, not three, C—H bonds in methane, and that they are all equivalent, suggesting that a single type of carbon orbital is involved. Furthermore, the methane bonds are disposed tetrahedrally, rather than being oriented along orthogonal axes.

In this predicament, we can achieve a model for suitable atomic orbitals in carbon simply by mixing the 2s and the three 2p orbitals to give four equivalent tetrahedral orbitals, each having one-quarter s character and three-quarters p character. These tetrahedral carbon atomic orbitals often are called sp^3 *hybrid* (that is, mixed) orbitals; each has roughly the shape shown in the figure. To gain some qualitative understanding of the origin of this shape, imagine combining an s orbital and a single p orbital. On one side of the p orbital constructive interaction makes the combined orbital fatter. On the other side, destructive interaction makes it slimmer. A point also needs to be made regarding overall geometry and coordinates. The directionality of the array as a whole is conserved. One started with a 2s orbital (non-directional) and three 2p orbitals that define direction in three dimensions. One ends with the three-dimensional tetrahedral array that solid geometry predicts for four equivalent vectors pointing outward in three dimensions:



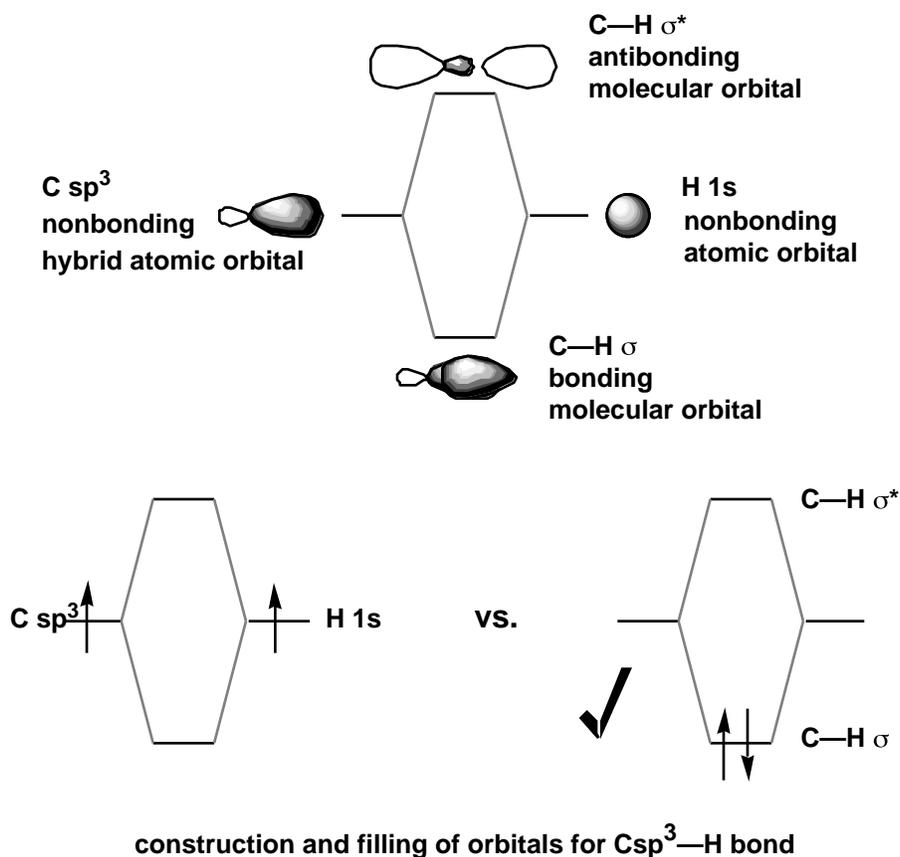
qualitative rationalization of shape:



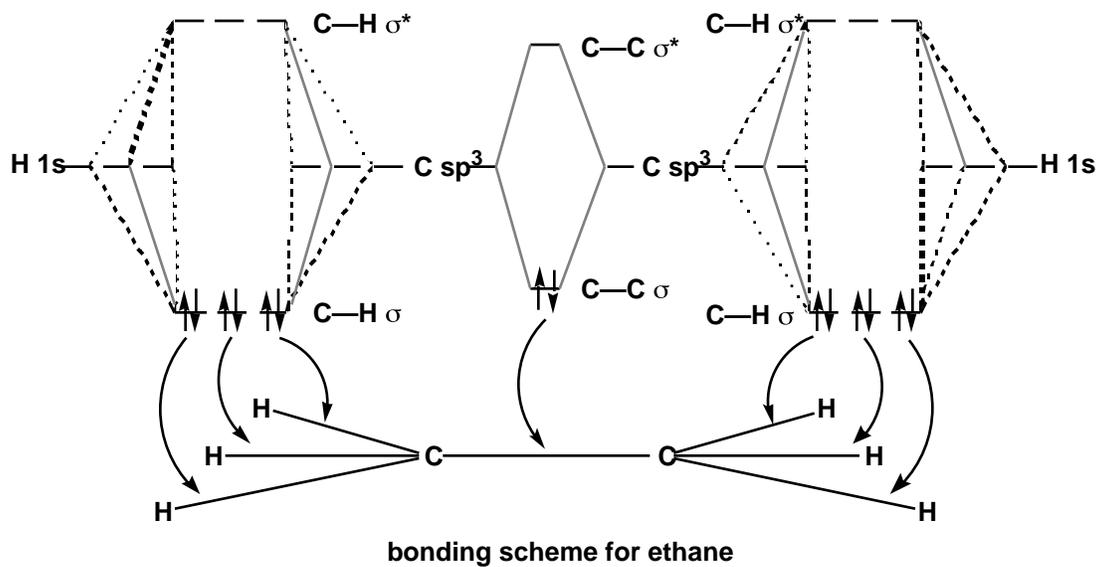
construction of sp^3 hybrid atomic orbitals
by mixing 2s and three 2p orbitals

Still considering methane, each of the tetrahedral carbon sp^3 hybrid atomic orbitals now can be mixed with a hydrogen 1s atomic orbital, to give Csp^3-H (bonding) and Csp^3-H^* (antibonding) molecular orbitals, four equivalent sets in all. The figure below summarizes the process for just one of these sets of orbitals in methane. In these orbitals we must accommodate eight electrons: four from carbon (the filled 1s shell of carbon is not at issue) and four from the four hydrogen atoms. Thus, we need only fill the four Csp^3-H bonding molecular orbitals, each with an electron pair, as diagrammed in the figure for one C—H bond. In sum, from eight original atomic orbitals, four from carbon and four from hydrogen, by way of the construct of sp^3 hybridization, we obtain eight molecular orbitals, four bonding and

four antibonding; and we place our eight available electrons in the four bonding orbitals to complete the bonding model for methane:



Tetrahedral sp^3 orbitals are sufficient for rationalizing the bonding to carbon in the molecules which we have considered until now. For example, the central bond in ethane (with a bond energy of about 82 kcal/mole) simply is modeled to involve the bonding of two carbon atoms by means of an sp^3 orbital and an electron from each atom; the remaining three orbitals of each carbon atom, as well as the residual electrons, are used for bonds with hydrogen:



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