

Chapter 32

ORBITALS, Part 3

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We continue with orbitals but we continue on a very different path. It is time to embark on the Molecular Orbital Approach (MOA).

32.1 The Molecular Orbital Approach

The Molecular Orbital Approach is very different from the Valence Bond Approach. VBA is inherently a localized approach: you start with resonance structures, each with localized bonds (on one bond connection) and localized lone pairs (on one atom), and you mix the various resonance structures to yield the final outcome. VBA can handle delocalization in the final result, but the individual resonance structures are localized. MOA is inherently a more delocalized approach. MOA starts at a very fundamental level with original atomic orbitals at each atom position in the polyatomic unit, and those are then combined mathematically in such a manner so as to obtain the "best" picture for that polyatomic unit. The resulting bond orbitals and lone pair orbitals are commonly delocalized, and these can even be spread over the entire molecule. For a simple illustration, consider H_2O .

VBA would describe the bonding as two separate, localized O–H bond orbitals of σ type.

MOA would describe the bonding as two delocalized orbitals of σ type, with each orbital encompassing both bond connections.

Which one is right? It's not necessarily a right vs. wrong issue. VBA and MOA are two ways of describing the bonds. They are two tools in the toolbox.

As we had done for VBA, we will work with MOA in a qualitative, pictorial fashion. The manner of doing so, however, will be vastly different. For one thing, be aware that MOA can be more complicated than VBA, even for simple molecules. For this reason, we will focus primarily on diatomic cases for MOA although we will see two examples of triatomic cases later in Chapter 33 to illustrate the delocalization aspects. The diatomics here will primarily be "homonuclear". Homonuclear means all nuclei in the unit are the same, which means that all atoms are of the same element. N_2 and O_2 are homonuclear diatomics. If atoms of different elements are present in the polyatomic unit, then it is "heteronuclear". CN is a heteronuclear diatomic. I'll mention a bit about heteronuclears in Chapter 33.

We will not use hybridization in our Molecular Orbital Approach. MOA can incorporate hybridization but it's an added complication which we don't need. Besides, it gives the same answer in the end anyway. Thus, we will do MOA using only original atomic orbitals.

Unlike VBA, the Molecular Orbital Approach develops an electron configuration for the polyatomic unit. Thus we will be returning to electron configurations, much like what we did in Chapter 22 for monatomics but now as applied to diatomics.

The Molecular Orbital Approach does not need a Lewis structure. Our Valence Bond Approach began with Lewis from which it derived bonding and nonbonding orbitals. MOA derives bonding and nonbonding orbitals, but it also derives antibonding orbitals. MOA determines the number of bonding, nonbonding and antibonding electrons directly from electron configurations. By the way, although MOA does nonbonding orbitals, these will not arise in our homonuclear diatomics. We will see one case of a triatomic molecule in Chapter 33 where this does arise.

32.2 More orbitals and notation

We need a bit of background, starting with the antibonding orbitals.

Antibonding orbitals do exactly what their name says: they diminish bonding. If there are electrons in antibonding orbitals, then this will weaken the bond. The whole idea of an antibonding orbital can seem a bit strange to students until they get used to the notion. Whether an orbital is bonding or antibonding depends on its energy relative to the energies of the atomic orbitals from which they are derived. This will be very important as we go.

Let me go back to the simplest of all orbital interactions, the one which arises from two hydrogen atoms. I want to repeat the intro from Chapter 30.

“



To begin, we start with two separate H atoms, each with $1s^1$ configuration. For as long as the atoms are too far apart for any interaction between each other, then the atomic orbitals stay their usual, spherical, $1s$ type.



Once the two atoms come into interaction range, the nucleus and electron of one atom sense the nucleus and electron of the other atom. Each orbital distorts toward the other atom as a result of this interaction.



As the atoms get closer, the interaction between the fields increases. This interaction results in substantial merging and overlapping of the AOs, resulting in the formation of a new field, the bonding orbital.



This interaction increases as the atoms get closer and closer. Eventually they achieve their optimum limit of approach, which corresponds to the bond length for H₂. Now you have a typical molecule of H₂.

The last orbital shown above is a bonding orbital. The bonding interaction can be derived as the sum of 1s orbitals from the two, separate hydrogen atoms. For our purposes, we will adopt a simplistic representation of this interaction as follows.



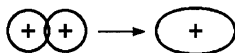
When I set that up in Chapter 30, I only gave you half the story. There's another half missing. Actually, I gave you a clue to this, but I used the clue for hybridization at that time.

“ The quantum realm demands orbital conservation: the number of orbitals is conserved in any mixing or in any hybridization or in any interaction whatsoever. ”

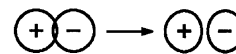
This statement includes interactions within a single atom (hybridization) and it includes interactions between atoms (molecular orbitals). The bonding orbital above for H₂ arose from the interaction of two atomic orbitals. That's only half the story. If TWO atomic orbitals interact to give a molecular orbital, then TWO molecular orbitals must be the result of the interaction. You cannot violate orbital conservation.

So where's the other molecular orbital?

For any interaction of two orbitals (one each from two atoms), an additive and a subtractive combination will result; this provides two molecular orbitals as required by orbital conservation. In order to better show additive and subtractive combinations, I'm going to bring back amplitude signs. The orbital shown upstairs for H₂ results from the additive combination of the separate 1s AOs: (H)1s + (H)1s. I depict this in a different way at left. This produces the bonding orbital.



Now let's look at the subtractive result, (H)1s - (H)1s, as shown at right. The overlap of orbitals of opposite signs decreases the amplitude and detracts from the MO, producing a node between the atoms. This gives an orbital which is higher energy than the original 1s AOs of the separate atoms. Since the orbital is higher energy in the diatomic than in the separate atoms, then the electrons would be better off in the separate atoms and this opposes bonding. Since this kind of MO would weaken the overall bond, this orbital is termed an antibonding orbital.



Now we have the total picture: the interaction of the two 1s atomic orbitals in H₂ produces one bonding orbital and one antibonding orbital. Does this change anything which we had previously discussed for the H₂ molecule? Nope, nothing's changed. Why? Keep in mind that the H₂ molecule has a total of two electrons. Both of these are in the bonding orbital and there are no electrons in the antibonding orbital. The bond order is still one. This is the same result as given by the Lewis structure and it's the same result as given by the Valence Bond Approach.

Now let's change the picture a bit: add one more electron to neutral H₂ in order to get the ion H₂⁻. That places one electron in the antibonding orbital. Now what? This would spell trouble to a Lewis structure and to VBA (within our coverage), but MOA can handle this easily. You must wait, however, before we can do that. We're jumping ahead and we need to take care of some other background first.

I mentioned upstairs that the MO Approach develops an electron configuration for the polyatomic unit. I will introduce this material with some parallel to the sequence which was used for monatomic configurations back in Chapters 21 and 22. Back then, we first developed a listing of all atomic orbitals, then we ranked these by energy, and then we derived configurations for monatomics. Now, we repeat the same sequence: first, we discuss the various molecular orbitals that are available, then we rank these by energy, and then we construct the configurations for diatomic units.

Before proceeding, I need to introduce orbital labels which are used within MOA.

Molecular orbitals are labeled first by whether they are σ or π type; then, we add a subscript in order to indicate their origin. Here's how we do this for the bonding orbital in H_2 : this orbital is σ type and it is derived from $1s$ AOs. We label this as σ_{1s} . The antibonding orbital in H_2 is also of σ type; although there is a gap in the orbital between the two nuclei, the orbital still lies on the bond axis and includes part of the bond axis, so it is σ type. For the label of an antibonding orbital, a star (asterisk) is commonly added; the antibonding orbital in H_2 is written as σ_{1s}^* . This is typically pronounced as "sigma-star-(one-ess)" or "sigma-(one-ess)-star"; either way is fine. Just remember that antibondings get a star.



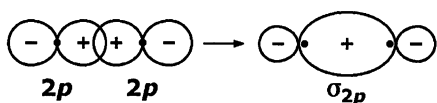
The bonding and antibonding orbitals which we have derived from $1s$ atomic orbitals in H_2 are fairly general; similar interactions can occur between any s orbitals in any n shell of any two atoms. Thus, the $2s$ orbitals of two atoms can interact and form σ_{2s} and σ_{2s}^* . These will be the same basic shape as for σ_{1s} and σ_{1s}^* but a bit larger, because larger $2s$ AOs are involved. Notice that the shell influence on size is carried through into the molecular orbitals which they form.

Now let's examine the interactions of $2p$ orbitals. This has some parallel to p 's in Valence Bond Approach.

Each atom will aim one p orbital at the other atom's p orbital, and this sets up a nose-to-nose interaction.

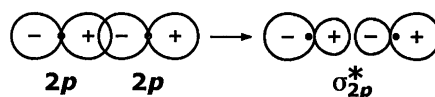
Each atom will still have two other p 's which are perpendicular to the bond axis and which can provide two side-to-side interactions.

We did that much in VBA, but now there's more to this story. Let's look at the interactions separately.

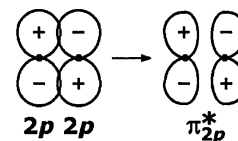
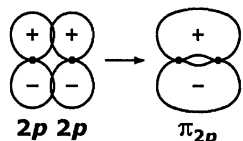


We begin with nose-to-nose. As we saw in the Valence Bond Approach, this interaction gives a σ -type bonding orbital, which is shown at left (with amplitude signs included). In the region of overlap with the same sign, the molecular orbital field is enhanced. In Molecular Orbital Approach, this orbital is

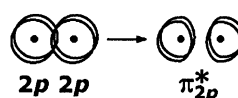
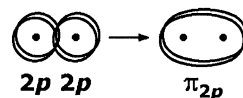
labeled σ_{2p} . We now also account for the antibonding orbital. This is derived from the subtractive combination of p orbitals, which is shown at right. In the overlap region with opposite signs, the orbital field is diminished. This orbital is destabilizing to the bond. This antibonding orbital is labeled σ_{2p}^* .



Now we move to the side-to-side p -to- p interactions. Each side-to-side interaction in the Valence Bond Approach gave us a π bonding orbital; we obtain this same bonding orbital in Molecular Orbital Approach. We label this as π_{2p} , shown at left. Now in MOA, we also obtain the antibonding result of that interaction, which is pictured at right. This orbital is also of π type. This orbital is destabilizing and opposes bonding. This orbital is labeled π_{2p}^* .



As we saw in VBA, there is a second side-to-side p -to- p interaction, perpendicular to the first; this produces a second π_{2p} bonding orbital. In MOA, we have this same π_{2p} bonding orbital and we also have a second antibonding orbital, π_{2p}^* . These are shown at left and at right; each of these orbitals projects forward and rearward. I didn't put the signs in those drawings for clarity, but the signs still apply.



Our grand result from all of these π interactions is that we have two π_{2p} bonding orbitals and we have two π_{2p}^* antibonding orbitals. Both π_{2p} bonding MOs have identical shape and they have identical energy; their only difference is that they are oriented perpendicularly to each other. Likewise, both π_{2p}^* antibonding MOs have identical shape and they have identical energy; their only difference is that they orient perpendicularly to each other. The energy aspects will be important momentarily.

This concludes all molecular orbitals derived from $1s$, $2s$ and $2p$ interactions. We will stop with these for our purposes. This will cover all diatomic molecules and ions of the First and Second Period elements. As in the past, we are concerned with the valence shell only. For First Period diatomics, we will need the

interactions of the valence 1s orbitals. For Second Period diatomics, the valence interactions involve the 2s and 2p orbitals. Here's a summary.

	AO interaction	MOs obtained
First Period:	1s/1s	one σ_{1s} and one σ_{1s}^*
Second Period:	2s/2s	one σ_{2s} and one σ_{2s}^*
	2p/2p	one σ_{2p} and one σ_{2p}^*
	nose-to-nose	two π_{2p} and two π_{2p}^*
	side-to-side	

For our next step towards configurations, we must rank these MOs by energy.

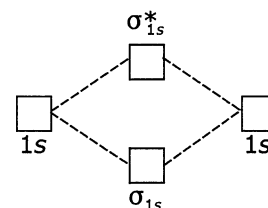
32.3 The relative energies of molecular orbitals

To begin the energy ranking for our MOs, we must take into account the following generality: for any specific interaction, bonding orbitals are lower in energy than antibonding orbitals. Keep in mind that lower energy is more favorable. Applying this to the above interactions, we have the following.

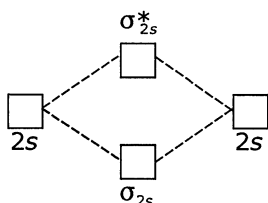
	AO interaction	MOs obtained	Relative energy
First Period:	1s/1s	one σ_{1s} and one σ_{1s}^*	$\sigma_{1s} < \sigma_{1s}^*$
Second Period:	2s/2s	one σ_{2s} and one σ_{2s}^*	$\sigma_{2s} < \sigma_{2s}^*$
	2p/2p	one σ_{2p} and one σ_{2p}^*	$\sigma_{2p} < \sigma_{2p}^*$
	nose-to-nose	two π_{2p} and two π_{2p}^*	$\pi_{2p} < \pi_{2p}^*$
	side-to-side		

This establishes a ranking within each specific type of interaction. That is all we need for the First Period interactions, but the Second Period involves different types of interactions and we will need to rank them among each other. We will start into this at this time, bringing in a figure which is called a Molecular Orbital Energy Diagram, MOED. The MOED shows the relative energies of the MOs and it also shows their AOs of origin.

Our first MOED will simply involve the 1s/1s interactions between two atoms, and it is shown at right. Let me point out a number of things. This is another energy diagram, so the vertical axis is energy; lower energy (lower position) is more favored. The MOs run up the middle column and that's the important part; the AOs are at the left and at the right. Dotted lines connect the orbitals within an interaction. Here's how we read the diagram: two 1s AOs interact to produce a σ_{1s} and a σ_{1s}^* orbital. The σ_{1s} orbital is lower energy than the original 1s AOs, while the σ_{1s}^* orbital is higher energy than the 1s orbitals. The lowering of σ_{1s} is close to, but not quite equal to, the raising of σ_{1s}^* . Thus, the antibonding effect is slightly greater than the bonding effect. The net result is that a bonding electron in σ_{1s} is offset by an antibonding electron in σ_{1s}^* . In other words, if you have an electron in σ_{1s} and one in σ_{1s}^* , then the total energy is slightly higher (worse) than having one electron in each of the separate 1s AOs; under these conditions, the atoms would not bond.



Note that, for the molecular orbitals (middle column), the energy sequence is $(\sigma_{1s})(\sigma_{1s}^*)$; this will be the fill sequence for electrons in these molecular orbitals. This MOED and this fill sequence is all we need for the diatomics of the First Period elements.



Moving to the Second Period diatomics, we first consider the analogous interactions between 2s orbitals of different atoms. You get the same basic outcome: σ_{2s} is lower energy than the original 2s atomic orbitals, and σ_{2s}^* is higher energy than the original 2s orbitals. (Again, antibonding is a slightly greater effect than bonding.) This is shown at left. The energy sequence for molecular orbitals (middle column) is $(\sigma_{2s})(\sigma_{2s}^*)$. This is the fill sequence for these orbitals.

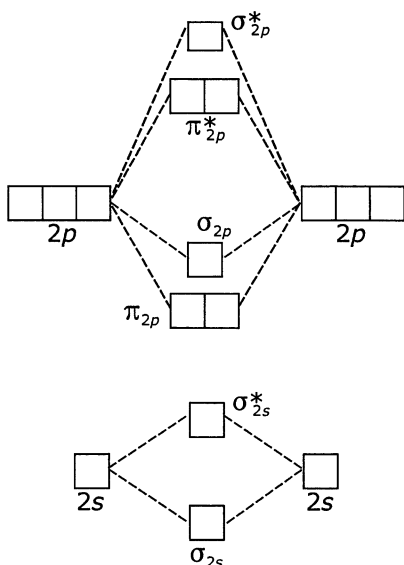
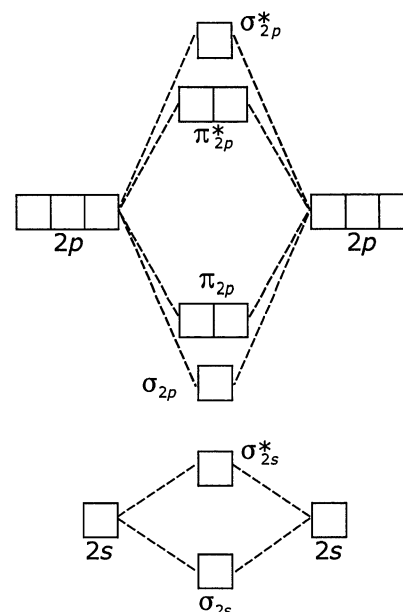
Now we bring in the p's. The interactions of the various 2p orbitals are a bit more complicated. Remember that we start with three 2p orbitals from each atom; from these, we have one nose-to-nose interaction to deal with (to give one σ_{2p} and one σ_{2p}^*) and we have two side-to-side interactions to deal with (to give two π_{2p} and two π_{2p}^*). Nose-to-nose is typically a stronger interaction than side-to-side; this

causes the σ_{2p} and σ_{2p}^* to spread apart more in energy than the spread for π_{2p} and π_{2p}^* . These $2p$ results are shown in the upper portion directly at right; the whole figure at right also includes the $2s/2s$ interactions at lower energy.

Notice in the MOED that both π_{2p} orbitals are the same energy and that both π_{2p}^* are the same energy. Notice that all of the $2p/2p$ interactions are cleanly above the energy of the $2s/2s$ interactions; this arises from the relative atomic orbital energies, $2p > 2s$.

Ranking the molecular orbitals so far, we have the energy sequence $(\sigma_{2s})(\sigma_{2s}^*)(\sigma_{2p})(\pi_{2p})(\pi_{2p}^*)(\sigma_{2p}^*)$.

Unfortunately, that's not the whole story. Some of the diatomics of the Second Period will indeed follow this energy sequence but some will not. The smaller atoms (O, F and Ne) will follow the sequence as shown. The larger atoms (Li, Be, B, C and N) however, have an extra complication.



The extra complication arises from a process called mixing, which involves mixing $2s/2s$ and nose-to-nose $2p/2p$ interactions together to obtain a lower energy result in the end. This shifts the energies of the MOs derived from those interactions, namely σ_{2s} , σ_{2s}^* , σ_{2p} and σ_{2p}^* . The energies of σ_{2s} and σ_{2s}^* shift downward to lower energy; the energies of σ_{2p} and σ_{2p}^* shift upward to higher energy. The really important one to note is σ_{2p} , since its energy ends up above the energy of π_{2p} . At left are the $2p/2p$ interactions when mixing is significant. Notice that σ_{2p} is now above π_{2p} in the energy lineup. This results in a modified sequence of $(\sigma_{2s})(\sigma_{2s}^*)(\pi_{2p})(\sigma_{2p})(\pi_{2p}^*)(\sigma_{2p}^*)$. This may look just like the prior sequence, but squint your eyeballs and take a closer look: the two sequences differ by the specific ordering of $\dots(\sigma_{2p})(\pi_{2p})\dots$ versus $\dots(\pi_{2p})(\sigma_{2p})\dots$. The (σ_{2p}) portion fell back one spot in the lineup. Subtle, eh?

Time to summarize.

We now have the listing of eight available MOs and their energies for homonuclear diatomics of the Second Period. There are two possible sequences, depending on whether there is significant mixing or not for a particular diatomic case. These two sequences are the following.

Without significant mixing: $(\sigma_{2s})(\sigma_{2s}^*)(\sigma_{2p})(\pi_{2p})(\pi_{2p}^*)(\sigma_{2p}^*)$

With significant mixing: $(\sigma_{2s})(\sigma_{2s}^*)(\pi_{2p})(\sigma_{2p})(\pi_{2p}^*)(\sigma_{2p}^*)$

For emphasis, I've underlined the parts that switch around. Although this switcheroo business may seem confusing, I'll show you how this all works out when we need it.

Now we're ready: we can proceed to electron configurations.

32.4 Configurations and consequences

Doing an electron configuration here for a diatomic is much the same as doing a monatomic configuration; here's how that was set up in Section 22.3.

“ In order to do configurations, you need three things: the general fill sequence ..., the total number of electrons in the atom ..., and the number of electrons allowed per subshell. ”

For diatomics in MOA, you again need three things:

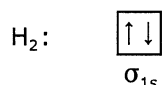
- ▶ the fill sequence,
- ▶ the total number of electrons in the diatomic unit, and,
- ▶ the number of electrons allowed per σ or π energy level

Let me explain that last entry. Notice in the MOEDs that every σ and σ^* level has one orbital; this means each (σ) and (σ^*) portion in the sequence can hold up to two electrons. Notice also in the diagrams that the π and π^* levels have two orbitals each; each (π) and (π^*) portion can hold up to four electrons. This is important and you need to remember this. While you're at it, you also have to remember all of the business about pairing: if two electrons are in one orbital, then they must be spin-paired. When dealing with the two orbitals in a (π) or (π^*) portion, one electron is located into each orbital first with the same spin, before pairing. We'll see how this stuff pans out in the various examples below and into the next Chapter.

We saw in Chapter 22 that there are two general ways to depict an electron configuration for monatomics: written format, such as $1s^22s^22p^6$, and box configuration. In the Molecular Orbital Approach, the configuration is often adapted right into the MOED, with electrons shown in the various energy levels. I want to keep things simple and focus only on the MOs without having AOs in the picture. Thus, we are simply going to stick with Chapter 22 methods, using written format and box format. We will not do full MOEDs each time.

OK, we go back to the beginning, First Period: H_2 .

As we have described so far, H_2 has two electrons and it has them in the σ_{1s} bonding orbital; we write this configuration as $(\sigma_{1s})^2$. In box notation, this is the following.



Both electrons are spin-paired, so the molecule is diamagnetic.

Time out. I need to re-introduce bond order right now; this is handled differently in Molecular Orbital Approach. Bond order is calculated as the difference between the number of bonding electron pairs and the number of antibonding electron pairs within the chemical unit.

$$\text{Bond order} = \text{number of bonding pairs} - \text{number of antibonding pairs}$$

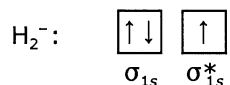
An alternative version counts electrons instead of electron pairs; that equation is the following.

$$\text{Bond order} = \frac{1}{2} \times \{\text{number of bonding electrons} - \text{number of antibonding electrons}\}$$

Bond order is still based on the notion of pairs but now we incorporate the effect of antibonding electrons. You need to catch the significance of these effects: in essence, each antibonding electron cancels the effect of one bonding electron. This is a very important aspect in the MO Approach.

Applying this to H_2 , there are two bonding electrons (one pair) and no antibonding electrons. This means that the bond order is one. The bonding electrons are in a σ -type orbital. This is exactly what the Lewis structure and the Valence Bond Approach tell us for H_2 : one single bond of σ type.

Let's return to the notion of the H_2^- ion which I had mentioned earlier in this Chapter. This has a total of three electrons. You enter three electrons into the fill sequence to get the configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^1$. The box notation is the following.



This critter is paramagnetic, with one unpaired electron. The bond order is determined as follows: there are two bonding electrons and one antibonding electron, for a difference of one. We take one-half of this, so the bond order is one-half.

One-half bond order? What's the significance of this? What in the world is the H_2^- ion?

Well, quite frankly, it's not much of an ion. Our MO Approach tells us that this diatomic ion can indeed exist and is stable by itself, but the bond would be weak because the bond order is only 0.5. Although stable by itself, it will be very reactive towards other molecules or ions at typical conditions.

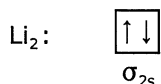
Just with these two simple examples, there are already several points to note.

- Comparing H_2 to H_2^- , we see that the impact of the antibonding electron is to reduce the strength of the bond, as reflected in the reduction in bond order. I said it just a moment ago and I'll say it again for emphasis: in essence, EACH ANTIBONDING ELECTRON CANCELS THE EFFECT OF ONE BONDING ELECTRON.
- Fractional bond orders can be obtained in the MO Approach: this will happen whenever there is an odd number of electrons.
- The MO Approach can tell us whether something can exist or not, based on bond order. In order for a diatomic to be able to exist (to be stable), then its bond order must be some number greater than zero. Notice that this only says that the diatomic is capable of existing; that doesn't mean it's something that will stay around long enough to sit in a jar at normal conditions.

Let's resume.

We'll do He_2 . How many total electrons are there in the diatomic unit? Helium atoms have two electrons each, so there would be four in a diatomic. What molecular orbitals are they in? Well, two will fill up σ_{1s} and the other two will fill up σ_{1s}^* , giving the configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^2$. Unfortunately, two antibonding electrons cancel the effect of the two bonding electrons completely. You can also see this in the calculated bond order: the bond order is zero. Zero bond order means no bond and no bond means no molecule. Period. End of story. The MO method tells us that He_2 cannot exist as a diatomic molecule. That's no surprise, since we know that helium is monatomic anyway.

Let's now drop down to the Second Period. We start with Li_2 . How many total valence electrons? Each lithium atom has one so the total is two. What molecular orbital are they in? Referring back to the configuration sequence, the first opening is in σ_{2s} and the two electrons will evenly fill that. The configuration is $(\sigma_{2s})^2$; the box format is the following.



The electrons are spin-paired and the compound is diamagnetic. The electrons are in a bonding orbital and there are no antibonding electrons; thus, the bond order is one. The bond order of one tells us that Li_2 can exist. No, it is not the common form of the element lithium but it has been studied and it follows the MOA expectations.

OK, another time out. We've covered a lot of turf here. I want to summarize where we are and what we're doing.

We have developed the Molecular Orbital Approach just barely into the Second Period. The general procedure is to determine the total number of valence electrons from the two atoms and to plug these into the MO fill sequence. If you're dealing with a polyatomic ion, you must also consider charge: you add to the count for an anion charge and you subtract for a cation charge. This much will get you the MO configuration. After you have the MO configuration, you can determine bond order and you can determine the magnetic properties of diamagnetism or paramagnetism. The question of diamagnetism and paramagnetism has parallel to the same notions used in Chapter 24 with monatomics; I'll explain this, but you need to go back to the blue star in Chapter 24 and re-read the clues. Those parts about odd versus even numbers of electrons and about exactly-filled versus partly-filled levels are still very important. Here's how we handle the exactly-filled versus partly-filled levels in MO Approach.

- ▶ Any (σ), (σ^*), (π) or (π^*) portion which is exactly filled will have all of its electrons paired.
- ▶ Any (σ), (σ^*), (π) or (π^*) portion which is partly filled will have one or more unpaired electrons.

Note! When considering how many electrons are unpaired in a diatomic unit, you need to look for the partly-filled levels only. This may sound confusing right now; hopefully this will get clearer when you see how this is applied.

This time-out is over.

Problems

1. What is the configuration of He_2^+ ? What is the bond order? How many unpaired electrons are there?
2. Is Li_2^+ capable of existence? What are the configuration and the bond order?