PH253: Molecular Orbitals

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Molecular orbitals

1.1 Linear combination of atomic orbitals

We used the variational method as a way to come up with reasonable guesses as to the wave function for a system, and then optimize our guesses. By considering the symmetry of the problem and basic mathematical constraints, we could make our guesses pretty good. Moreover, if we were willing to sacrifice complexity in favor of a few extra adjustable constants (say, by including more terms in our wave functions), we could improve our accuracy considerably.

The point of all that was to get to a position of understanding molecules and molecular orbitals. The idea is the following: if we want to figure out the molecular orbitals for, say, an H_2 molecule, we can't do it exactly. We can use the variational principle and make a decent guess. How to guess? Basically the same way we explained the periodic table, and the way we've talked qualitatively about bonding: assume a good guess for the molecule is a linear combination of H atom orbitals. That is, specifically, if φ_i are the correct ground-state wave functions for each atom i in the molecule, we presume a good guess for the wave function of the whole molecule is

$$\psi_{\text{molecule}} = \sum_i c_i \varphi_i \tag{1.1}$$

here the c_i are the relative weights for each atomic orbital. In the case of a hydrogen molecule H_2, one might reasonably (and correctly) imagine $c_1 = |c_2|$, and we know $\varphi_i(r) = \frac{1}{\sqrt{\pi a_o^3}} e^{-r_i/a_o}$ where a_o is the Bohr radius and r_i the distance from atom i to the electron position in question. The one surprising result, spoiler alert, is that $c_1 = c_2$ and $c_1 = -c_2$ are both solutions: the former is the favorable bonding situation, the latter is the unfavorable anti-bonding state.

The essential idea is that we are assuming that *bonding is a relatively weak perturbation*, i.e., the coupling (energy gain) of the atoms to make a molecule is weak compared to the coupling of the electrons and protons to form an atom in the first place. That's not a highly accurate assumption, frankly. However, more accurate but less transparent schemes reproduce the basic idea. The advantage of the LCAO approach is that it is simple enough to understand on physical grounds, but just complicated enough to give reasonable and decent answers.

1.1.1 Homo-nuclear diatomic molecule

The title just means we have a molecule like X_2. Imagine it is H_2 for the moment. We have two hydrogen atoms, and their ground state wave functions *before* bonding are φ_1 and φ_2. The LCAO

proposal is that the wave function for the resulting H_2 molecule is a weighted linear combination of the ground state wave functions,

$$\psi = c_1\varphi_1 + c_2\varphi_2 \tag{1.2}$$

In the case of H atoms, we know $\varphi_i(r) = \frac{1}{\sqrt{\pi a_o^3}}e^{-r_i/a_o}$ as noted above. The variational method using a trial wave function ψ prescribes that we optimize the functional

$$E[\psi] = \frac{\int \psi^* H\psi \, dV}{\int |\psi|^2 \, dV} \tag{1.3}$$

That is, the minimum of $E[\psi]$ with respect to the adjustable parameters c_1 and c_2 is the closest approximation to the ground state energy of the molecule we can come up with for a given trial function ψ.[i] If you use Eq. 1.2 in Eq. 1.3, the general result is

$$E = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1c_2 H_{12}}{c_1^2 + c_2^2 + 2c_1c_2 S_{12}} \tag{1.4}$$

where the H_{ij} are the *bond integrals* defined by

$$H_{ij} = c_i c_j \int \varphi_i H\varphi_j \, dV \tag{1.5}$$

where H is the Hamiltonian operator from the Schrödinger equation. Keep in mind: the bond integrals in the end are just numbers. They may not be easy to calculate, but that does not concern us for the moment. The S_{12} term is the *overlap integral*

$$S_{12} = \int \varphi_1 \varphi_2 \, dV \tag{1.6}$$

Again, the overlap integral is also, given some particular system, just a number. Its value does not concern us, nor do the values of the H_{ij}, the mere fact that they are constants is all we need to know for now.

Still, there is a lot to unpack here. First, if we are talking about a homo-nuclear system X_2 where both atoms are the same, then $H_{11} = H_{22} \equiv H$ are just the kinetic plus potential energies of the individual atoms before bonding. Using H $1s$ orbitals, the calculation is straightforward but fussy. The result is:

$$H_{11} = H_{22} = E_o + \frac{ke^2}{R}\left(1 + \frac{R}{a_o}\right)e^{-2R/a_o} \tag{1.7}$$

where E_o is the ground state energy of the hydrogen atom. Neglecting the constant term E_o, here is a plot:

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[i]We can do a much better job in the case of hydrogen by making the decay constant a variable as well, i.e., for the atomic wave function replace r_i/a_o by $c_j r_i/a_o$, where c_j is another adjustable constant. But that is a lot of added complexity for no added clarity at this point.

$H_{11}(R)$
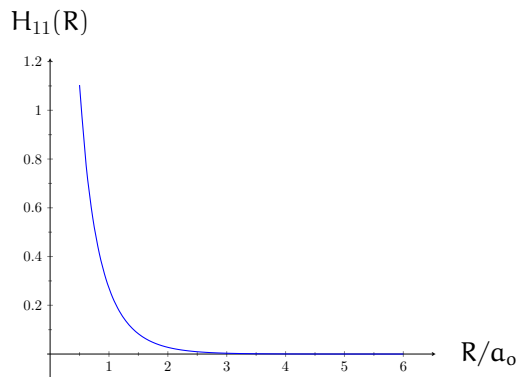
Without including any interactions, if we just jam everything closer together the energy of the system increases. Since we are considering a homo-nuclear system, either of the integrals can be denoted by just $H = H_{11} = H_{22}$.

The $H_{12} = H_{21}$ term is the *bonding* or *exchange integral*, sometimes also called the *resonance* integral. Explicitly,

$$H_{12} = 2c_1 c_2 \int \varphi_1 H \varphi_2 \, dV \tag{1.8}$$

This term is called an exchange integral because on one side of the H operator we have an orbital on a given site, and on the other side we have exchanged sites. In a way, you can think of it as the cost required to switch orbitals. If you've taken chemistry, you can think of it as similar to resonance structures. Using H $1s$ orbitals one can evaluate it explicitly for a separation distance R:

$$H_{12}(R) = \frac{a_o}{R} S_{12}(R) - e^{-R/a_o} \left(1 + \frac{R}{a_o} \right) = e^{-R/a_o} \left(\frac{a_o}{R} - \frac{2R}{3a_o} \right) \tag{1.9}$$

where S_{12}, the overlap integral, is discussed below. The next figure shows a plot of $H_{12}(R)$.

$H_{12}(R)$
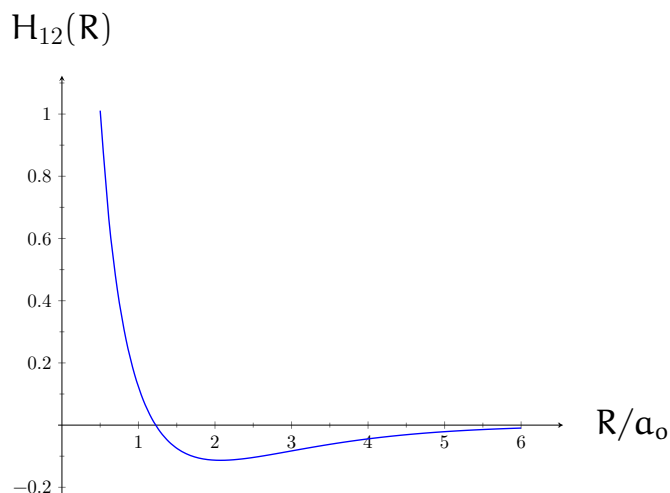
What is interesting in this case is that when the nuclei get too close together, the exchange integral

is positive, meaning it is an unfavorable contribution to the energy. We already discussed how this made sense in terms of the proton-proton repulsion and reduced electron screening at small separations.

Finally, the S_{12} term, the overlap integral, is just what it sounds like: a measure of the degree to which the atomic orbitals situated on different atoms. It is the area under the curve φ_1 that is also under φ_2. Using H 1s orbitals, one can evaluate it explicitly, and one finds for a separation R of the nuclei

$$S_{12}(R) = e^{-R/a_0} \left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2} \right) \tag{1.10}$$

Here is a plot of $S(R)$:
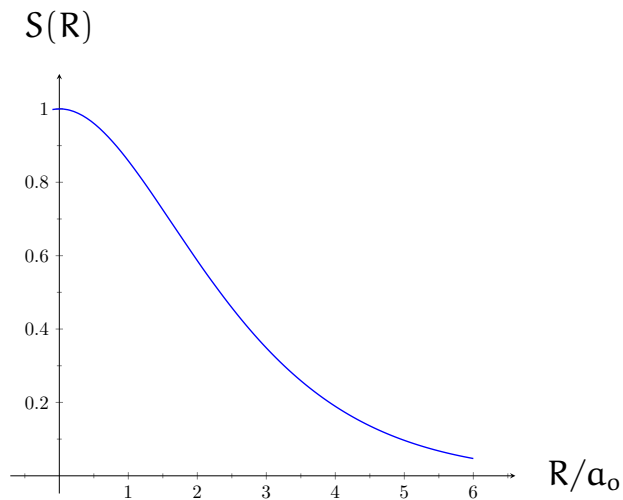
Following the variational approach, the idea is to minimize the energy with respect to the adjustable parameters c_1 and c_2 we have left ourselves. One should set $\partial E/\partial c_i = 0$ in each case, which is straightforward but tedious. The result is two solutions

$$E_b = \frac{H - H_{12}}{1 - S_{12}} \tag{1.11}$$

$$E_a = \frac{H + H_{12}}{1 + S_{12}} \tag{1.12}$$

With a bit of algebra, you can rewrite these as

$$E_b = H - \frac{H_{12} - HS_{12}}{1 - S_{12}} \tag{1.13}$$

$$E_a = H + \frac{H_{12} - HS_{12}}{1 + S_{12}} \tag{1.14}$$

This has the form "molecule energy = (atom energy) ± (bonding gain or loss)", which the picture we've had for a while now. Atoms wouldn't come together to form molecules unless it was energetically favorable, in the same say electrons and protons wouldn't come together to form atoms unless it was energetically favorable. You've seen this before too: these are the bonding (E_b) and anti-bonding (E_a) energy levels you saw in introductory chemistry.

We can also the qualitative behavior in the limit the separation distance tends toward infinity (no molecule). In that case, the atomic orbitals don't overlap at all, so any integral involving both sites will be zero, i.e., $H_{12} = S_{12} = 0$. In that case, the energy reduces to $E = H$ in both cases, each atom just has its original pre-bonding energy. More importantly, what was originally two degenerate energy levels - the bare atoms both had the same ground state energy - are now two distinct energy levels E_a and E_b, with $E_a > E_b$ and the difference is

$$\Delta E = E_a - E_b = 2\left(\frac{H_{12} - HS_{12}}{1 - S_{12}^2}\right) \tag{1.15}$$

Looking at the form of the energy difference, we can conclude that increasing overlap of the wave functions is favorable since $S > 0$ everywhere, and smaller distances are favored since S decreases monotonically as separation increases. However, we know that H_{12} is positive below a critical distance, adding to the overall energy, which tells us the minimum energy is at some finite separation of the two nuclei.

From two individual atoms, we now have a combination, a molecule, that has a more favorable energy state where the two atoms bond. We also have an unfavorable configuration, the anti-bonding state, and so long as more electrons are in the bonding state vs the anti-bonding state, we expect molecules to form. We're on our way to molecular orbitals. Schematically, here are two pictures. First, the energy vs separation.
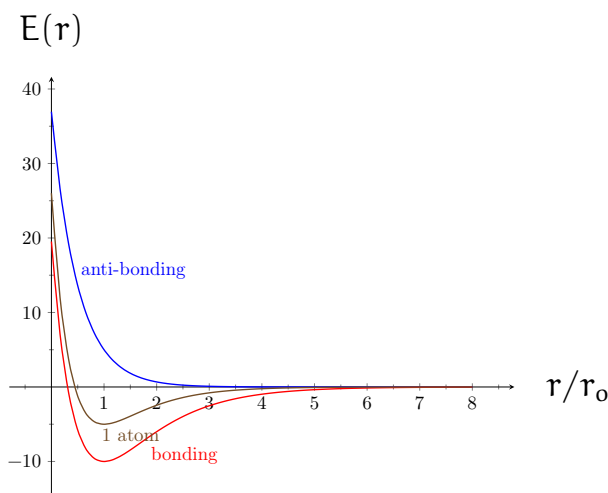

Figure 1.1: *Schematic energy vs. separation for a diatomic molecule*

The bonding state clearly has a minimum energy, corresponding to a favorable bond which has a lower energy than the individual atoms. The antibonding state is clearly unfavorable for all separations, and their occupation tend to pull the molecule apart. This is the situation we talked about in H_2 where both electrons stuck to the outside of the molecule - in that case the two protons repelled each other, and we were better off having two separate atoms. We also can't have both electrons between the protons, as the electrons would just repel each other. The happy medium is spreading the electron density around, meaning a tradeoff between the bonding and overlap integrals hinted at in Eq. 1.15. This is what the energy levels do:
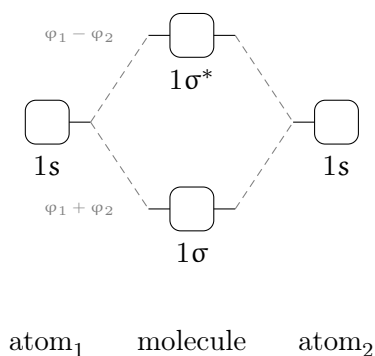
Figure: Molecular orbitals: σ orbitals from 1s states

The overall ground state energy of the molecule reduces, at the expense of the first excited state. In general, when two s states overlap, we call the resulting combination a σ molecular orbital. The $*$ superscript indicates the unfavorable anti-bonding case. The lowest states are 1s atomic orbitals adding or subtracting in equal weight, resulting in 1σ bonding and $1\sigma^*$ antibonding molecular orbitals. Here is what the molecular wave functions look like for the case of H_2:
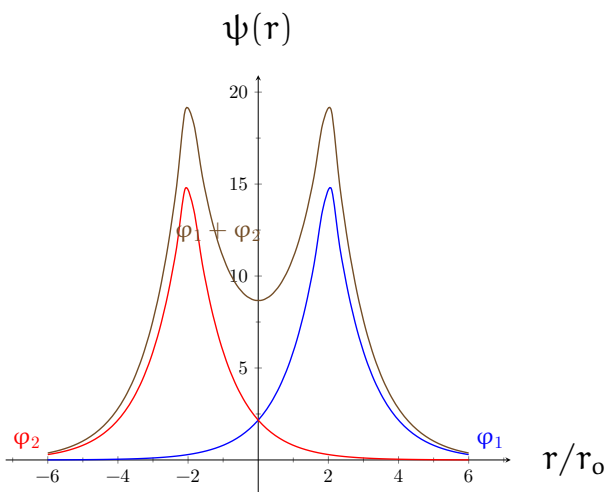
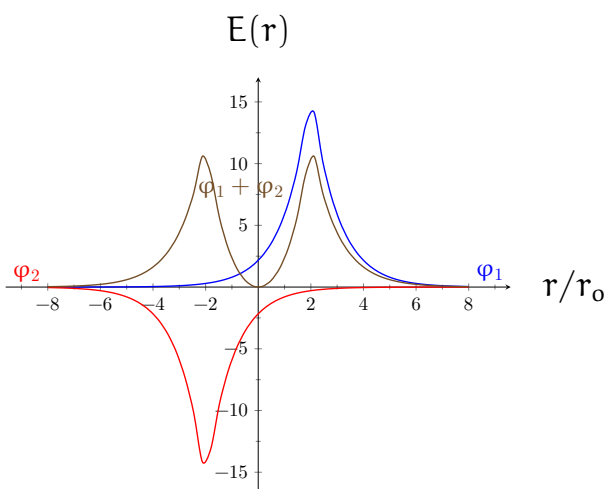**Figure 1.2:** *Bonding molecular wave function*

Figure 1.3: *Anti-bonding molecular wave function*

Looking at the electron density $|\psi|^2$, one can visualize the constructive and destructive overlap of the orbitals a bit better. Adding two $1s$ orbitals in phase creates a σ orbital, adding them out of phase creates a σ^* orbital:
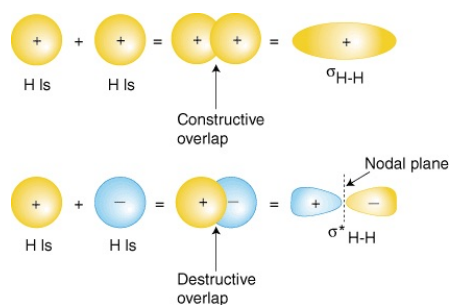

Figure 1.4: *Two atomic $1s$ orbitals combine to form bonding and anti-bonding molecular orbitals. Via* https://www.sparknotes.com/chemistry/bonding/molecularorbital/section1/
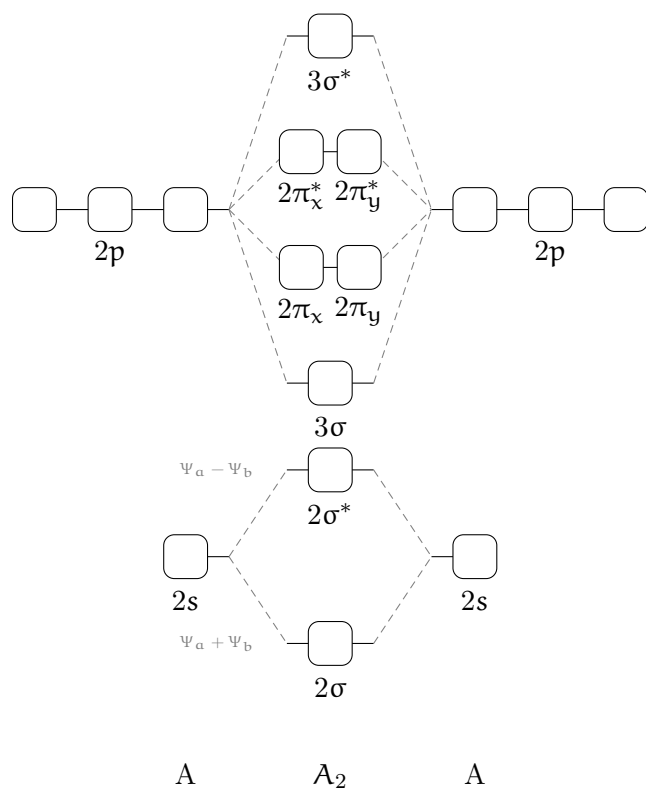
Overall, the competition between bonding and antibonding orbitals is captured by the *bond order*, defined as

$$\text{bond order} = \frac{1}{2}\left(\text{number of } e^- \text{ in bonding orbitals} - \text{number of } e^- \text{ in antibonding orbitals}\right)$$
$$(1.16)$$

The higher the bond order, the stronger the bond. For example, H_2 has 2 electrons that both occupy the 1σ orbital, so the bond order is $\frac{1}{2}(2-0) = 1$. He_2^+ has three electrons, one of which must be in the $1\sigma^*$ orbital, giving a bond order of $\frac{1}{2}(2-1) = \frac{1}{2}$. Thus He_2^+ should have a weaker bond than H_2.

One can continue this method for heavier atoms, or higher excited states of H, where the outermost electron participating in bonding is in a p or d orbital. For example, we can combine 2 p_z atomic orbitals to make 2σ molecular orbitals, and p_x or p_y to form π molecular orbitals as shown below.

Figure 1.5: *Two atomic* p_z *orbitals combine to form bonding and anti-bonding* σ *molecular orbitals. Via* https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/09._Molecular_Geometry_and_Bonding_Theories/9.7%3A_Molecular_Orbitals

Figure 1.6: *Two atomic* p_x *or* p_y *orbitals combine to form bonding and anti-bonding* π *molecular orbitals. Via* https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/09._Molecular_Geometry_and_Bonding_Theories/9.7%3A_Molecular_Orbitals

When one does this, one comes up with the following energy level picture. Here $*$ denotes antibonding orbitals, and the 1σ and $1\sigma*$ orbitals have been omitted.

Generic diatomic system

For a diatomic system then it is just a matter of counting electrons. For example: oxygen (O) has an electron configuration of $1s^2 2s^2 2p^4$, a total of 8 electrons. Diatomic oxygen O_2 thus has 16 electrons in total. Based on the atomic orbitals, one might expect that all electron spins would be paired, meaning O_2 should be diamagnetic and thus not respond strongly to a magnetic field. If we fill up the molecular orbitals, remembering to first fill in as many spin up electrons at a given energy before pairing electrons, we get the following:
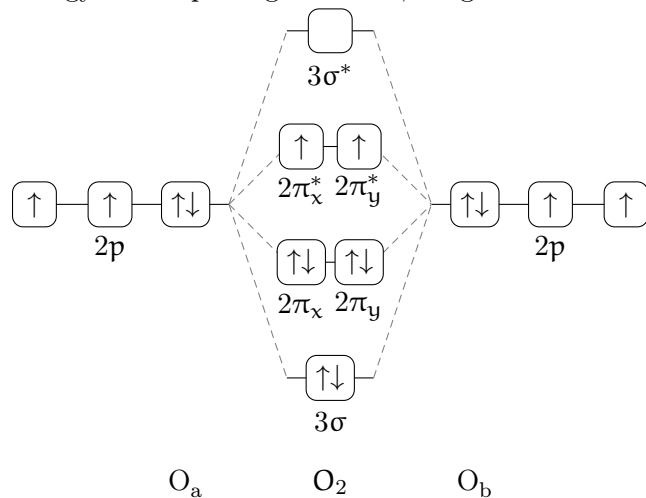
Dioxygen ($|S| = 1$)

The 1σ and 2σ orbitals are not shown for brevity. Diatomic oxygen in fact doesn't have all electrons paired, the two $2\pi^*$ orbitals each have one unpaired electron. The unpaired spins mean that diatomic oxygen is in reality paramagnetic, meaning it is attracted to a permanent magnet.