In recent years, great progress has been made in quantum-mechanical calculations of the properties of small organic molecules by so-called *ab initio* methods, which means calculations from basic physical theory using only fundamental constants, without calibration from known molecular constants. Calculations that are calibrated by one or more known properties and then used to compute other properties are called "semiempirical" calculations.

It should be made clear that there is no single, unique *ab initio* method. Rather, there is a multitude of approaches, all directed toward obtaining useful approximations to mathematical problems for which no solution in closed form is known or foreseeable. The calculations are formidable, because account must be taken of several factors: the attractive forces between the electrons and the nuclei, the interelectronic repulsions between individual electrons, the internuclear repulsions, and the electron spins.

The success of any given *ab initio* method usually is judged by how well it reproduces known molecular properties with considerable premium for use of tolerable amounts of computer time. Unfortunately, many *ab initio* calculations do not start from a readily visualized physical model and hence give numbers that, although agreeing well with experiment, cannot be used to enhance one's qualitative understanding of chemical bonding. To be sure, this should not be regarded as a necessary condition for making calculations. But it also must be recognized that the whole qualitative orbital and hybridization approach to chemical bonding presented in this chapter was evolved from mathematical models used as starting points for early *ab initio* and semiempirical calculations.

Electron-amplitude contour diagrams of the GVB orbitals for ethene are shown in Figure 6-22. Let us be clear about what these contour lines represent. They are lines of *equal electron amplitude* analogous to topological maps for which contour lines are equal-altitude lines. The electron amplitudes shown are those calculated *in the planes containing the nuclei* whose positions are shown with crosses. In general, the amplitudes decrease with distance from the nucleus. The regions of *equal-electron amplitude* for \(\ell(s)\)-like orbitals (middle-right of Figure 6-22) surround the nuclei as a set of concentric shells corresponding to the surfaces of the layers of an onion (Figure 6-23). With the \(\ell(sp^2)\)-like orbitals, the amplitude is zero at the nucleus of the atom to which the orbital belongs.
Figure 6-22: Generalized valence-bond orbitals calculated for ethene by the ab initio method. The nuclei are located in the \((x), (y)\) plane of the coordinate system at the positions indicated by crosses. The long dashes correspond to locations of change of phase. The dotted lines are contour lines of electron amplitude of opposite phase to the solid lines. Top shows both \((\text{\textsigma})\)-bonding carbon orbitals (almost \((\text{sp}^2)\)), middle-left is the carbon orbital and middle-right the hydrogen orbital of one of the \((\text{C-H})\) bonds, and bottom represents a side view of the \((\text{\textpi})\) orbitals in perpendicular section to the \((x), (y)\) plane. (Drawings furnished by Dr. W. A. Goddard, III.)

The physical significance of electron amplitude is that its square corresponds to the electron density, a matter that we will discuss further in Chapter 21. The amplitude can be either positive or negative, but its square (the electron density) is positive, and this is the physical property that can be measured by appropriate experiments.

Looking down on ethene, we see at the top of Figure 6-22 two identical \((\text{C-C})\) \((\text{\textsigma})\)-bonding orbitals, one on each carbon, directed toward each other. The long dashed lines divide the space around the atom into regions of opposite orbital phase (solid is positive and dotted is negative). The contours for one of the \((\text{C-H})\) bonding orbitals are in the middle of the figure, and you will see that the orbital centered on the hydrogen is very much like an \((\text{s})\) orbital, while the one on the carbon is a hybrid orbital with considerable \((\text{p})\) character. There are three other similar sets of orbitals for the other ethene \((\text{C-H})\) bonds.

When we look at the molecule edgewise, perpendicular to the \((\text{C-C})\) \((\text{\textsigma})\) bond, we see the contours of the individual, essentially \((\text{p})\)-type, orbitals for \((\text{\textpi})\) bonding. Ethyne shows two sets of these orbitals, as expected.
What is the difference between the GVB orbitals and the ordinary hybrid orbitals we have discussed previously in this chapter? Consider the $(sp^2)$-like orbitals (upper part of Figure 6-22) and the $(sp^2)$ hybrids shown in Figure 6-9. The important point is that the $(sp^2)$ hybrid in Figure 6-9 is an atomic orbital calculated for a single electron on a single atom alone in space. The GVB orbital is much more physically realistic, because it is an orbital derived for a molecule with all of the nuclei and other electrons present. Nonetheless, the general shape of the GVB $(sp^2)$-like orbitals will be seen to correspond rather closely to the simple $(sp^2)$ orbital in Figure 6-9. This should give us confidence in the qualitative use of our simple atomic-orbital models.