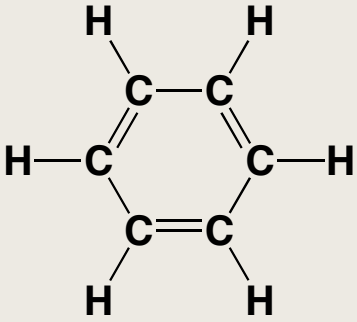
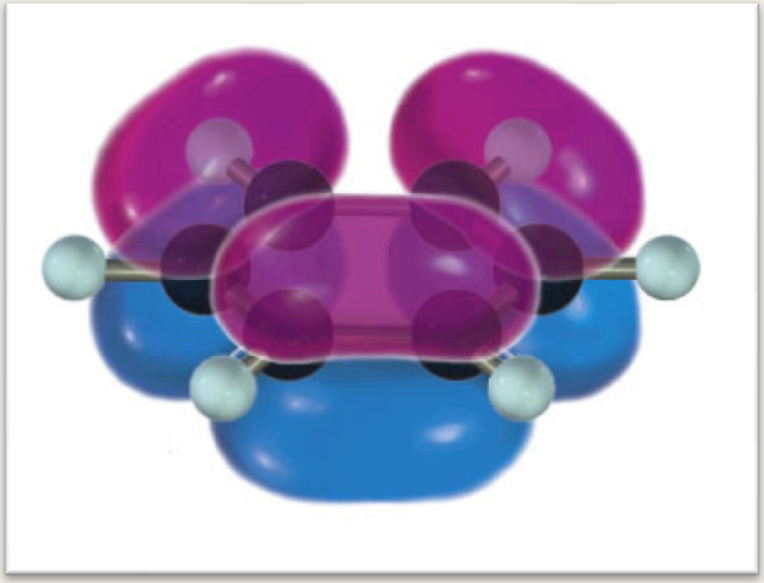
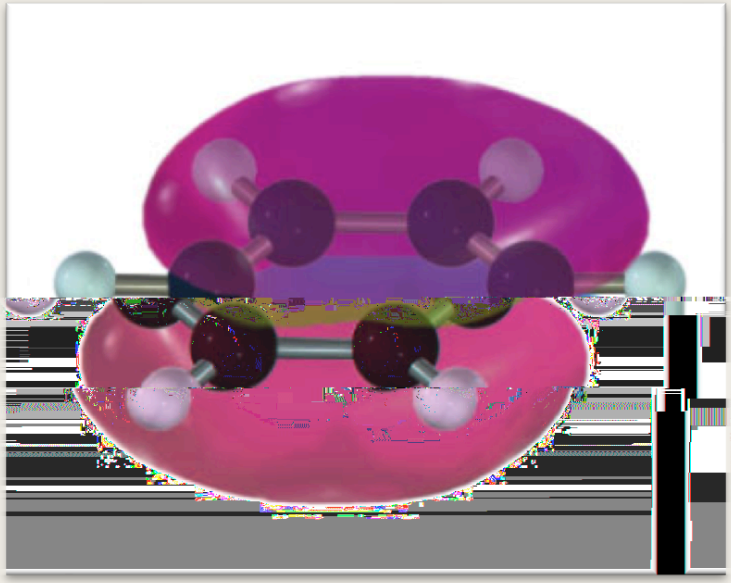
Molecular Orbital Theory



A more accurate theory than valence bond theory is **molecular orbital (MO) theory**. In molecular orbital theory, we imagine that electronic orbitals cover the whole molecule and are not localised on one atom. These diagrams show the difference between valence bond theory and molecular orbital theory when considering the orbitals of benzene.



Valence bond theory: three sets of **localised** π-bonds (the σ-bonds are shown as sticks).

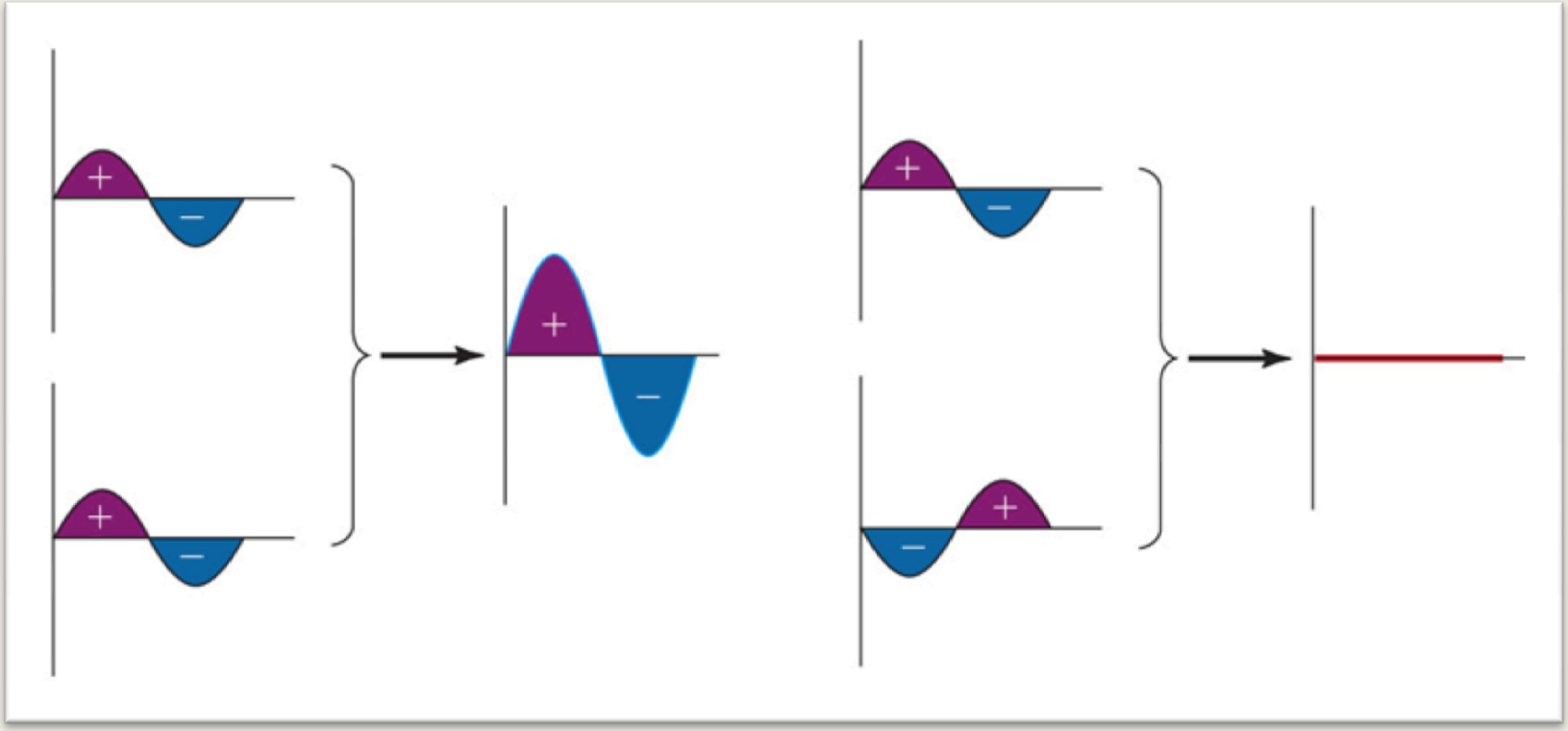


Molecular orbital theory: orbitals are spread over whole molecule.

MO Theory Basics

Whilst we can imagine the hybrid orbitals of valence bond theory very easily, we need computers to visualise molecular orbitals. However, elements of molecular orbital theory are necessary for many discussions of chemical and physical properties and so will will discuss some basic principles here.

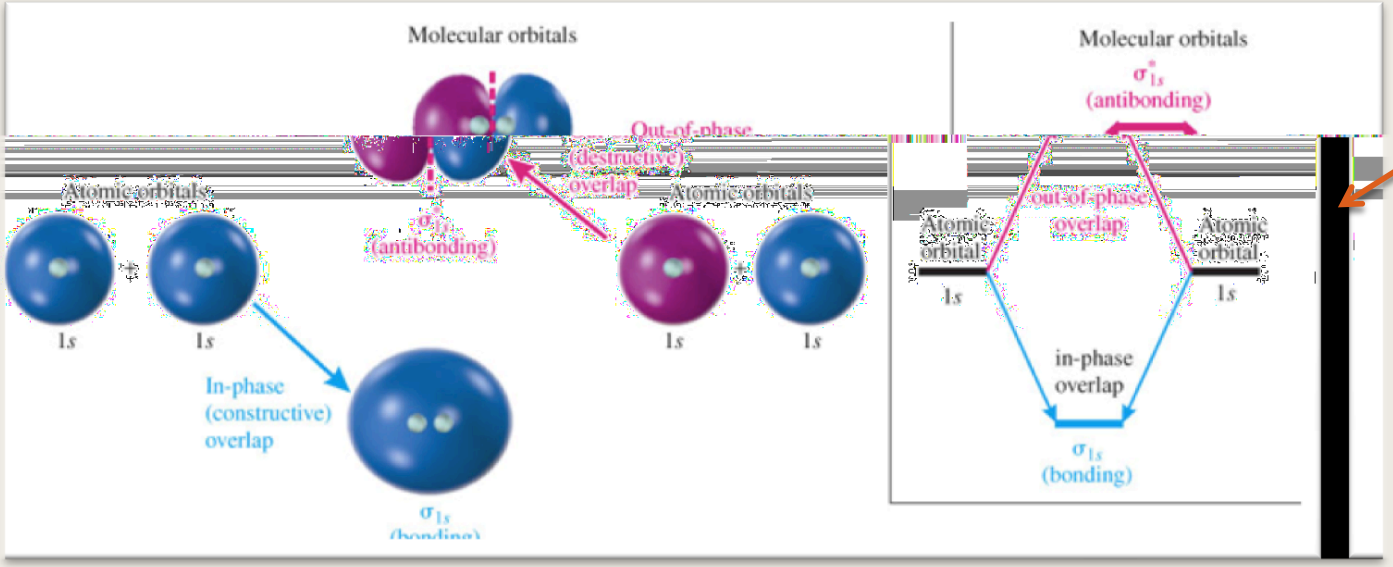
Lets begin by looking again at **wave superimposition**. We have already seen that waves with the same phase will **interfere constructively** and increase their **amplitude**. Waves with opposite phases interfere **destructively** to decrease their amplitude.



Energy Diagrams

Now let's look at the simplest molecule, dihydrogen (H_2). A H_2 molecule is made by superimposing (overlapping) the 1s orbitals of two H atoms. If the orbitals have the same phase, they will interfere constructively and form a molecular orbital with greater electron density between the positively charged nuclei. It will require less energy to hold the atoms together if there are electrons in this orbital and the orbital is called a **bonding orbital**.

Energy required



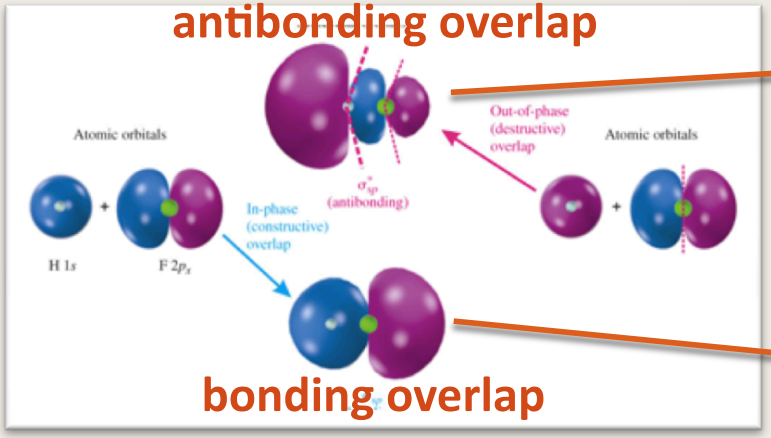
Energy diagram

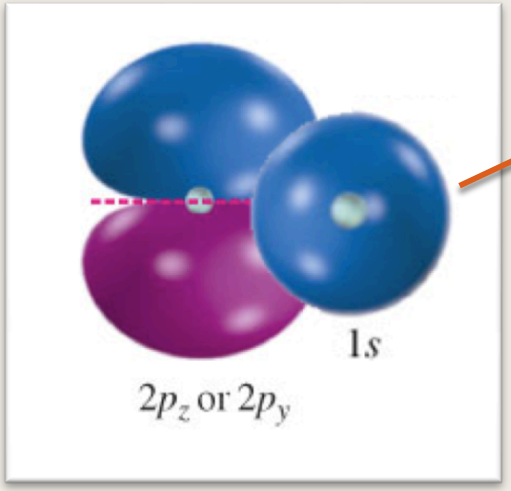
If the atomic orbitals are of opposite phase, they will interfere destructively and form a molecular orbital with less electron density between the nuclei. Because the nuclei repel each other, it will take more energy to hold the atoms together in this configuration. This forms an **anti-bonding orbital** and the molecule will need more energy to stay together if electrons occupy the anti-bonding orbital.

In short, the two atomic orbitals of H_2 can make two **molecular orbitals**: one bonding orbital and one anti-bonding orbital. These orbitals can be represented simply by an **energy diagram**. **Note:** only atomic orbitals that are close in energy can form bonding/anti-bonding orbitals.

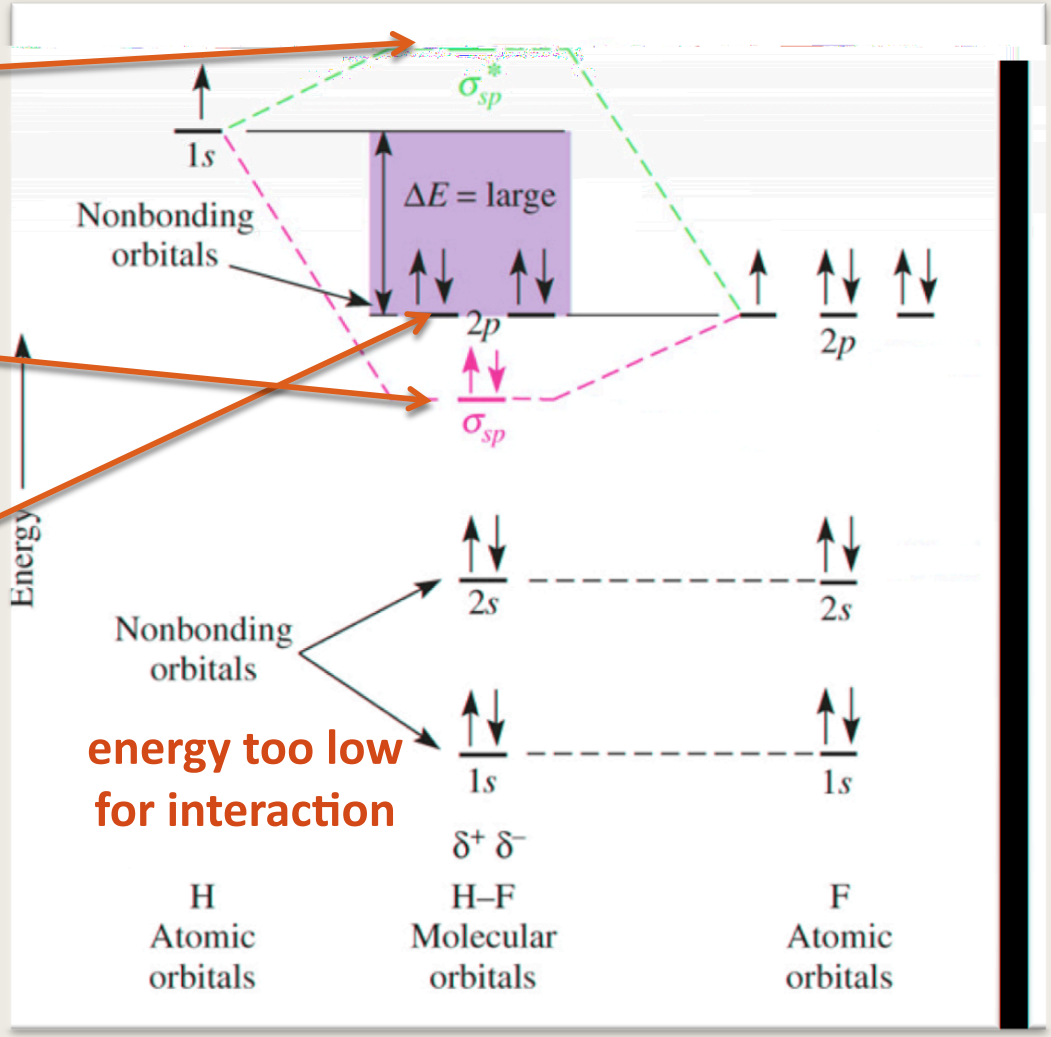
Non-bonding Orbitals

If an atomic orbital does not form a bonding or anti-bonding orbital, it is called a **non-bonding orbital**. There are two common reasons that atomic orbitals form non-bonding orbitals: 1) they do not have a similar energy to an orbital on another atom or 2) constructive interference with one lobe of an orbital is cancelled by destructive interference with another lobe of that orbital. The following diagrams illustrate the case with hydrogen fluoride.





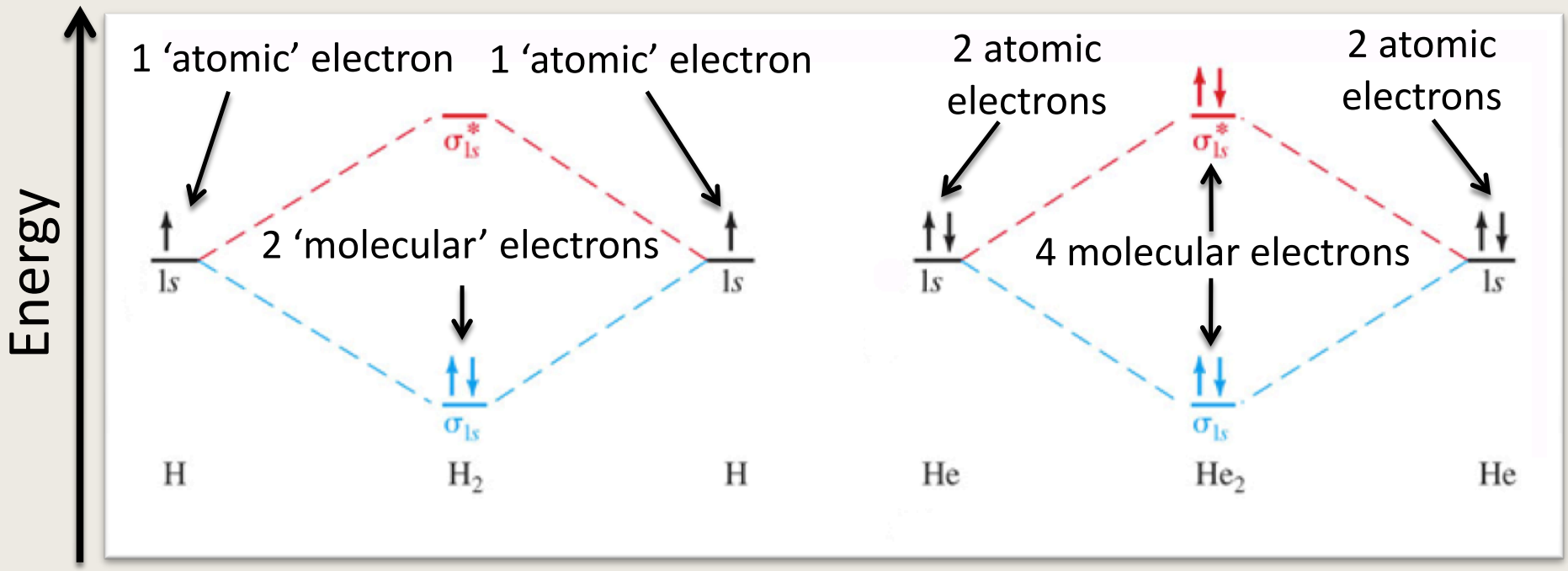
non-bonding overlap



Completing Simple Energy Diagrams

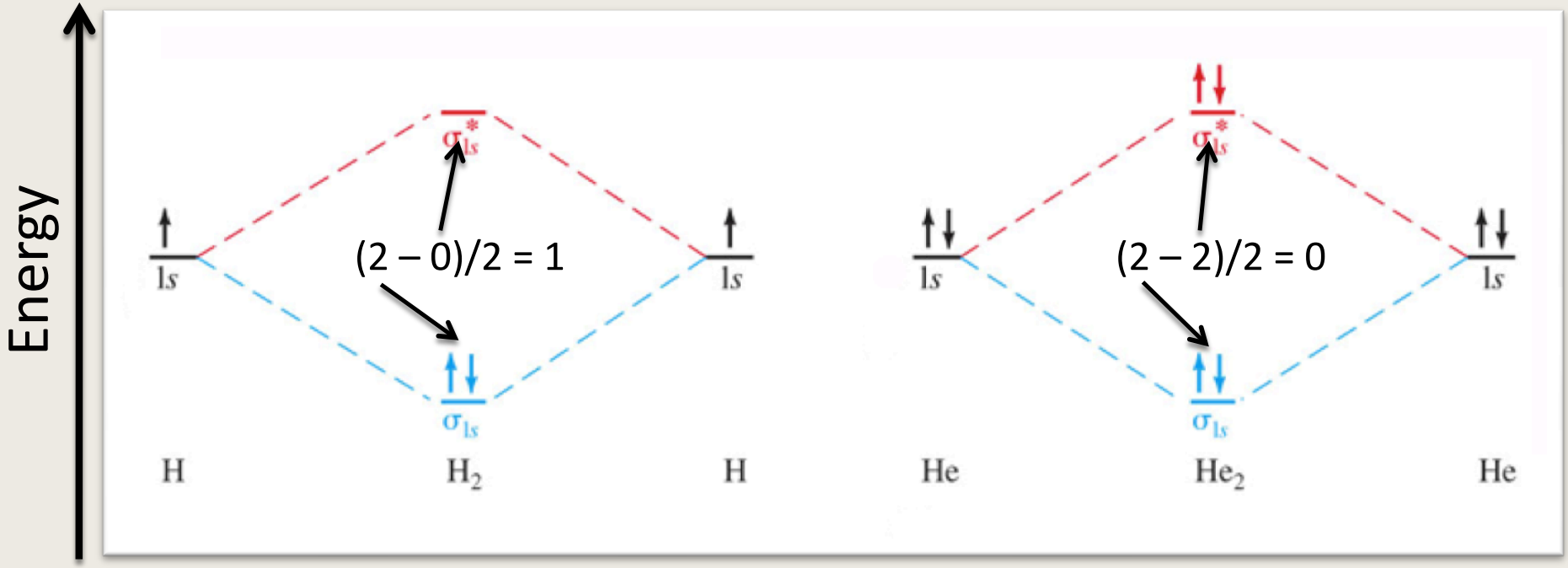
We will not look at making energy diagrams in this course but it is useful to know how to complete them with electrons.

The energy diagram tells us which molecular orbitals are created in a molecule but to know which orbitals are occupied, we need to add electrons. The total number of electrons we can use is equal to the number of valence electrons on all the atoms. If the molecule has an electric charge, we must add/remove electrons to match the charge (i.e. OH^- will have one more electron than neutral O and H atoms separately). We complete molecular orbital diagrams in the same way we complete atomic orbital diagrams: fill from the bottom to the top, fill degenerate orbitals with unpaired electrons first, and pair up electrons before filling higher energy levels.



Bond Order and Stability

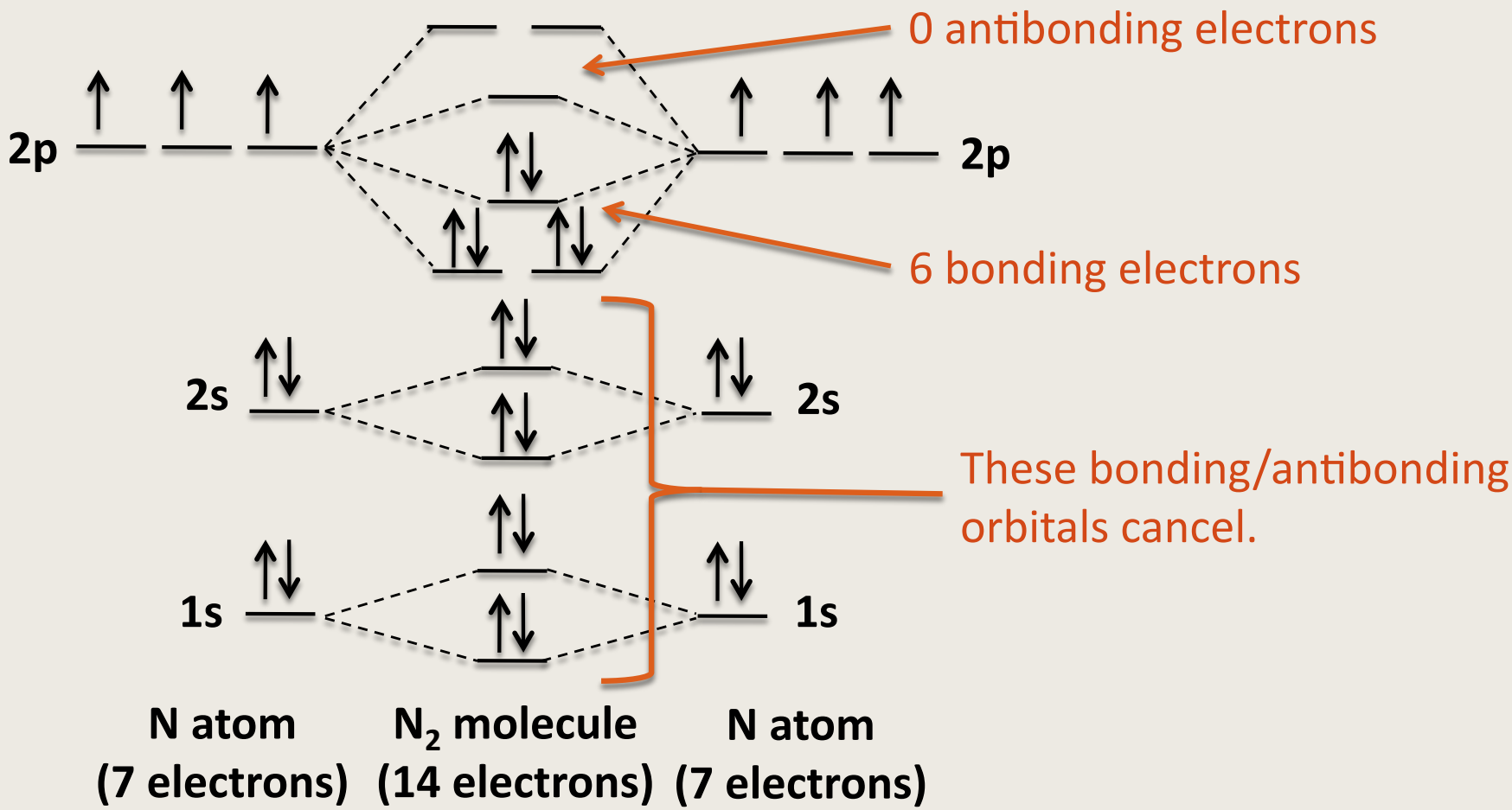
In MO theory, there are no single, double or triple bonds, instead there is **bond order**. Bond order is calculated as: (no. of bonding electrons – no. of antibonding electrons)/2. Look at the diagrams for H_2 and He_2: we can see that H_2 has a bond order of one and that He_2 would have a bond order of zero. Higher bond orders usually correspond to greater stability. (Note: bond order is NOT the same as single/double/triple bonds. Bond order is only used with MO theory and single/double/triple bonds are only used with valence bond theory.)



We can use bond order to predict the stability or instability of molecules. For instance, we can see that a H_2 molecule, with two electrons in a bonding orbital, will have lower energy (and therefore be more stable) than two separate H atoms. However, two He atoms will not make a stable molecule because their electrons fill both the bonding and the antibonding orbitals. This arrangement results in no extra stability compared with separate atoms.

N_2

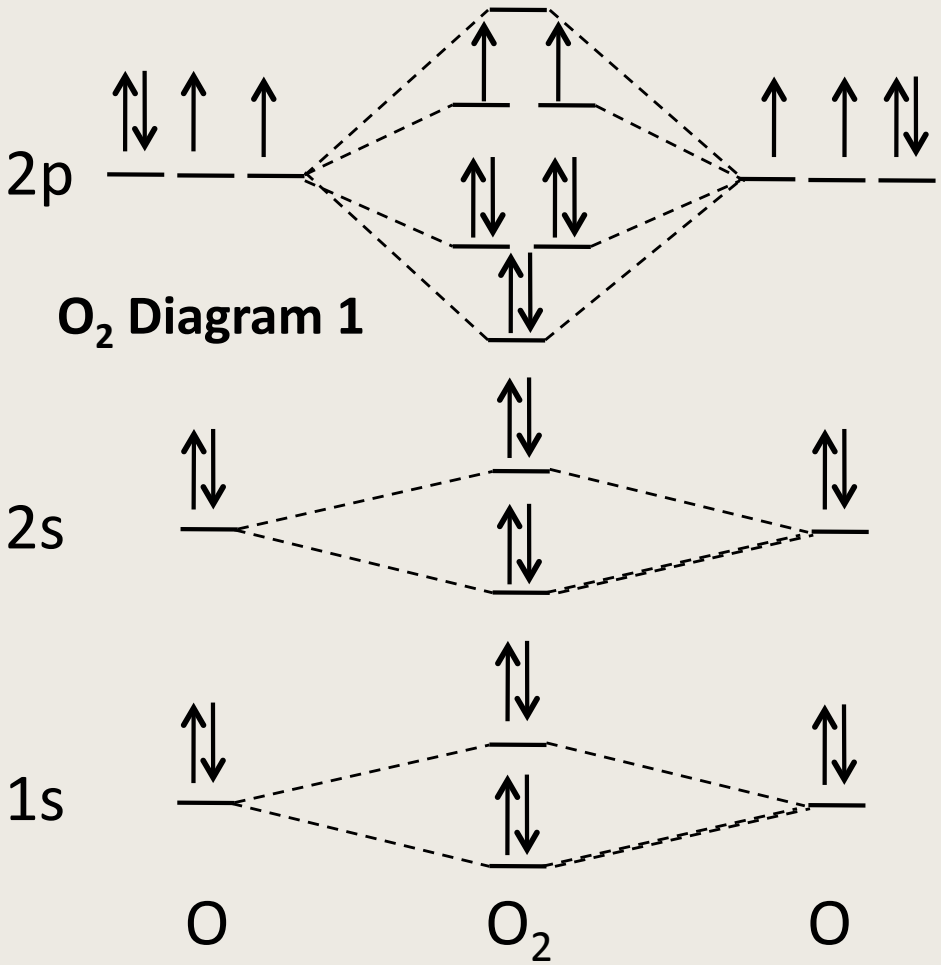
Let's look at a slightly more complex case: dinitrogen (N_2)



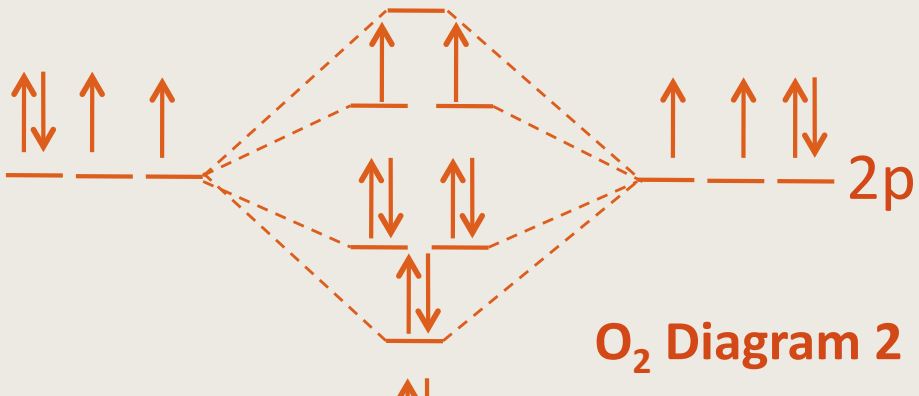
$(6 - 0)/2 = 3$ so N_2 has a bond order of 3. This explains why dinitrogen is so stable. In fact, the only things that can break molecules of N_2 at room temperature are enzymes found in a few kinds of bacteria.

Abbreviated Diagrams

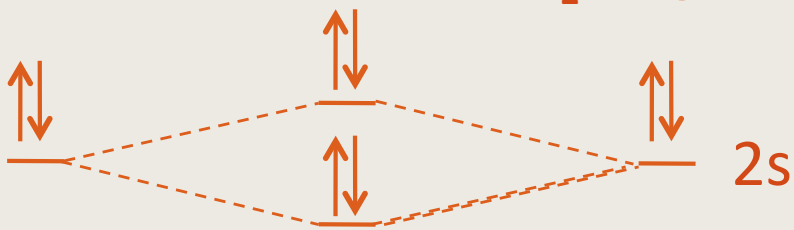
Since lower sets of bonding/antibonding orbitals cancel each other out, we usually do not include them when making MO diagrams. In the case of O_2, that means we might show only the 2s and 2p orbitals or even just the 2p orbitals (note that MO theory easily explains why O_2 has 2 unpaired electrons). Any one of the three diagrams below can be used to represent O_2.

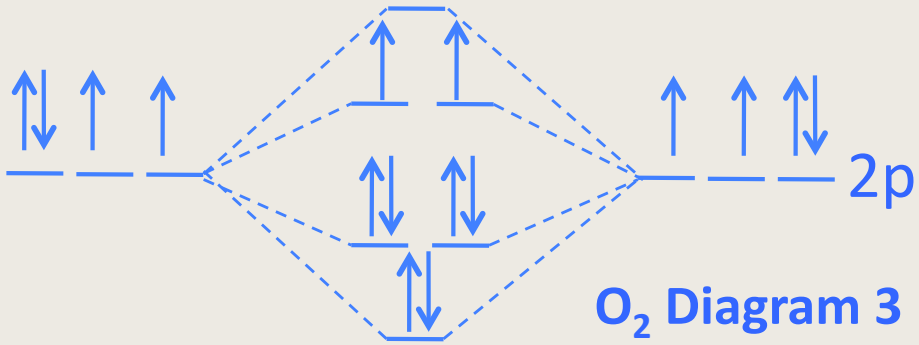


O_2 Diagram 1



O_2 Diagram 2





O_2 Diagram 3

(‘Stability’ v. ‘Reactivity’)

We will make a brief diversion at this point to explain that ‘stability’ and ‘reactivity’ are different concepts and should not be confused when interpreting molecular orbital diagrams.

A bond between two atoms is more stable if more energy is required to break it up. This stability usually corresponds directly to the bond order.

The definition of a reactive molecule is that it easily reacts with other particles. There are many factors that affect the reactivity of a molecule — one factor is the stability of its bonds but configuration (i.e. shape) and the presence of unpaired electrons are also important. Note that this means that a molecule with energetically stable bonds might still be reactive. A good example is oxygen, which has a bond order of 2 but also has two unpaired electrons. In cases such as these, we must be careful not to say that oxygen is unstable because of its unpaired electrons — it is *reactive* because of its unpaired electrons. Conversely, the peroxide ion (O_2^{2-}) is more reactive than oxygen, despite having no unpaired electrons, because it is less stable with a bond order of only one.

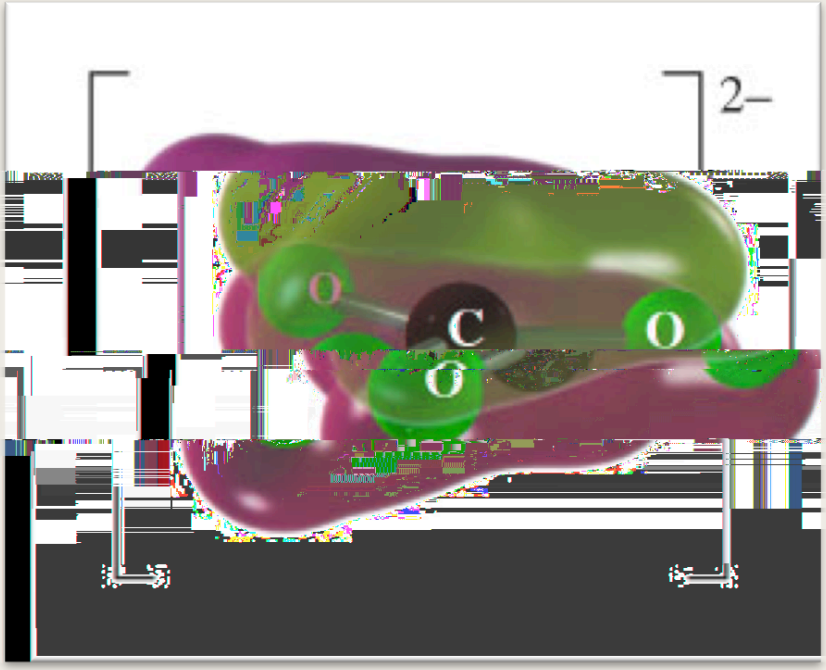
Many experienced chemists mistake the concepts of stability and reactivity.

Using Molecular Orbital Theory

But how do we know the energies of the orbitals and hence, which orbitals are bonding, non-bonding and antibonding? And how do we know the shapes of those orbitals?

For simple diatomic molecules, we can make rough estimates of the relative energies of molecular orbitals by following a few rules. You may study those rules on later courses.

However, for triatomic molecules and above, we can only calculate the energies and shapes of molecular orbitals by solving the Schrodinger equation for the whole molecule. This is extremely complicated so we have to rely on computers and experimental data. For now, it is enough to understand the basics of molecular orbital theory.



Though it is quite complex, MO theory explains many phenomena that valence bond theory cannot, for instance, why benzene (C_6H_6) is extremely stable but cyclooctatetrene (C_8H_8) is not, or how certain catalysts work. It also forms the basis of band theory, which we shall briefly look at later.

(Warning!)

Valence bond theory and molecular orbital theory are different theories. Valence bond theory makes imaginary hybrid orbitals around atoms that overlap to make discrete bonding orbitals and lone pair orbitals. The bonding orbitals form single, double and triple bonds. Molecular orbital theory uses the Schrodinger equation to make orbitals around an entire molecule, usually with unpredictable orbital shapes. A molecular orbital can be bonding, non-bonding, antibonding or somewhere in between (for instance 90% anti-bonding and 10% non-bonding). Single/double/triple bonds are replaced by the concept of bond order, which can be fractional (e.g. 1½).

Chemists use valence bond theory because it is simple and molecular orbital theory because it is accurate. Unfortunately, this leads many chemists, and even text books, to mix their uses of *both* theories. This is only allowable if we are very careful about what we are saying.

Bad Examples:

Concise Inorganic Chemistry, P. D. Lee, 5th edition, p. 112.

In a discussion of the application of molecular orbital theory to the carbonate anion (CO_3^{2-}): "The structure of the carbonate ion is a planar triangle with bond angles of 120°. The C atom at the centre uses sp^2 orbitals."

Inorganic Chemistry, D. F. Shriver, P. W. Atkins, C. H. Langford, 2nd edition, pp. 85 & 88.

When discussing molecular orbital theory and SF_6: "The important point is that the bonding in the hypervalent SF_6 molecule can be explained without using sulphur d-orbitals to expand the octet." Later, when discussing hybrid orbitals in the context of molecular orbital theory: "To match the arrangements of bonds in molecules with [octahedral] shapes, it is necessary to use d-orbitals as well as s- and p-orbitals."

Molecular Modeling

Using a mixture of VB theory, MO theory and **classical** Newtonian mechanics, chemists often make computational models of molecules. These models are used for calculations that help chemists to design new molecules and understand interesting properties of molecules already synthesised.

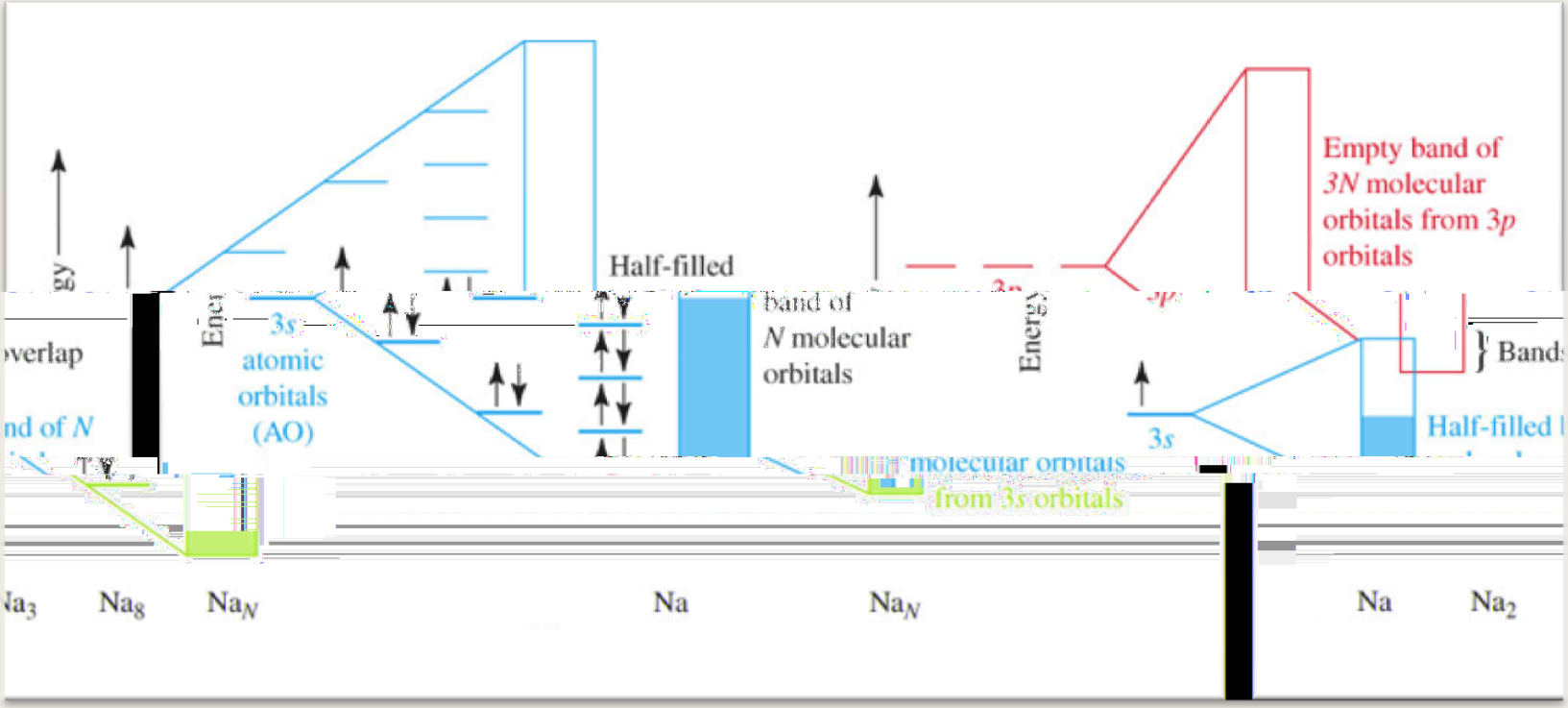
Molecular mechanics calculations use valence bond theory to fix the possible shapes of a molecule and then use classical Newtonian mechanics to see how the molecule can twist and vibrate. They are very fast and easy to set up so they are best for simple **conformational modeling**, where we simply want to know what shapes a molecule is most likely to take.

Ab initio calculations calculate everything beginning from the Schrodinger Equation. They take a lot of computational time and are a little more difficult to set up. Chemists usually use this kind of calculation when they want to know details of the molecular orbitals.

Semi-empirical calculations use some data from experiments and calculate other parts using the Schrodinger equation. They are more accurate than molecular mechanics but don't take as long as ab initio calculations.

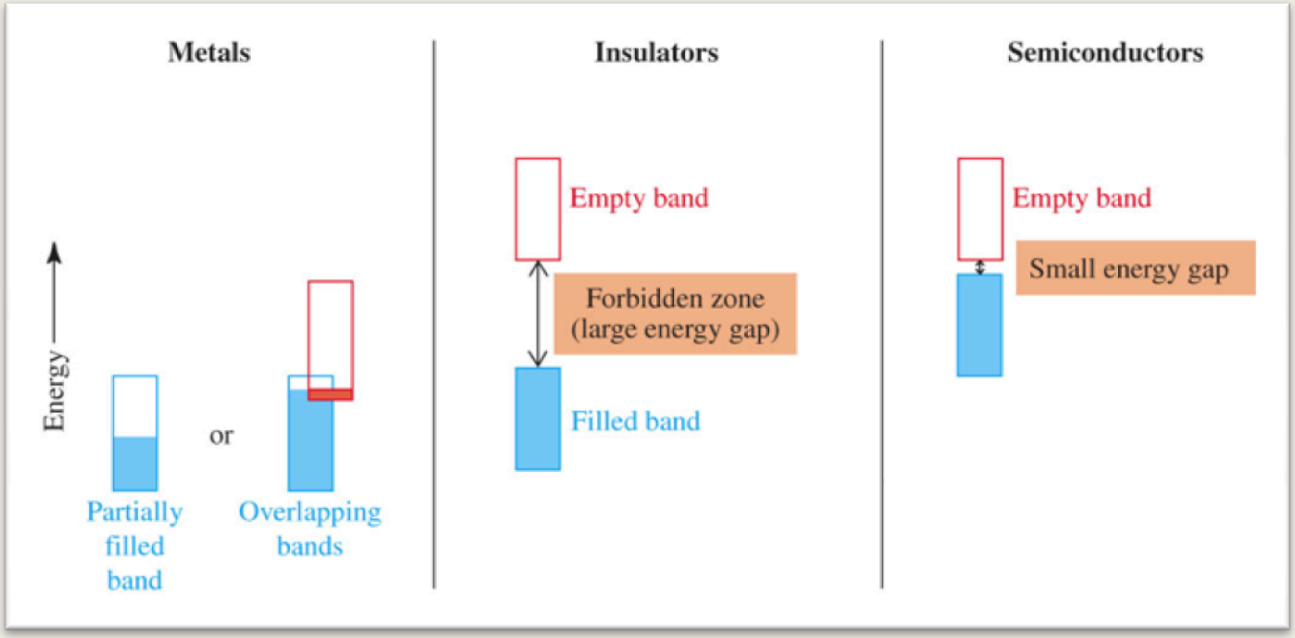
Band Theory

We have seen that the energy of orbitals around atoms can be represented by an energy diagram and that atomic orbitals can be extended over whole molecules. The same principle can also be applied to crystal lattices. In a simple approximation, three things happen when electronic orbitals are made for a whole lattice: 1) Orbitals of the same energy separate to make an equal number of orbitals above and below their separate energies 2) The difference in energy between the highest and lowest molecular orbitals gets larger, and 3) the separation between neighbouring molecular orbital energies gets smaller. In other words, the spread of energy levels gets larger but the levels also get denser. For a typical crystal lattice, the states are so densely packed that we can think of them as being a solid **band** of full or empty orbitals. In some cases, orbitals that are widely separated in separate atoms spread out enough to overlap as bands.



Metals, Insulators and Semi-Conductors

Band theory helps us understand the differences between electrical **conductors**, **semi-conductors** and **insulators**. For electrons to move through a lattice, there must be a convenient empty orbital for them to move into. If a band is only partially filled, an electron at the top of the filled band can move into an empty orbital at an energy level immediately above and travel through the lattice for a tiny amount of extra energy. If an empty band overlaps with a full band, electrons will transfer into the empty band and create space for electrons to travel. Insulators, on the other hand, have a large energy gap between the top of a full band and the bottom of an empty band. It therefore takes a lot of energy move electrons into empty orbitals and insulators do not normally conduct electricity.



Semi-conductors have a smaller energy gap between the top of the full band and the bottom of the empty band, meaning electrons can enter an empty orbital with a little extra energy. This explains why semi-conductors conduct electricity better when energy (as heat, light or electricity) is added to the lattice.