Essential Molecular Orbital Theory for the Study of Pyrotechnics

R. B. Lowry

School of Earth, Ocean and Environmental Sciences, Univ. of Plymouth, Drake Circus, Plymouth PL4 8AA UK

ABSTRACT

The Linear Combination of Atomic Orbitals (LCAO) model is presented as it applies to small heterogeneous molecules. A non-mathematical approach is used to enable the discussion of the terminology used. The production of light and the rules that govern it are examined.

Keywords: linear combination of atomic orbitals, LCAO, energy level, electronic transitions, color, molecular orbital theory

Introduction

The purity of colors produced by pyrotechnic compositions, together with the intensity of the light, is of utmost importance if a display is to capture the audience. The chemistry behind the production of these effects is not understood fully, but to make further improvements it will be necessary to consider the basic physical processes that lead to luminescence. This article considers the changes in energy of the electrons within the molecules of interest. To do so, the fundamental model of bonding within molecules will be considered so that the energy of the electrons can be evaluated. Only the essential parts of the model, as is necessary to the study of flame colors, will be discussed. The transitions between these energy levels are what leads to the production of light and, hopefully, a high-impact display.

Molecular Orbitals

When atoms come together to form molecules, and bonds form between them, the bonding electrons are "shared" between the atoms. In other words, these electrons are no longer held by one atom only, but orbit two (or more) atoms. There are a variety of different methods of considering this, but the most useful one when considering the energies of these orbitals is the so-called *Linear Combination of Atomic Orbitals* (LCAO) method. This assumes that *molecular orbitals* (MOs) can be "built" by combining two or more atomic orbitals. The mathematical method involves adding the wave functions that describe the individual atomic orbitals. For the purposes of this paper, it will be sufficient to consider the shapes of the atomic orbitals and their resultant MOs.

When two atomic orbitals interact to form molecular orbitals, two MOs are formed. One of these is lower in energy and hence stabilises the molecule. This is the *bonding orbital* and one way of looking at this is that the two atomic orbitals interfere constructively to form one MO. The other MO is higher in energy, hence destabilises the molecule and is called the *antibonding orbital*. This can be viewed as the two atomic orbitals interfering destructively to form two half-orbitals that repel each other. Figure 1 illustrates these two processes. Atomic orbitals that do not interact to participate in bonding are called *non-bonding orbitals* and the bonding process does not affect their energies.

Energy and Symmetry

For the majority of molecules, the number of possible interactions between atomic orbitals to form MOs is huge. However, several considerations reduce the number of possibilities:

- Only atomic orbitals of similar energies can combine to form MOs.
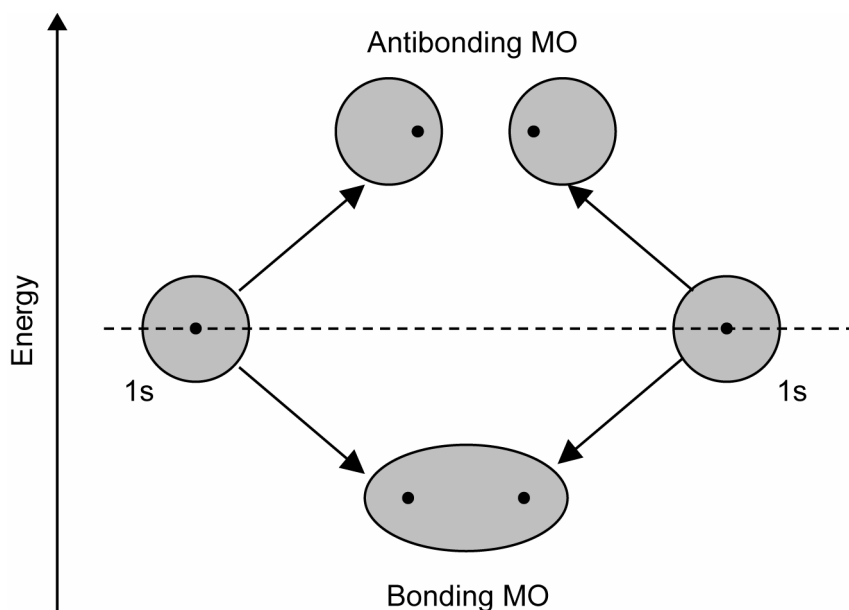
Figure 1. Combination of two atomic orbitals to form two molecular orbitals.

- Atomic orbitals from filled shells from two very different elements do not interact due to the difference in energies.

- Atomic orbitals from filled shells from similar elements can combine to form MOs, but there is no net effect upon bonding (see below).

- Only atomic orbitals of similar symmetry can combine to form MOs.

The notion of symmetry arises because there must be a significant overlap of the two atomic orbitals if a MO is to form. In addition, in heavier atoms, as the nuclear charge rises, the energy of each of the shells changes due to the increase in attraction between the nucleus and the electrons. Thus, it is possible to get sufficient overlap between orbitals from different shells providing there is a significant diffe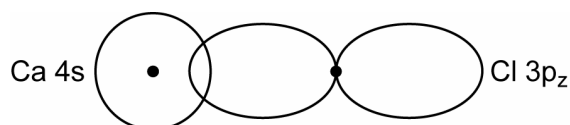re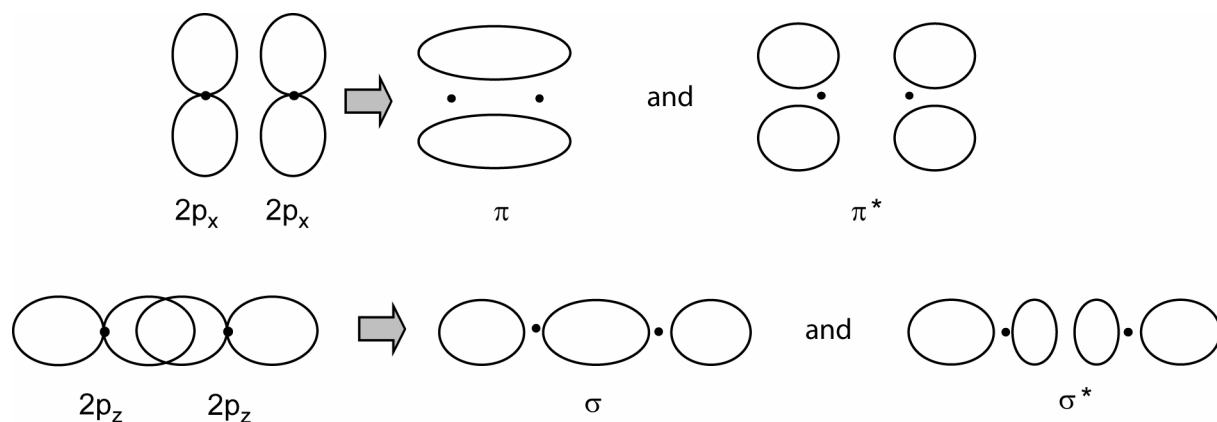nce in the atomic masses. Figure 2 shows how the $3p_z$ orbital of Cl can interact with the 4s orbital of Ca. The $3p_y$ or $3p_x$ orbitals would not overlap significantly and hence cannot form MOs under these circumstances.

MO Labels

To identify particular MOs, we ascribe labels to them. These labels have three parts:

1) σ, π or n. This denotes whether the MO is a single envelope along the internuclear axis (σ) or one with two lobes—one above and one below the axis (π). Each MO can contain only two electrons, even if it has two lobes, much like a p orbital can only accept 2 electrons. A π bond is the second bond in a double bond, the first being a σ bond. n denotes a non-bonding orbital.

2) If a MO is marked with a superscript asterisk, it denotes that the MO is an anti-bonding one. Bonding MOs are unmarked

3) MOs are numbered consecutively from 1, with 1 being the orbital with the lowest energy. σ and π type MOs each have their own numeric series.

Unfortunately, there is more than one labelling scheme in place for MOs. The differences

Figure 2. Illustration of how the $3p_z$ orbital of chlorine can interact with the 4s orbital of calcium.

Note: the 2p$_y$ orbitals will combine in a similar way to the 2p$_x$ orbitals, through 90° (into and out of the page)

Figure 3. Example of the molecular orbitals and labels that arise when 2p orbitals from two atoms overlap.

are small, but significant care must be taken when comparing data from different sources.

Figure 3 shows the MOs and labels that arise when the 2p orbitals from two atoms overlap. These MOs would be involved in the bonding of the O_2 molecule, together with the σ and σ* MOs formed from the combination of the 2s orbitals. Diagrams such as that in Figure 3 are useful to visualise a MO, but give no indication of the energy and therefore whether the MO contains any electrons. To demonstrate this, an energy level diagram similar to that in Figure 4 is used. In this figure, the diagram for the O_2 molecule is shown. The order of the MOs is not fixed, but varies as their energies change due to different elements. Another contributing factor is that the 2s and 2p$_z$ atomic orbitals can interact, providing their energies are sufficiently similar. This is not the case in the O_2 molecule.

Figure 4 shows that there are 12 electrons involved in the MOs shown in the diagram. However, some are in bonding orbitals and some are in anti-bonding orbitals. The net effect of a filled bonding orbital and a filled anti-bonding orbital is no bond. Thus, the 1σ and 2σ* orbitals cancel one another. Similarly, there are four 1π electrons and two 2π* electrons which results in one

bond. The 3σ MO is filled, whilst the 4σ* is not. Hence this is another bond. Therefore, the O_2 molecule is held together by a double bond. The electronic configuration of the molecule can be quoted in a similar way to that used for atoms, O_2 having the configuration $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$.

The oxygen molecule also illustrates another property that exists in molecular orbitals. The two highest energy electrons exist in two MOs that are degenerate (have the same energy). Under these conditions, Hund's rule operates, just as it does in single atoms. Thus, the lowest energy state possible (the ground state) has the two electrons in separate MOs. Since these two electrons are not paired, they are free to take up (and change) any spin direction. This means that there are three possible situations: both spin "up", both spin "down" and one spin "up" and one "down". Note that "up"/"down" is the same as "down"/"up" as it is impossible to tell the difference between the two electrons. Therefore this electronic state can exist in three different ways and is called a triplet state. If the electrons were forced to pair up, then there is only one possible way that this can happen and so this is called a singlet state. The number of ways that a state can exist is called the *multiplicity*.
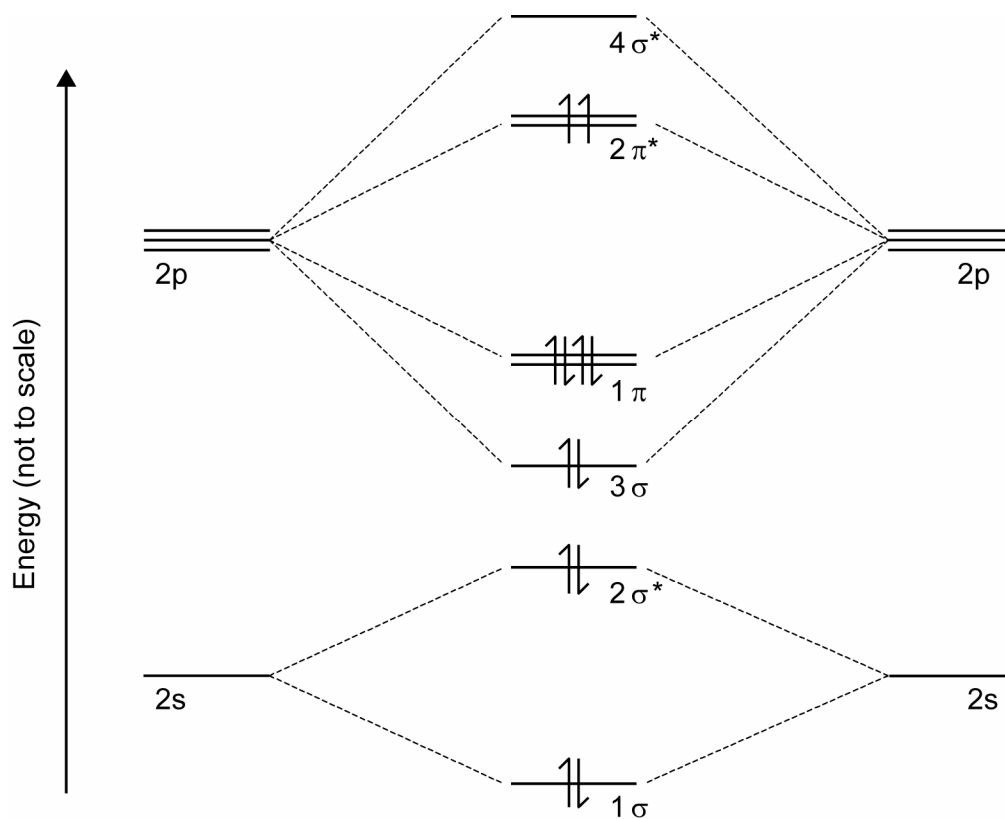
Figure 4. The MO diagram for O$_2$.

Excited States

If a molecule absorbs energy, or is created in such a way that it is not in a state of minimal energy, it is described as being in an excited state. This excess energy is manifested within the bonding of the molecule as the electrons are being distributed amongst the MOs in a way that is different to the ground state. This will involve more electrons existing in higher energy MOs. Thus, for O$_2$ the configuration $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^3 2\pi^{*3}$ is an excited state.

Term Symbols

Electronic configurations can be abbreviated and further information incorporated using *term symbols*. Filled orbitals do not contribute to the information in term symbols. The main part of the symbol is a capital Greek letter; Σ, Π or Δ. This part of the symbol contains information about which MOs are occupied. Each σ electron contributes 0 and each π electron +1. If there are

two degenerate π orbitals, one contributes +1 and the other −1. These values are summed and written according to the code $\Sigma = 0$, $\Pi = 1$ and $\Delta = 2$. The other part of the symbol is the multiplicity and is written as a superscript before the Greek letter. The ground state of O$_2$ is therefore described as $^3\Sigma$. Other information can be attached to the term symbol, but is concerned with the mathematical representation of the MOs and will not concern us here.

Transitions

The emission of light from small molecules is caused by the relaxation of the molecule from an excited state to a lower (frequently ground) state. However, not all transitions are allowed, but are constrained by a series of selection rules. These rules specify which transitions are allowed based upon the term symbols of the excited and ground state. The selection rules for transitions between MOs are:

1) The Greek letter is allowed to remain the same, or change by one.

2) The multiplicity must not change.

In effect, the first rule forbids transitions from Σ to Δ or vice versa. In fact, these transitions can be observed, but occur rarely. This results in very weak output of light and is therefore not of interest in this context. The second rule can also be broken when one or more heavy atoms are present. The pyrotechnic emitters SrCl, BaOH, etc. are in this class.

The color of the light emitted as the molecule relaxes from excited state to ground state depends upon the difference in energy between the two states. Thus, the light emitted by SrOH at 606 nm can be used to calculate the difference in energy between the ground state and the excited state. In this case, it is 3.28×10^{-19} J. The ground state of SrOH is $^2\Sigma$ and applying the selection rules above leads to the deduction that the excited state is probably a $^2\Sigma$ state as well.

Studying Electronic Transitions

Electronic transitions can be studied by the use of a spectrometer, which measures the intensity of the incident light as a function of wavelength. Given the transitory nature of the species responsible for producing light in pyrotechnics, the study of these species has not been easy. Some studies have been performed that generate the species continuously under very specific conditions.[1,2] However, the growth of video technology has allowed real pyrotechnic events to be captured and then the data studied later.[3] Studies such as these can allow the correct iden-tification of the species involved in the production of light and the conditions necessary for the efficient manufacture of the correct excited state. This can only lead to purer, brighter pyrotechnics.

References

1) M. A. Anderson, M. D. Allen, W. L. Barclay, Jr. and L. M. Ziurys, "The Millimeter and Sub-Millimeter Spectrum of the BaOH Radical", *Chemical Physics Letters,* Vol. 205 (1993) p 415.

2) M. A. Anderson, W. L. Barclay, Jr., and L. M. Ziurys, "The Millimeter-Wave Spectrum of the SrOH and SrOD Radicals", *Chemical Physics Letters,* Vol. 196 (1992) p 166.

3) K. L. and B. J. Kosanke, "Development of a Video Spectrometer", *Journal of Pyrotechnics*, No. 7 (1998) p 37.

Bibliography

W. G. Richards, and P. R. Scott, *Energy Levels in Atoms and Molecules.,* Oxford Science Publications, 1994.

J. M. Hollas, *Basic Atomic and Molecular Spectroscopy,* Royal Society of Chemistry, 2002.

R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, John Wiley, 1976.

P. Atkins and J. de Paula, *Physical Chemistry,* Oxford University Press, 2002.