

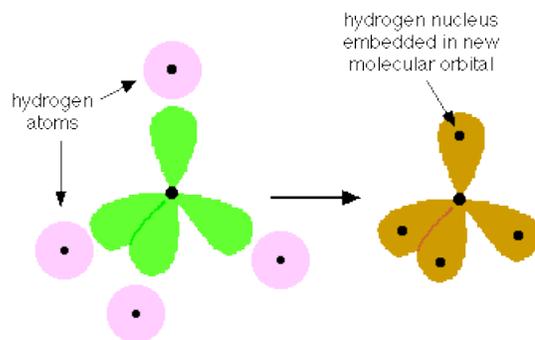
QUANTUM-MECHANICAL MODELS

These models of bonding take into account the fact that a particle as light as the electron cannot really be said to be in any single location. The best we can do is define a region of space in which the probability of finding the electron has some arbitrary value which will always be less than unity. The shape of this volume of space is called an orbital and is defined by a mathematical function that relates the probability to the (x,y,z) coordinates of the molecule.

Like other models of bonding, the quantum models attempt to show how more electrons can be simultaneously close to more nuclei. Instead of doing so through purely geometrical arguments, they attempt this by predicting the nature of the orbitals which the valence electrons occupy in joined atoms.

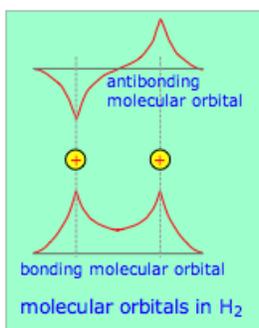
The hybrid orbital model

This was developed by Linus Pauling in 1931 and was the first quantum-based model of bonding. It is based on the premise that if the atomic s, p, and d orbitals occupied by the valence electrons of adjacent atoms are combined in a suitable way, the hybrid orbitals that result will have the character and directional properties that are



consistent with the bonding pattern in the molecule. The rules for bringing about these combinations turn out to be remarkably simple, so once they were worked out it became possible to use this model to predict the bonding behavior in a wide variety of molecules. The hybrid orbital model is most usefully applied to the p-block elements in the first few rows of the periodic table, and is especially important in organic chemistry.

The molecular orbital model



This model takes a more fundamental approach by regarding a molecule as a collection of valence electrons and positive cores.

Just as the nature of atomic orbitals derives from the spherical symmetry of the atom, so will the properties of these new

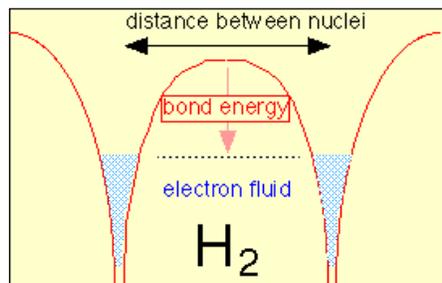
molecular orbitals be controlled by the interaction of the valence electrons with the multiple positive centers of these atomic cores.

These new orbitals, unlike those of the hybrid model, are delocalized; that is, they do not “belong” to any one atom but extend over the entire region of space that encompasses the bonded atoms. The available (valence) electrons then fill these orbitals from the lowest to the highest, very much as in the Aufbau principle that you learned for working out atomic electron configurations.

For small molecules (which are the only ones we will consider here), there are simple rules that govern the way that atomic orbitals transform themselves into molecular orbitals as the separate atoms are brought together. The real power of molecular orbital theory, however, comes from its mathematical formulation which lends itself to detailed predictions of bond energies and other properties.

The electron-tunneling model

A common theme uniting all of the models we have discussed is that bonding depends on the fall in potential energy that occurs when opposite charges are brought together. In the case of covalent bonds,



the shared electron pair acts as a kind of “electron glue” between the joined nuclei. In 1962, however, it was shown that this assumption is not strictly correct, and that instead of being concentrated in the space between the nuclei, the electron orbitals become even more concentrated around the bonded nuclei. At the same time however, they are free to “move” between the two nuclei by a process known as tunneling.

This refers to a well-known quantum mechanical effect that allows electrons (or other particles small enough to exhibit wavelike properties) to pass (“tunnel”) through a barrier separating two closely adjacent regions of low potential energy. One result of this is that the effective volume of space available to the electron is increased, and according to the uncertainty principle this will reduce the kinetic energy of the electron.

According to this model, the bonding electrons act as a kind of fluid that concentrates in the region of each nucleus (lowering the potential energy) and at the same time is able to freely flow between them (reducing the kinetic energy). Despite its conceptual simplicity and full acknowledgment of the laws of quantum mechanics, this model is less known than it deserves to be and is unfortunately absent from most textbooks.

Source: <http://www.chem1.com/acad/webtext/chembond/cb02.html>