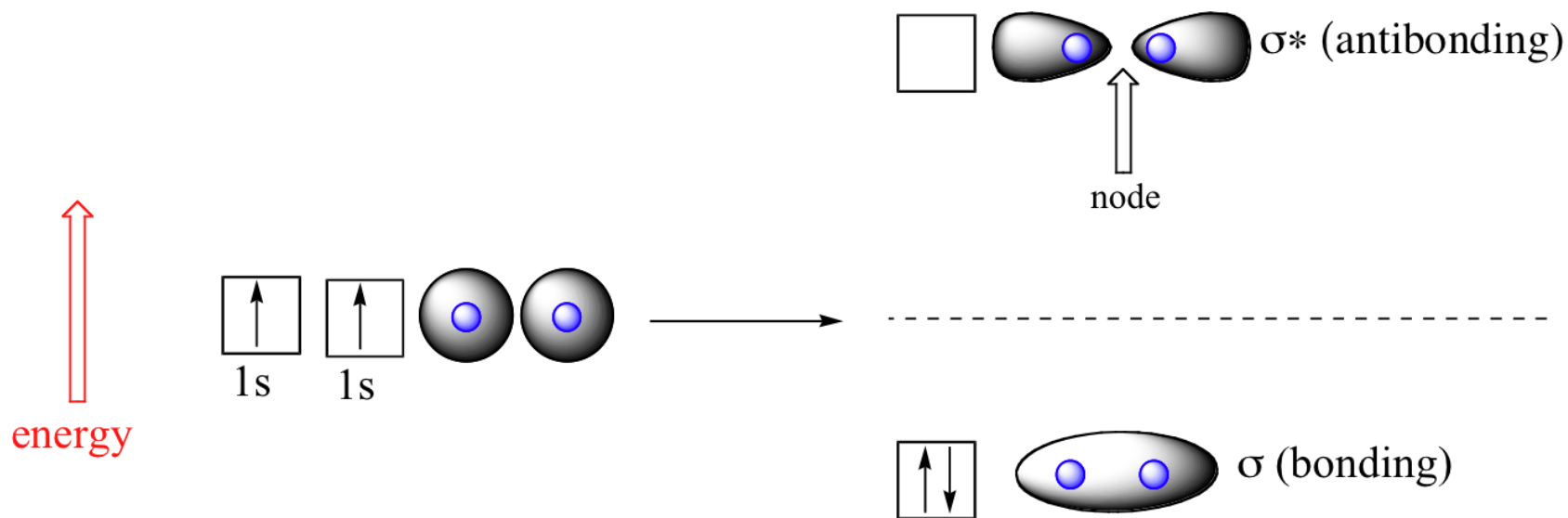


Chemical Bonds- Molecular Orbital Theory

H₂ molecule: bonding and anti-bonding sigma molecular orbitals

Let's consider again the simplest possible covalent bond: the one in molecular hydrogen (H₂). When we described the hydrogen molecule using valence bond theory, we said that the two 1s orbitals from each atom overlap, allowing the two electrons to be shared and thus forming a covalent bond. In molecular orbital theory, we make a further statement: we say that the two atomic 1s orbitals don't just overlap, they actually *combine to form two completely new orbitals*. These two new orbitals, instead of describing the likely location of an electron around a single nucleus, describe the location of an electron pair around two or more nuclei. The bonding in H₂, then, is due to the formation of a new molecular orbital (MO), in which a pair of electrons is delocalized around two hydrogen nuclei.

An important principle of quantum mechanical theory is that when orbitals combine, the number of orbitals before the combination takes place must equal the number of new orbitals that result – orbitals don't just disappear! We saw this previously when we discussed hybrid orbitals: one s and three p orbitals make four sp³ hybrids. When two atomic 1s orbitals combine in the formation of H₂, the result is two molecular orbitals called sigma (σ) orbitals. According to MO theory, the first sigma orbital is lower in energy than either of the two isolated atomic 1s orbitals – thus this sigma orbital is referred to as a bonding molecular orbital. The second, sigma-star (σ*) orbital is higher in energy than the two atomic 1s orbitals, and is referred to as an anti-bonding molecular orbital. In MO theory, a star (*) sign always indicates an anti-bonding orbital.



Following the *aufbau* ('building up') principle, we place the two electrons in the H_2 molecule in the lowest energy molecular orbital, which is the (bonding) sigma orbital.

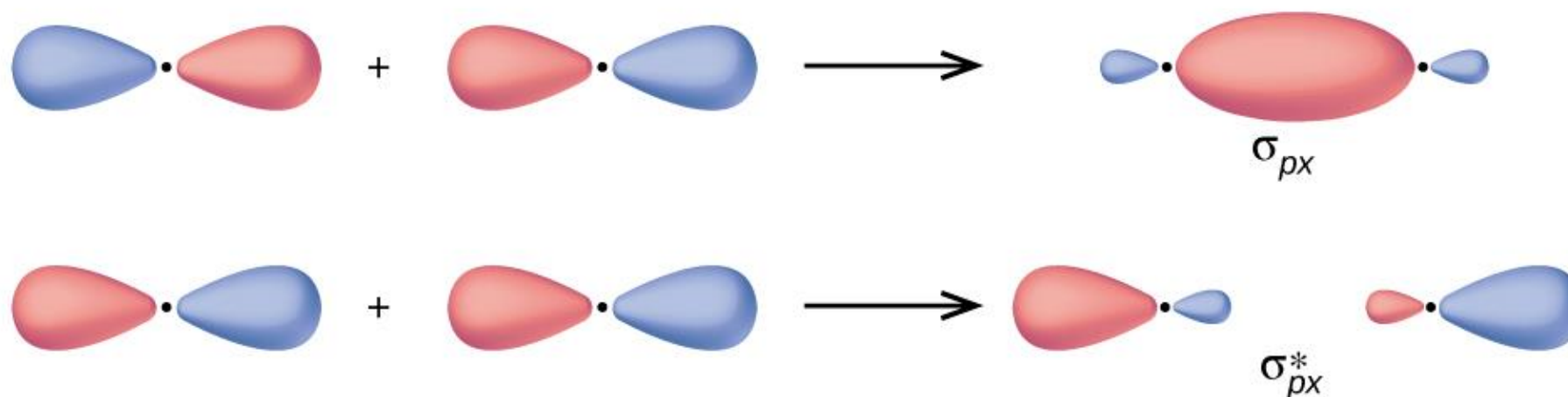
The bonding sigma orbital, which holds both electrons in the ground state of the molecule, is egg-shaped, encompassing the two nuclei, and with the highest likelihood of electrons being in the area between the two nuclei. The high-energy, anti-bonding sigma-star orbital can be visualized as a pair of droplets, with areas of higher electron density near each nucleus and a 'node', (area of zero electron density) midway between the two nuclei.

Remember that we are thinking here about electron behaviour as *wave behaviour*. When two separate waves combine, they can do so with what is called constructive interference, where the two amplitudes reinforce one another, or destructive interference, where the two amplitudes cancel one another out. Bonding MO's are the consequence of constructive interference between two atomic orbitals which results in an attractive interaction and an increase in electron density between the nuclei. Anti-bonding MO's are the consequence of

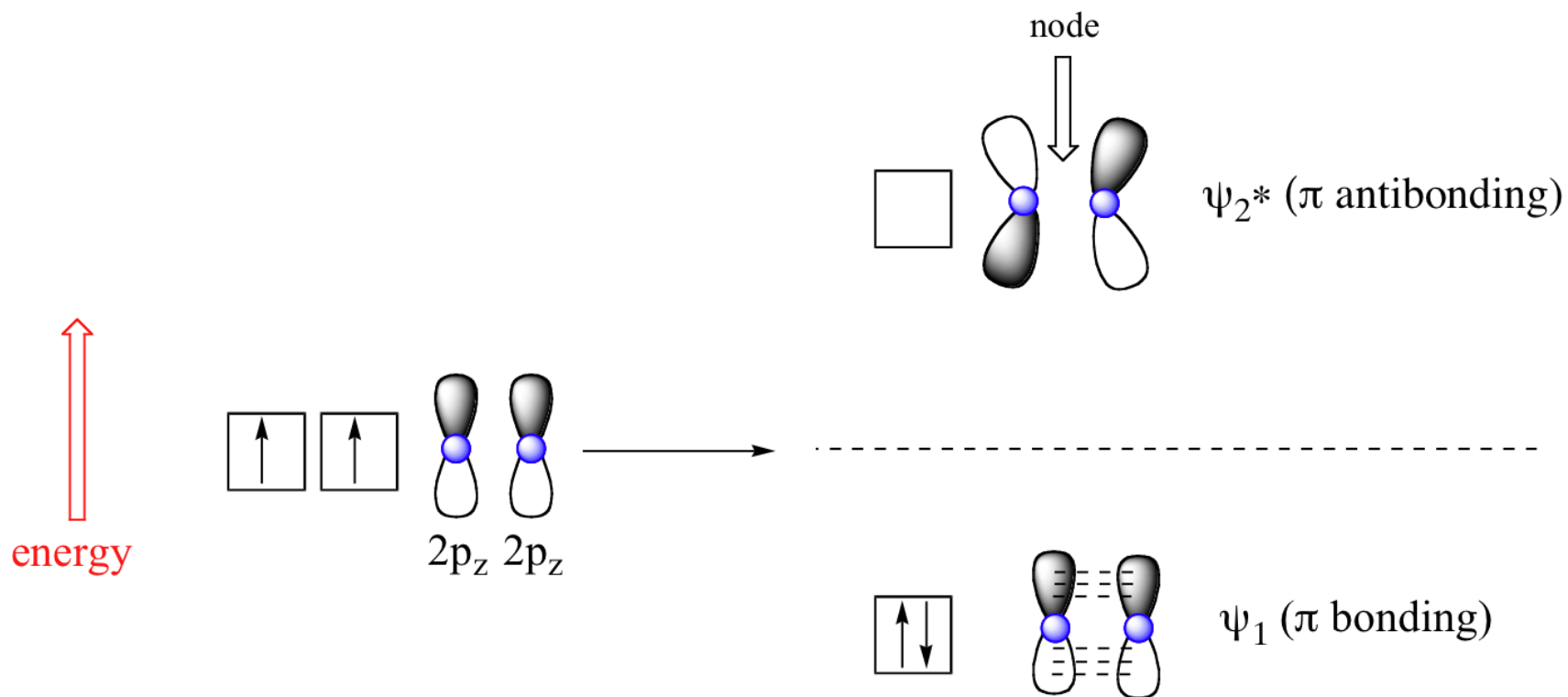
destructive interference which results in a repulsive interaction and a 'canceling out' of electron density between the nuclei (in other words, a node).

MO theory and pi bonds

In p orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When p orbitals overlap end to end, they create σ and σ^* orbitals. If two atoms are located along the x-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and σ^*_{px} (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with s-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.



The advantage of MO theory becomes more apparent when we think about pi bonds, especially in those situations where two or more pi bonds are able to interact with one another. Let's first consider the pi bond in ethene from an MO theory standpoint (in this example we will be disregarding the various sigma bonds, and thinking *only* about the pi bond). According to MO theory, the two atomic $2p_z$ orbitals combine to form two pi (π) molecular orbitals, one a low-energy π bonding orbital and one a high-energy π -star (π^*) anti-bonding molecular orbital. These are sometimes denoted, in MO diagrams like the one below, with the Greek letter psi (Ψ) instead of π .



In the bonding Ψ_1 orbital, the two shaded lobes of the $2p_z$ orbitals interact constructively with each other, as do the two unshaded lobes (remember, the shading choice represents mathematical (+) and (-) signs for the wavefunction). Therefore, there is increased electron density between the nuclei in the molecular orbital – this is why it is a bonding orbital.

In the higher-energy anti-bonding Ψ_2^* orbital, the shaded lobe of one $2p_z$ orbital interacts destructively with the unshaded lobe of the second $2p_z$ orbital, leading to a node between the two nuclei and overall repulsion.

By the *aufbau* principle, the two electrons from the two atomic orbitals will be paired in the lower-energy Ψ_1 orbital when the molecule is in the ground state.