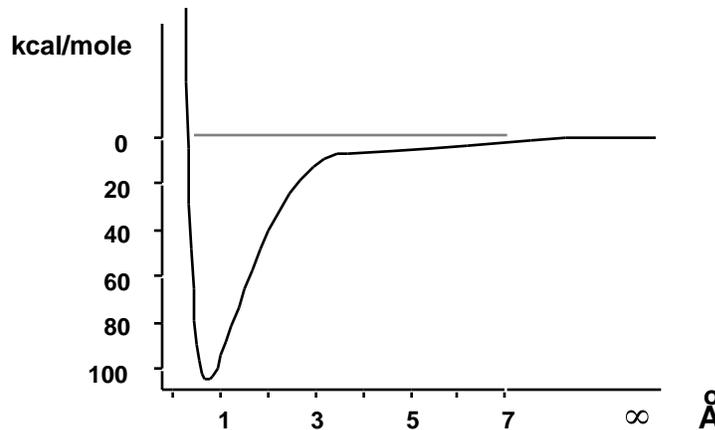


Text Related to Segment 7.01 ©2002 Claude E. Wintner

To make a simple analogy which is not meant to be stretched too far, the elements comprise a chemist's alphabet. It is necessary to understand how to arrange the letters of an alphabet (atoms) correctly, so that they form words (molecules). There are rules. Only certain words are allowed: we must learn how to spell! Words (molecules) can be grouped in a proper order to form sentences (reactions). Again, there are rules. Only certain sentences are allowed: we must learn grammar! On the basis of a primitive "ball-and-stick" model, and some fundamental geometrical precepts, but without the benefit of any consideration of how or why the atoms in molecules are joined, we have worked through a fairly detailed introduction to the stereochemistry of saturated hydrocarbon systems. It is time now to embark on a brief discussion of "spelling," that is, the rules of bonding which determine how atoms are held in association with one another. Only then will we be able to proceed to the study of "grammar" — the rules governing the transformations of molecules, or reactions, that are the specific domain of the chemist.

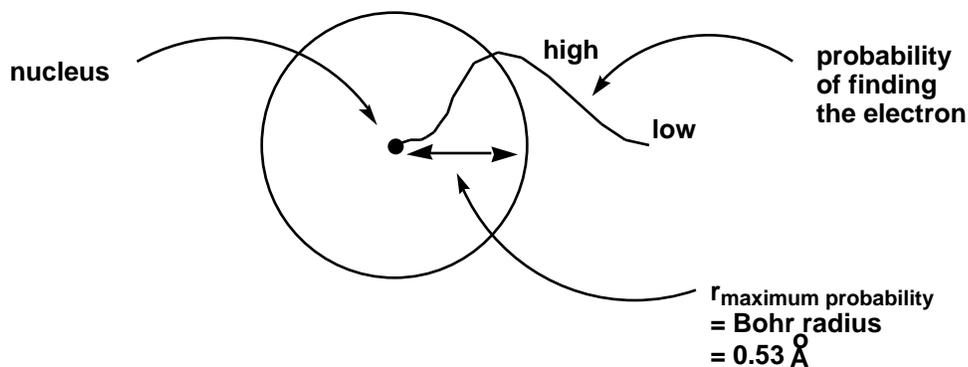
When two hydrogen atoms are brought together from "infinite" distance, they form a hydrogen molecule, with the release of a large amount of energy: 104 kcal/mole. We refer to this energy as the covalent bond energy of the hydrogen molecule. To put the number in some perspective, a temperature of 2000°C is necessary to break a reasonable fraction of the bonds in a sample of H₂ at a reasonable rate. From suitable empirical potential functions it is estimated that some very small interaction starts already at a mutual distance of approximately 8Å (8 x 10⁻¹⁰m); the energy minimum occurs at 0.74Å (the mean bond distance); if the atoms come together further, a penalty for compression begins to be manifested, and then rapidly becomes intolerable:



potential function for the hydrogen molecule, plotting vibrational potential energy vs. nuclear separation, and used as a model for bond strength vs. nuclear separation

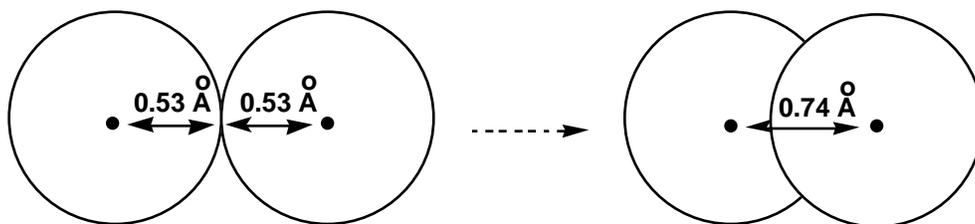
How is it that the bond is so strong? This question has been, and continues to be, central to all of chemistry. The problem certainly is not "solved," although extraordinarily close approximations to a quantitative solution have been achieved. Here we will be satisfied with the briefest and most qualitative of treatments. Each hydrogen atom may be described as a hydrogen nucleus (proton) with an associated electron which may be found with maximum probability in a spherical shell 0.53\AA from the nucleus. (It is worth keeping in mind that the radius of this spherical shell — the so-called Bohr radius of the hydrogen atom — is a factor of 10^5 larger than the radius of the nucleus. In other words, if the nucleus were to be thought of as a marble, the electron would be found with maximum probability somewhere in a spherical shell about one kilometer away!) Probability functions (wave functions) that attempt to describe the whereabouts of electrons in atoms are called atomic orbitals. Those that attempt to describe the whereabouts of electrons in molecules are termed molecular orbitals. For the hydrogen atom we say that the electron resides in the 1s atomic orbital of the atom. The ensuing figure endeavors to

communicate the probability of finding the electron at any given distance from the nucleus in the hydrogen atom (in its ground state):



1s orbital of the hydrogen atom

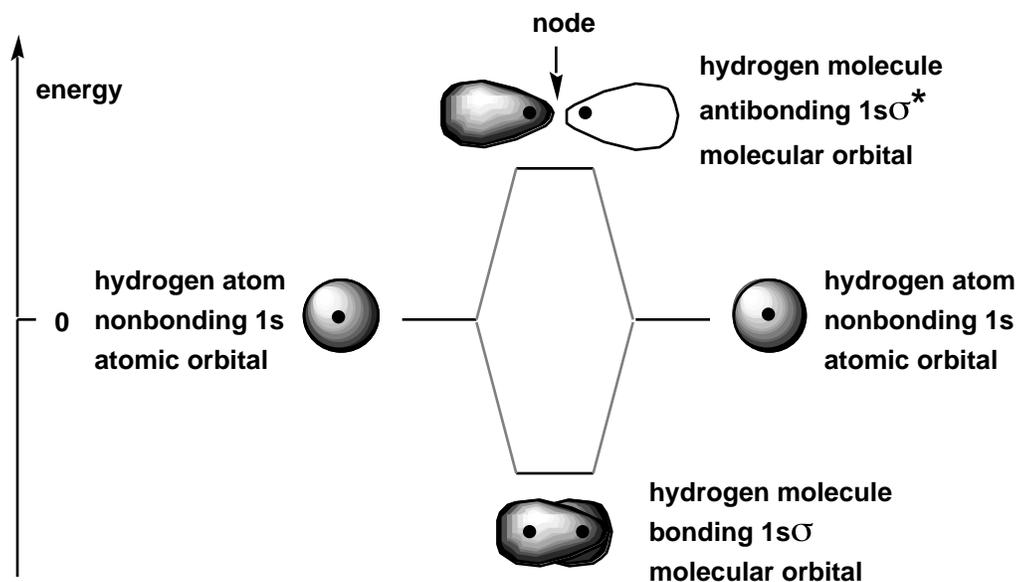
Now suppose that we have brought two hydrogen atoms together so that the two protons are held at the mean mutual H—H bond distance of 0.74\AA . What happens to the electrons? Under this circumstance there is considerable overlap of the two Bohr radii, whose sum would be 1.06\AA :



the radial maxima of probable locations of the electrons in two hydrogen atoms are overlapping in the hydrogen molecule

We could imagine that each electron simply would be localized in its own 1s atomic orbital, but this is precisely the nonbonding situation of two hydrogen atoms. On the other hand, by mixing the two atomic orbitals (mathematically, the wave functions are combined either in-phase or out-of-phase) we can use them to form

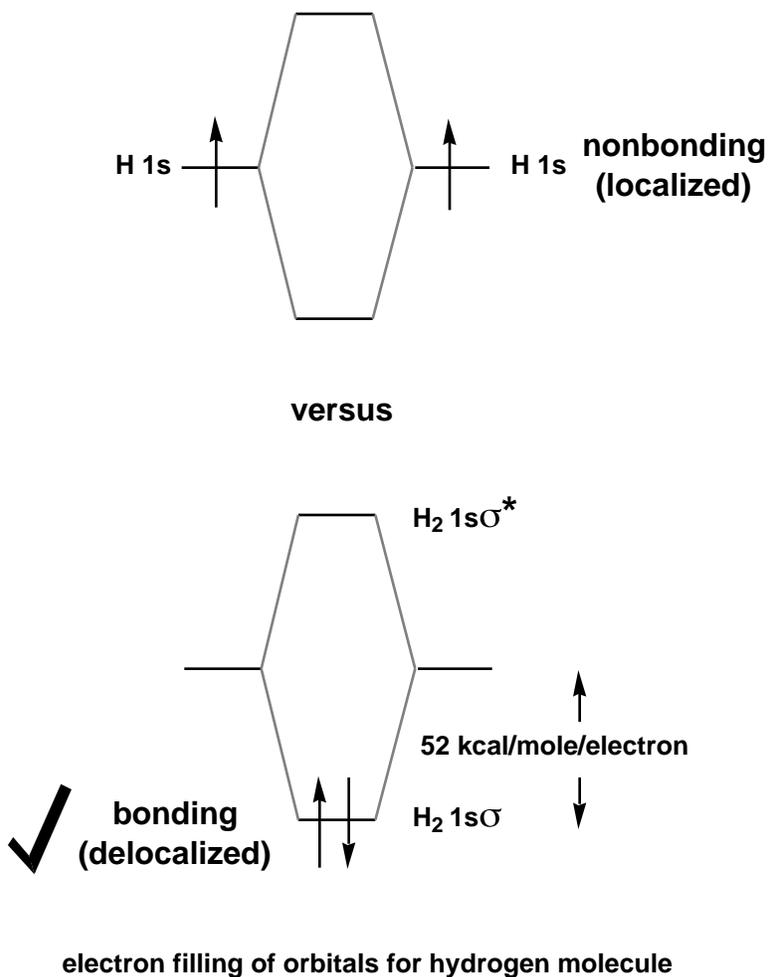
two new orbitals — *delocalized* molecular orbitals, one bonding and one antibonding:



construction of orbitals for molecular hydrogen from hydrogen atomic orbitals

Note that the overall number of orbitals is conserved. The two atomic orbitals no longer are considered as relevant; the two molecular orbitals have taken their place. However, the new orbitals are rearranged as to energy, with one ("bonding") at lower energy and the other ("antibonding") at a corresponding higher energy, relative to the starting null situation. The figure also gives an indication of the orbital shapes. The high-energy antibonding orbital has a node. An analogy with vibrating strings is useful: if one bows a violin string while establishing a node by touching a finger to the center of the string, the frequency — a function of the energy — rises by an octave. These molecular orbitals are named 1s (bonding) and 1s* (antibonding), or σ and σ^* for short, to recognize their provenance from the mixing of 1s atomic orbitals. As a matter of general convention, a star is used to designate an antibonding orbital.

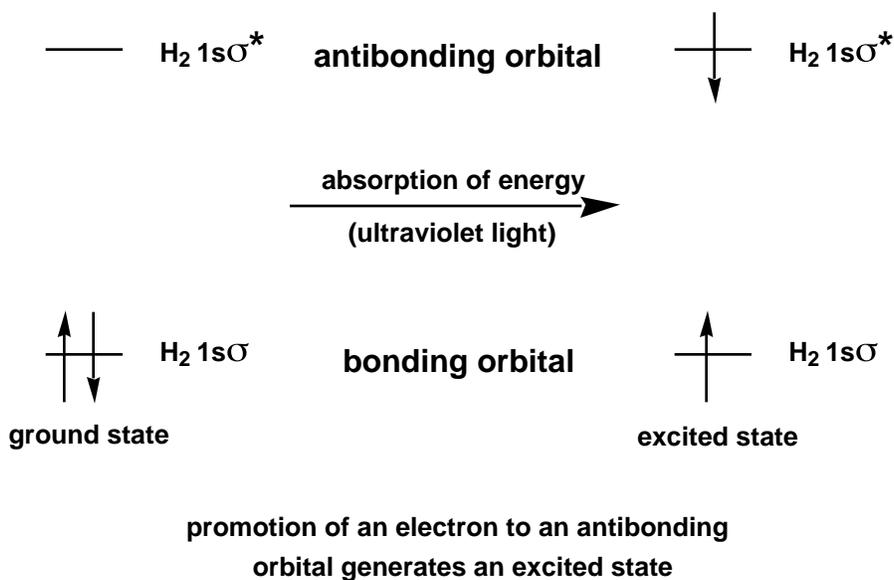
Until now our molecular orbital construction has considered, so to speak, the homes for the electrons, but not the electrons themselves. As is true of all orbitals, each of the two new orbitals in our model can hold two, and only two, electrons. By filling the bonding orbital with the two electrons from our two hydrogen atoms, we gain 104 kcal/mole over the localized situation:



The beauty is that both electrons of the hydrogen molecule can be placed (with paired spins) in the bonding orbital, leaving the antibonding orbital vacant. In molecular hydrogen it is no longer the case that either electron "belongs" to either hydrogen nucleus. We say that the two electrons are *delocalized* in the bonding molecular orbital, as opposed to *localized* in the nonbonding atomic orbitals. *By*

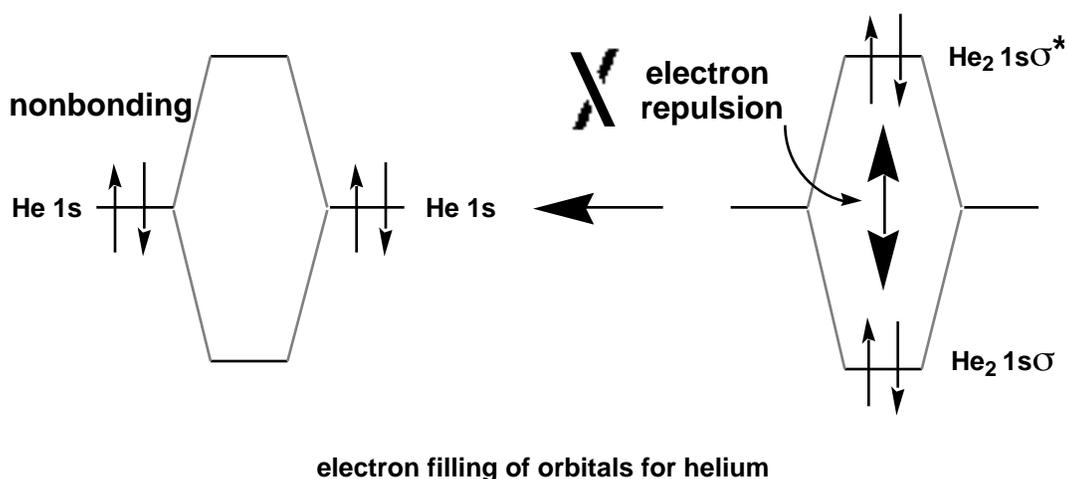
delocalizing the electrons we lower the energy of the system. There is an important corollary to be enunciated here: if a model of a molecular system is constructed, but delocalization of electrons is neglected, then the energy which is predicted by the model will be incorrect, and it always will be too high. We will have many occasions to apply these ideas in the ensuing discussion.

It needs to be emphasized that promotion of an electron to the antibonding orbital is by no means an imaginary or unattainable process. Given the requisite large amount of energy — for example, from absorption of ultraviolet radiation of wavelength corresponding to the correct energy for the transition — an electron can be promoted from the bonding to the antibonding orbital, yielding an excited state:



Such states are short-lived, and can lead, for example, to dissociation of the molecule; but their existence is confirmed by, and in fact is the underlying basis of, spectroscopy. For the case of isolated helium atoms versus a species He—He, we must deal with a total of four — not just two — electrons in total, because the helium atom's 1s orbital is filled with two electrons to begin with. Here there is no net gain from delocalized bonding because of the necessity of filling the antibonding orbital.

Furthermore, the situation is somewhat worse for the molecular species in terms of energy because electron repulsion between electron pairs becomes considerable as two helium atoms attempt to approach each other to form an He_2 entity. Thus, in this instance the prediction of the model is that He_2 should not be favored relative to free helium atoms, as is indeed confirmed by experience: in the world around us, while hydrogen exists as the molecular hydrogen species H_2 , helium occurs as single atoms:



It needs to be emphasized that the foregoing discussion properly cannot be termed an *explanation* of the phenomenon of covalent bonding; rather, we have developed a model — but one which has proved to have very significant predictive value. Indeed, these ideas can be extended nicely to rationalize the bonding in the important diatomic molecules of the second row of the periodic table — molecular nitrogen, molecular oxygen, and molecular fluorine — as well as the existence of neon as single atoms. (See 7.01 Text Addendum.)