Chapter 8
Molecules

(We have only three days for chapter 8!)

8.1 The Molecular Bond

A molecule is an electrically neutral group of atoms held together strongly enough to behave as a single particle.

A molecule always has a definite composition and structure.

The total energy of the molecule is less than the total energy of the separate, noninteracting atoms.

If the energy of the system is greater than the energy of the isolated components, no molecule is formed.

For example, He contains two 1s electrons. To form He$_2$ would require (according to the Pauli exclusion principle) promoting two of the four 1s electrons to p-states. This would result in an increase in the system energy. Hence, He$_2$ is not formed.

Some molecular bonds involve sharing of electrons between atoms. These are covalent bonds.

Covalently bonded solids take up more space than closely-packed arrays of atoms. The volume increase is energetically favorable because of the directional dependence of the bonds.

Dipole moments are not of primary importance in these bonds.

Some bonds involve transfer of electrons between atoms. These are ionic bonds.

The atoms become partially ionic. The structure is then held together by electrostatic forces.

It is interesting that ionic bonds do not result in the formation of molecules. You can still talk about the NaCl structure, for example, but it is not correct to talk about a molecule of NaCl.

In the real world, most bonding has both ionic and covalent character. You can calculate the percent of ionicity or covalency of a bond.

8.2 Electron Sharing

When adjacent atoms are close enough that the "tails" of their wave functions overlap, electrons can tunnel between atoms.
Which wave functions are we talking about?  Atomic electronic wave functions.

When atomic wave functions overlap, we must write the system wave function as a linear combination of the overlapping wave functions, since there can only be one wave function at any point.

Depending on the symmetry of the linear combination under particle exchange, the probability distribution for finding an electron in the region between the two atoms may be enhanced or reduced.

Enhanced probability (show figure 8.5d) results in bonding.

Reduced probability (show figure 8.6e) results in antibonding.

8.3 The H$_2^+$ molecular ion.

This is the most complex molecule for which an exact solution for Schrödinger's equation is possible! We can't even do it for H$_2$.

That doesn't mean there's anything "wrong" with the state of our knowledge. It just means exact solutions are not obtainable. Physicists can certainly calculate approximate solutions which are "good enough" for the time being.

We won't do exact solutions here, just qualitative discussions.

Molecular H$_2^+$ consists of two protons and a single electron. We must write our electron wave function as a linear combination of two 1-electron wave functions centered on each of the two hydrogen nuclei.

When the two protons are far apart, we know what the 1s electron wave functions look like:

(Show Figure 8.5.)

This is a linear combination of two 1s wave functions. It is also a symmetric combination, because exchanging a and b does not change the combination.

(Anybody see anything strange here? We are talking about two wave functions, only one electron. Anything wrong with that?)

As we bring the protons closer together, the wave functions overlap, like this.

(Illustrate on transparency.)
Finally, when we let the proton-proton separation approach zero, our linear combination wave function looks like this.

(Illustrate on transparency.)

Anybody see any problems with figure 8.5e?

One would expect a Coulomb repulsion between the two protons; He$^+$ ion is not easy to get. In fact, H$_2^+$ is more like figure 8.5d.

There is another possibility for H$_2^+$, which would result from an antisymmetric combination of 1s wave functions.

Show and discuss figure 8.6.

Now let's step back and think about what we've done.

We've modeled in our heads symmetric and antisymmetric H$_2^+$ wave functions.

Does either actually exist? Can we predict? How would we predict?

We can make some quantitative predictions by adding up all contributions to the system energy.

We need to include the proton-proton repulsion; this is simply

$$V_p = \frac{e^2}{4 \pi \varepsilon_0 r}.$$  

We also need to include the electron energy, for either symmetric or antisymmetric wave functions.

For symmetric wave functions, when the proton-proton separation R approaches 0, the energy $E_S$ is that of the He$^+$ ion, which is 4(-13.6) eV = -54.4 eV. (This is $Z^2$ times the hydrogen energy.)

When R is large, $E_S$ approaches the -13.6 eV for the hydrogen atom

Here's a plot of the dependence of $E_S$ on the proton-proton separation (show transparency of Figure 8.7).

When we add together the energies, we end up with a shallow minimum in $E_{\text{total}}$, with the minimum value equal to -2.65 eV.

Now let's consider the energy versus proton-proton separation for antisymmetric wave functions.

$E_A$ for R approaching 0 is -13.6 eV (like the 2p state of He; see Beiser). $E_A$ is approximately
$Z^2 \text{ times } -13.6 \text{ eV/n}^2$, or $-13.6 \text{ eV}$.

$E_A$ for $R$ approaching infinity is also $-13.6 \text{ eV}$; just the binding energy of a single hydrogen atom, because there is only one electron.

Calculations show that there is a small dip in between.

Figure 8.7 shows the results for the antisymmetric combination; there is no bonding in this case.

Notice the difference between the total energy of $\text{H}_2^+$ and the bond energy of $\text{H}_2^+$.

The total energy is $-16.3 \text{ eV}$. The total energy of $\text{H}+\text{H}^+$ is $-13.6 \text{ eV}$. The difference is $-2.65 \text{ eV}$, the bond energy of $\text{H}_2^+$, which is the energy decrease upon bonding of $\text{H}$ and $\text{H}^+$.

### 8.4 The Hydrogen Molecule

We can repeat the above analysis for the hydrogen molecule, with minor differences.

Two electrons contribute, so the bond energy is $E=2(2.65\text{eV})-(\text{electron-electron repulsion energy})$.

The result is about $4.5 \text{ eV}$.

For $\text{H}_2$, $S$ leads to bonding, $A$ does not.

Oops -- I thought we said electrons in a system are described by antisymmetric wave functions.

They are: $?=? \text{ times s, where s is the spin part of the wave function, and the total wave function } ? \text{ must be antisymmetric.}$

Since $?$ is symmetric, it follows that $s$ must be antisymmetric.

In other words, in this 2-electron system, the spin function is antisymmetric, and the electron spins therefore must be antiparallel (if they were parallel, you wouldn't be able to tell them apart).

One can calculate the total energies for symmetric and antisymmetric hydrogen molecule wave functions. The result is:
Show plot in Figure 8.8...very much like total energies for H₂⁺.

The absence of bonding for Eₐ is a consequence of the Pauli exclusion principle. When the available states are S orbitals, the “different” state will have to be an S or P orbital from the next shell (hydrogen atom example) If the “different” orbitals are from a subshell, such as the d orbitals, the electrons manage to have parallel spins and occupy perhaps the full set of d orbitals. This is the case for Hund’s Rule atoms in which the magnetic moment increases until the subshell is half filled, then decreases until the filled subshell atom is in fact, non magnetic.

8.5 Complex Molecules

Some facts:

? Inner electrons are tightly bound.

? Repulsive interatomic forces become predominant when inner shells are still far apart.

Why? In this case, when outer shells begin to overlap there are more than enough available electrons to fill the shell. The remaining electrons must occupy higher states, thus raising the total energy of the molecule with decreasing distance: this is the definition of a repulsive force.

Bonding is primarily due to the favorable interaction of outer (valence) electrons.

Guess what bonds made up of s orbitals are like?

They are non-directional.

Example: soft, ductile metals.

In contrast, p and d orbitals form strong, brittle bonds.

The p, d, and f wave functions are not spherically symmetric, so their bonds are directional; see figures 8.9 and 8.10.

Note the example of sp³ hybrid orbitals. The tiny blip of wavefunction probability is called a “back bond” in chemistry. Physics too.

Note that the Px, Py, and Pz wavefunctions are shown with positive amplitude along their respective axes. When a combination of S and Px wavefunctions are formed, the electron “center of gravity” is shifted along the +x axis. With four wave functions in sp³ bonding, one can make four equivalent linear combinations.
Can you see that the positive sum “points” along the [111] direction? Study the other three combinations to understand the tetragonal result for CH₄.

SP2 bonding accounts for the graphite structure and SP for the long hydrocarbon chains with transverse H bonding.

STOP HERE, PLEASE. THANK YOU SO MUCH.

8.6 Rotational Energy Levels -- skip this section.
8.7 Vibrational Energy Levels -- skip this section.
8.8 Electronic Spectra of Molecules – skip this section.

Vibrational energy levels:

Consider two masses hooked together by spring. Describe their vibrations. Answer: probably a variation on the harmonic oscillator.

Hooke's law type forces hold for small amplitudes.

Vibrational energies depend on masses, so again we are talking vibrations of atoms or nuclei, and not of electrons.

These are just quantum mechanical harmonic oscillators, so everything we talked about before applies.

$$E = (\nu + \frac{1}{2}) \ h - \nu_0 \ .$$

where ν=0,1,2,3,... is the vibrational quantum number.

Electronic spectra. (Note spectra implies photons.)

Rotational states contribute in the meV (microwave) region of the spectrum.
Vibrational states contribute in the tenths of eV (infrared) region of the spectrum.

**Molecular** electronic states contribute in the several eV (visible and ultraviolet) region of the spectrum.

There are many transitions between different rotational and vibrational states for each electronic state.

There are also transitions between electronic states.

The result is a series of closely spaced lines, which appear as a band, see Figure 4.13.

**Fluorescence.**

A molecule can absorb a photon, and undergo a transition to an excited electronic state.

It can give off some of its energy in a series of transitions without the release of photons (via collisions) to successively lower vibrational states of the excited electronic state.

Finally, it can give off a lower energy, lower frequency photon in a transition back to the electronic ground state.

The result is visible light containing many wavelengths of light; e.g., a fluorescent lamp.

It's interesting that underneath the white spectrum of a fluorescent lamp, you ought to see the line spectrum of mercury or argon.

**Phosphorescence.**

A molecule in a molecular S=0 ground state can absorb a photon and go to a S=0 excited state.

The molecule can then undergo radiationless transitions (how? vibrational transitions again) to the S=1 excited state.

The S=1 excited state to S=0 ground state transition may be "forbidden" (i.e., may have a very low but still nonzero probability), but after a long time, the forbidden transition may occur.

The emitted photons are called phosphorescent radiation.