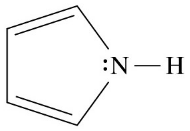
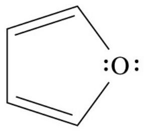
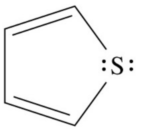
An Introduction to
Molecular Orbital Theory



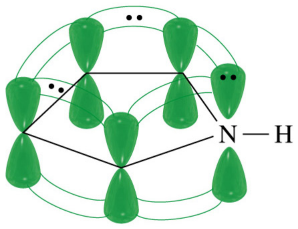
pyrrole



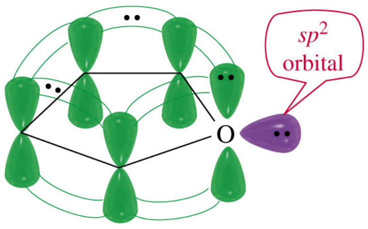
furan



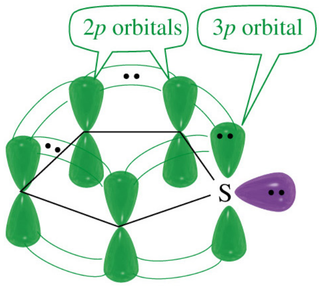
thiophene



six pi electrons


O
sp^2 orbital

six pi electrons


2*p* orbitals
3*p* orbital
S

six pi electrons

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1. Introduction

1.1. Localized and Non-localized Approaches to Bonding

There are two main ways of trying to explain how the electrons of a molecule are involved in bonding.

1. *Localized bond approach* (also known as the *valence bond theory*): involves regarding all bonds as localized interactions involving two electrons shared between two atoms. In polyatomic molecules this leads to the use of orbital hybridization as a convenient mathematical (and pictorial) procedure of manipulating the atomic orbitals to permit the bonding to be described in terms of a collection of simple two-center, two-electron bonds.
2. *Molecular orbital approach* (also known as MO theory): involves the assignment of electrons to molecular orbitals[1] which are, in general, delocalized over the whole molecule.

Which approach is better?

There is no straightforward answer to this question - neither approach is exact.

- In some instances, such as in the description of bonding in diatomic molecules, the two approaches give essentially identical results.
- The valence bond approach is the approach with which you will be most familiar - it is conceptually simpler and is widely used in organic chemistry, but it fails to adequately explain the bonding in certain classes of molecules, including aromatic compounds.
- The MO approach is generally harder to implement but better explains the bonding in those molecules where the valence bond approach fails, and is generally more consistent with the results of spectroscopic measurements.

This course will provide an introduction to the molecular orbital (MO) approach.

---

[1] Vividly speaking one can imagine an atomic orbital as an "electron cloud".

1.2. Some remarks on orbitals in chemistry

During this course, two important notations are used: *Atomic Orbital* and *Molecular Orbital*. These different types of orbitals play a crucial role in chemical bonding between atoms in molecules, molecular structure and in theoretical organic and anorganic chemistry (e.g. Molecular orbital (MO) theory). The term orbital was introduced by Robert S. Mulliken (7 June 1896 - 31 October 1986) in 1932 as an abbreviation for *one-electron orbital wave function*. However, the idea that electrons might revolve around a compact nucleus with definite angular momentum was convincingly argued at least 19 years earlier by Niels Bohr (7 October 1885 - 18 November 1962) and the Japanese physicist Hantaro Nagaoka (15 August 1865 - 11 December 1950). They published an orbit-based hypothesis for electronic behavior as early as 1904. Explaining the behavior of these electron "orbits" was one of the driving forces behind the development of quantum mechanics.

1.2.1. Atomic Orbitals

An atomic orbital is a mathematical function that describes the wave-like behavior of either one electron or a pair of electrons in an atom. This function can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus. The term may also refer to the physical region or space where the electron can be calculated to be present, as defined by the particular mathematical form of the orbital. In short, atomic orbitals predict the location of an electron in an atom. Any orbital can be occupied by a maximum of two electrons, each with its own spin quantum number (Pauli principle). The simple names s orbital, p orbital, d orbital and f orbital refer to orbitals with angular momentum quantum number l = 0, 1, 2 and 3 respectively. These names, together with the value of n, are used to describe the electron configurations of atoms. They are derived from the description by early spectroscopists of certain series of alkali metal spectroscopic lines as **s**harp, **p**rincipal, **d**iffuse, and **f**undamental. Orbitals for $l > 3$ continue alphabetically, omitting j (g, h, i, k, ...). Atomic orbitals are the basic building blocks of the atomic orbital model. Orbitals are given names in the form:

$$X\,\text{type}^{y}$$

where X is the energy level corresponding to the principal quantum number n[2], type is a lower-case letter denoting the shape or subshell of the orbital and it corresponds to the angular quantum number l, and y is the number of electrons in that orbital.

---

[2] The principal quantum number, symbolized as n, is the first of a set of quantum numbers (which includes: the principal quantum number n, the azimuthal quantum number (or orbital angular momentum quantum number) l, the magnetic quantum number m_l, and the spin quantum number m_s) of an atomic orbital. The principal quantum number n can only have positive integer values, i.e. $n = 1, 2, 3, \ldots$ As n increases, the orbital becomes larger and the electron spends more time farther from the nucleus. As n increases, the electron is also at a higher potential energy and is therefore less tightly bound to the nucleus.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called sp hybrids because they are formed from one s and one p orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure s and p orbitals.

1.2.2. Molecular Orbitals

In chemistry, a molecular orbital (or MO) is a mathematical function describing the wave-like behavior of an electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region or a representation of the regions in a molecule where an electron occupying that orbital is likely to be found respectively. At an elementary level, it is used to describe the region of space in which the function has a significant amplitude. Molecular orbitals are usually constructed by combining atomic orbitals or hybrid orbitals from each atom of the molecule, or other molecular orbitals from groups of atoms. They can be quantitatively calculated using the Hartree-Fock or self-consistent field (SCF) methods. A molecular orbital can specify the electron configuration of a molecule: the spatial distribution and energy of one (or one pair of) electron(s). Most commonly a MO is represented as a linear combination of atomic orbitals (the LCAO-MO method, see Chapter 4), especially in qualitative or very approximate usage. They are invaluable in providing a simple model of bonding in molecules, understood through molecular orbital theory.

The type of interaction between atomic orbitals can be further categorized by the molecular-orbital symmetry labels σ (sigma), π (pi), δ (delta), ϕ (phi), γ (gamma) etc. paralleling the symmetry of the atomic orbitals s, p, d, f and g. The number of nodal planes containing the internuclear axis between the atoms concerned is zero for σ MOs, one for π, two for δ, etc.

A MO with σ symmetry results from the interaction of either two atomic s-orbitals or two atomic p_z-orbitals. An MO will have σ-symmetry, if the orbital is symmetrical with respect to the axis joining the two nuclear centers, the internuclear axis. This means that rotation of the MO about the internuclear axis does not result in a phase change. A σ^* orbital, sigma antibonding orbital, also maintains the same phase when rotated about the internuclear axis. The σ^* orbital has a nodal plane that is between the nuclei and perpendicular to the internuclear axis.

A MO with π symmetry results from the interaction of either two atomic p_x orbitals or p_y orbitals. A MO will have π-symmetry, if the orbital is asymmetrical with respect to rotation about the internuclear axis. This means that rotation of the MO about the internuclear axis will result in a phase change. There is one nodal plane containing the internuclear axis, if real orbitals are considered. A π^* orbital, pi antibonding orbital, will also produce a phase change when rotated about the internuclear axis. The π^* orbital

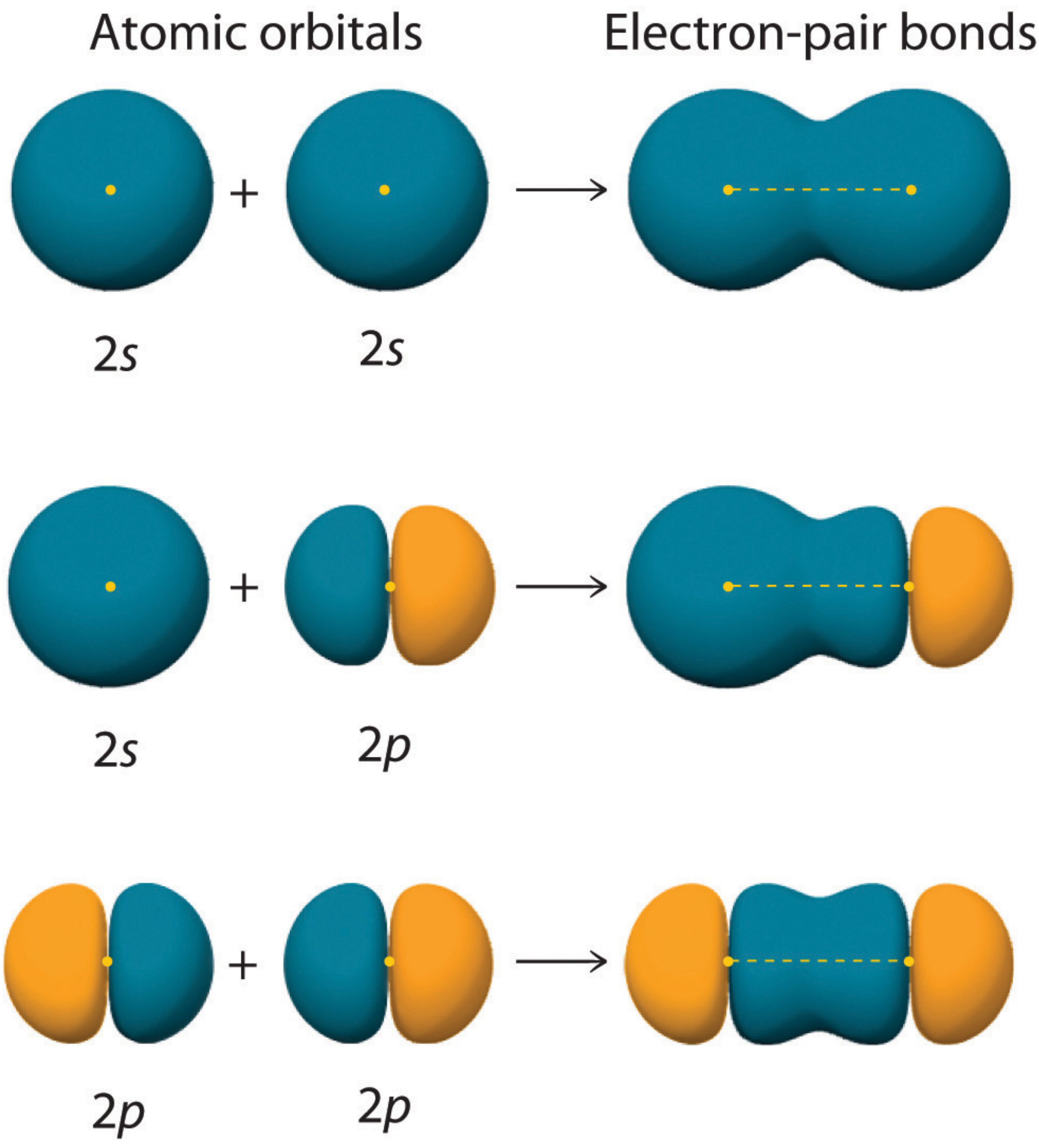

Atomic orbitals
Electron-pair bonds
+
2s
2s
+
2s
2p
+
2p
2p

Figure 1.1.
Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where n = 2. The positive lobe is indicated in yellow, and the negative lobe is in blue.

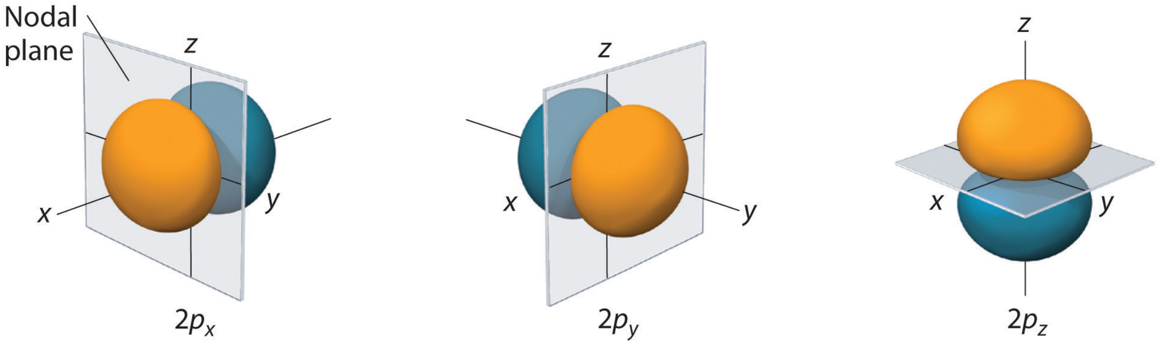

Nodal plane
z
x
y
$2p_x$
z
x
y
$2p_y$
z
x
y
$2p_z$

Figure 1.2.
Illustration of p_x-, p_y- and p_z-Orbitals

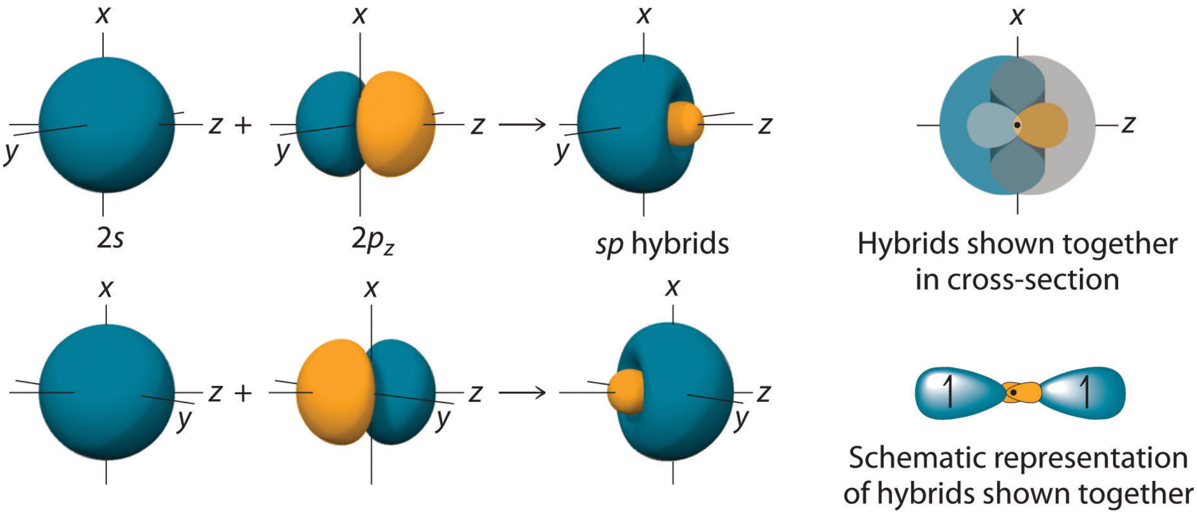

x
y
z +
2s
x
y
z →
$2p_z$
x
y
z
sp hybrids
x
z
Hybrids shown together in cross-section
x
z +
y
x
z →
y
x
z
y
Schematic representation of hybrids shown together

Figure 1.3.
The Formation of sp Hybrid Orbitals. Taking the mathematical sum and difference of an ns and an np atomic orbital where n = 2 gives two equivalent sp hybrid orbitals oriented at 180°C to each other.

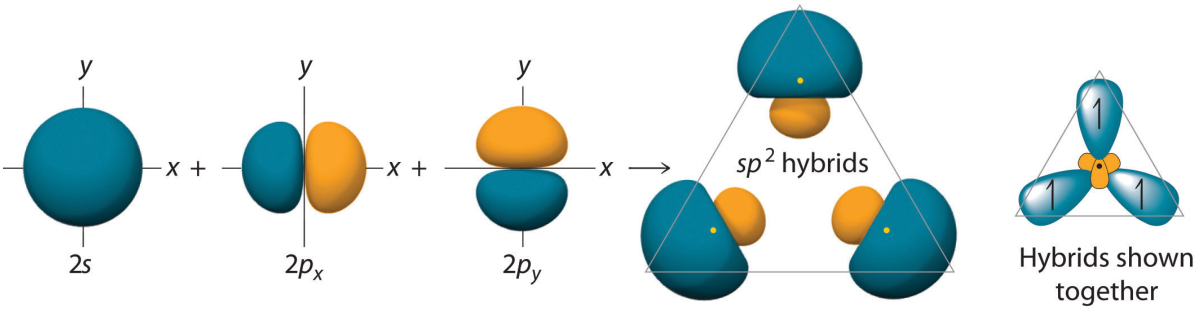

y
x +
2s
y
x +
2p_x
y
x
2p_y
sp² hybrids
Hybrids shown together

Figure 1.4.
Formation of sp^2 *Hybrid Orbitals Combining one ns and two np atomic orbitals gives three equivalent* sp^2 *hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120°C to one another.*

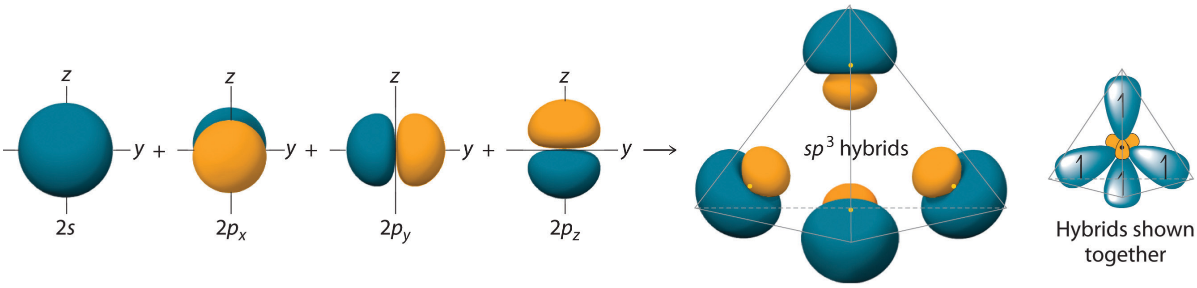

z
y +
2s
z
y +
2p_x
z
y +
2p_y
z
y
2p_z
sp³ hybrids
Hybrids shown together

Figure 1.5.
Formation of sp^3 *Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four* sp^3 *hybrid orbitals oriented at 109.5°C to one another in a tetrahedral arrangement.*

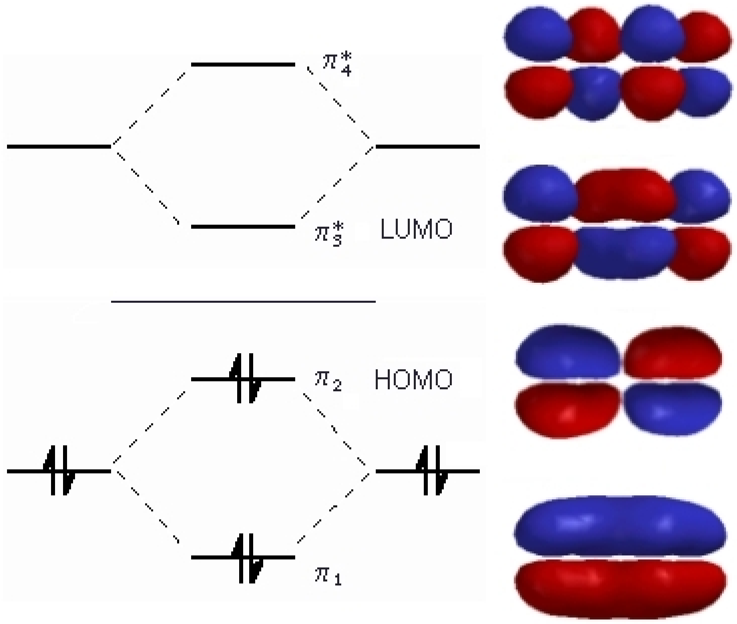


Figure 1.6.
Relative energies of π molecular orbitals of 1,3-butadiene and electron configuration

also has a second nodal plane between the nuclei.

Figure 1.6 shows the relative energies of the π molecular orbitals of 1,3-butadiene (derived from ethene) and the electron configuration. The horizontal center line denotes the energy of a C atomic p-orbital. Orbitals below that line are bonding those above are anti-bonding. We now have 4 electrons to arrange, 1 from each of the original atomic p orbitals. These are all paired in the two stabilized π-bonding orbitals, π_1 and π_2. The highest occupied molecular orbital or HOMO is π_2 in 1,3-butadiene (or any simple conjugated diene). In contrast, the anti-bonding π^* orbitals contain no electrons. The lowest unoccupied molecular orbital or LUMO is π_3 in 1,3-butadiene (or any simple conjugated diene).

The relative energies of these orbitals can be accounted for by counting the number of bonding and anti-bonding interactions in each:

π_1 has bonding interactions between C1-C2, C2-C3 and C3-C4
Overall = 3 bonding interactions

π_2 has bonding interactions between C1-C2 and C3-C4 but anti-bonding between C2-C3
Overall = 1 bonding interaction

π_3 has bonding interactions between C2-C3 but anti-bonding between C1-C2 and C3-C4
Overall = 1 anti-bonding interaction

π_4 has anti-bonding interactions between C1-C2, C2-C3 and C3-C4
Overall = 3 anti-bonding interactions

1.2.3. Synopsis

The following important statements can be made:

- The positions and energies of electrons in atoms can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in molecules can be described in terms of *molecular orbitals* (MOs).
- Molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a delocalized approach to bonding.
- A molecular orbital exhibits a particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.
- In a molecular orbital, the electrons are allowed to interact with more than one atomic nucleus at a time.
- A molecule must have as many molecular orbitals as there are atomic orbitals.
- Antibonding orbitals contain a node (regions of zero electron probability) perpendicular to the internuclear axis; bonding orbitals do not.
- A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).
- Electrons in non-bonding molecular orbitals have no effect on bond order.

2. Exact Solutions to the Schrödinger Equation?

In quantum mechanics, the Schrödinger equation is a partial differential equation that describes how the quantum state of a physical system changes with time. It was formulated in late 1925, and published in 1926, by the Austrian physicist Erwin Schrödinger (12 August 1887 - 4 January 1961).
To illustrate how difficult it is to solve the Schrödinger wave equation, consider the H_2 (hydrogen) molecule: this consists of just two protons (A,B) and two electrons (1,2).
The time-independent Schrödinger equation predicts that wave functions can form standing waves, called stationary states (also called "orbitals", as in atomic orbitals or molecular orbitals). These states are important in their own right, and if the stationary states are classified and understood, then it becomes easier to solve the time-dependent Schrödinger equation for any state. The time-dependent Schrödinger equation (single non-relativistic particle in three dimensions) reads as

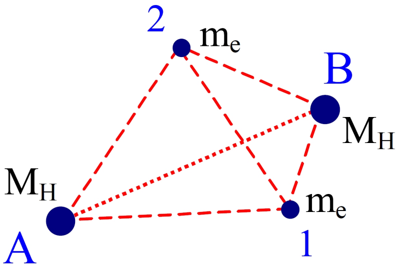


Figure 2.1.
The Hydrogen atom

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r},t)\right]\Psi(\mathbf{r},t)}\ , \tag{2.1}$$

where μ is the particle's "reduced mass"[1], V is its potential energy, ∇^2 is the Laplacian, and Ψ is the wave function.

---

[1] In the case of our example, hydrogen, the reduced mass μ reads as

$$\mu = \frac{m_e \cdot M_H}{m_e + M_H}\ ,$$

where m_e is the mass of the electron and M_H the mass of the proton (nuclei).

The time-independent Schrödinger equation is deceptively simple, and is stated as

$$E\Psi = \mathscr{H}\Psi \ . \tag{2.2}$$

or, more precisely, as

$$\boxed{E\Psi(\mathbf{r}) = \left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r})} \ . \tag{2.3}$$

The Hamiltonian $\mathscr{H}$ is defined as

$$\mathscr{H} \equiv \frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})$$

for particles in three dimensions. The vector $\mathbf{r}$ is the distance between the particles and $\hbar = \frac{h}{2\pi}$, where h is the Planck constant with a value of $6.62606957(29) \cdot 10^{-34}$ J s.
The equation describes, as mentioned above, stationary states and is only used when the Hamiltonian itself is not dependent on time. In general, the wave function still has a time dependency. It's theoretical derivation is shown in Appendix A.
In words, the time-independent Schrödinger equation states:

When the Hamiltonian operator $\mathscr{H}$ acts on a certain wave function Ψ, and the result is proportional to the same wave function Ψ, then Ψ is a *stationary state*, and the proportionality constant, E, is the energy of the state Ψ.

But even in the case for a hydrogen molecule, $\mathscr{H}$ is an operator of a relatively complex form, containing kinetic energy (KE) terms for each of the four particles (two electrons and two protons) and potential energy (PE) terms for each of the six electrostatic pairwise interactions. More specifically, in the case of hydrogen, $\mathscr{H}$ consists of the following terms:

$$\begin{aligned}
\mathscr{H} = {} & \frac{-\hbar^2}{2M_H}\cdot\left(\nabla_A^2+\nabla_B^2\right) \quad \text{KE of nuclei A and B} \\
& + \frac{-\hbar^2}{2m_e}\cdot\left(\nabla_1^2+\nabla_2^2\right) \quad \text{KE of electrons 1 and 2} \\
& + \frac{e^2}{4\pi\varepsilon_0\cdot\mathbf{R}_{AB}} \quad \text{Internuclear electrostatic PE (repulsive)} \\
& + \frac{e^2}{4\pi\varepsilon_0\cdot\mathbf{r}_{12}} \quad \text{Interelectronic electrostatic PE (repulsive)} \\
& - \left(\frac{e^2}{4\pi\varepsilon_0\mathbf{r}_{1A}}+\frac{e^2}{4\pi\varepsilon_0\mathbf{r}_{1B}}+\frac{e^2}{4\pi\varepsilon_0\mathbf{r}_{2A}}+\frac{e^2}{4\pi\varepsilon_0\mathbf{r}_{2B}}\right) \quad \text{Electron-nuclear PE terms (attractive)} \\
& \qquad \text{Neglect initially} \\
& + \text{other terms (spin-orbit coupling, etc.)}\ ,
\end{aligned}$$

where

KE	kinetic energy
PE	potential energy
∇^2	$= \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$ the Laplace operator
ε_0	vacuum permittivity constant.

The value of ε_0 is defined as

$$\varepsilon_0 \overset{\text{def}}{=} \frac{1}{c_0^2\mu_0} = \frac{1}{35950207149.4727056\cdot\pi}\,\frac{\text{F}}{\text{m}} \approx 8.8541878176\ldots\times 10^{-12}\ \text{F/m}$$

where c_0 is the speed of light in free space and μ_0 is the vacuum permeability.

If the Hamiltonian is this complex for H_2, then one could imagine what it is like for a more complex molecule containing several atoms and many electrons!

The two available electrons (one from each H atom) in **figure 2.2** fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

In summary, to make any progress and to calculate the MO of more complex molecules than hydrogen, we need to simplify the problem. Therefore, three simplifying assumptions are made.

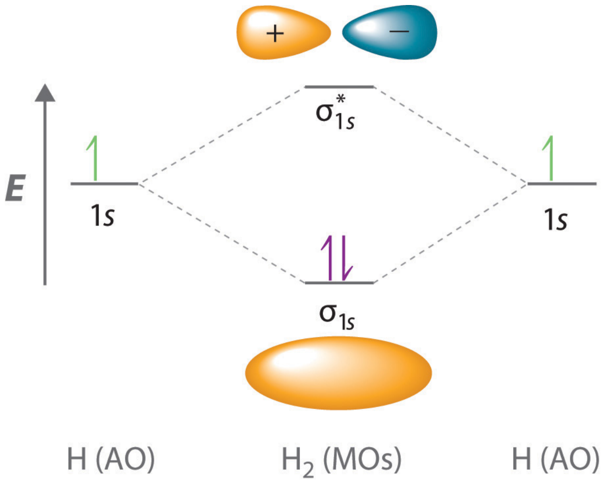

+
−
E
1s
σ^*_{1s}
1s
σ_{1s}
H (AO)
H_2 (MOs)
H (AO)

Figure 2.2.
Molecular Orbital Energy-Level Diagram for H_2

3. The Way Forward - Assumptions and Approximations

3.1. First Simplification

The electrons move much faster than the nuclei (since they are much lighter) - we will therefore treat the nuclear and electronic motion entirely independently. This is the **Born-Oppenheimer approximation**.

In quantum chemistry and molecular physics, the Born-Oppenheimer (BO) approximation is the assumption that the motion of atomic nuclei and electrons in a molecule can be separated. The approach is named after Max Born (11 December 1882 - 5 January 1970) and J. Robert Oppenheimer (22 April 1904 - 18 February 1967). In mathematical terms, it allows the wave function of a molecule to be broken into its electronic and nuclear (vibrational, rotational) components.

$$\Psi_{\mathrm{total}} = \psi_{\mathrm{electronic}} \cdot \psi_{\mathrm{nuclear}}$$

Computation of the energy and the wave function of an average-size molecule is simplified by the approximation. For example, the benzene molecule consists of 12 nuclei and 42 electrons. The time-independent Schrödinger equation, which must be solved to obtain the energy and wave function of this molecule, is a partial differential eigenvalue equation in 162 variables - the spatial coordinates of the electrons and the nuclei. The BO approximation makes it possible to compute the wave function in two less complicated consecutive steps.

The approach for a hydrogen atom is:

1. Freeze the molecule with a fixed internuclear separation ($\mathbf{R}_{AB}$, hereafter called $\mathbf{R}$); then carry out calculations to obtain the total energy, V, and wave functions for that $\mathbf{R}$ value.
2. Repeat for different values of $\mathbf{R}$, to obtain the complete *potential energy function*, $V(\mathbf{R})$.

This gives results of the following form:

The total energy of the free ("unfrozen") bound-molecule is then given by:

$$E_{\mathrm{total}} = E_{\mathrm{electronic}} + E_{\mathrm{v,r,t}} \quad ,$$

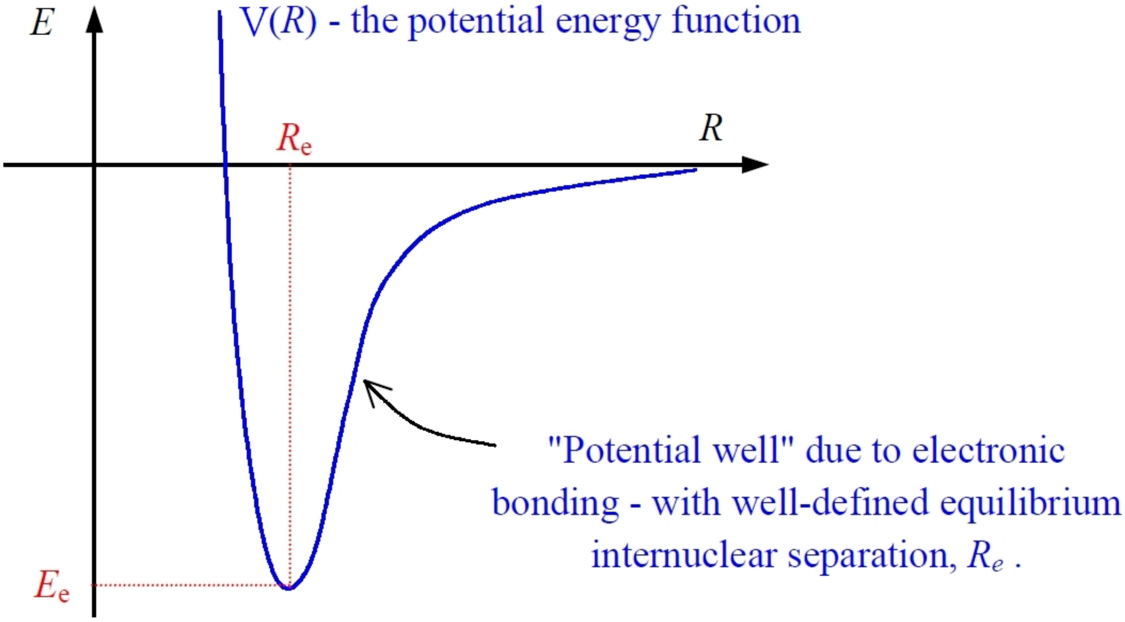


Figure 3.1.
Potential energy as a function of interatomic distance

where $E_{\text{electronic}}$ is the electronic energy (incl. total energy of electrons in molecular environment and internuclear repulsion) and $E_{\text{v,r,t}}$ is the vibrational, rotational and translational energy of the molecules.
To actually determine the electronic energy we still have to solve a Schrödinger equation, but this first approximation means that it is now a much simpler equation. For a particular value of **R** (the internuclear separation), the equation is:

$$\mathscr{H}_e \Psi_e (\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2) = V(\mathbf{R}) \Psi_e (\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2)$$

or

$$\mathscr{H}_e \Psi_e (\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2) = E_e \Psi_e (\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2) \quad \text{at} \quad \mathbf{R} = \mathbf{R}_e ,$$

where:

$\mathscr{H}_e$ is the electronic Hamiltonian, i.e. the full Hamiltonian, $\mathscr{H}$, but without the nuclear KE terms.

$\Psi_e (\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2)$ is the *electronic wave function* for the molecule (which is a function of the vectorial positions of the two electrons).

Unfortunately, the Schrödinger equation is still impossible to solve, because the interelectronic repulsion term

$$V_{12} = \left(\frac{e^2}{4\pi\varepsilon_0 \cdot \mathbf{r}_{12}}\right)$$

(opposite) depends upon the positions of both electrons (since $\mathbf{r}_{12} = |\underline{\mathbf{r}}_1 - \underline{\mathbf{r}}_2|$).

3.2. Second Simplification

This is known as the independent electron model or orbital approximation.
Consider each electron to move in some sort of "average potential" which incorporates the interactions with the two nuclei and an "averaged interaction" with the other electron. The electronic Hamiltonian can then be separated into two parts:

$$\mathscr{H}_e = \mathscr{H}_1 + \mathscr{H}_2 \ , \tag{3.1}$$

where

$\mathscr{H}_1$ is dependent only upon the properties of electron (1) and upon R,
$\mathscr{H}_2$ is dependent only upon the properties of electron (2) and upon R.

This is a major step forward since we can now look for solutions of the form:

$$\Psi_e\left(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2\right) = \psi_{\mathrm{a}}(1) \cdot \psi_{\mathrm{b}}(2) \ , \tag{3.2}$$

where

$\mathscr{H}_1 \psi_{\mathrm{a}} = \varepsilon_a \psi_{\mathrm{a}}$ and ε_a is the energy of orbital "a",
$\mathscr{H}_2 \psi_{\mathrm{b}} = \varepsilon_b \psi_{\mathrm{b}}$ and ε_b is the energy of orbital "b" .

Then the total electronic energy (at the equilibrium bond length) is given by:

$$E_e = \varepsilon_a + \varepsilon_b \ , \tag{3.3}$$

i.e. by the sum of the energies of the individual occupied molecular orbitals.

Consequences of the Orbital Approximation:

$$\begin{aligned}\mathscr{H}_e \Psi_e &= (\mathscr{H}_1 + \mathscr{H}_2) \cdot \left(\psi_a(1) \cdot \psi_b(2)\right) \\ &= \mathscr{H}_1 \cdot \left(\psi_a(1) \cdot \psi_b(2)\right) + \mathscr{H}_2 \cdot \left(\psi_a(1) \cdot \psi_b(2)\right) \\ &= \left(\mathscr{H}_1 \cdot \psi_a(1)\right) \cdot \psi_b(2) + \left(\mathscr{H}_2 \cdot \psi_b(2)\right) \cdot \psi_a(1)\end{aligned}$$

since $\mathscr{H}_1$ acts only upon the wave function for electron 1, i.e. on $\psi_a(1)$, etc.

$$\begin{aligned}\Rightarrow \mathscr{H}_e \Psi_e &= \varepsilon_a \cdot \psi_a(1)\psi_b(2) + \varepsilon_b \cdot \psi_b(2)\psi_a(1) \\ &= (\varepsilon_a + \varepsilon_b)\, \psi_a(1)\psi_b(2) \\ \text{i.e. } \mathscr{H}_e \Psi_e &= E_e \Psi_e \quad \text{where } E_e = \varepsilon_a + \varepsilon_b\end{aligned}$$

In actual fact, a wave function of the form $\Psi_e\left(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2\right) = \psi_a(1)\psi_b(2)$ is unacceptable since:

- it permits the two electrons to be distinguished,
- the wave function is not antisymmetric upon exchange of the two electrons

This is a result of the The Pauli exclusion principle, which states, that two identical fermions, i.e. electrons (particles with half-integer spin, e.g. $\frac{1}{2}\hbar$, $\frac{3}{2}\hbar$, $\frac{5}{2}\hbar$, $\ldots$) cannot occupy the same quantum state simultaneously. In the case of electrons, it can be stated as follows: it is impossible for two electrons of a poly-electron atom to have the same values of the four quantum numbers (n, l, m_l and m_s). For two electrons residing in the same orbital, n, l, and m_l are the same, so m_s (the spin quantum number) must be different and the electrons have opposite spins[1]. This principle was formulated by Austrian physicist Wolfgang Pauli (25 April 1900 - 15 December 1958) in 1925. A more rigorous statement is that the total wave function for two identical electrons (which are grouped under the name fermions) is anti-symmetric with respect to exchange of the particles. This means that the wave function $\Psi_e\left(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2\right)$ changes its sign if the space and spin co-ordinates of any two particles are interchanged.
The wave function $\Psi_e\left(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2\right)$ can therefore be modified to meet these criteria according to

$$\Psi_e\left(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2\right) = \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)$$

without compromising the additional simplicity afforded by the orbital approximation.

---

[1] The spin quantum number describes the unique quantum state of an electron and is designated by the letter s. It describes the energy, shape and orientation of orbitals.

3.3. Third Simplification

So all we now need to do is to solve the one-electron Schrödinger equation:

$$\mathscr{H}_1 \psi_a = \varepsilon_a \psi_a \quad , \tag{3.4}$$

in which the term on the left stands for the *Effective one-electron Hamiltonian* and the term on the right for the *one-electron wave function, a Molecular Orbital*.
The solutions are the molecular orbital wave functions, $\{\psi_a\}$, and molecular orbital energies, $\{\varepsilon_a\}$. To actually do this we make one final approximation which is called the **linear combination of atomic orbitals (LCAO) approximation**.
This supposes that we can construct molecular orbitals from linear superpositions of atomic orbitals centered on individual atoms,

$$\text{i.e. } \psi = \sum_i \left(c_i \cdot \phi_i\right)$$

where ψ designates a *Molecular Orbital*, c_i the *Mixing Coefficient* and ϕ_i an *Atomic Orbital*. In its simplest form a molecular orbital may be constructed from a summation of one orbital on one atom, with a second orbital on a different atom.

Example:
Hydrogen (H_2): Each hydrogen atom has a single valence orbital, this being the 1s orbital. Two molecular orbitals may be formed by the constructive and destructive overlap (constructive interference between two waves and destructive interference between two waves) of these two atomic orbitals (see **figure 3.2**) according to:

$$\text{MO}(1) = \text{AO}(\text{atom A}) + \text{AO}(\text{atom B})$$
$$\text{MO}(1) = \text{AO}(\text{atom A}) - \text{AO}(\text{atom B})$$

The molecular orbitals created from the above equation are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals), see **figure 3.3**. A molecule must have as many molecular orbitals as there are atomic orbitals.
While for constructive overlap the internuclear electron probability density is increased, it is reduced in intensity and causes a decrease in the internuclear electron probability density for destructive overlap.
This interaction of atomic orbitals, which gives rise to the molecular orbitals, may also be represented in the form of an orbital (electron) energy diagram which shows the relative energies of the orbitals. In the specific case of hydrogen each of the isolated atoms has one electron in its 1s orbital and when the atoms combine to form H_2 the two electrons

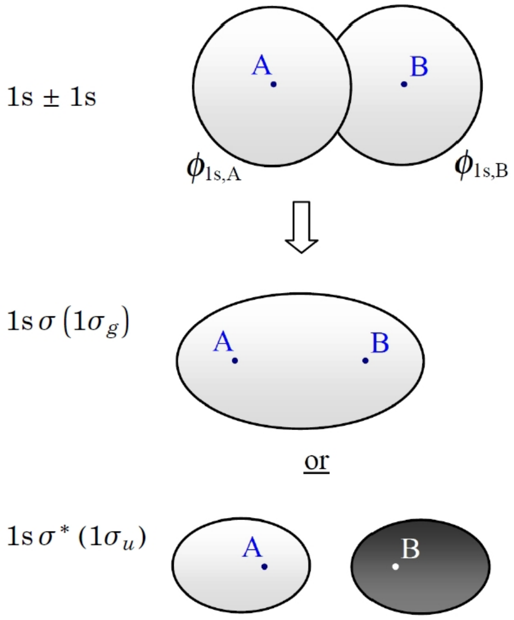

1s ± 1s
A
B
$\phi_{1s,A}$
$\phi_{1s,B}$
$1s\,\sigma\,(1\sigma_g)$
A
B
or
$1s\,\sigma^*\,(1\sigma_u)$
A
B

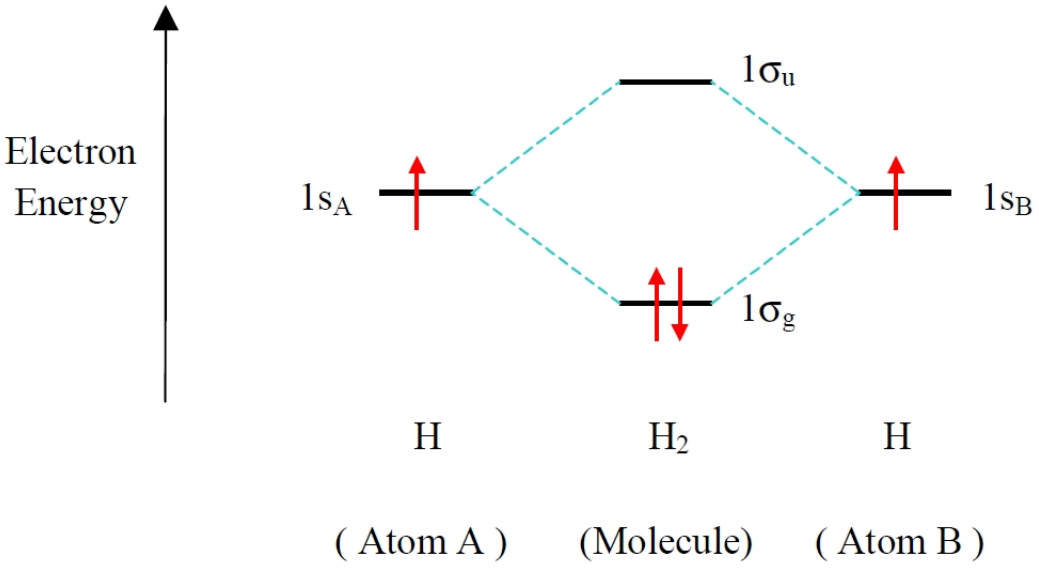
Diagram showing the superposition of the two 1s atomic orbitals

Bonding molecular orbital $\psi_+ = c_+\phi_{1s,A} + c_+\phi_{1s,B} = c_+\cdot\left(\phi_{1s,A} + \phi_{1s,B}\right)$

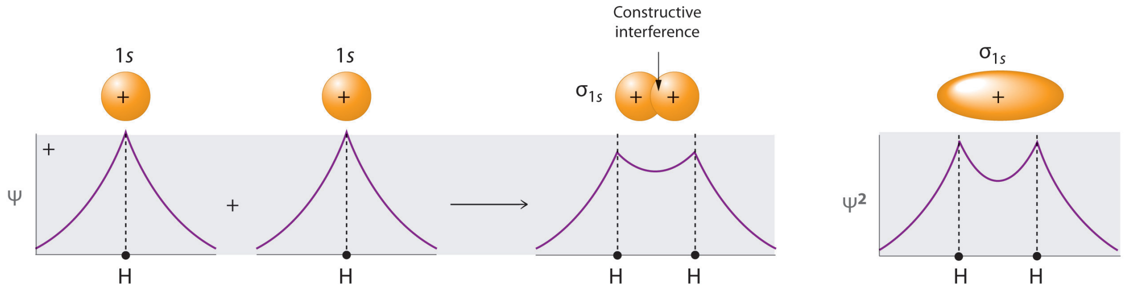
Antibonding molecular orbital $\psi_- = c_-\phi_{1s,A} - c_-\phi_{1s,B} = c_-\cdot\left(\phi_{1s,A} - \phi_{1s,B}\right)$

Figure 3.2.
Forming of MO in H_2 by LCAO

may be accommodated (with opposite spins) in the bonding molecular orbital, as illustrated below.

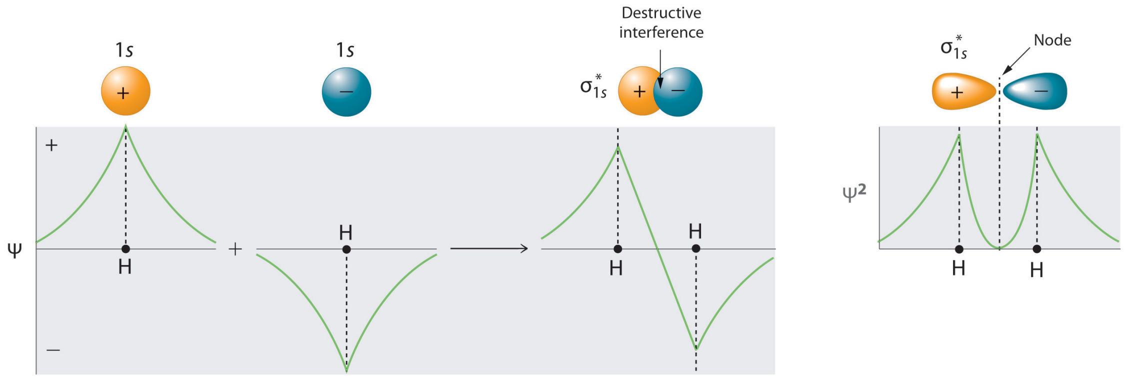

Electron Energy
$1\sigma_u$
$1s_A$
$1s_B$
$1\sigma_g$
H
H_2
H
(Atom A)
(Molecule)
(Atom B)

Note that in this instance two atomic orbitals give rise to two molecular orbitals - we shall see later that this is a general characteristic, i.e. linear combinations of n atomic orbitals give rise to n molecular orbitals. However this pictorial approach fails to answer some important questions, namely:



(a) Wave functions combined for σ_{1s}

(b) Bonding probability density



(c) Wave functions combined for σ^*_{1s}

(d) Antibonding probability density

Figure 3.3.
Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

1. what are the values of the mixing coefficients?
2. what are the exact energies of the molecular orbitals?

NOTE

From hereon, we will switch to using numerical labels for the atomic orbitals and their associated coefficients, e.g.

$$\psi = c_1\phi_1 + c_2\phi_2$$

where ϕ_i simply represents a specific atomic orbital on a specific atom (i).

4. LCAO and the Variational Principle

A linear combination of atomic orbitals or LCAO is a quantum superposition of atomic orbitals and a technique for calculating molecular orbitals in quantum chemistry. In quantum mechanics, electron configurations of atoms are described as wave functions. In a mathematical sense, these wave functions are the basis set of functions, the basis functions, which describe the electrons of a given atom. In chemical reactions, orbital wave functions are modified, i.e. the electron cloud shape is changed, according to the type of atoms participating in the chemical bond.
It was introduced in 1929 by Sir John Lennard-Jones (27 October 1894 - 1 November 1954) with the description of bonding in the diatomic molecules of the first main row of the periodic table, but had been used earlier by Linus Pauling (28 February 1901 - 19 August 1994) for H_2^+.
An initial assumption is, that the number of molecular orbitals ψ is equal to the number of atomic orbitals ϕ_i included in the linear expansion. In a sense, n atomic orbitals combine to form n molecular orbitals, which can be numbered $i = 1$ to n and which may not all be the same. The expression (linear expansion) for the ith molecular orbital would be:

$$\begin{aligned} \psi_i &= c_{1i}\phi_1 + c_{2i}\phi_2 + c_{3i}\phi_3 + \cdots + c_{ni}\phi_n \\ &\text{or} \\ \psi_i &= \sum_r c_{ri}\phi_r \quad , \end{aligned}$$

where ψ_i represents a specific molecular orbital given as the sum of n atomic orbitals ϕ_r, each multiplied by a corresponding coefficient c_{ri} , and r (numbered 1 to n) represents which atomic orbital is combined in the term. The coefficients are the weights of the contributions of the n atomic orbitals to the molecular orbital. The orbitals are thus expressed as linear combinations of basis functions, and the basis functions are one-electron functions centered on nuclei of the component atoms of the molecule.
However, LCAO does **not** give exact solutions to the one-electron Schrödinger equation (3.4), only approximate solutions. How do we make these approximate solutions as good as possible?

4.1. The Variational Principle

For a particular wave function, the estimate (expectation value) of the orbital energy E (previously referred to as ε) is given by:

$$E = \frac{\int \psi^* \mathscr{H} \psi \cdot \mathrm{d}\tau}{\int \psi^* \psi \cdot \mathrm{d}\tau} \tag{4.1}$$

where

ψ molecular orbital wave function (expressed as LCAO),
ψ^* complex conjugate of ψ ($\psi^* = \psi$, if the wave function is entirely real),
$\mathscr{H}$ effective one-electron Hamiltonian,
$\mathrm{d}\tau$ integral over all space.

The variational principle states that the value of E given by equation (4.1) is always greater than the true energy for the exact solution, from which it follows that the best approximate solution (i.e. the best values for the coefficients in the LCAO construction) can be obtained by minimizing the value of the energy, E, given by this equation.

4.2. Procedure for Implementing the Principle

1. Decide which atomic orbitals might contribute to the MO (symmetry considerations are of immense value at this point) and construct the summation for ψ, i.e. $\psi = c_1\phi_1 + c_2\phi_2 + \dots$.
2. Obtain an expression for E where

   $$E = \frac{\int \psi^* \mathscr{H} \psi \cdot \mathrm{d}\tau}{\int \psi^* \psi \cdot \mathrm{d}\tau} \quad .$$

   If ψ is entirely "real" (i.e. has no imaginary components) then

   $$\psi^* = \psi, \text{ and } \frac{\int \psi \mathscr{H} \psi \cdot \mathrm{d}\tau}{\int \psi^2 \cdot \mathrm{d}\tau} \quad .$$
3. Find the values of c_1, c_2, ... that minimize the value of E; once you have obtained these coefficients, then the wave function is obtained as $\psi = \sum_i (c_i\phi_i)$, the orbital energy as $\varepsilon = E_{min}$.

4.3. Overlap of Two Atomic Orbitals

When just two orbitals are permitted to interact, then the general expression for the molecular orbital expressed as a linear combination of atomic orbitals

$$\psi = \sum_i \left(c_i \phi_i\right)$$

simplifies to

$$\psi = c_1\phi_1 + c_2\phi_2 \ ,$$

where the first summand designates *Atomic orbital on atom 1* and the second summand *Atomic orbital on atom 2*. The expression for E now becomes:

$$E = \frac{\int \psi \mathscr{H} \psi \cdot \mathrm{d}\tau}{\int \psi^2 \cdot \mathrm{d}\tau} = \frac{\int \left(c_1\phi_1 + c_2\phi_2\right) \mathscr{H} \left(c_1\phi_1 + c_2\phi_2\right) \cdot \mathrm{d}\tau}{\int \left(c_1\phi_1 + c_2\phi_2\right)^2 \cdot \mathrm{d}\tau} \tag{4.2}$$

(1) Consider first the top line of the fraction.

$$\begin{aligned}\int \psi \mathscr{H} \psi \cdot \mathrm{d}\tau = & \int \left(c_1\phi_1 + c_2\phi_2\right) \mathscr{H} \left(c_1\phi_1 + c_2\phi_2\right) \cdot \mathrm{d}\tau \\ = & c_1^2 \cdot \int \phi_1 \mathscr{H} \phi_1 \cdot \mathrm{d}\tau + c_1 c_2 \cdot \phi_1 \mathscr{H} \phi_2 \cdot \mathrm{d}\tau \\ & + c_1 c_2 \cdot \phi_2 \mathscr{H} \phi_1 \cdot \mathrm{d}\tau + c_2^2 \cdot \int \phi_2 \mathscr{H} \phi_2 \cdot \mathrm{d}\tau\end{aligned}$$

where the first and last integral designate *An integral, α_1 (α_2), which corresponds to the energy of an electron in atomic orbital 1 (2) (albeit in the molecular environment)* and the second and third integrals designate *Two integrals, β_{12} and β_{21}, whose size is a measure of the strength of the bonding interaction arising as a result of overlap of ϕ_1 and ϕ_2.* From this it follows, that:

$$\int \psi \mathscr{H} \psi \cdot \mathrm{d}\tau = c_1^2 \alpha_1 + c_1 c_2 \beta_{12} + c_1 c_2 \beta_{21} + c_2^2 \alpha_2 \ .$$

As long as the ϕ_i-functions are entirely real, then $\beta_{12} = \beta_{21}$ (since $\mathscr{H}$ is an Hermitian operator) and this simplifies to

$$\int \psi \mathscr{H} \psi \cdot \mathrm{d}\tau = c_1^2 \alpha_1 + 2 c_1 c_2 \beta_{12} + c_2^2 \alpha_2 \ .$$

(2) Now consider the bottom line of the fraction.

$$\begin{aligned}\int \psi^2 \cdot \mathrm{d}\tau &= \int \left(c_1\phi_1 + c_2\phi_2\right) \cdot \left(c_1\phi_1 + c_2\phi_2\right) \cdot \mathrm{d}\tau \\ &= c_1^2 \cdot \int \phi_1^2 \cdot \mathrm{d}\tau + c_1 c_2 \cdot \int \phi_1\phi_2 \cdot \mathrm{d}\tau + c_1 c_2 \cdot \int \phi_2\phi_1 \cdot \mathrm{d}\tau + c_2^2 \cdot \int \phi_2^2 \cdot \mathrm{d}\tau\end{aligned}$$

where the first and last integral equals 1, since the atomic orbitals are "**normalized**" and the second and third integrals are equal. This integral is known as the "overlap integral", denoted as S (it is positive)and is a quantitative measure of the overlap of two atomic orbitals.
From this it follows, that:

$$\int \psi^2 \cdot \mathrm{d}\tau = c_1^2 + c_2^2 + 2 c_1 c_2 \cdot S \quad .$$

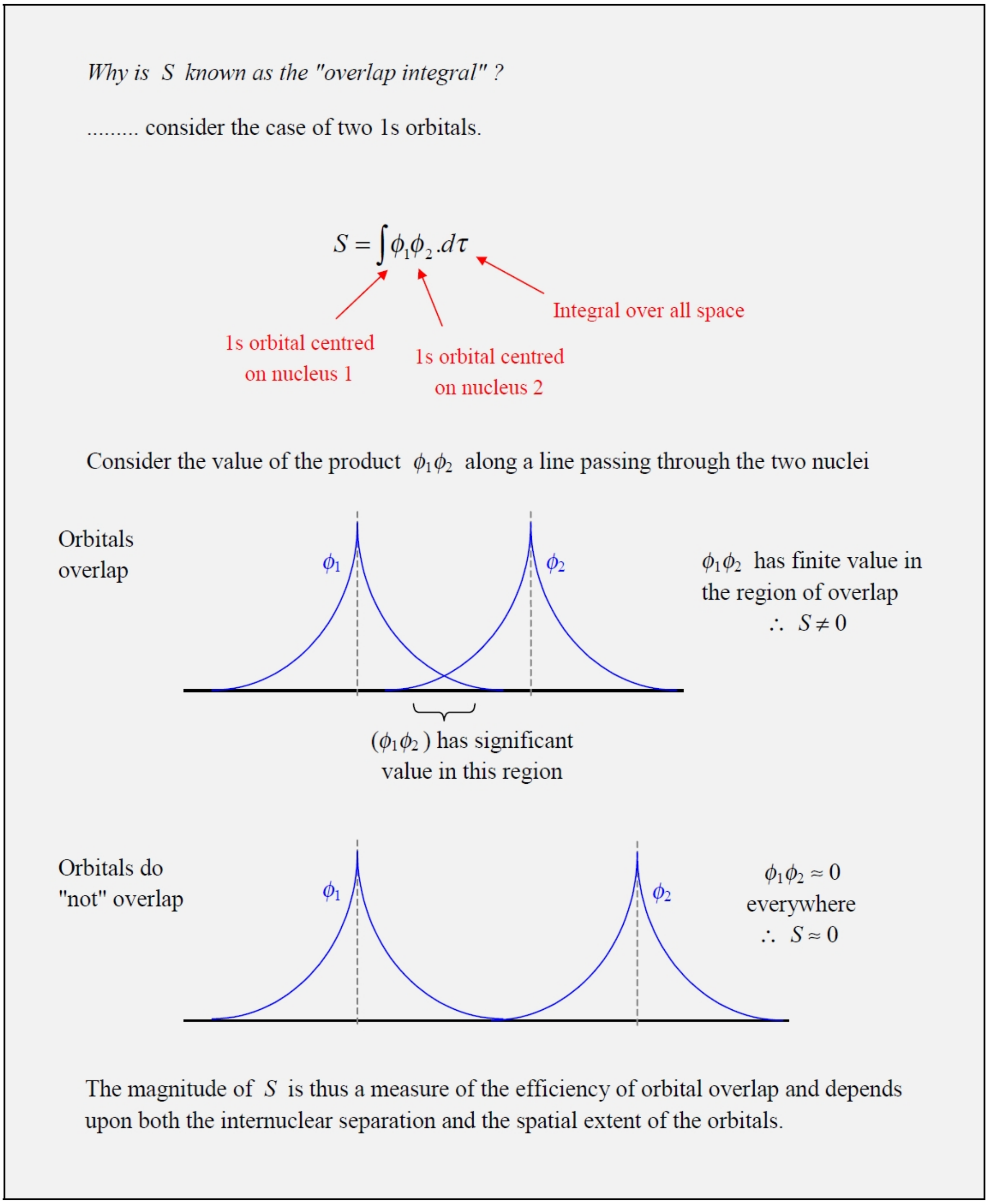
Substitution of the expressions for the integrals into equation (4.2) therefore gives:

$$\frac{c_1^2 \alpha_1 + 2 c_1 c_2 \beta_{12} + c_2^2 \alpha_2}{c_1^2 + c_2^2 + 2 c_1 c_2 \cdot S} \quad . \tag{4.3}$$

We now need to find the values of c_1, c_2 that minimize the value of E.

4.4. Summary of Terminology

α_i	is known as the Coulomb integral: it is equal to the energy of an electron in the corresponding atomic orbital, i, albeit with the atom in the molecular environment, it is negative.
β_{ij}	is known as the resonance integral: it is a measure of the strength of the bonding interaction as a result of the overlap of orbitals i and j, it is negative for constructive overlap of orbitals.
S	is known as the overlap integral: it is a measure of the effectiveness of overlap of the orbitals (its magnitude is always significantly less than one, i.e. $S \ll 1$).



Why is S known as the "overlap integral" ?

.... consider the case of two 1s orbitals.

$$S = \int \phi_1 \phi_2 . d\tau$$

1s orbital centred on nucleus 1

1s orbital centred on nucleus 2

Integral over all space

Consider the value of the product $\phi_1\phi_2$ along a line passing through the two nuclei

$\phi_1\phi_2$ has finite value in the region of overlap $\therefore\ S \neq 0$

$(\phi_1\phi_2)$ has significant value in this region

$\phi_1\phi_2 \approx 0$ everywhere $\therefore\ S \approx 0$

The magnitude of S is thus a measure of the efficiency of orbital overlap and depends upon both the internuclear separation and the spatial extent of the orbitals.

Figure 4.1.
Illustration of the overlap integral

4.5. The Secular Equations and Secular Determinant

Rearrangement of equation (4.3) yields

$$E\cdot\left(c_1^2+c_2^2+2c_1c_2\cdot S\right)=c_1^2\alpha_1+2c_1c_2\beta_{12}+c_2^2\alpha_2$$

To minimize E with respect to c_1 and c_2 we need to set both

$$\begin{aligned}\frac{\partial E}{\partial c_1}&=0\\ \frac{\partial E}{\partial c_2}&=0\ .\end{aligned}$$

(See Appendix B for details)
Differentiation with respect to c_1 and setting the derivative equal to zero gives

$$c_1\cdot(\alpha_1-E)+c_2\cdot\left(\beta_{12}-ES\right)=0\ . \tag{4.4}$$

Differentiation with respect to c_2 and setting the derivative equal to zero gives

$$c_1\cdot\left(\beta_{12}-ES\right)+c_2\cdot(\alpha_2-E)=0\ . \tag{4.5}$$

Equations (4.4) and (4.5) are simultaneous equations in c_1 and c_2, known as the "**secular equations**". These equations need to be solved to obtain the appropriate values for c_1 and c_2. For non-trivial solutions (i.e. solutions other than $c_1 = c_2 = 0$) we require (see Appendix C) that the corresponding "**secular determinant**" be equal to zero, i.e.:

$$\begin{vmatrix}\alpha_1-E & \beta_{12}-ES\\ \beta_{12}-ES & \alpha_2-E\end{vmatrix}=0\ . \tag{4.6}$$

Solving this equation will tell us for what values of E we can get non-trivial solutions.

4.5.1. Case 1: Overlap of Two Identical Orbitals

This is the simplest possible case - the classic example would be H_2 , but the approach is also a reasonable approximation for the bonding in any homonuclear diatomic molecule, X_2, and can also be applied to certain types of localized, two-centre bonding in more complex molecules.
Since ϕ_1 and ϕ_2 are the same type of orbital (e.g. both hydrogen 1s orbitals):

$$\alpha_1=\alpha_2=\alpha$$

and for simplicity let the resonance integral β_{12} simply be represented by β. The secular determinant now simplifies to

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \ . \tag{4.7}$$

4.5.1.1. The Simplest Solution

It is now possible to make a further simplification, namely that $S \ll 1$ (i.e. the *overlap integral* is very small, or, if you prefer, $S \approx 0$) - this is the neglect of overlap approximation (and, as we shall see later, also one of the Hückel approximations) and the result is that the determinant simplifies to

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \tag{4.8}$$

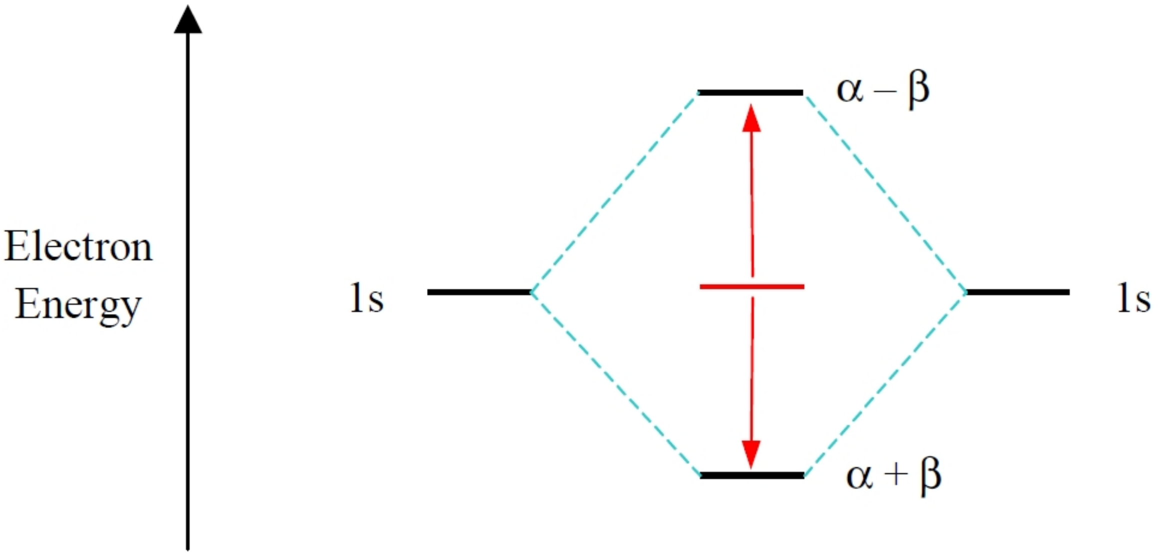
Expanding the determinant (see Appendix C) gives:

$$\begin{aligned} (\alpha - E)^2 - \beta^2 &= 0 \\ \Rightarrow (\alpha - E)^2 &= \beta^2 \\ \Rightarrow (E - \alpha) &= \pm\beta \end{aligned}$$

which yields

$$\boxed{E_+ = (\alpha + \beta)} \quad \text{or} \quad \boxed{E_- = (\alpha - \beta)}$$

Given that β is negative (see page 28), then it is clear that E_+ is lower in energy than E_- and therefore that E_+ corresponds to the energy of the bonding molecular orbital.



At this level of approximation the bonding and antibonding molecular orbitals are symmetrically distributed above and below the original atomic orbitals on the orbital energy diagram.

An example of a homonuclear diatomic would be ethylene (C_2H_4). In this molecule, the H-C-H and H-C-C angles are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C-H (sp^2 + s) and one C-C (sp^2 + sp^2), see **figure 4.2**. After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron, see **figure 4.3**. The two singly occupied $2p_z$ orbitals can overlap to form a π-bonding orbital and a π^*-antibonding orbital. With the formation of a π-bonding orbital, electron density increases in the plane between the carbon nuclei. The π^* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π^* orbital empty. Consequently, the C-C bond in ethylene consists of a s bond and a π bond, which together give a C=C double bond.

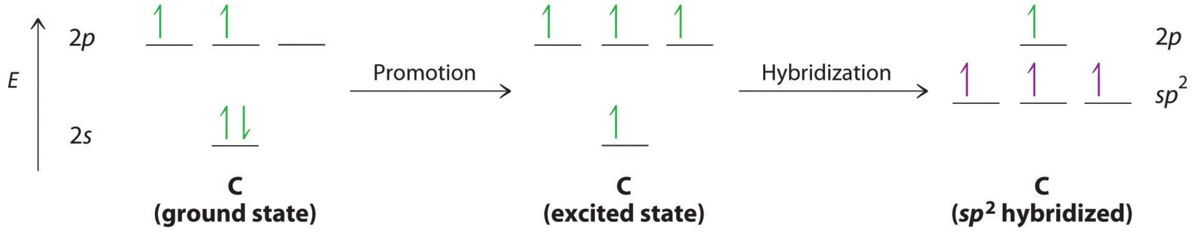

E
2p
2s
Promotion
Hybridization
2p
sp2
C
(ground state)
C
(excited state)
C
(sp2 hybridized)

Figure 4.2.
Illustration of hybridization in ethylene

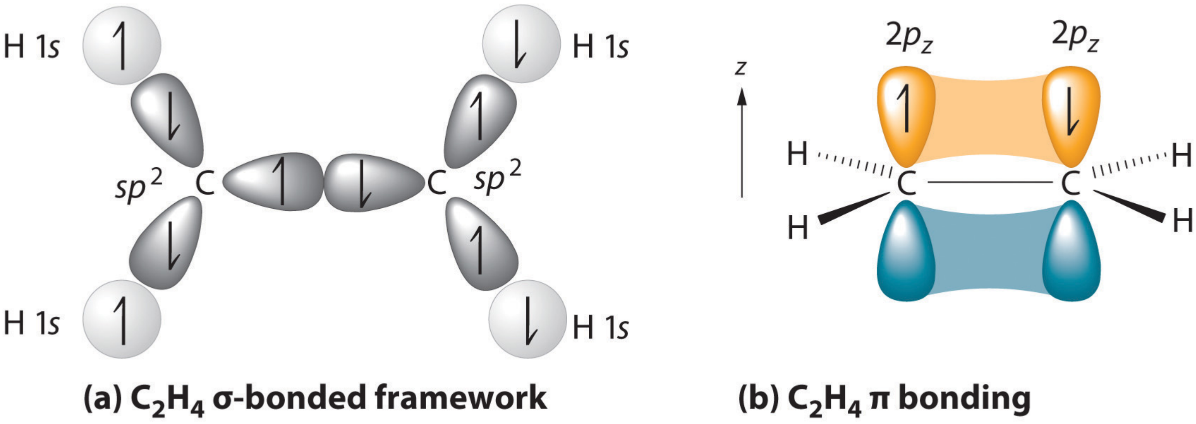

H 1s
H 1s
H 1s
H 1s
sp2
sp2
C
C
(a) C2H4 σ-bonded framework
z
2pz
2pz
H
H
H
H
C
C
(b) C2H4 π bonding

Figure 4.3.
Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C-H bonds and one C-C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon-carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the z-axis.)

4.5.1.2. The More Realistic Solution

If we are not prepared to neglect the orbital overlap then expanding the determinant of equation (4.9) gives the following equation:

$$\begin{aligned}
&(\alpha - E)^2 - \left(\beta - ES\right)^2 = 0 \\
&\qquad \Rightarrow (\alpha - E)^2 = \left(\beta - ES\right)^2 \\
&\qquad \Rightarrow (\alpha - E) = \sqrt{\left(\beta - ES\right)^2} = -\left(\beta - ES\right) \text{ or } + \left(\beta - ES\right) \\
&\qquad \Rightarrow (E - \alpha) = \pm\left(\beta - ES\right) \\
&\quad \Rightarrow E \cdot (1 \pm S) = \alpha \pm \beta \ .
\end{aligned}$$

So, the energy of the bonding molecular orbital is given by

$$\boxed{E_+ = \frac{\left(\alpha + \beta\right)}{(1 + S)}}$$

whilst the energy of the antibonding molecular orbital is given by

$$\boxed{E_- = \frac{\left(\alpha - \beta\right)}{(1 - S)}} \ .$$

Once again, given that β is negative (see page 28, then it is clear that E_+ is still lower in energy than E_- and therefore that E_+ corresponds to the energy of the bonding molecular orbital.

The expressions for the orbital energies may be reformulated as follows to better illustrate the values relative to the energy of the constituent atomic orbitals:

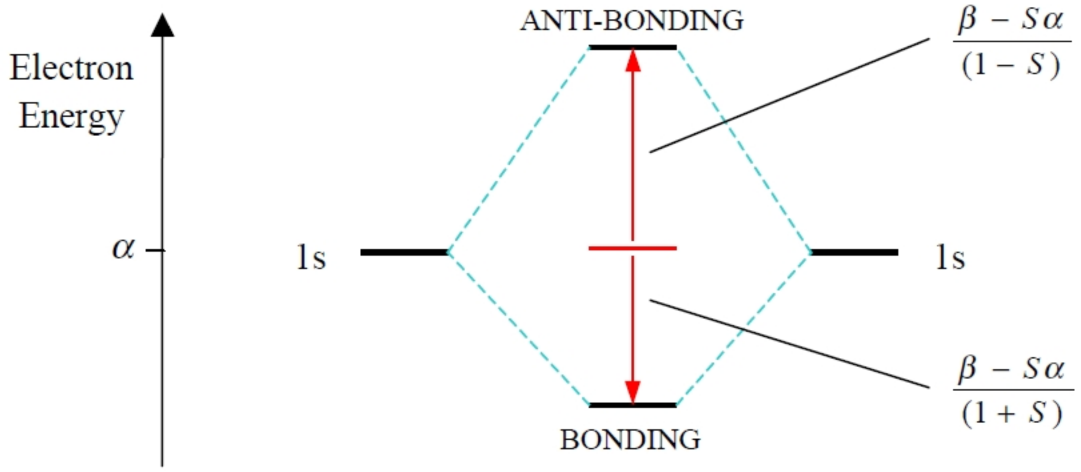
$$\begin{aligned}
E_+ &= \frac{\left(\alpha + \beta\right)}{(1 + S)} = \alpha + \frac{\left(\beta - S\,\alpha\right)}{(1 + S)} \\
E_- &= \frac{\left(\alpha - \beta\right)}{(1 - S)} = \alpha - \frac{\left(\beta - S\,\alpha\right)}{(1 - S)} \ .
\end{aligned}$$

Since $S > 0$, $(1 + S) > (1 - S)$ and hence the above equations for E_+ and E_- demonstrate that

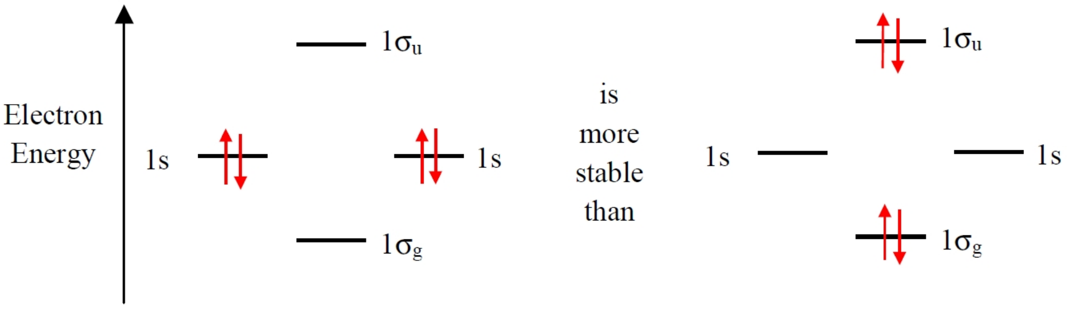
... the antibonding orbital is more strongly antibonding than the bonding orbital is bonding.

We may again represent this situation diagrammatically using an orbital energy diagram, noting that the bonding and antibonding molecular orbitals are now **asymme-**

trically distributed about the original atomic orbitals on the orbital energy diagram.


Electron Energy
α
1s
1s
ANTI-BONDING
BONDING
$\frac{\beta - S\alpha}{(1-S)}$
$\frac{\beta - S\alpha}{(1+S)}$

One consequence of the asymmetry is that He_2, for example, is not a stable molecule, i.e.


Electron Energy
1s
$1\sigma_u$
1s
$1\sigma_g$
is more stable than
1s
$1\sigma_u$
1s
$1\sigma_g$

This is reflected in the comparison of the potential energy curves for hydrogen and helium.

4.5.2. Case 2: Overlap of Two Dissimilar Orbitals

An example of this type would be the bonding in a heteronuclear diatomic molecule such as CO. For the sake of simplicity we will neglect overlap (i.e. assume, as we have done before, that $S \approx 0$) in which case the secular determinant of equation (4.6) simplifies to:

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{12} & \alpha_2 - E \end{vmatrix} = 0$$

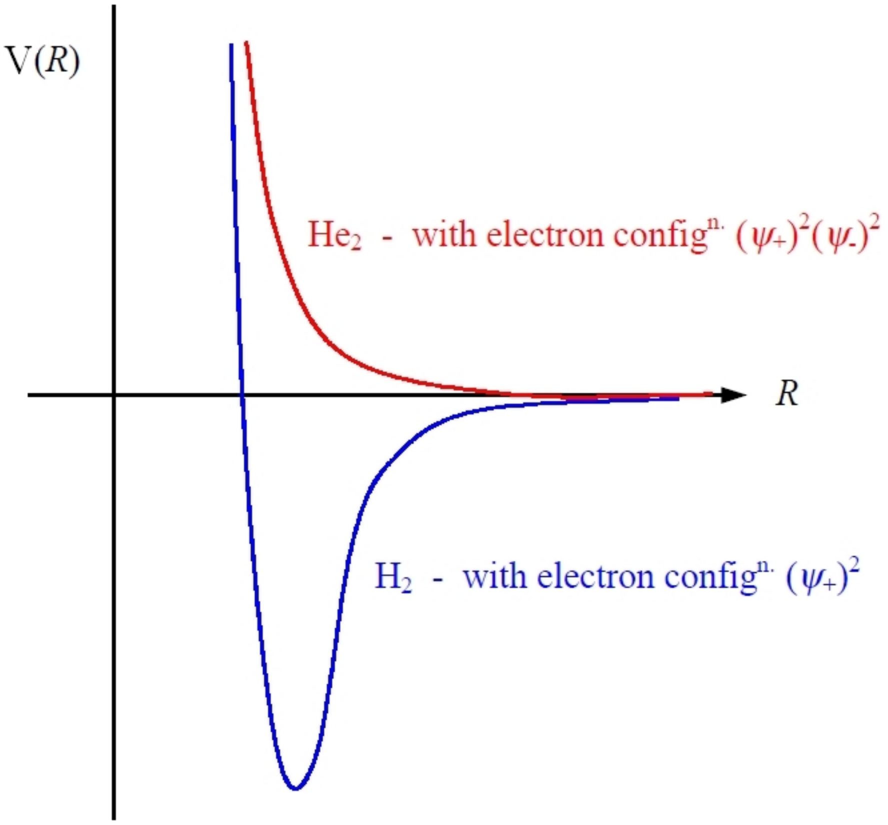


Figure 4.4.
Potential energy curves for hydrogen and helium

Expanding the determinant (see Appendix C), again replacing β_{12} by β for ease of writing, gives:

$$(\alpha_1 - E)\cdot(\alpha_2 - E) - \beta^2 = 0$$
$$\Rightarrow E^2 - E\cdot(\alpha_1 + \alpha_2) + \left(\alpha_1\alpha_2 - \beta^2\right) = 0$$

This is a quadratic equation in E (comparable to $a\,x^2 + b\,x + c = 0$) and applying the general solution for such equations gives:

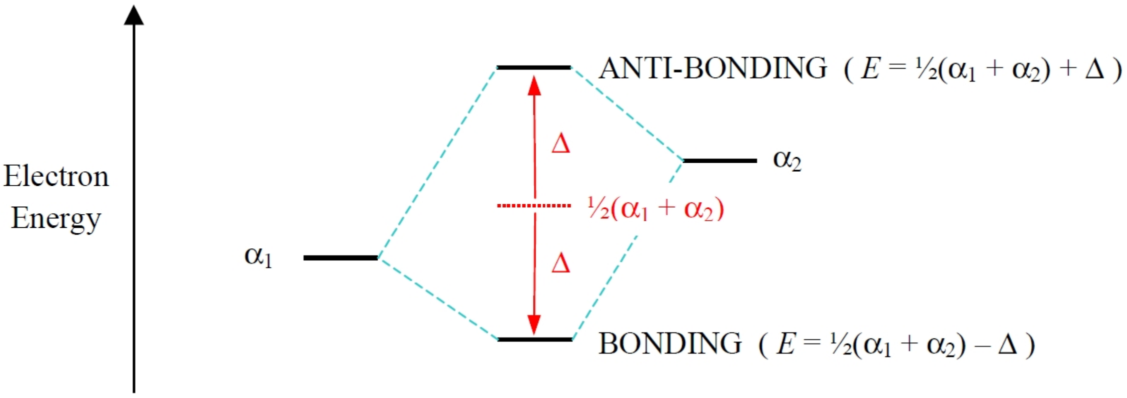
$$
\begin{aligned}
E &= \frac{(\alpha_1+\alpha_2)\pm\sqrt{(\alpha_1+\alpha_2)^2-4\cdot\left(\alpha_1\alpha_2-\beta^2\right)}}{2}\\
\Rightarrow E &= \frac{(\alpha_1+\alpha_2)\pm\sqrt{(\alpha_2-\alpha_1)^2+4\cdot\beta^2}}{2}
\end{aligned}
$$

which finally gives

$$E=\frac{1}{2}\cdot(\alpha_1+\alpha_2)\pm\Delta \ ,$$

where

$$\Delta=\frac{1}{2}\cdot\sqrt{(\alpha_2-\alpha_1)^2+4\cdot\beta^2}>0 \ .$$


Electron Energy
ANTI-BONDING ($E = \frac{1}{2}(\alpha_1+\alpha_2)+\Delta$)
α_2
Δ
$\frac{1}{2}(\alpha_1+\alpha_2)$
Δ
α_1
BONDING ($E = \frac{1}{2}(\alpha_1+\alpha_2)-\Delta$)

As an example, the bonding orbitals in methanal or formaldehyde (H_2CO) are shown. Sigma bonding between hydrogen s orbitals and carbon sp^2 hybrids. Sigma bond between carbon sp^2 and oxygen sp^2 (lone pairs occupy other sp^2 orbitals). π-bond between p orbitals of carbon and oxygen.

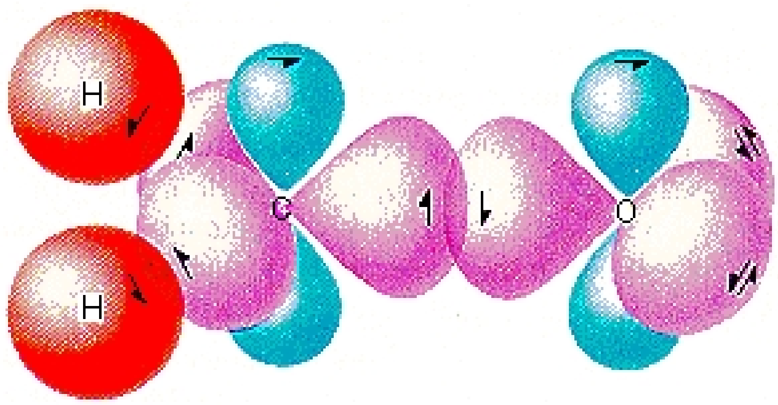


Figure 4.5.
Depiction of bonding orbitals in methanal

4.6. What are the Molecular Orbital Wave functions?

The *systematic Approach* to finding the wave functions themselves requires us to:

1. Substitute the values of E back into the secular equations to obtain two simultaneous equations for c_1 and c_2,
2. Solve these simultaneous equations for c_1 and c_2.

4.6.1. Case 1: Homonuclear Bonding

If we neglect overlap then the secular determinant is (see equation (4.9))

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \tag{4.9}$$

and the corresponding secular equations are:

$$\begin{aligned} c_1 \cdot (\alpha - E) + c_2 \beta &= 0 \\ c_1 \beta + c_2 \cdot (\alpha - E) &= 0 \ . \end{aligned}$$

For the bonding MO,

$$\begin{aligned} E_+ &= (\alpha + \beta) \\ \Rightarrow (\alpha - E) &= -\beta \end{aligned}$$

and substituting into the secular equations gives:

$$\begin{aligned} -c_1\beta + c_2\beta = 0 &\;\Rightarrow -c_1 + c_2 = 0 \\ c_1\beta - c_2\beta = 0 &\;\Rightarrow \quad c_1 - c_2 = 0 \ , \end{aligned}$$

i.e.

$$c_1 = c_2$$

and so the coefficients for the bonding MO of a homonuclear diatomic molecule are of the same sign and of equal magnitude.

Using the same approach, it can easily be shown that the coefficients for the antibonding MO of a homonuclear diatomic molecule are of equal magnitude but opposite sign.

These results should not be a great surprise - the high symmetry of the molecule itself means that the wave functions must also possess a high degree of symmetry. To get the actual value of the coefficients we need to "normalize" the molecular orbitals. Let both coefficients of the bonding MO be denoted c_+ - the wave function for the bonding MO may then be written as:

$$\psi_+ = c_+ \cdot (\phi_1 + \phi_2) \ .$$

If a wave function is normalized (see Appendix D), then the requirement on the wave function is that:

$$\int \psi^* \psi \cdot \mathrm{d}\tau = \int |\psi|^2 \cdot \mathrm{d}\tau = 1 \ .$$

For ψ_+ therefore:

$$c_+^2 \cdot \int (\phi_1+\phi_2)^2 \cdot \mathrm{d}\tau = 1$$

$$\Rightarrow c_+^2 \cdot \left(\underbrace{\int \phi_1^2 \cdot \mathrm{d}\tau}_{=1} + 2 \underbrace{\int \phi_1 \phi_2 \cdot \mathrm{d}\tau}_{=S\approx 0} + \underbrace{\int \phi_2^2 \cdot \mathrm{d}\tau}_{=1} \right) = 1$$

$$\Rightarrow 2c_+^2 = 1 \quad \Rightarrow \quad c_+ = \frac{1}{\sqrt{2}}$$

$$\text{i.e. } \psi_+ = \frac{1}{\sqrt{2}}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 = \frac{1}{\sqrt{2}}(\phi_1+\phi_2) \quad .$$

Similarly, one obtains for the antibonding MO:

$$\psi_- = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_2 = \frac{1}{\sqrt{2}}(\phi_1-\phi_2) \quad .$$

Note: these values of the coefficients could also be obtained using the general normalization condition of a molecular orbital (see Appendix D), which states that when overlap is neglected

$$\sum_i c_i^2 = 1 \quad ,$$

e.g. for ψ_+:

$$\psi_+ = c_+\phi_1 + c_+\phi_2 \text{ i.e. } c_1 = c_+ \text{ and } c_2 = c_+$$

$$\sum_i c_i^2 = c_1^2 + c_2^2 = c_+^2 + c_+^2 = 1$$

$$\Rightarrow 2c_+^2 = 1$$

$$\Rightarrow c_+ = \frac{1}{\sqrt{2}} \quad .$$

4.6.2. Case 2: Heteronuclear Bonding

We can again proceed as in the previous case by substituting the values of E back into the secular equations, thereby obtaining two simultaneous equations for c_1 and c_2.
. . . but there is also a "general solution".

4.6.3. General solution to the two-orbital problem

For $\alpha_1 \leqslant \alpha_2$, the general solutions for the wave functions (no proof will be given) are:

$$\begin{aligned}\psi_- &= -\sin\left(\theta \cdot \phi_1\right) + \cos\left(\theta \cdot \phi_2\right) \\ \psi_+ &= \quad \cos\left(\theta \cdot \phi_1\right) + \sin\left(\theta \cdot \phi_2\right)\end{aligned}$$

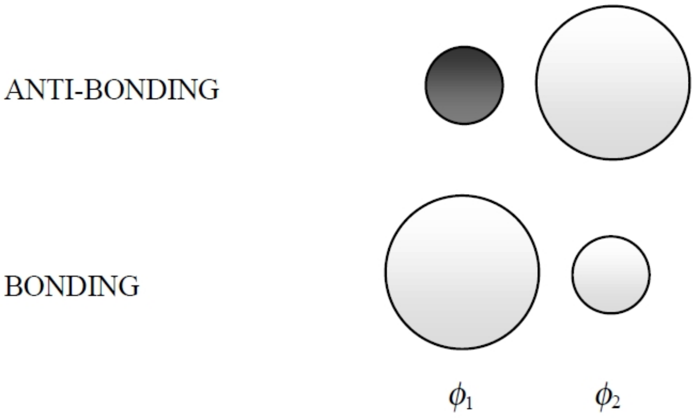
where

$$\tan(2\theta) = \frac{\beta}{\frac{1}{2} \cdot (\alpha_1 - \alpha_2)} \quad .$$

Note: β and $(\alpha_1 - \alpha_2)$ are both negative, hence $\tan(2\theta)$ is positive, hence

$$\begin{aligned}&\Rightarrow \; 0 < 2\theta < 90^\circ \\ &\Rightarrow \; 0 < \theta < 45^\circ \\ &\Rightarrow \; |\cos\theta| > |\sin\theta| \quad .\end{aligned}$$

The coefficients for the wave functions are therefore such that their character is as illustrated below:



i.e. the electron density in the occupied bonding MO is concentrated around the nucleus associated with the atomic orbital of lower energy (for orbitals of the same type on atoms of a particular period, this corresponds to the more electronegative nucleus and also that possessing the higher nuclear charge, Z). This effect can be seen in a comparison of the π-bonding molecular orbitals of oxygen (O_2) and carbon monoxide (CO).

It may be noted, that the coefficients of these "general solutions" automatically incorpo-

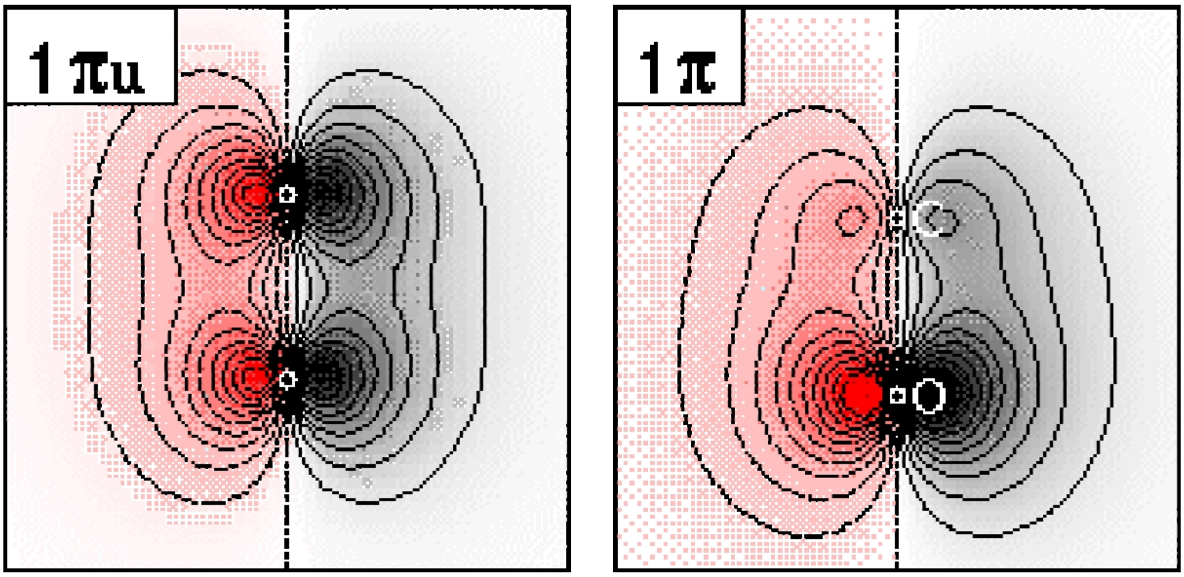


Figure 4.6.
Electron density of the π-bonding molecular orbitals of O_2 and CO

rate the *normalization condition*. The normalization condition for molecular orbitals (see Appendix D) formed by the combination of just two atomic orbitals, as in this instance, is:

$$\sum_i c_i^2 = 1 \;\Rightarrow\; c_1^2 + c_2^2 = 1 \; .$$

For the wave function:

$$\begin{aligned} \psi_- &= -\sin(\theta \cdot \phi_1) + \cos(\theta \cdot \phi_2) \\ \psi_+ &= \quad \cos(\theta \cdot \phi_1) + \sin(\theta \cdot \phi_2) \end{aligned}$$

it follows that

$$c_1^2 + c_2^2 = \sin^2\theta + cos^2\theta$$

and since $\sin^2\theta + cos^2\theta = 1$ (one of the standard trigonometric relationships) it follows that

$$c_1^2 + c_2^2 = 1 \; ,$$

i.e. the wave functions (ψ_+ and ψ_-) given by the formulae quoted above, are already normalized.
We can also use the general solution to look at certain special (limiting) cases.

4.6.3.1. Special Case 1

If $|\beta| \gg \frac{1}{2}\cdot(\alpha_2-\alpha_1)$ then

$$\Delta = \frac{1}{2}\cdot\sqrt{(\alpha_2-\alpha_1)^2+4\beta^2} \approx \frac{1}{2}\cdot\sqrt{4\beta^2} \ ,$$

i.e. $\Delta \to |\beta|$ and since $E_+ = \frac{1}{2}\cdot(\alpha_1+\alpha_2)\mp\Delta$ (where Δ is positive), it follows that

$$\begin{aligned} E_+ &\to \frac{1}{2}\cdot(\alpha_1+\alpha_2)+\beta \\ E_- &\to \frac{1}{2}\cdot(\alpha_1+\alpha_2)-\beta \ . \end{aligned}$$

Furthermore $\tan(2\theta) = \frac{\beta}{\frac{1}{2}\cdot(\alpha_1-\alpha_2)} \to \infty$ since $|\beta| \gg \frac{1}{2}\cdot(\alpha_2-\alpha_1)$, which leads to the conclusion, that

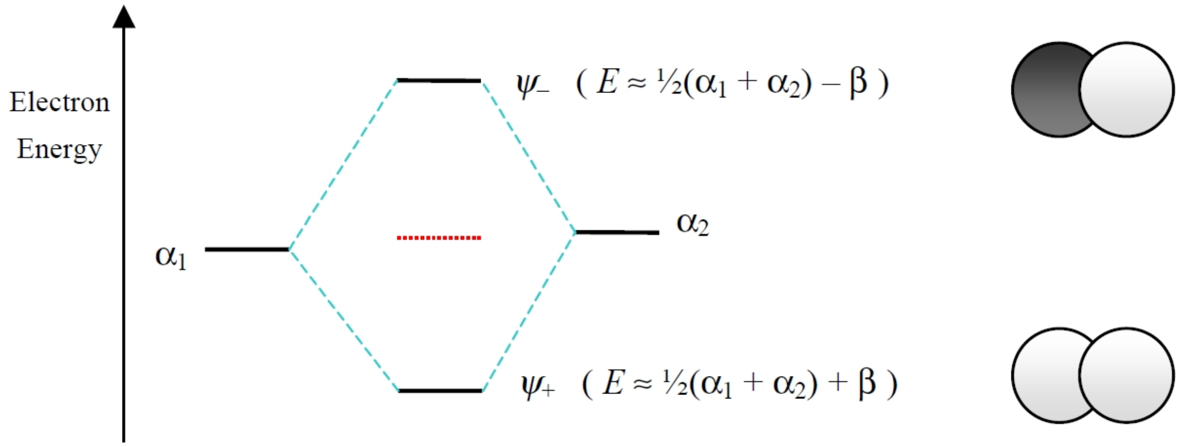
$$2\theta \to 90^\circ,\ \theta \to 45^\circ \ ,$$

in which case

$$\cos\theta \to \frac{1}{\sqrt{2}} \ \text{and} \ \sin\theta \to \frac{1}{\sqrt{2}}$$

and

$$\psi_+ \to \frac{1}{\sqrt{2}}\cdot(\phi_1+\phi_2),\ \psi_- \to \frac{1}{\sqrt{2}}\cdot(\phi_1-\phi_2) \ .$$


Electron Energy
ψ_- ($E \approx ½(\alpha_1 + \alpha_2) - \beta$)
α_2
α_1
ψ_+ ($E \approx ½(\alpha_1 + \alpha_2) + \beta$)

i.e. if the interaction energy (β) is much larger than the difference between the energies of the original overlapping orbitals, then we are rapidly approaching the situation which pertains when $\alpha_1 = \alpha_2 = \alpha$ (i.e. the special case of overlap of two identical orbitals that we considered initially).

4.6.3.2. Special Case 2

If $|\beta| \ll \frac{1}{2} \cdot (\alpha_2 - \alpha_1)$ then

$$\Delta = \frac{1}{2} \cdot \sqrt{(\alpha_2 - \alpha_1)^2 + 4\beta^2} \approx \frac{1}{2} \cdot \sqrt{(\alpha_2 - \alpha_1)^2} \ ,$$

i.e. $\Delta \to \frac{1}{2} \cdot (\alpha_2 - \alpha_1)$ and since $E_{+} = \frac{1}{2} \cdot (\alpha_1 + \alpha_2) \mp \Delta$ (where Δ is positive), it follows that

$$\begin{aligned} E_{+} &\to \frac{1}{2} \cdot (\alpha_1 + \alpha_2) - \frac{1}{2} \cdot (\alpha_2 - \alpha_1) = \alpha_1 \\ E_{-} &\to \frac{1}{2} \cdot (\alpha_1 + \alpha_2) + \frac{1}{2} \cdot (\alpha_2 - \alpha_1) = \alpha_2 \ . \end{aligned}$$

Furthermore $\tan(2\theta) = \frac{\beta}{\frac{1}{2} \cdot (\alpha_1 - \alpha_2)} \to 0$ since $|\beta| \ll \frac{1}{2} \cdot (\alpha_2 - \alpha_1)$, which leads to the conclusion, that

$$2\theta \to 0^\circ, \ \theta \to 0^\circ \ ,$$

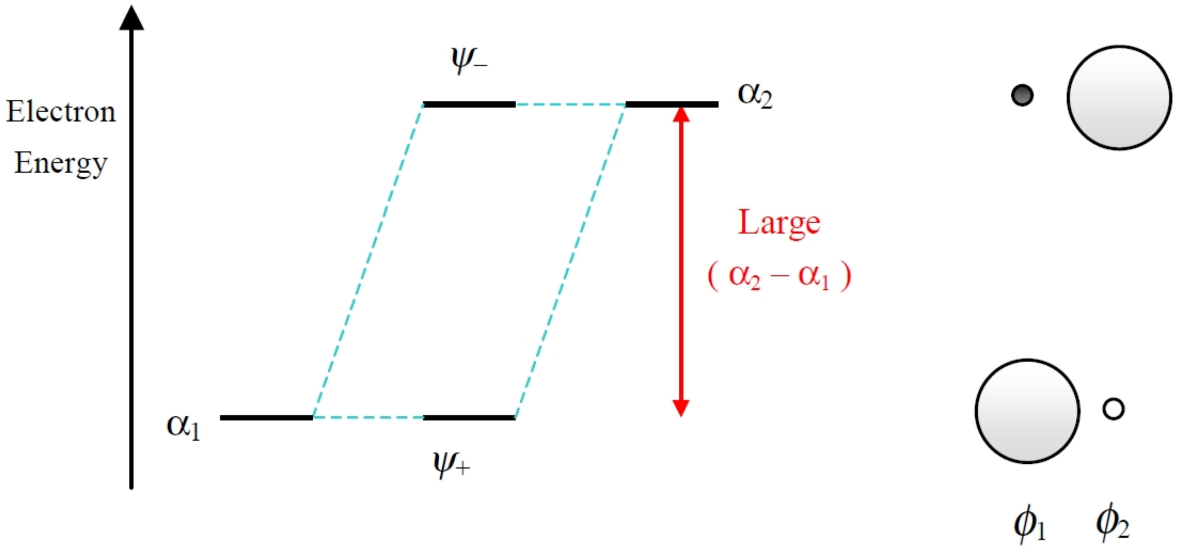
in which case

$$\cos\theta \to 1 \ \text{and} \ \sin\theta \to 0$$

and

$$\psi_{+} \to \phi_1, \ \psi_{-} \to \phi_2 \ ,$$

i.e. the orbitals and their energies are almost unchanged.


Electron
Energy
ψ_-
α_2
Large
$(\alpha_2 - \alpha_1)$
α_1
ψ_+
ϕ_1
ϕ_2

Important Conclusion
Bonding interactions arising from orbital overlap can be neglected if the energy separation of the overlapping orbitals is large compared to the interaction energy, β.

5. Partial Charges and Bond Orders

When we view a molecule as a chemist and consider its possible reactions, two of the most important questions are:

1. how strong are the various bonds in the molecule?
2. is the charge uniformly distributed or is the molecule polar with centers of positive and negative character?

so we need to know how to extract this information when the bonding in a molecule is considered using molecular orbital theory.

5.1. Partial Charges

A neutral, isolated atom has an overall charge of zero since the positive charge of the nucleus is exactly balanced by the negative charge of the electrons in the area surrounding the nucleus. In a molecule the formation of bonds leads to a redistribution of the valence electron density, and this can lead to regions where there is an imbalance between the ion core charge (the positive charge associated with the nucleus and the inner shell/ core electrons) and the immediately-surrounding valence electron charge. This leads to the concept that atoms in a molecule may have "partial charges" (i.e. fractional electronic charge).

5.1.1. Calculation of the partial charge on an atom

The electron density, q_i, on atom, i, due to one particular MO is given by (see Appendix D):

$$q_i = n \cdot c_i^2$$

where

n number of electrons in the MO (i.e. 0, 1 or 2),

c_i coefficient of the atomic orbital on this atom , i, in the LCAO representation of the molecular orbital.

The total valence electron density, Q_i, on atom, i, due to all the molecular orbitals is given by:

$$Q_i = \sum_{MOs} q_i \quad ,$$

where the summation must be carried out over all the occupied molecular orbitals in which this atom participates.

The partial charge on atom, i, is given by the difference between the positive ion core charge, V_i, (equal to the net charge of the nucleus and all inner-shell electrons of the atom) and the total valence electron density, Q_i, around the atom.

$$\text{Partial charge on atom} = V_i - Q_i \quad .$$

5.2. Bond Orders

In simplistic considerations of bonding in molecules the bond order between two atoms can be calculated using the equation:

$$\begin{aligned}\text{Bond Order} = \; & \text{No. of pairs of electrons in bonding MOs} \\ & - \text{No. of pairs of electrons in antibonding MOs} \quad .\end{aligned}$$

This approach works perfectly well for homonuclear diatomic molecules but to calculate bond orders in heteronuclear diatomic molecules and in polyatomic molecules, where the molecular orbitals span several atoms, we need a more sophisticated approach, as outlined below.

The bond order between two atoms, i and j, due to one particular MO is given by (see Appendix D):

$$p_{i,j} = n \cdot c_i \cdot c_j$$

where

n number of electrons in the MO (i.e. 0, 1 or 2),

c_i coefficient of the atomic orbital on atom , i, in the molecular orbital,

c_j coefficient of the atomic orbital on atom , j, in the molecular orbital.

The total bond order between two atoms, i and j, due to all the molecular orbitals is given by:

$$P_{i,j} = \sum_{MOs} p_{i,j} \quad ,$$

where the summation must be carried out over all the occupied molecular orbitals which involve both the atoms.

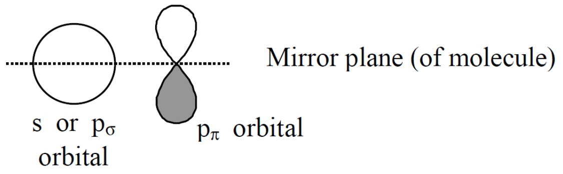
6. Hückel Theory

The Hückel method or Hückel molecular orbital method (HMO), proposed by Erich Hückel (August 9, 1896, Berlin - February 16, 1980, Marburg) in 1930, is a very simple linear combination of atomic orbitals molecular orbitals (LCAO MO) method for the determination of energies of molecular orbitals of π-electrons in conjugated hydrocarbon systems, such as ethene, benzene and butadiene. It is the theoretical basis for the Hückel's rule. It was later extended to conjugated molecules such as pyridine, pyrrole and furan that contain atoms other than carbon, known in this context as heteroatoms. The theory was originally introduced to permit qualitative study of the π-electron systems in planar, conjugated hydrocarbon molecules (i.e. in "flat" hydrocarbon molecules which possess a mirror plane of symmetry containing all the carbon atoms, and in which the atoms of the carbon skeleton are linked by alternating double and single carbon-carbon bonds when the bonding is represented in a localized fashion). It is thus -as mentioned above- most appropriate for molecules such as benzene or butadiene, but the approach and concepts have wider applicability.

6.1. Basic Assumptions

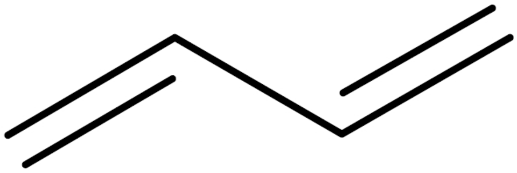
First Assumption

The atomic orbitals contributing to the π-bonding in a planar molecule (e.g. the so-called p_x-orbitals in a molecule such as benzene) are antisymmetric with respect to reflection in the molecular plane; they are therefore of a different symmetry to the atomic orbitals contributing to the σ-bonding and may be treated independently.



Second Assumption

The Coulomb integrals for all the carbon atoms are assumed to be identical, i.e. small differences in α-values due to the different chemical environment of carbon atoms in a molecule such as



are neglected.

Third Assumption

All resonance integrals between directly-bonded atoms are assumed to be the same; whilst those between atoms that are not directly bonded are neglected, i.e.

$$\begin{aligned}\int \phi_i \mathscr{H} \phi_j \cdot \mathrm{d}\tau &= \beta \ \text{: if atoms } i \text{ and } j \text{ are directly } \sigma\text{-bonded,} \\ &= 0 \ \text{: if atoms } i \text{ and } j \text{ are non-bonded.}\end{aligned}$$

Fourth Assumption

Alle overlap integrals representing the overlap of atomic orbitals centered on different atoms are neglected, i.e.

$$\int \phi_i \phi_j \cdot \mathrm{d}\tau = 0 \ \text{: if } i \neq j \ .$$

Note, that if $i \neq j$, then

$$\int \phi_i \phi_j \cdot \mathrm{d}\tau = 1 \ ,$$

since it is assumed that the atomic orbitals are normalized.

6.2. A Closer Look at the Secular Determinant

The basic form of the secular determinant for the bonding arising from the overlap of two orbitals (from page 35) is reproduced below:

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{12} & \alpha_2 - E \end{vmatrix} = 0$$

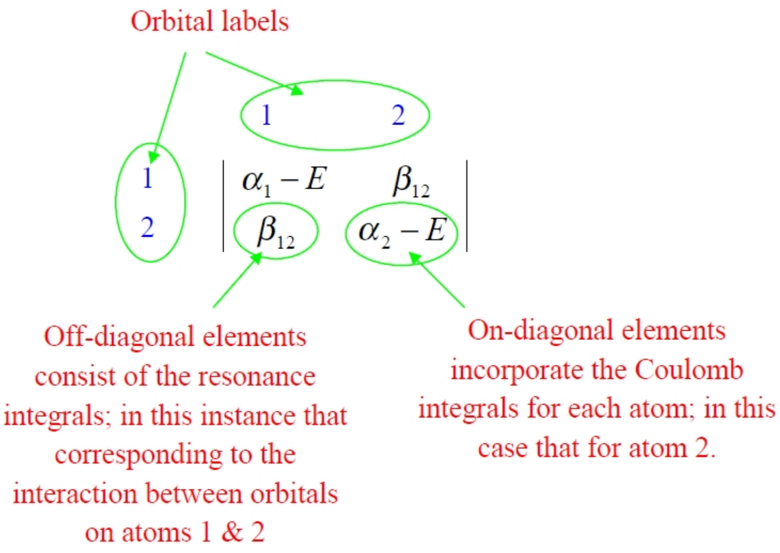
For three overlapping orbitals the approach outlined in Chapter 4 leads to a secular determinant of the form:

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} \\ \beta_{12} & \alpha_2 - E & \beta_{23} \\ \beta_{13} & \beta_{23} & \alpha_3 - E \end{vmatrix} = 0$$

From a comparison of the two secular determinants given above, it is becoming clear that all such secular determinants have a characteristic structure:

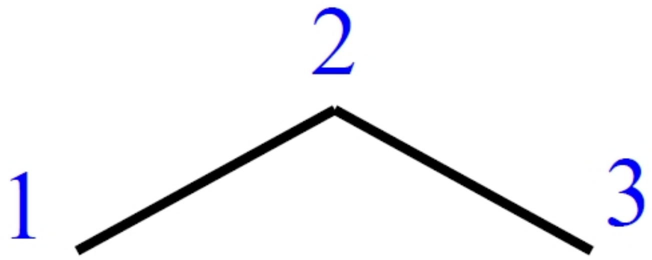
1. Each row and column may be associated with one of the atomic orbitals; thus the first row and first column contain information about the nature of orbital 1 and its interactions with the other orbitals, the second row and second column contain information about the nature of orbital 2 and its interactions with the other orbitals.
2. The diagonal set of elements (comprised of those elements where row 1 intersects column 1, row 2 intersects column 2, . . . and so on) include the values of the relevant Coulomb integrals (α_1, α_2, etc.).
3. The off-diagonal elements (comprised of those elements having different row numbers and column numbers) are equal to the relevant resonance integrals (e.g. β_{12} at the intersection of row 1 and column 2).

This structure is summarized below, where the rows and columns have been labeled with numbers identifying the associated atomic orbital:


Orbital labels
1
2
1
2
$\alpha_1 - E$
β_{12}
β_{12}
$\alpha_2 - E$
Off-diagonal elements consist of the resonance integrals; in this instance that corresponding to the interaction between orbitals on atoms 1 & 2
On-diagonal elements incorporate the Coulomb integrals for each atom; in this case that for atom 2.

6.3. Linear Conjugated Hydrocarbons

6.3.1. C_3 Molecules (3-atom chain)



Secular Determinant / Equation

$$\begin{array}{c|ccc|}
 & 1 & 2 & 3 \\
1 & \alpha - E & \beta & 0 \\
2 & \beta & \alpha - E & \beta \\
3 & 0 & \beta & \alpha - E
\end{array} = 0$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \text{ where } x = \frac{(\alpha - E)}{\beta}$$

$$\Rightarrow 0 = x \cdot (x \cdot x - 1 \cdot 1) - 1 \cdot (1 \cdot x - 1 \cdot 0) + 0 \cdot (1 \cdot 1 - x \cdot 0)$$

$$\Rightarrow 0 = x^3 - x - x$$

$$\Rightarrow 0 = x^3 - 2x$$

$$\Rightarrow 0 = x \cdot \left(x^2 - 2\right)$$

$$\Rightarrow x_1 = 0 \text{ or } x_{2,3} = \pm\sqrt{2}$$

i.e. $x = +\sqrt{2}, 0, -\sqrt{2}$.

Now, from the equation above, the following is valid:

$$E = \alpha - x \cdot \beta \ . \tag{6.1}$$

So the energies of the molecular orbitals are:

$$\begin{aligned}
&E = \alpha - \sqrt{2} \cdot \beta \ \text{Highest Energy} \\
&E = \alpha \\
&E = \alpha + \sqrt{2} \cdot \beta \ \text{Lowest Energy}
\end{aligned}$$

The secular equations are:

$$\begin{aligned}
c_1 \cdot (\alpha - E) + c_2 \beta + 0 &= 0 \\
c_1 \beta + c_2 \cdot (\alpha - E) + c_3 \beta &= 0 \\
0 + c_2 \beta + c_3 \cdot (\alpha - E) &= 0
\end{aligned}$$

or, in terms of x:

$$c_1 x + c_2 + 0 = 0 \tag{6.2}$$

$$c_1 + c_2 x + c_3 = 0 \tag{6.3}$$

$$0 + c_2 + c_3 x = 0 \tag{6.4}$$

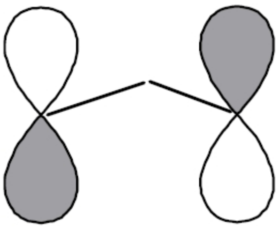
For $x = 0$, i.e. $E = \alpha$, it follows from equation (6.2), (6.3) and (6.4):

$$\begin{aligned}
(6.2) &\Rightarrow c_2 = 0 \\
(6.3) &\Rightarrow c_1 + c_3 = 0 \quad \Rightarrow c_1 = -c_3 \ .
\end{aligned}$$

If we now apply the normalization condition $\left(\sum_i c_i^2 = 1\right)$, then it follows, that

$$|c_1| = |c_3| = \frac{1}{\sqrt{2}} \ ,$$

i.e.



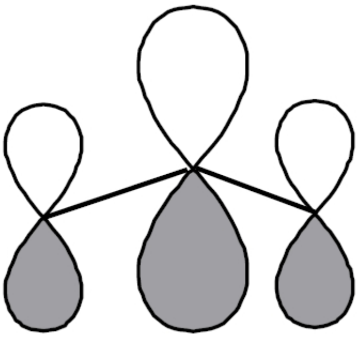
For $x = -\sqrt{2}$, i.e. $E = \alpha + \sqrt{2}\cdot\beta$, the following results according to equation (6.2), (6.3) and (6.4) are obtained:

$$\begin{aligned} (6.2)-(6.4) &\Rightarrow c_1 - c_3 = 0 \quad \Rightarrow c_1 = c_3 \\ (6.2) &\Rightarrow -\sqrt{2}\cdot c_1 + c_2 = 0 \quad \Rightarrow c_2 = \sqrt{2}\cdot c_1 \quad . \end{aligned}$$

If we now apply the normalization condition $\left(\sum_i c_i^2 = 1\right)$, then it follows (see Appendix C), that

$$\begin{aligned} &\sum_i c_i^2 = c_1^2 + c_2^2 + c_3^2 = c_1^2 + \left(\sqrt{2}\cdot c_1\right)^2 + c_1^2 = 4\cdot c_1^2 \\ &\Rightarrow c_1^2 = \frac{1}{4} \\ &\Rightarrow c_1 = c_3 = \frac{1}{2} \\ &\Rightarrow c_2 = \sqrt{2}\cdot\frac{1}{2} = \frac{1}{\sqrt{2}} \quad , \end{aligned}$$

i.e.



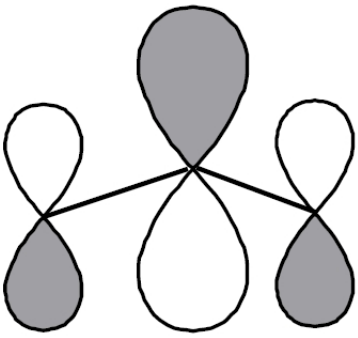
For $x = +\sqrt{2}$, i.e. $E = \alpha - \sqrt{2} \cdot \beta$, the following results according to equation (6.2), (6.3) and (6.4) are obtained:

$$\begin{aligned} (6.2) - (6.4) &\Rightarrow c_1 - c_3 = 0 \quad \Rightarrow c_1 = c_3 \\ (6.2) &\Rightarrow \sqrt{2} \cdot c_1 + c_2 = 0 \quad \Rightarrow c_2 = -\sqrt{2} \cdot c_1 \quad . \end{aligned}$$

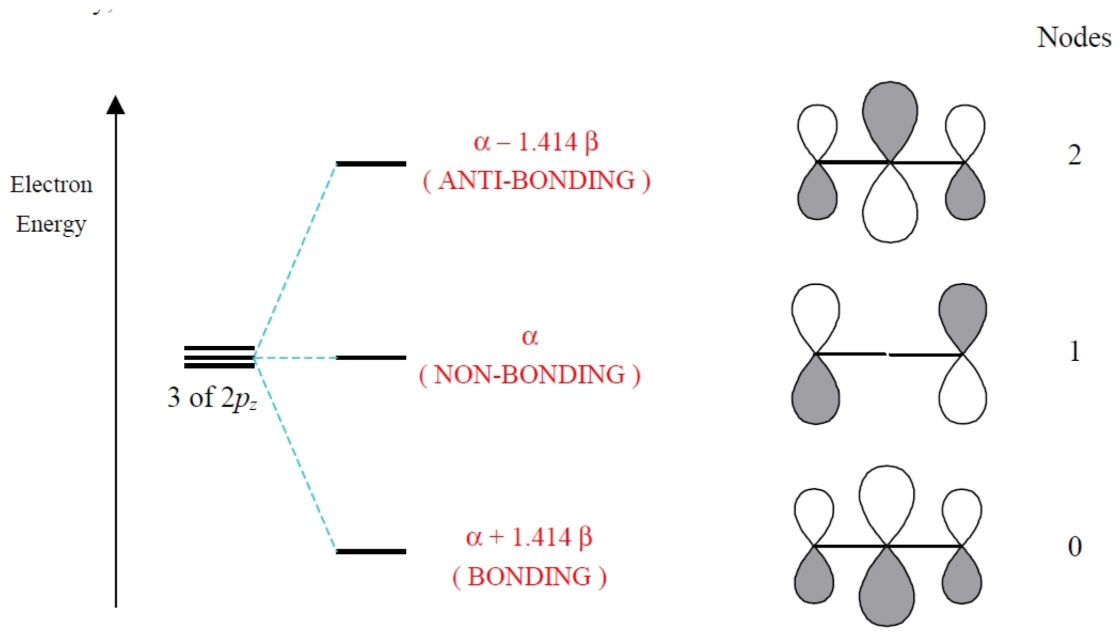
If we now apply the normalization condition $\left(\sum_i c_i^2 = 1\right)$, then it follows (see Appendix C), that

$$\begin{aligned} &\Rightarrow c_1 = c_3 = \frac{1}{2} \\ &\Rightarrow c_2 = -\frac{1}{\sqrt{2}} \quad , \end{aligned}$$

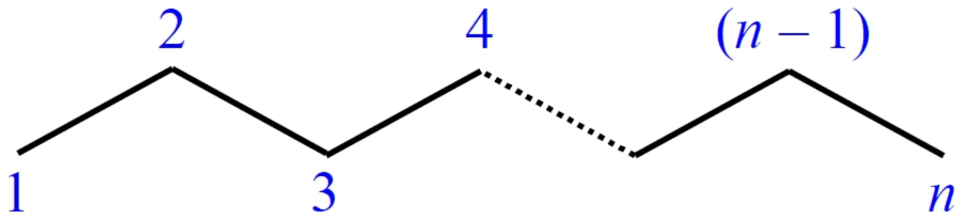
i.e.



In summary, it follows the bond order and charge distribution calculations for allylic species.


Nodes
Electron
Energy
α − 1.414 β
(ANTI-BONDING)
2
α
(NON-BONDING)
1
3 of $2p_z$
α + 1.414 β
(BONDING)
0

6.3.2. General Solution (n-atom chain, e.g. C_nH_{n+2} conjugated polyenes)



The secular determinant has the same basic form, whatever the chain length, as illustrated below:

$$
\begin{array}{c|cccccc|}
 & 1 & 2 & 3 & & & n \\
1 & x & 1 & 0 & 0 & \dots & 0 \\
2 & 1 & x & 1 & & & \\
3 & 0 & 1 & x & & & \\
 & 0 & & & & & \\
 & & & & & x & 1 \\
n & 0 & \dots & \dots & \dots & 1 & x
\end{array}
$$

Consequently the solutions also have the same basic form, whatever the chain length, and it can be demonstrated that the **Orbital Coefficients** are given by

$$c_s \propto \sin\left(\frac{\pi k s}{n+1}\right) \quad , \tag{6.5}$$

where

n	total number of atoms in the conjugated chain,
s	atom number (i.e. 1, 2, $\dots n$),
k	quantum number, identifying the MO ($= 1, 2, \dots, n$)

and the constant of proportionality can be determined by applying the normalization condition.
Example: consider the highest energy MO ($k = 3$) of the three carbon chain ($n = 3$). Then it follows that

$$c_s \propto \sin\left(\frac{3\pi s}{4}\right) \quad ,$$

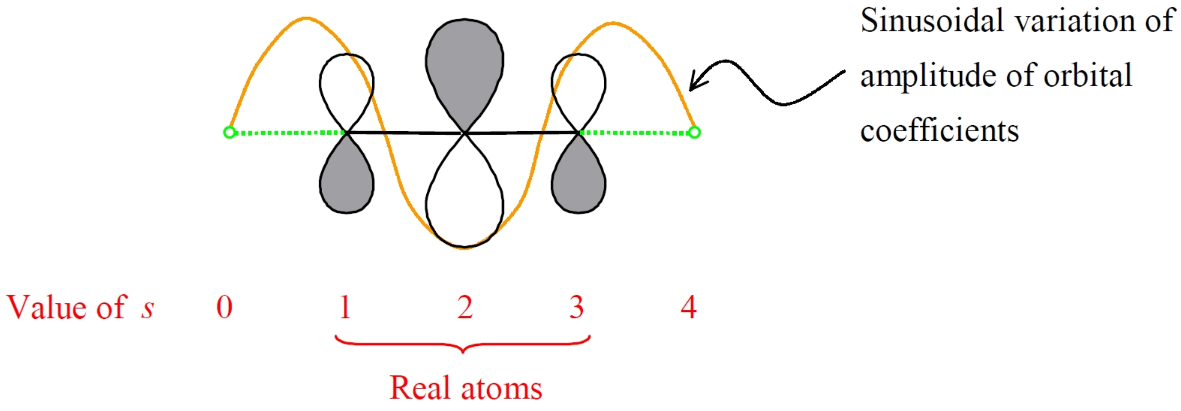
i.e.

$$c_1 \propto \sin\left(\frac{3\pi}{4}\right) = \frac{1}{\sqrt{2}}, \ c_2 \propto \sin\left(\frac{6\pi}{4}\right) = -1, \ c_3 \propto \sin\left(\frac{9\pi}{4}\right) = \frac{1}{\sqrt{2}} \ .$$

These coefficients are not normalized. To achieve this, we need to multiply them all by the same constant value, chosen to ensure that the new values of the coefficients satisfy the condition that $\sum_i c_i^2 = 1$. From the general expression for the coefficients given above it can be seen that the relative signs and sizes can also be visualized using the following trigonometric construction.
Procedure:

1. Draw the n-regularly spaced atoms (1, 2, ..., n) in a straight line and then add two imaginary atoms (labeled 0 and $(n+1)$) at either end of the chain.
2. Sketch portions of sine waves between these two imaginary end atoms, ensuring that the imaginary end atoms correspond to nodes of the sine wave.
3. The lowest energy MO has no other nodes and corresponds to half a sine wave; the next MO has one additional node in the middle and corresponds to a complete sine wave; the next MO has two additional nodes ... and so on.

E.g., for the third MO ($k = 3$) of the three carbon chain ($n = 3$), the result is:



The **Orbital Energies** are given by

$$E = \alpha + 2\beta \cdot \cos\left(\frac{\pi k}{n+1}\right) \ , \tag{6.6}$$

where

n total number of atoms in the conjugated chain,
k quantum number, identifying the MO $(= 1, 2, \ldots, n)$.

Note that the cosine function varies only between the limiting values of -1 and $+1$, i.e.

$$-1 \leqslant \cos\left(\frac{\pi k}{n+1}\right) \leqslant +1 \quad ,$$

hence

$$(\alpha + 2\beta) \leqslant E \leqslant (\alpha - 2\beta) \quad .$$

Consequently, all molecular orbital energies must lie within an energy range of 4β, $\pm 2\beta$ of the original atomic orbital energy.
Recall also that for an n-atom chain, in which each atom contributes one atomic orbital to the conjugated π-system, there will be n overlapping atomic orbitals giving rise to n molecular orbitals. Since all these MOs are confined to a fixed energy range, it follows that the average energy separation must decrease as n increases. This is illustrated below in an electron energy diagram which also shows the electron occupancy (for the neutral molecule) for the first three members of the series:

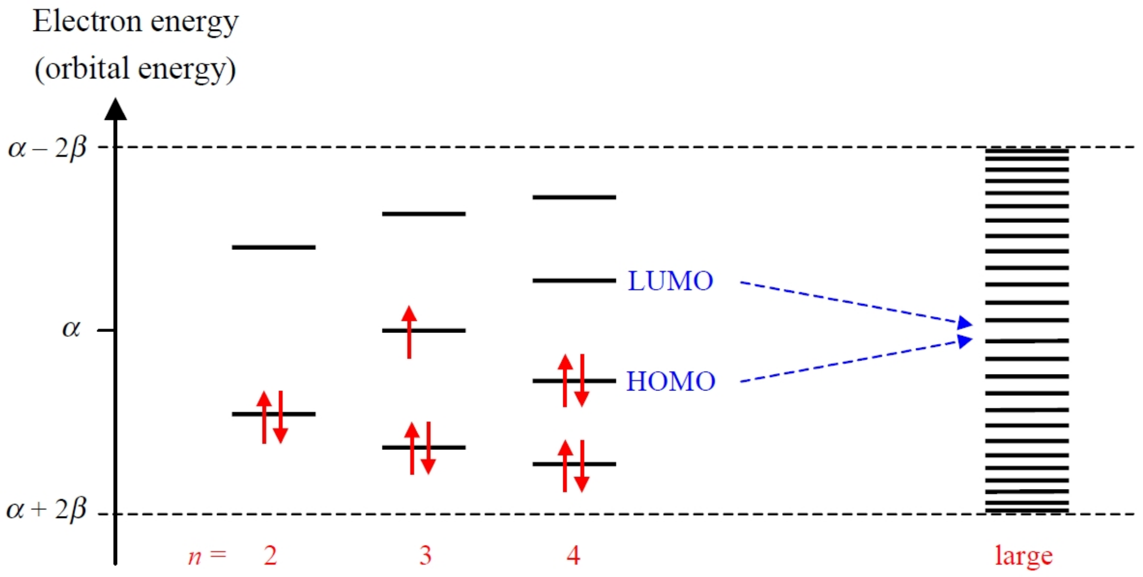


Figure 6.1.
Electron energy diagram

Note:

1. As n increases: the HOMO-LUMO[1] separation decreases - consequently the photon energy required to excite an electron from the HOMO to LUMO also decreases. I.e., $h \cdot v = \Delta E = E_{HOMO} - E_{LUMO}$ decreases as n increases. For conjugated carbon atom chains the photon energy changes from the ultra violet[2] (for small n) to the visible range of light[3] (large n). Consequently, molecules with extended conjugated systems are colored.
2. As $n \rightarrow \infty$: the separation between any two energy levels decreases towards zero and the energy levels (although still discrete in principle) effectively merge to give a continuous band of energy levels. The width of this band is 4β and is therefore determined by the effectiveness of overlap of the individual atomic orbitals and hence the strength of interaction and the magnitude of the resonance integral β. The system approaches the *metallic state* - that is to say that electrical conduction can readily occur (since the HOMO-LUMO separation is essentially zero) and all wavelengths λ of visible light are readily absorbed.

---

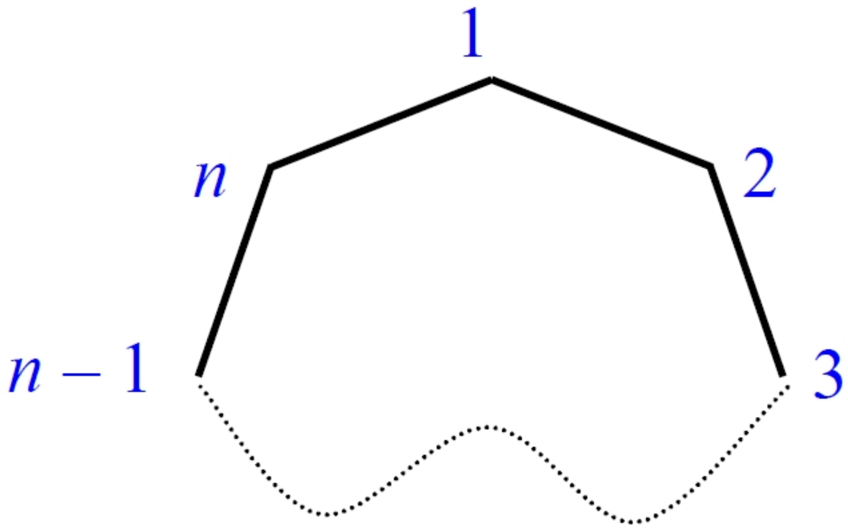
[1] HOMO - Highest Occupied Molecular Orbital, LUMO - Lowest Unoccupied Molecular Orbital

[2] λ = 400 nm to 10 nm

[3] λ = 400 nm to 700 nm

6.4. Cyclic Conjugated Hydrocarbons

6.4.1. General Solution (n-atom ring; C_nH_n, cyclic conjugated hydrocarbons)



The secular determinant has the same basic form, whatever the ring size, as illustrated below:

$$\begin{array}{c|cccccc|} & 1 & 2 & 3 & & & n \\ 1 & x & 1 & 0 & 0 & \dots & 1 \\ 2 & 1 & x & 1 & & & \\ 3 & 0 & 1 & x & & & \\ & 0 & & & & & \\ & & & & & x & 1 \\ n & 1 & \dots & \dots & \dots & 1 & x \end{array} = 0$$

Consequently, the solutions also have the same basic form, whatever the ring size, and it can be demonstrated that the **Orbital Energies** are given by

$$E = \alpha + 2\beta \cdot \cos\left(\frac{2\pi k}{n}\right) \ , \tag{6.7}$$

where

n total number of atoms in the conjugated ring system,
k quantum number, identifying the MO $(= 1, 2, \ldots, n-1)$,

but, given the periodic and "even" (symmetrical about $\theta = 0$) nature of the cosine function, this permitted range of k-values may also be written in the form

$$k = 0,\ \pm1,\ \pm2,\ \ldots,\ \left(\frac{n}{2}\right) \ \text{for even } n,$$
$$k = 0,\ \pm1,\ \pm2,\ \ldots,\ \pm\left(\frac{n-1}{2}\right) \ \text{for odd } n.$$

Note, that the cosine function varies only between the limiting values of -1 and $+1$, and because the cosine function is an even function, the energy depends only on $|k|$, i.e.

$$-1 \leqslant \cos\left(\frac{2\pi k}{n}\right) \leqslant +1$$

hence

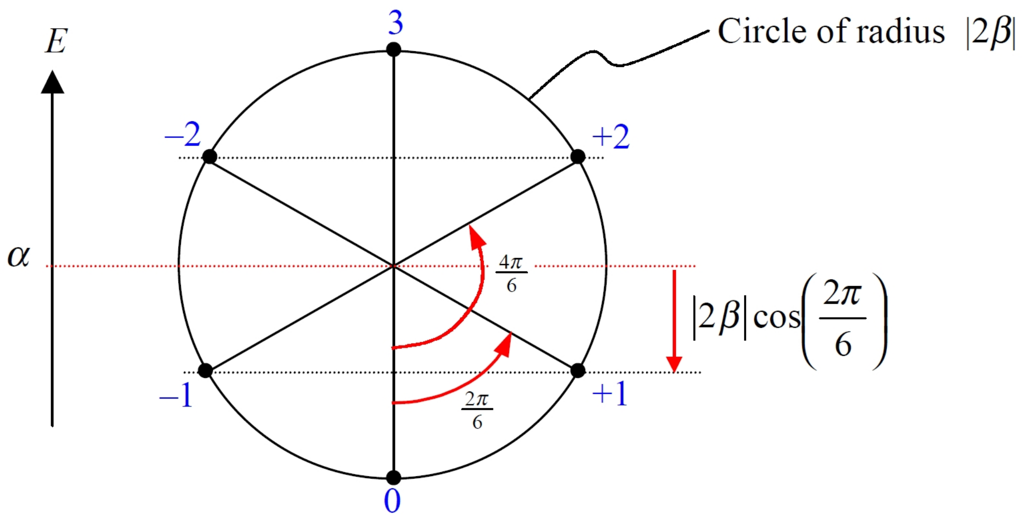
$$(\alpha + 2\beta) \leqslant E \leqslant (\alpha - 2\beta) \ .$$

It is possible to represent equation (6.7) as a geometrical construction, and this is illustrated below. Consider $n = 6$ (e.g. C_6H_6 - benzene). The expression for E is then given by

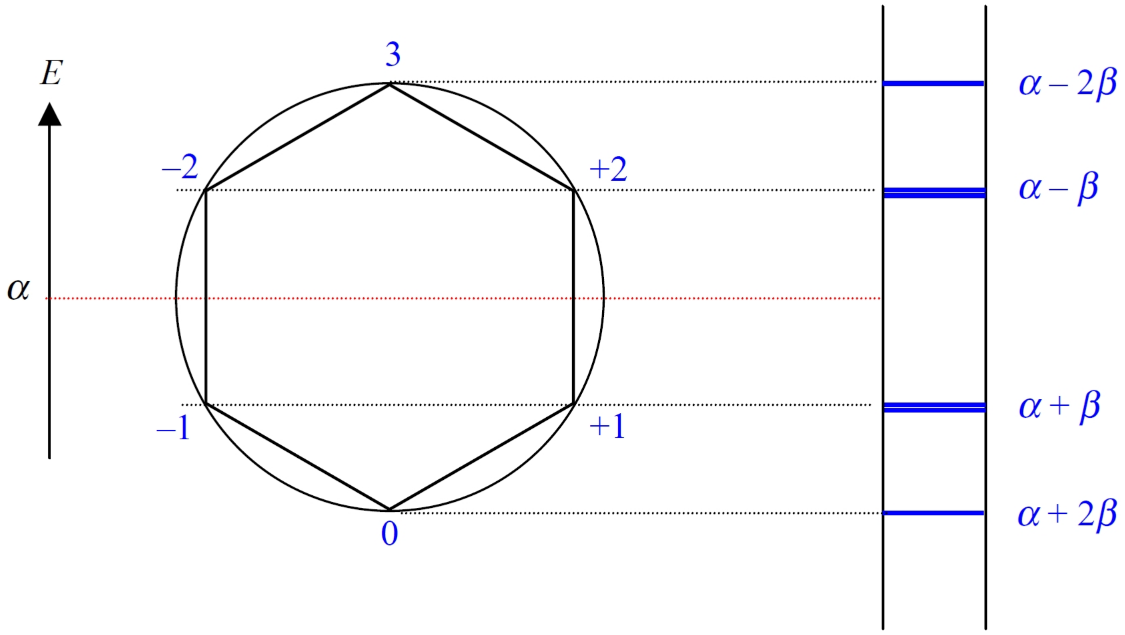
$$E = \alpha + 2\beta \cdot \cos\left(\frac{2\pi k}{6}\right) \ ,$$

where

$$k = 0,\ \pm1,\ \pm2,\ 3 \ \text{ since } n \text{ is even.}$$


E
α
3
−2
+2
−1
+1
0
Circle of radius $|2\beta|$
$\frac{4\pi}{6}$
$\frac{2\pi}{6}$
$|2\beta|\cos\left(\frac{2\pi}{6}\right)$

Whilst the above diagram highlights the relationship between the geometrical construction and the equation for E, it also suggests that the energies of the orbitals may also be obtained using a simpler construction, namely by drawing the corresponding regular polyhedron (i.e. a hexagon for $n = 6$) inscribed inside the circle with one apex coincident with the bottom of the circle.


E
α
3
−2
+2
−1
+1
0
$\alpha - 2\beta$
$\alpha - \beta$
$\alpha + \beta$
$\alpha + 2\beta$

Note: for these cyclic conjugated systems

1. The lowest energy MO is always non-degenerate.
2. The highest energy MO may be non-degenerate (if n is even) or degenerate (if n is odd).
3. All the remaining solutions form pairs of degenerated MOs.

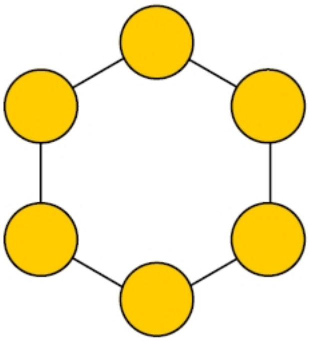
One consequence of this arrangement of the MOs is, that only specific numbers of electrons can be accommodated if a stable molecule is to result. This important observation is embodied in the . . .

Hückel Rule
A stable, closed-shell conjugated cyclic structure is obtained for $(4N+2,\ N \in \mathbb{N}_0 = \mathbb{N} \cup \{0\})$ electrons, i.e. stable structures are obtained for 2, 6, 10, . . . electrons.

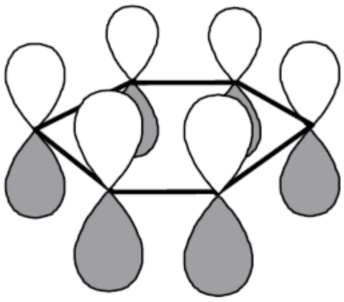
6.4.2. What are the wave functions?

The wave functions are generally complex (i.e. contain imaginary parts), the exceptions being the non-degenerate solution(s).

- The MO of lowest energy ($k = 0$) is always non-degenerate (irrespective of whether n is even or odd) and has the same coefficient for each and every contributing atomic orbital - there are therefore no angular nodes in the wave function. E.g. for $n = 6$ this gives



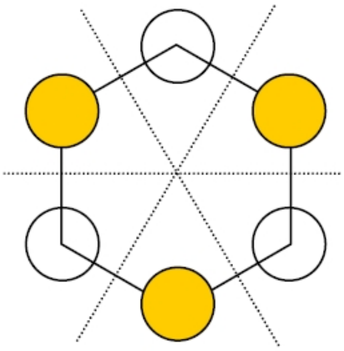
Top view



Side view

The molecular plane is a nodal plane for all the π-MOs, but for this particular MO there are no angular nodal planes in the wave function and all the interactions between orbitals on adjacent atoms are of a bonding nature.

- The highest energy MO of even n systems is also non-degenerate. The magnitude of the coefficient is the same for each and every contributing atomic orbital but the sign changes between adjacent atoms. E.g. for $n = 6$ this gives



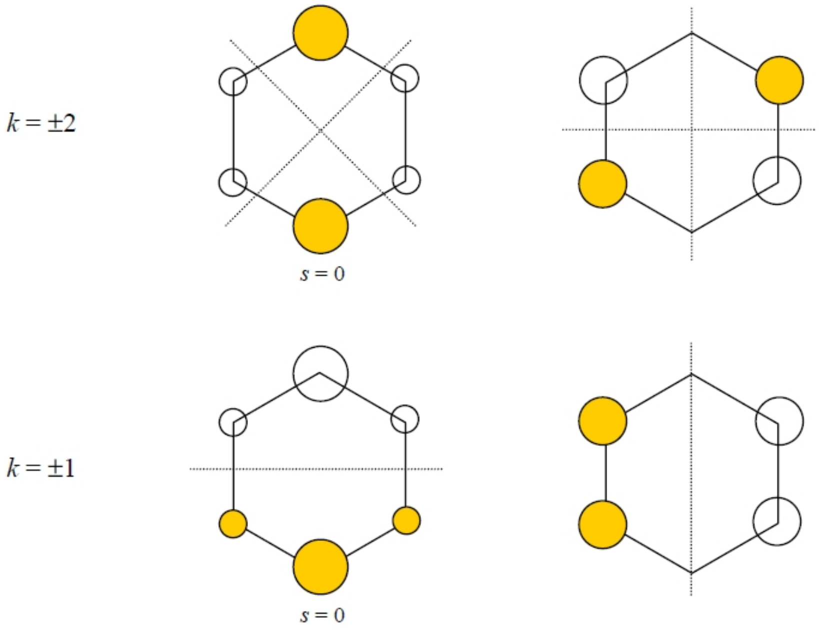
  In this case there are three angular nodal planes as marked (—) on the diagram - the wave function thus changes sign between each pair of atoms and all the interactions between orbitals on adjacent atoms are of an anti-bonding nature.

- The remaining degenerate pairs of solutions are complex wave functions, but it is possible to generate completely real linear combinations of these which are still solutions of the Schrödinger equation with the same energies (in the same way that the p_x and p_y atomic orbitals may be constructed from the p_+ and p_- atomic orbitals). The coefficients for the real functions are:

$$\psi_{k+} \propto \sum_s \left(\cos\left(\frac{2\pi k s}{n}\right)\right) \cdot \phi_s$$

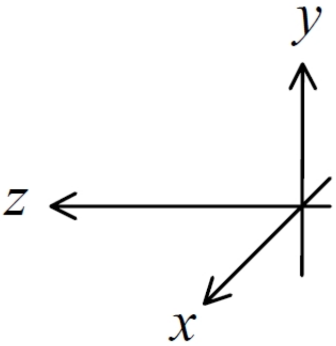
$$\psi_{k-} \propto \sum_s \left(\sin\left(\frac{2\pi k s}{n}\right)\right) \cdot \phi_s$$

E.g. for $n = 6$ this gives



7. Symmetry and Hybridisation

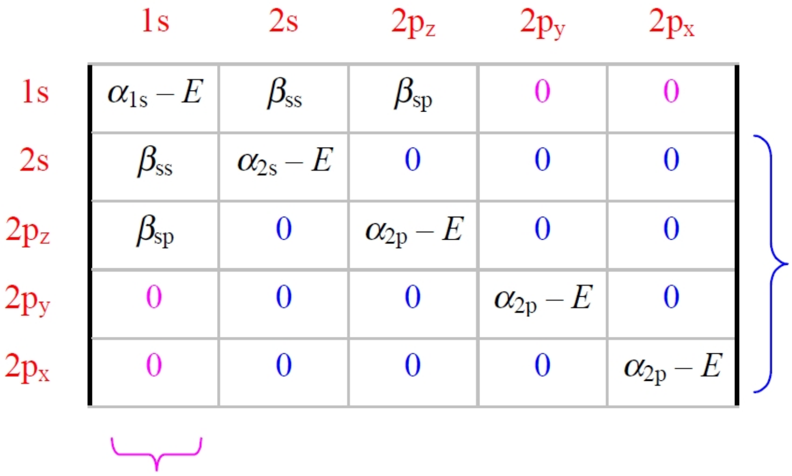
As the size of a molecule increases (and the number of valence atomic orbitals contributing to the bonding increases) then the solution of the secular equations can become rather difficult. But consideration of molecular symmetry can be used to greatly simplify the problem.
To illustrate this, consider a simple example - a diatomic molecule HX (where X = Li, Be, B, C, N, O, F).



The valence orbitals of the atoms concerned are:

H	1s
X	2s, $2p_x$, $2p_y$, $2p_z$, .

The interactions of the five valence orbitals can be described using a (5 × 5) secular determinant.



$$\begin{array}{c|ccccc|}
 & 1s & 2s & 2p_z & 2p_y & 2p_x \\
\hline
1s & \alpha_{1s} - E & \beta_{ss} & \beta_{sp} & 0 & 0 \\
2s & \beta_{ss} & \alpha_{2s} - E & 0 & 0 & 0 \\
2p_z & \beta_{sp} & 0 & \alpha_{2p} - E & 0 & 0 \\
2p_y & 0 & 0 & 0 & \alpha_{2p} - E & 0 \\
2p_x & 0 & 0 & 0 & 0 & \alpha_{2p} - E \\
\hline
\end{array}$$

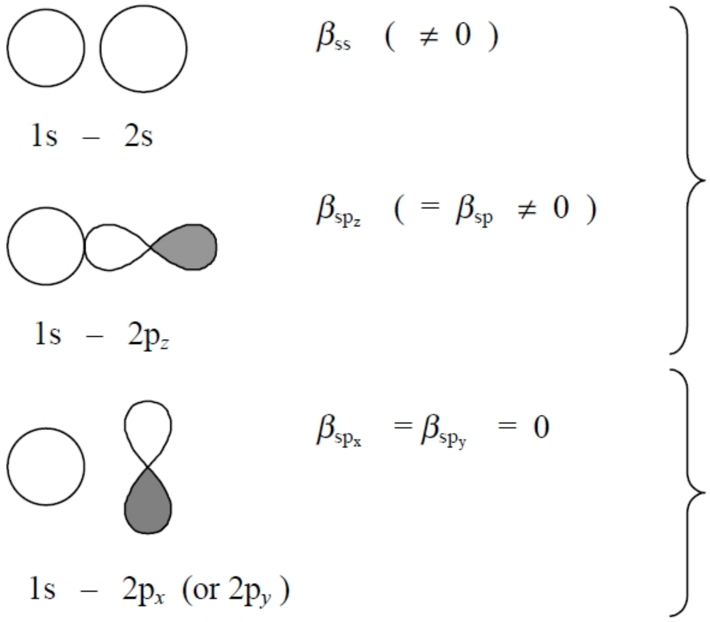
AOs of the X-atom are orthogonal - hence they "can't interact with each other"

H 1*s* will only give a non-zero resonance integral when it overlaps with the 2*s* and 2p_z orbitals of the X atom - see below.

The off-diagonal elements in the determinant may be obtained by noting that:

1. Integrals involving two different orbitals of the X atom are exactly zero, since the atomic orbitals are orthogonal to one another.
2. The resonance integrals due to the interactions of the H 1s orbital with the orbitals of the X atom are only non-zero if the orbitals have the "same symmetry" (that is, the same symmetry within the point group of the molecule).
   Conversely, if the two overlapping orbitals are of different symmetries then any constructive overlap of the orbitals is always exactly counterbalanced by an equal amount of destructive overlap and the net interaction is always exactly zero.

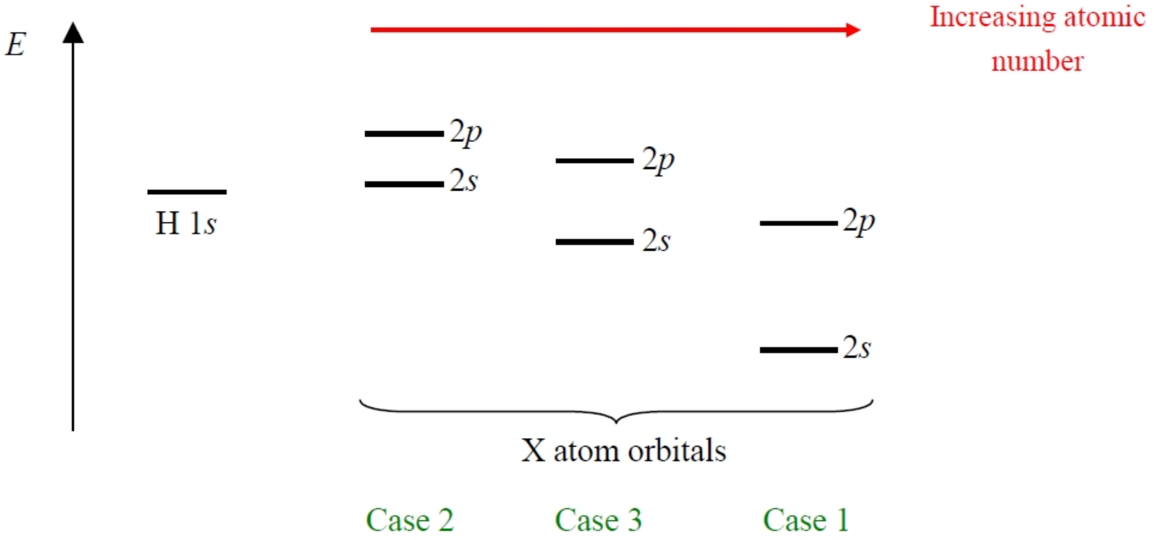
. . . these two contrasting situations are illustrated below.


β_{ss} ($\neq 0$)
1s – 2s
β_{sp_z} ($= \beta_{sp} \neq 0$)
1s – 2p$_z$
$\beta_{sp_x} = \beta_{sp_y} = 0$
1s – 2p$_x$ (or 2p$_y$)

The H 1s orbitals and the X 2s and $2p_z$ orbitals all have the same symmetry (σ^+) in the molecular point group ($C_{\infty v}$)

The H 1s orbitals and X $2p_x$, $2p_y$ orbitals have different symmetries (σ^+ and π respectively in $C_{\infty v}$)

Consequently, in this case, rows 4 and 5 have no (non-zero) off-diagonal elements, because the $2p_x$ and $2p_y$ orbitals are of different symmetry to the H 1s orbital. The (5 × 5) secular determinant can therefore be simplified to two trivial (1 × 1) determinants and a (3 × 3) determinant.

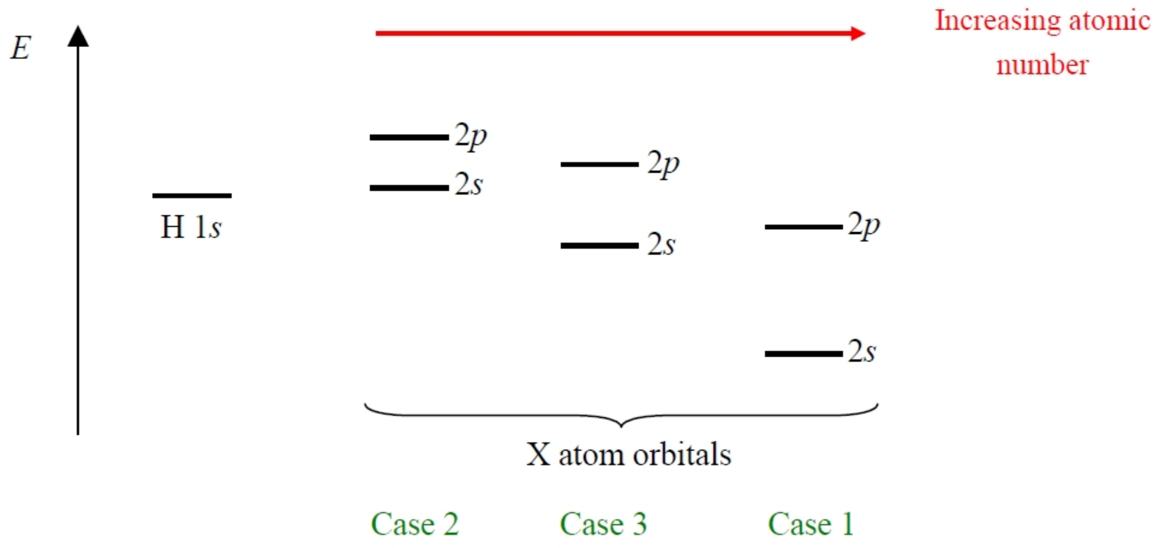

E
Increasing atomic number
H 1s
2p
2s
2p
2s
2p
2s
X atom orbitals
Case 2
Case 3
Case 1

$$\left|(5\times 5)\right| = 0 \quad \begin{cases} |\alpha_{2p} - E| = 0 \quad \Rightarrow E = \alpha_{2p_x} \\[2ex] |\alpha_{2p} - E| = 0 \quad \Rightarrow E = \alpha_{2p_y} \\[2ex] \begin{vmatrix} \alpha_{1s} - E & \beta_{ss} & \beta_{sp} \\ \beta_{ss} & \alpha_{2s} - E & 0 \\ \beta_{sp} & 0 & \alpha_{2p} - E \end{vmatrix} = \quad 0 \end{cases}$$

We can conclude that in this molecule, the $2p_x$ and $2p_y$ orbitals of the X atom are non-bonding, and more generally that it is only necessary to consider interactions between orbitals possessing the same symmetry in the molecular environment.

7.1. Solution of the (3×3) Determinant

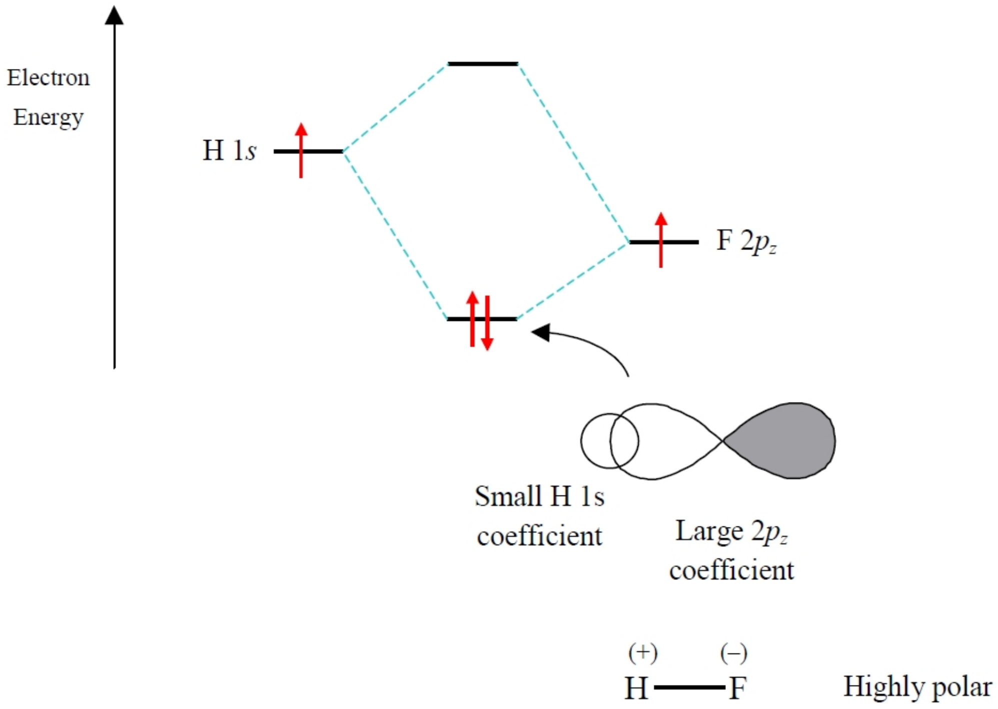
Strictly any solution necessarily involves both the 2s and $2p_z$ orbitals of the X atom. However, the extent to which each is involved depends upon the energies of the orbitals relative to that of the 1s orbital of the H atom, and this varies significantly across the periodic table.



The above diagram illustrates how the relative orbital energies might vary for different X atoms; we now need to remember (see 45) that there is only a significant bonding interaction between two orbitals if the energy separation, $|\alpha_2 - \alpha_1|$ is not large compared

to the interaction energy, as represented by the resonance integral, β_{12}.
We can therefore identify three "limiting" cases:

Case 1:
The main interaction is H 1s - X $2p_z$, . . . and if we completely neglect any interaction with X 2s then the problem simplifies to a 2×2 determinant. E.g. for HF (Hydrogen fluoride) we get


Electron
Energy
H 1s
F $2p_z$
Small H 1s coefficient
Large $2p_z$ coefficient
(+) (−)
H—F
Highly polar

Case 2:
The main interaction is H 1s - X 2s . . . and if we completely neglect any interaction with X $2p_z$ then the problem again simplifies to a (2×2) determinant. This limiting case is most closely approached for LiH (Lithium hydride).

Case 3:
This is the intermediate case. To illustrate what sort of solutions might be obtained in this case we can consider a "model" system (obtained by making some drastic simplifying assumptions). Let us suppose that:

$$\alpha_{2s} = \alpha_{1s} + \frac{1}{2} \cdot \beta$$
$$\alpha_{2p} = \alpha_{1s} - \frac{1}{2} \cdot \beta$$

and $\beta_{ss} = \beta_{sp}$ and, for simplicity, we just call this β.

Then

$$\begin{vmatrix} \alpha_{1s} - E & \beta_{ss} & \beta_{sp} \\ \beta_{ss} & \alpha_{2s} - E & 0 \\ \beta_{sp} & 0 & \alpha_{2p} - E \end{vmatrix} = 0$$

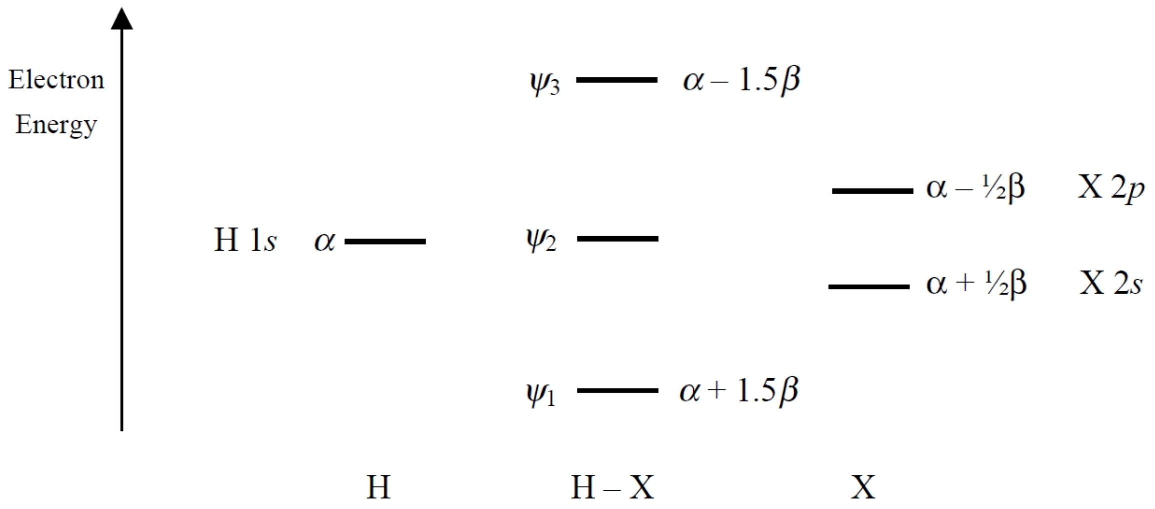
simplifies to

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \left(\alpha + \frac{1}{2} \cdot \beta\right) - E & 0 \\ \beta & 0 & \left(\alpha - \frac{1}{2} \cdot \beta\right) - E \end{vmatrix} = 0$$

where α is the value for α_{1s}. This yields, by dividing through β, and with the definition of x according to equation (6.1) the following determinant:

$$\begin{vmatrix} x & 1 & 1 \\ 1 & \left(x + \frac{1}{2}\right) & 0 \\ 1 & 0 & \left(x - \frac{1}{2}\right) \end{vmatrix} = 0$$

to which the solutions are

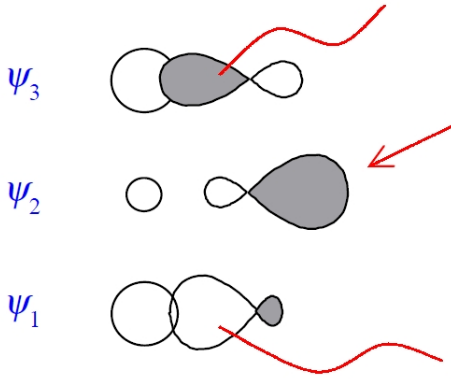

Electron Energy
ψ_3
$\alpha - 1.5\beta$
$\alpha - ½\beta$
X 2*p*
H 1*s*
α
ψ_2
$\alpha + ½\beta$
X 2*s*
ψ_1
$\alpha + 1.5\beta$
H
H – X
X

Now consider the MO coefficients

	H 1s	X 2s	X $2p_z$
ψ_3	0.67	–0.33	–0.67
ψ_2	0.33	–0.67	0.67
ψ_1	0.67	0.67	0.33

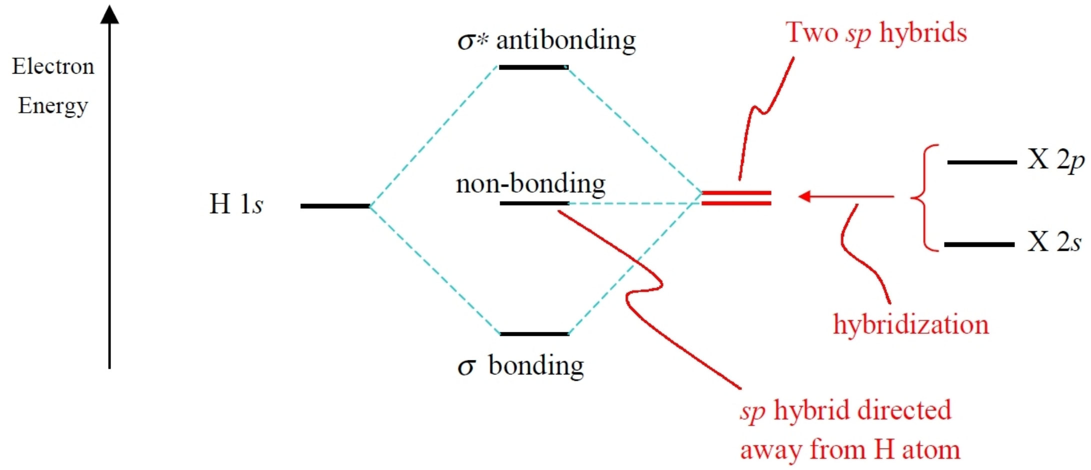
Equivalent to an "sp"-hybrid orbital pointing away from the H atom

More *p* than *s* character.


ψ_3
ψ_2
ψ_1

More *s* than *p* character.

Note, that similar, but not identical, MO energies and orbital coefficients would be predicted using a valence bond approach (as illustrated below) in which we first "hybridize" the 2s and $2p_z$ orbitals of the X atom to give two sp hybrid orbitals and then let the one pointing towards the H atom interact with the H 1s orbital whilst the other is considered to undergo no interaction with the H 1s orbital and may thus be labeled a non-bonding orbital, i.e.


Electron
Energy
H 1s
σ* antibonding
non-bonding
σ bonding
Two sp hybrids
X 2p
X 2s
hybridization
sp hybrid directed
away from H atom

A. The Schrödinger Equation

A.1. The Wave Equation – Explanatory notes

The wave equation is an important second-order linear hyperbolic partial differential equation for the description of waves - as they occur in physics - such as sound waves, shock waves, light waves and water waves. It arises in fields like acoustics, electromagnetic field theory, and fluid dynamics. It is second order with respect to the time like Newton's law, which is stated (with constant mass) as

$$\vec{F}(t) = m \cdot \frac{\mathrm{d}^2 \vec{s}(t)}{\mathrm{d}t^2} \quad .$$

The wave equation in one space dimension can be written according to

$$\frac{\partial^2 y}{\partial t^2} = c^2 \cdot \frac{\partial^2 y}{\partial x^2} \quad . \tag{A.1}$$

It typically contains a time variable t, one or more spatial variables $x_1, x_2, \ldots, x_n$ and a scalar function $\psi = \psi(x_1, x_2, \ldots, x_n; t)$, whose values could model the displacement of a wave. The wave equation in general form for ψ is

$$\frac{\partial^2 \psi}{\partial t^2} = c^2 \Delta^2 \psi \quad , \tag{A.2}$$

where for the scalar function ψ Δ is a scalar differential operator defined by

$$\begin{aligned} \Delta^2 \psi = \frac{1}{h_1 h_2 h_3} \Bigg[& \frac{\partial}{\partial u_1} \left(\frac{h_2 h_3}{h_1} \cdot \frac{\partial}{\partial u_1} \right) \\ & + \frac{\partial}{\partial u_2} \left(\frac{h_1 h_3}{h_2} \cdot \frac{\partial}{\partial u_2} \right) + \frac{\partial}{\partial u_3} \left(\frac{h_1 h_2}{h_3} \cdot \frac{\partial}{\partial u_3} \right) \Bigg] \psi, \end{aligned} \tag{A.3}$$

or (also in Cartesian coordinates in 3 dimensions)

$$\Delta f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \quad , \tag{A.4}$$

that is called the Laplace operator or Laplacian[1] and which is a operator given by the divergence of the gradient of a function on Euclidean space. h_i are the scale factors of the coordinate system and c is a fixed constant.

Solutions of this equation, that are initially zero outside some restricted region propagate out from the region at a fixed speed in all spatial directions, as do physical waves from a localized disturbance. The constant c is therefore usually identified with the propagation speed of the wave, i.e.

$$c = \nu \cdot \lambda \quad , \tag{A.5}$$

and with the period T, defined by

$$T = \frac{1}{\nu} \tag{A.6}$$

is given as

$$c = \frac{\lambda}{T} \quad . \tag{A.7}$$

The Wave equation is linear, as the sum of any two solutions is again a solution of the wave equation. In physics this property is called the superposition principle.

A.2. Derivation of the time independent one-dimensional Schrödinger Wave Equation

Though there is no "real" derivation of the Schrödinger wave equation, it can be done theoretically.

We start with the wave equation in one dimension

$$\frac{\partial^2 y}{\partial t^2} \cdot \mathbf{C} = \frac{\partial^2 y}{\partial x^2} \tag{A.8}$$

for which we seek a solution $y = y(x,t)$, that fulfills the superposition principle. $\mathbf{C}$ is a constant to be determined next. From the above mentioned, it follows, that the solution is assumed to be a sinusoidal function of the form

$$y(x,t) = \sin(\mathbf{k} \cdot x) \cdot \sin(\omega \cdot t) \tag{A.9}$$

---

[1] The Laplace operator is named after the French mathematician Pierre-Simon de Laplace (1749 - 1827)

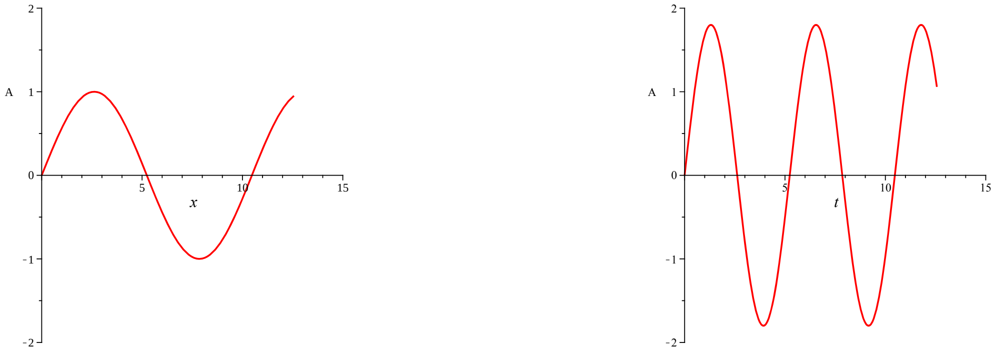


Figure A.1.
1D-Wave Equation in space and time

which is written with the following two expressions

$$\mathbf{k} = \frac{2\pi}{\lambda}$$
$$\omega = 2\pi\nu$$

as

$$y(x,t) = \sin\left(\frac{2\pi}{\lambda}\cdot x\right)\cdot\sin(2\pi\nu\cdot t) \ , \tag{A.10}$$

where ω is the angular frequency and $\mathbf{k}$ is the wave number. Inserting equation (A.10) in equation (A.8) and calculating the first order derivative yields

$$2\pi\nu\cdot\sin\left(\frac{2\pi}{\lambda}\cdot x\right)\cdot\cos(2\pi\nu\cdot t)\cdot\mathbf{C} = \frac{2\pi}{\lambda}\cdot\cos\left(\frac{2\pi}{\lambda}\cdot x\right)\cdot\sin(2\pi\nu\cdot t)$$

in which we have used the laws of differential calculus

$$
\begin{aligned}
&(f \cdot g)' = f' \cdot g + f \cdot g' \\
&(a \cdot f)' = a \cdot f' \\
&\cos'(x) = -\sin(x) \\
&\sin'(x) = \cos(x) \quad .
\end{aligned}
$$

The second order derivative of equation (A.10) is

$$4\pi^2 \nu^2 \cdot \sin\left(\frac{2\pi}{\lambda} \cdot x\right) \cdot -\sin(2\pi\nu \cdot t) \cdot \mathbf{C} = \frac{4\pi^2}{\lambda^2} \cdot -\sin\left(\frac{2\pi}{\lambda} \cdot x\right) \cdot \sin(2\pi\nu \cdot t)$$

which yields

$$\mathbf{C} = \frac{1}{\nu^2 \cdot \lambda^2} \quad . \tag{A.11}$$

This can be rewritten according to equation (A.6) as

$$\mathbf{C} = \frac{1}{\frac{\lambda^2}{T^2}}$$

and using relation (A.7) we finally have

$$\mathbf{C} = \frac{1}{v^2} \quad , \tag{A.12}$$

where v is the propagation speed of the wave.
The a priori unknown solution to the Schrödinger wave equation is assumed to have the sinusoidal form

$$\Psi(x,t) = \psi(x) \cdot \sin(2\pi\nu \cdot t) \quad . \tag{A.13}$$

Inserting equation (A.13) in equation (A.8) and recognizing equation (A.12) gives

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2} \cdot \frac{\partial^2 \Psi}{\partial t^2} \quad . \tag{A.14}$$

Calculation of the first and second order derivatives of equation (A.13) yields

$$\begin{aligned}
\frac{\partial \Psi}{\partial x} &= \frac{\partial \psi(x)}{\partial x} \cdot \sin(2\pi\nu \cdot t) \\
\frac{\partial^2 \Psi}{\partial x^2} &= \frac{\partial^2 \psi(x)}{\partial x^2} \cdot \sin(2\pi\nu \cdot t) \\
\frac{\partial \Psi}{\partial t} &= \psi(x) \cdot 2\pi\nu \cdot \cos(2\pi\nu \cdot t) \\
\frac{\partial^2 \Psi}{\partial t^2} &= \psi(x) \cdot 4\pi^2\nu^2 \cdot -\sin(2\pi\nu \cdot t) \ .
\end{aligned}$$

By inserting the second order derivatives in equation (A.14), we get the following result:

$$\begin{aligned}
\frac{\partial^2 \psi(x)}{\partial x^2} \cdot \sin(2\pi\nu \cdot t) &= 4\pi^2 \cdot \frac{\nu^2}{v^2} \cdot -\sin(2\pi\nu \cdot t) \cdot \psi(x) \\
\frac{\partial^2 \psi(x)}{\partial x^2} + 4\pi^2 \cdot \frac{\nu^2}{v^2} \cdot \psi(x) &= 0 \ . \qquad \text{(A.15)}
\end{aligned}$$

Now we make use of the de Broglie equation, which relates the wavelength λ to the momentum p. We have

$$\lambda = \frac{h}{p} \qquad \text{(A.16)}$$

where h is Planck's constant. For the total energy of the particle we have

$$\mathscr{E}_{tot} = \mathscr{E}_{kin} + \mathscr{E}_{pot} \ ,$$

which is to be determined. Remembering that the momentum p is given by the relation $p = m \cdot v$ and using the energy equation of classical mechanics for a particle and expanding $\mathscr{E}_{tot}$ by $\frac{m}{m}$, we have

$$\begin{aligned}
\mathscr{E}_{kin} &= \frac{1}{2} \cdot m \cdot v^2 \\
&= \frac{1}{2} \cdot m \cdot \frac{m \cdot v \cdot v}{m} \\
&= \frac{p^2}{2 \cdot m} \ .
\end{aligned}$$

As a temporary result we get the following expression for $\mathscr{E}_{tot}$ and p^2 respectively:

$$\begin{aligned} \mathscr{E}_{tot} &= \frac{p^2}{2\cdot m} + \mathscr{E}_{pot} \\ p^2 &= 2\cdot m \cdot \left(\mathscr{E}_{tot} - \mathscr{E}_{pot}\right) \quad . \end{aligned} \tag{A.17}$$

With the de Broglie equation (A.16) written as

$$\lambda^2 = \frac{h^2}{p^2}$$

and setting

$$\frac{v^2}{\nu^2} = \frac{h^2}{p^2} \quad ,$$

because $v = \lambda \cdot \nu$, and inserting this relation in equation (A.15) while bearing in mind relation (A.17) we get

$$\begin{aligned} \frac{\partial^2 \psi(x)}{\partial x^2} + 4\pi^2 \cdot \frac{p^2}{h^2} \cdot \psi(x) &= 0 \\ \frac{\partial^2 \psi(x)}{\partial x^2} + 4\pi^2 \cdot \frac{2m}{h^2} \cdot \left(\mathscr{E}_{tot} - \mathscr{E}_{pot}\right) \cdot \psi(x) &= 0 \quad . \end{aligned}$$

Finally, we get the classical form of the time-independent Schrödinger wave equation in one dimension for a particle:

$$\boxed{\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2} \cdot \left(\mathscr{E}_{tot} - \mathscr{E}_{pot}\right) \cdot \psi(x) = 0} \quad . \tag{A.18}$$

Substituting

$$\hbar = \frac{h}{2\pi} \quad , \tag{A.19}$$

rearranging and multiplying equation (A.18) with (-1), we get

$$-\frac{\hbar}{2\cdot m} \cdot \frac{\partial^2 \psi(x)}{\partial x^2} + \mathscr{E}_{pot} \cdot \psi(x) = \mathscr{E}_{tot} \cdot \psi(x) \quad . \tag{A.20}$$

This again can be rearranged to give

$$\underbrace{\left[-\frac{\hbar}{2\cdot m} \cdot \frac{\partial^2}{\partial x^2} + \mathscr{E}_{pot}\right]}_{Hamiltonian} \cdot \underbrace{\psi(x)}_{Eigenfunction} = \underbrace{\mathscr{E}_{tot}}_{Eigenvalue} \cdot \psi(x) \quad . \tag{A.21}$$

The Hamiltonian operator is the operator corresponding to the total energy of the quantum mechanical system. It is denoted by $\mathscr{H}$, also $\hat{H}$ and is named after Sir William Rowan Hamilton (4 August 1805 - 2 September 1865), an Anglo-Irish physicist, astronomer, and mathematician. $\mathscr{H}$ is the quantum mechanical analogon to the Hamiltonian operator in classical physics. Its spectrum is the set of possible outcomes when one measures the total energy of a system. Because of its close relation to the time-evolution of a system, it is of fundamental importance in most formulations of quantum theory. In general, the Hamiltonian (or any other operator in physics) is a function over the space of physical states. As a result of its application on a physical state, another physical state is obtained, very often along with some extra relevant information.
The Hamiltonian $\mathscr{H}$ is the sum of the kinetic energies of all the particles, plus the potential energy $\mathscr{E}_{pot}$ of the particles associated with the system. For different situations or number of particles, the Hamiltonian is different since it includes the sum of kinetic energies of the particles, and the potential energy function corresponding to the situation.
The eigenfunction of the linear operator $\mathscr{H}$ (defined on some function space) is a non-zero function $\psi(x)$ in that space, such that the application of $\mathscr{H}$ on $\psi(x)$ gives $\psi(x)$ again, times a constant $\mathbf{k}$. The constant $\mathbf{k}$ is called the eigenvalue.

B. Minimization of the Expression for the Orbital Energy

Rearrangement of the equation for determining the expectation value of the orbital energy yields:

$$E \cdot \int \psi^2 \cdot \mathrm{d}\tau = \int \psi \mathscr{H} \psi \cdot \mathrm{d}\tau \quad , \tag{B.1}$$

which, as shown on page 30, may (for two orbital overlap) be written in the form

$$E \cdot \left(c_1^2 + c_2^2 + 2c_1c_2 \cdot S\right) = c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2 \tag{B.2}$$

To minimize E with respect to c_1, we need to differentiate equation (B.2) with respect to c_1 and set

$$\frac{\partial E}{\partial c_1} = 0 \quad .$$

The derivative of the lhs of equation (B.2) yields, by using the chain rule $(f(g(x)))' = f'(g(x)) \cdot g'(x)$,

$$E \cdot (2c_1 + 2c_2 \cdot S) + \frac{\partial E}{\partial c_1} \cdot \left(c_1^2 + c_2^2 + 2c_1c_2 \cdot S\right) \quad .$$

The derivative of the rhs of equation (B.2) is obtained as

$$2c_1\alpha_1 + 2c_2\beta_{12} \quad .$$

Hence, when we set $\frac{\partial E}{\partial c_1} = 0$, the differentiated form of equation (B.2) becomes

$$E \cdot (2c_1 + 2c_2 \cdot S) = 2c_1\alpha_1 + 2c_2\beta_{12} \quad , \tag{B.3}$$

which finally gives

$$\boxed{c_1 \cdot (\alpha_1 - E) + c_2 \cdot \left(\beta_{12} - ES\right) = 0} \quad . \tag{B.4}$$

To minimize E with respect to c_2, we need to differentiate equation (B.2) with respect to c_2 and set

$$\frac{\partial E}{\partial c_2} = 0 \quad .$$

The derivative of the lhs of equation (B.2) yields, by using the chain rule,

$$E\cdot(2c_2+2c_1\cdot S)+\frac{\partial E}{\partial c_2}\cdot\left(c_1^2+c_2^2+2c_1c_2\cdot S\right)\quad .$$

The derivative of the rhs of equation (B.2) is obtained as

$$2c_2\alpha_2+2c_1\beta_{12}\quad .$$

Hence, when we set $\frac{\partial E}{\partial c_2}=0$, the differentiated form of equation (B.2) becomes

$$E\cdot(2c_2+2c_1\cdot S)=2c_2\alpha_2+2c_1\beta_{12}\quad , \tag{B.5}$$

which finally gives

$$\boxed{c_1\cdot\left(\beta_{12}-ES\right)+c_2\cdot(\alpha_2-E)=0}\quad . \tag{B.6}$$

C. Determinants and Simultaneous Equations

C.1. 2×2 Determinants

Value:
The value of a (2×2) determinant is given by

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = (a\cdot d - b\cdot c)$$

or, using a slightly different notation

$$\begin{vmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{vmatrix} = (m_{11}\cdot m_{22} - m_{12}\cdot m_{21}) \; .$$

Properties:
Multiplying each and every term of the determinant by a common factor, is the same as multiplying the determinant by the same factor taken to a power equal to the order of the determinant, i.e.

$$\begin{vmatrix} ya & yb \\ yc & yd \end{vmatrix} = y^2\cdot \begin{vmatrix} a & b \\ c & d \end{vmatrix}$$

Proof:

$$\begin{vmatrix} ya & yb \\ yc & yd \end{vmatrix} = (ya\cdot yd)-(yb\cdot yc) = y^2\cdot[(a\cdot d)-(b\cdot c)] = y^2\cdot \begin{vmatrix} a & b \\ c & d \end{vmatrix}$$

C.2. 3×3 Determinants

Value:
The value of a (3×3) determinant is given by

$$\begin{vmatrix} i & j & k \\ a & b & c \\ d & e & f \end{vmatrix} = i\cdot\begin{vmatrix} b & c \\ e & f \end{vmatrix} - j\cdot\begin{vmatrix} a & c \\ d & f \end{vmatrix} + k\cdot\begin{vmatrix} a & b \\ d & e \end{vmatrix} = i\cdot(bf-ce) - j\cdot(af-cd) + k\cdot(ae-bd)$$

or, using a slightly different notation

$$\begin{vmatrix} m_{11} & m_{12} & m_{13} \\ m_{21} & m_{22} & m_{23} \\ m_{31} & m_{32} & m_{33} \end{vmatrix} = m_{11}\cdot\begin{vmatrix} m_{22} & m_{23} \\ m_{32} & m_{33} \end{vmatrix} - m_{12}\cdot\begin{vmatrix} m_{21} & m_{23} \\ m_{31} & m_{33} \end{vmatrix} + m_{13}\cdot\begin{vmatrix} m_{21} & m_{22} \\ m_{31} & m_{32} \end{vmatrix}$$

$$= m_{11}\cdot(m_{22}m_{33} - m_{23}m_{32}) - m_{12}\cdot(m_{21}m_{33} - m_{23}m_{31}) + m_{13}\cdot(m_{21}m_{32} - m_{22}m_{31})$$

C.3. $n \times n$ Determinants

Value:
The value of a $(n \times n)$ determinant is given by progressively breaking it down into smaller determinants using the procedure outlined below:

$$\begin{vmatrix} m_{11} & m_{12} & m_{13} & \cdots & m_{1n} \\ m_{21} & m_{22} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ m_{n1} & m_{n2} & m_{n3} & \cdots & m_{nn} \end{vmatrix} = m_{11}\cdot\begin{vmatrix} m_{22} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ m_{n2} & m_{n3} & \cdots & m_{nn} \end{vmatrix} - m_{12}\cdot\begin{vmatrix} m_{21} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ m_{n1} & m_{n3} & \cdots & m_{nn} \end{vmatrix}$$
$$+ \ldots$$

where the sign preceding each term alternates between + and −, and the terms themselves are formed by taking each element from the top row and multiplying it by the smaller determinant formed by excluding the row and column in which this element occurs.

Properties:
Multiplying each and every term of the determinant by a common factor, is the same as multiplying the determinant by the same factor taken to a power equal to the order of the determinant (in this case n), i.e.

$$\begin{vmatrix} ym_{11} & ym_{12} & ym_{13} & \cdots & ym_{1n} \\ ym_{21} & ym_{22} & ym_{23} & \cdots & ym_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ ym_{n1} & ym_{n2} & ym_{n3} & \cdots & ym_{nn} \end{vmatrix} = y^n \cdot \begin{vmatrix} m_{11} & m_{12} & m_{13} & \cdots & m_{1n} \\ m_{21} & m_{22} & m_{23} & \cdots & m_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ m_{n1} & m_{n2} & m_{n3} & \cdots & m_{nn} \end{vmatrix}$$

C.4. Solving Simultaneous Equations

Consider a set of simultaneous equations of the form:

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n &= b_1 \\ a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n &= b_2 \\ a_{31}x_1 + a_{32}x_2 + \cdots + a_{3n}x_n &= b_3 \\ &\text{etc.} \end{aligned}$$

These equations may also be represented in a matrix form as indicated below:

$$\mathbf{AX} = \mathbf{B} \quad , \tag{C.1}$$

where

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ a_{31} & a_{32} & \cdots & a_{3n} \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \quad ,$$

$$\mathbf{X} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \cdots \end{pmatrix}$$

and

$$\mathbf{B} = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ \cdots \end{pmatrix} .$$

The desired solutions are the set of x_i values that satisfy these equations. The approach to obtaining the solutions when using the matrix representation is to pre-multiply both sides of the matrix equation by $\mathbf{A}^{-1}$, the inverse of matrix $\mathbf{A}$. This gives,

$$\mathbf{A}^{-1}\mathbf{A}\mathbf{X} = \mathbf{A}^{-1}\mathbf{B} \ . \tag{C.2}$$

Now,

$$\mathbf{A}^{-1}\mathbf{A} = \mathbf{I} \ ,$$

where $\mathbf{I}$ is the identity matrix (the matrix equivalent of multiplying by one) according to:

$$\mathbf{I} = \begin{pmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \end{pmatrix} .$$

Hence it follows (since $\mathbf{IX} = \mathbf{X}$), that the matrix $\mathbf{X}$ (corresponding to the required set of x_i-values) may simply be obtained from:

$$\mathbf{X} = \mathbf{A}^{-1}\mathbf{B} \ .$$

What is the inverse matrix $\mathbf{A}^{-1}$?
It may be shown that

$$\mathbf{A}^{-1} = \frac{\mathrm{adj}(\mathbf{A})}{|\mathbf{A}|} \ ,$$

where adj($\mathbf{A}$) is the adjoint matrix for the matrix $\mathbf{A}$. $|\mathbf{A}|$ (or det($\mathbf{A}$)) is the determinant of the matrix $\mathbf{A}$.

What happens, if $\mathbf{B} = 0$ (i.e. **all** the b_i-values are equal to zero)?

$$\mathbf{X} = \mathbf{A}^{-1}\mathbf{B} = \frac{\mathrm{adj}(\mathbf{A})}{|\mathbf{A}|} \cdot 0 \ .$$

There are two possible solutions:

(i) $\mathbf{X} = 0$, i.e. all the x_i values are equal to zero,
or
(ii) $|\mathbf{A}| = 0$, i.e. the determinant is zero.

The first is the trivial solution (not of much interest), whilst the second defines the condition which must be satisfied for a set of non-trivial x_i-values to exist (but does not actually provide these solutions).

Example:
Consider the simultaneous equations:

$$\begin{aligned} (2-E)\cdot x_1 + 2x_2 &= 0 \\ x_1 + (1+E)\cdot x_2 &= 0 \end{aligned}$$

which in matrix form becomes

$$\begin{pmatrix} (2-E) & 2 \\ 1 & (1+E) \end{pmatrix} \cdot \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} = 0$$

The trivial solutions are $x_1 = 0$ and $x_2 = 0$. Non-trivial solutions only exist when

$$\begin{aligned} \begin{vmatrix} (2-E) & 2 \\ 1 & (1+E) \end{vmatrix} &= 0 \\ (2-E)\cdot(1+E) - 2 &= 0 \\ \Rightarrow -E^2 + E &= 0 \\ \Rightarrow E \cdot (1-E) &= 0 \\ \Rightarrow E = 0 \ \text{ or } \ (1-E) &= 0 \\ \Rightarrow E = 0 \ \text{ or } \ E &= 1 \ . \end{aligned}$$

What are the non-trivial solutions ?

(i) If $E = 0$, the simultaneous equations become

$$\begin{aligned} 2x_1 + 2x_2 &= 0 \\ x_1 + x_2 &= 0 \quad , \end{aligned}$$

i.e., any pairs of values such that $x_1 = x_2$.

(ii) If $E = 1$, the simultaneous equations become

$$\begin{aligned} x_1 + 2x_2 &= 0 \\ x_1 + 2x_2 &= 0 \quad , \end{aligned}$$

i.e., any pairs of values such that $x_1 = -2x_2$.

Note that,

1. the non-trivial solutions correspond to those situations where the simultaneous equations become equivalent.
2. unique solutions (i.e. specific values of x_1 and x_2) only arise if additional constraints are applied, such as the normalization condition in quantum mechanics.

D. Normalization of MOs and Electron Density Distribution

D.1. Normalization of Molecular Orbitals

You should recall, that the probability of finding a particle at a particular point in space is proportional to the value of ψ^2 at that point, where ψ is the wave function used to describe the properties of that particle.
For a correctly normalized wave function, the integral of ψ^2 over all space must therefore be unity since the particle must be located somewhere in this all-encompassing region (or, to put it another way, if we consider all possible outcomes then the total probability must be equal to one). This leads to the normalization condition, namely that:

$$\int \psi^2 \cdot \mathrm{d}\tau = 1 \ . \tag{D.1}$$

Within the LCAO approximation, where the molecular orbital is represented as a linear combination of atomic orbitals, $\psi = \sum_i c_i \cdot \phi_i$, it therefore follows that:

$$\int \left(\sum_i c_i \cdot \phi_i \right)^2 \cdot \mathrm{d}\tau = 1 \ . \tag{D.2}$$

If we set

$$\int \phi_i \phi_j \cdot \mathrm{d}\tau = 1 \ \ (\text{if} \ \ i = j) \ \ \text{i.e. assume the atomic orbitals are normalized,}$$
$$\int \phi_i \phi_j \cdot \mathrm{d}\tau = 0 \ \ (\text{if} \ \ i \neq j) \ \ \text{i.e. neglect all overlap integrals,}$$

then equation (D.2) simplifies to

$$\sum_i c_i^2 = 1 \ , \tag{D.3}$$

which is the normally-quoted *normalization condition* for the coefficients of a molecular orbital.

D.2. Electron Density Distribution

To quantify the partial charges on the atoms in a molecule, we need to have a procedure for allocating a fraction of the electrons in a particular MO to a particular atom (remember that MOs are typically delocalized across several, or indeed many, atoms).
For a molecular orbital, $\psi = \sum_i c_i \cdot \phi_i$, containing n electrons ($n = 0, 1$ or 2), it follows from equation (D.3) by simple multiplication that:

$$n \cdot \sum_i c_i^2 = n \quad , \tag{D.4}$$

or, to write it the other way around,

$$\text{No. of valence electrons in the MO, } n = n \cdot \sum_i c_i^2$$

or

$$\text{No. of valence electrons in the MO, } n = n \cdot \sum_i n \cdot c_i^2 \quad .$$

The right hand side effectively consists of a sum over all the atoms of the amount of electron density associated with this MO in the vicinity of those atoms, i.e.

$$\text{No. of valence electrons in the MO, } n = \sum_i q_i \quad ,$$

where q_i is the electron density on atom i, due to this particular MO.
It follows therefore that the electron density, q_i, on atom i due to one particular MO is given by:

$$q_i = n \cdot c_i^2 \quad . \tag{D.5}$$

D.3. Bond Order

To quantify the bond order, p_{ij}, between two atoms (i and j) arising as a result of occupancy of a molecular orbital, we need a model which must meet the basic requirement that a pair of electrons shared equally between the two atoms corresponds to a single bond (i.e. it yields a bond order of one).
It is clear, that for an MO wave function of the form $\psi = c_1\phi_1 + c_2\phi_2$

- if there are no electrons in the MO then the bond order must be zero,
- if either coefficient is zero, then the bond order must be zero.

It also seems reasonable to assume that the bond order scales directly with the number, n, of electrons in the MO, i.e. $p_{ij} \propto n$.
The simplest formula for calculating a bond order that meets all these requirements is

$$p_{ij} = n \cdot c_i \cdot c_j \quad , \tag{D.6}$$

where

n	number of electrons in the MO (i.e. 0, 1 or 2),
c_i	coefficient of the atomic orbital on atom i in the molecular orbital,
c_j	coefficient of the atomic orbital on atom j in the molecular orbital.

List of Symbols

h	Planck constant
λ	Wavelength
a	Acceleration
ω	Angular frequency
$\phi_1 \phi_2$	Atom-1s-wavefunctions of atom 1 and atom 2
β	Resonance integral. Measure of the strength of the bonding (interaction energy)
$x\,y\,z$	Cartesian coordinates in Euclidian space
q_i	Electron density of the i-atom
$\mathscr{E}\,E$	Energy (of electrons, of the orbital, etc.)
ν	Frequency
$\hbar$	Reduced Planck constant. Planck's constant divided through 2π
m	Mass
$c_1\,c_2\,c_i$	Mixing coefficients. They specify, to which extend the atomic orbitals contribute to the molecular orbital
p	Momentum
n	Number of atoms, number of electrons in the Molecular Orbital
S	overlap Integral
T	Time Period
k	Principal quantum number
t	Time
v	Velocity
c	Velocity (of light)
$\mathbf{k}$	Wave number