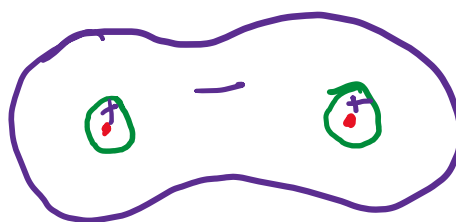
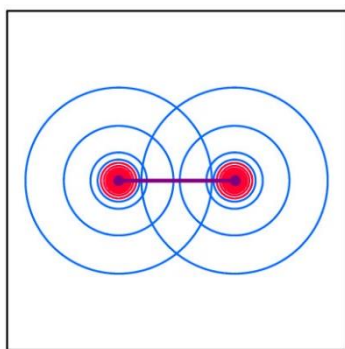
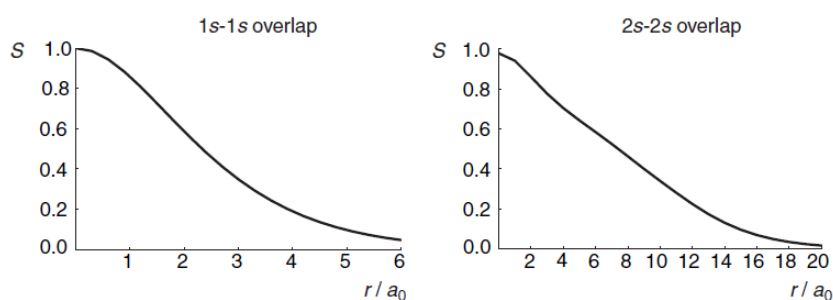


FAQ: Molecular Orbitals

1. How would you construct an MO from the overlap of two 2s orbitals.

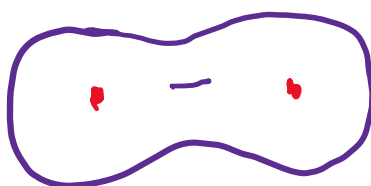
Let us first understand how we understand the strength of interaction between two AO's. It is done by looking at the overlap integral between two AO's, which is obtained by multiplying together the two wavefunctions and taking the integral of this product over all space. If the two AO's are far apart, there is no region of space where the two wavefunctions both have a significant value. Hence the product of the two wavefunctions is small everywhere leading to a small integral.

For 2s orbitals, since they are larger than the corresponding 1s orbitals, they do not get so close in order to overlap so significantly. Hence for relatively large separations the overlap between two 2s orbitals will be larger than the overlap integral between two 1s orbitals. At $R=0$, both overlap and the integral will be 1 by definition. The overall plot for two 1s and two 2s orbitals will be similar as shown below, since the radial node in the 2s AO does not have a large effect on the overall form of the overlap integral. This is because the positive form of the 2s wavefunction is very compact and only occupies a small region of space close to the nucleus.



Bonding MO contour plot constructed from two 2s orbitals.

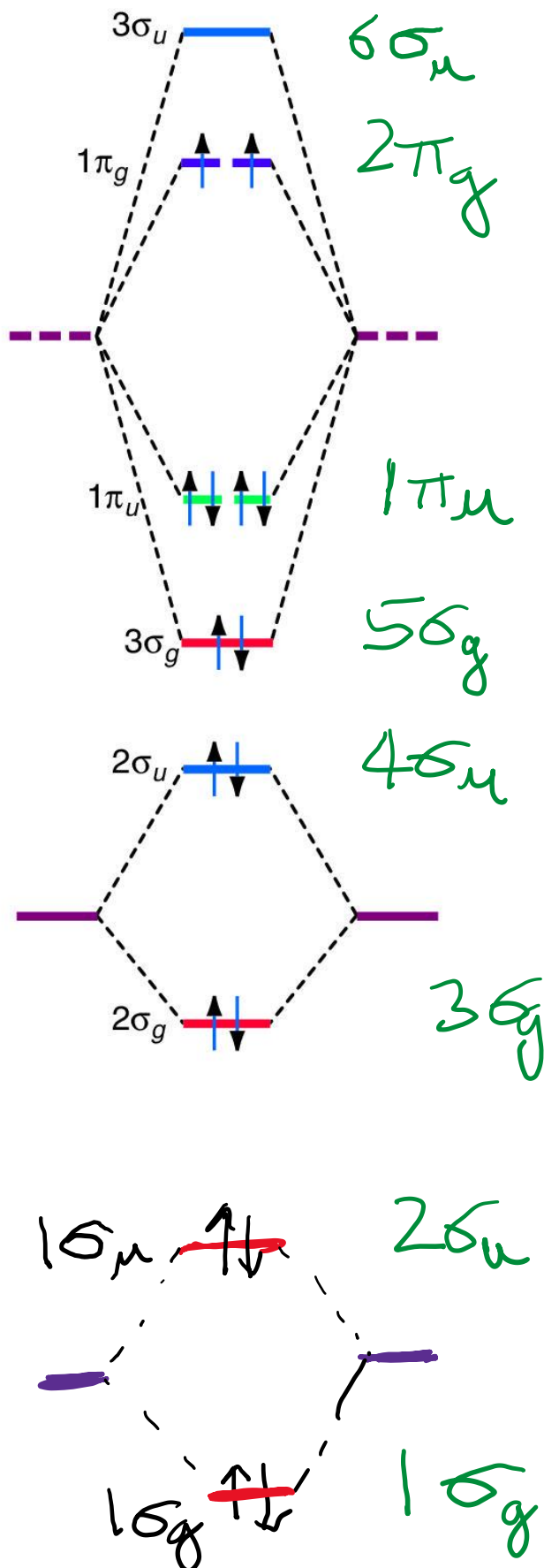
Since the positive part of the wavefunction will not have any effect in the overlap integral as shown above, representing the σ bonding MO of the two 2s orbitals by the diagram shown below is not very inaccurate (the inner part is omitted in this drawing)



Note the positive part of the wavefunction is not shown

2. What do the numbers in the prefix of MO's represent, e.g., the number 3 in $3\sigma_g$.

They really do not mean much other than identifying the particular molecular orbital. For example, two different numbering schemes are shown below. Both are acceptable and found in different books.



3. Since the sum of the energies of the bonding MO and anti-bonding MO is greater than the total energy of atomic orbitals, why does chemical bonding happen?

There is no relation between the energies of the MOs and AO's to apply conservation of energy principle. The energies of the bonding and anti-bonding MO's are real and can be probed by photo-electron spectroscopy. What we show in the MO interaction diagrams is that these MO's can be constructed *via* the linear combination of atomic orbitals (this is a hypothesis which works to a good approximation). We also put it in an energy scale to give us some idea of the relative energies of MO's and AO's.

4. Why do atomic orbitals overlap to form MO's? How do they know they have to positively or negatively overlap?

The answer is like FAQ 3. The atomic orbitals do not overlap out of will....this is a hypothesis we use to construct the MO's so that we can avoid rigorous calculations to determine their exact wavefunction.