

A Rigorous Introduction to Molecular Orbital Theory and its Applications in
Chemistry

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Contents

1 Preface	4
2 Introduction to Quantum Mechanics	5
2.1 Fundamentals	5
2.2 Wavefunctions	7
2.3 Observables and Operators	9
2.4 Schrodinger Equation	11
3 Structure of Atomic Orbitals	14
3.1 Quantum Numbers	14
3.1.1 Principal Quantum Number n	14
3.1.2 Angular Quantum Number l	14
3.1.3 Magnetic Quantum Number m_l	15
3.1.4 Electron Spin Quantum Number m_s	15
3.2 Hydrogenic Wavefunctions	16
3.3 Nodes	17
3.3.1 Radial Nodes	17
3.3.2 Angular Nodes	18
4 Valence-Bond Theory	19
4.1 Types of bonding	19
4.1.1 σ bonds	19
4.1.2 π bonds	19
4.1.3 Orders of bonding	20
4.2 Hybridization	20
4.2.1 Hybridization of s and p orbitals	21
5 Linear Combinations of Atomic Orbitals and Molecular Orbital Theory	22
5.1 Introduction to Molecular Orbital Theory	22
5.2 Schrodinger Equation for MOs and the Variational Principle	23
5.3 Orbital overlap and mixing	29
5.4 Two orbital problem (degenerate case)	29
5.5 Two orbital problem (nondegenerate case)	30
5.5.1 F_2 molecular orbitals	31
5.6 Three (or more) orbital mixing problem	32
5.6.1 N_2 molecular orbitals	33

6	Constructing MOs from Fragments and Perturbation Theory	34
7	Molecular Symmetry and Group Theory	37
7.1	Symmetry operations	37
7.2	Basic Group Theory	37
7.3	Assigning point groups	38
7.3.1	C_n point group	39
7.3.2	C_{nv} point group	40
7.3.3	C_{nh} point group	40
7.3.4	D_n point group	40
7.3.5	D_{nh} point group	40
7.3.6	D_{nd} point group	40
7.3.7	O_h and T_d point groups	40
7.4	Similarity transformations and classes	41
7.5	Group representations	41
8	Symmetry-Adapted Linear Combinations	44
8.1	Determining molecular orbitals from character tables	44
8.2	Molecular orbitals of H_2O	45
9	Crystal Field Theory	46
10	Ligand Field Theory	47
10.1	π -donating effects	48
10.2	π -accepting effects	49
10.3	Spectrochemical Series	49
10.4	Other effects	50
11	References	52

1 Preface

The following document aims to elucidate the fundamental principles of molecular orbital theory and describe some of its applications to chemistry. Molecular orbital theory is central to understanding chemical reactivity and behavior; an intuitive grasp of the subject is vital in order to obtain clear insight regarding the properties of compounds and the dynamics of chemical reactions.

2 Introduction to Quantum Mechanics

2.1 Fundamentals

Electromagnetic radiation is the propagation of energy through oscillations in the electric and magnetic fields. Visible light, radio waves, and x-rays are a few examples of electromagnetic radiation; although they all behave drastically differently (in terms of how they interact with matter), they are all governed by the same physical mechanism. The electric field at a particular point in space can be represented as a vector: a quantity with both magnitude (strength) and direction. As an electric field vector moves through space, a periodic fluctuation in its magnitude and direction results in a sinusoidally varying electric field, visualized in the diagram below. The oscillating electric field induces a complimentary oscillation in the magnetic field, which propagates in a plane perpendicular to the electric field.

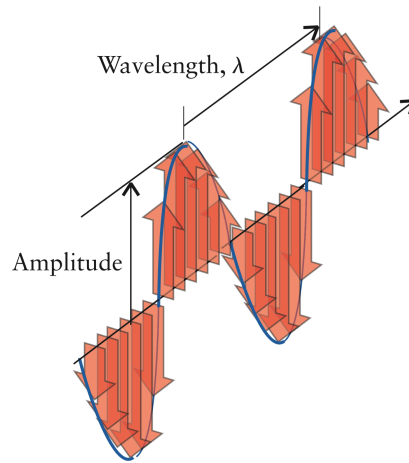


Figure 1: The electric field of electromagnetic radiation oscillates in space and time. This diagram represents a “snapshot” of an electromagnetic wave at a given instant. The length of an arrow at any point represents the strength of the force that the field exerts on a charged particle at that point. The distance between the peaks is the wavelength of the radiation, and the height of the wave above the center line is the amplitude.^[1]

All forms of electromagnetic radiation propagate through space at the speed of light (represented by the letter c , equivalent to $3 \times 10^8 \text{ m/s}$). A particular electromagnetic wave can be characterized by three main quantities: its amplitude, wavelength, and frequency. The *amplitude* is correlated with the strength of the oscillation; that is, it measures the maximum magnitude of the electric field vector during one cycle of the wave. The *wavelength* represents the distance traversed between two corresponding points on two sequential cycles of the wave. The *frequency* of an electromagnetic wave is the number of cycles completed per unit time.

An important relationship between the wavelength and frequency is that their product is always equal to the speed of light, c . This is represented by the following equation:

$$\lambda \times \nu = c$$

where λ is the wavelength, and ν is the frequency. One can gain a more intuitive understanding of the above relation with dimensional analysis: since λ is in units of meters (m) and ν is in units of cycles per second (s^{-1}), the units on the left side

of equation multiply to meters per second (m/s), which is the correct unit for c , the speed of light.

Different varieties of electromagnetic radiation are characterized by their wavelengths—they can thus be organized into a spectrum, as seen below:

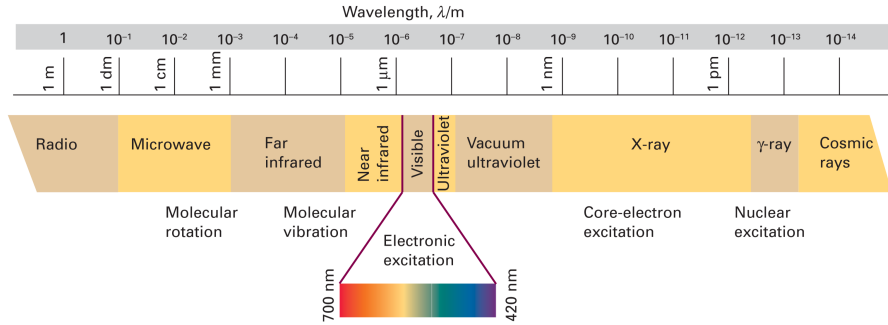


Figure 2: The electromagnetic spectrum^[2]

When two waves are added together (that is, when they overlap in space), a phenomenon called *interference* occurs. When two waves overlap such that the peaks of one wave coincide with the peaks of the other, the amplitude of the summed wave increases—this is called *constructive interference*. In contrast, when two waves overlap such that the peaks of one wave coincide with the troughs of the other, the positive portions of one wave counteract the negative portions of the other, and the overall amplitude of the summed wave decreases. This is known as *destructive interference*. In the following diagram, a) represents constructive interference, while b) represents destructive interference:

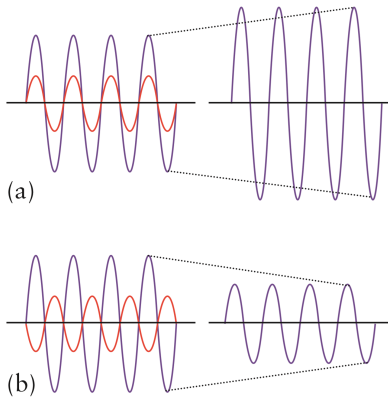


Figure 3: Constructive and destructive wave interference^[1]

Electromagnetic radiation transmits energy in bursts, or quanta, called *photons*. In other words, the energy is neither transmitted continuously as a wave, nor in a stream of individual particles; rather, it is transmitted in packets that are discrete (like particles) but still retain the characteristics of waves (such as a distinct amplitude and frequency). The energy of a photon is given by the following equation:

$$E = h\nu$$

where h is Planck's constant, equal to $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$. Since $\lambda\nu = c$, the equation can also be written as,

$$E = hc/\lambda.$$

The general idea that energy can only be transferred in discrete, quantized amounts is of crucial importance to quantum mechanics—for example, it is ultimately responsible for the fact that electrons can only occupy specific, distinct energy levels in atoms and molecules.

Another critical, fundamental postulate of quantum mechanics is the *wave-particle duality*—the idea that all quantum-scale objects have characteristics of both waves and particles. This idea is an extension of the concept of photons—all matter behaves analogously to light, in the sense that it can be associated with a wavelength (like a wave) as well as a position and momentum (like a particle). In fact, the wavelength and momentum are correlated through what is known as the *de Broglie relation*:

$$\lambda = h/p$$

where λ is the wavelength of the object, h is Planck's constant, and p is the object's momentum. An object's *momentum*, specifically linear momentum, is the product of its mass and velocity:

$$p = mv$$

Thus, the de Broglie relation can be rewritten as,

$$\lambda = h/mv$$

From the above equation, it can be deduced that very massive objects (on a quantum scale) will have a very short wavelength. For this reason, everyday objects (like people and cars) do not experience significant wave-particle duality; their wavelengths are short enough that they can be treated as essentially classical systems. On the other hand, objects like electrons (with very small masses in comparison), have significant wavelengths, leading to significant ambiguity in their exact position. This ambiguity of position as a result of a non-negligible wavelength is manifested in the *Heisenberg uncertainty principle*, which states that the uncertainty in a particle's momentum is inversely proportional to the uncertainty in its position. In other words, if a particle's momentum is known to great certainty, then its position must be largely ambiguous, and vice versa.

2.2 Wavefunctions

In general, the behavior of macroscopic, day-to-day objects can be described with classical mechanics—the study of particles with definite, exact positions and momenta. Classical mechanics is largely governed by Newton's laws of motion. In a classical system, the momentum and energy of a particle can be described as a function of the position vector and its

derivatives with respect to time. For example:

$$p = mv = m \frac{dx}{dt}$$
$$E = \frac{p^2}{2m} = \frac{1}{2}mv^2 = \frac{1}{2}m \left(\frac{dx}{dt} \right)^2$$

However, since particles on the quantum scale do not have precise positions (and are instead distributed through space like a wave), the range of possible positions they may occupy is instead mathematically described with a probabilistic approach. This probabilistic description of position is accomplished using the particle's *wavefunction* (represented by the Greek letter psi, ψ), which is a mathematical function defined over the space that the particle may occupy.

A wavefunction must contain all of the dynamical information about the system it describes. Firstly, as mentioned above, the wavefunction encodes information about the location of the particle. The *Born interpretation* of the wavefunction links the probability of finding a particle within a certain small region of space to the square of its wavefunction. A more rigorous definition of the Born interpretation is given below:

If the wavefunction of a particle has the value ψ at some point x , then the probability of finding the particle between x and $x + dx$ is proportional to $|\psi|^2 dx$.

Note: The square modulus of the wavefunction, $|\psi|^2$, is the magnitude of the wavefunction vector in the complex plane, equal to the wavefunction (ψ) times its complex conjugate (ψ^*):

$$|\psi|^2 = \psi^* \psi.$$

If the wavefunction is real (as they will be in the remainder of this document), with no imaginary component, then the wavefunction equals its complex conjugate, and the square modulus is simply equal to the wavefunction squared:

$$|\psi|^2 = \psi^* \psi = \psi^2.$$

The square modulus, $|\psi|^2$, is a probability density, or probability per unit length (in one dimension). In two or three dimensions, $|\psi|^2$ would instead represent probability per unit area or unit volume, respectively (for simplicity, the discussion of wavefunctions that follows in the remainder of this section will be limited to one dimension). In order to determine the probability of finding an electron within a small region of space, dx , the probability density over that region of space must be multiplied by the length of the region. Thus, the probability of finding the electron within the region is $|\psi|^2 dx$.

The probability of finding an electron within an infinitesimally small region can be easily computed with $|\psi|^2 dx$ because the value of ψ is constant over such a small region of space. To calculate the probability of finding an electron over a non-infinitesimal region of space, Δx , divide the region into many infinitesimal regions (each of size dx), compute the individual probabilities over each, and sum them up to determine the total probability. This operation is represented mathematically with the following integral:

$$\int_{\Delta x} |\psi(x)|^2 dx.$$

In other words, the probability of finding the electron over a region Δx is the integral of the wavefunction squared with

respect to x . It should be noted that the sign of the wavefunction has no effect on the probability distribution of the electron because the probability is related to the square of the wavefunction (which must always be positive).

A *node* is a point where the wavefunction passes through zero. At this point, the probability density is also zero; thus, there is always zero probability of finding the particle at a node.

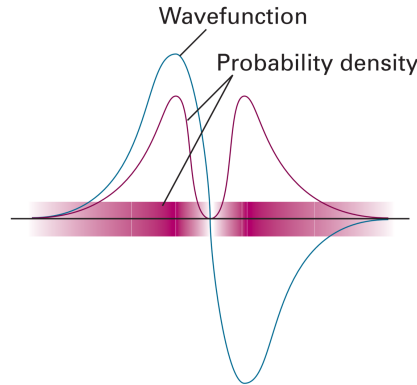


Figure 4: A plot of a wavefunction, ψ , and its corresponding probability density, $|\psi|^2$. There is a node in the center where ψ equals zero.^[2]

Because the total probability of finding an electron over all space must be equal to 1, the integral of its square modulus over all space must also equal 1:

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 1$$

A wavefunction is said to be *normalized* if the above integral evaluates to 1. Although atomic wavefunctions are generally already normalized, it is occasionally necessary to multiply an unnormalized wavefunction by some calculable constant value in order to satisfy the above normalization condition (for example, in the construction of molecular orbitals).

Finally, in order for a wavefunction to satisfy the Born interpretation, it must obey a few mathematical restrictions:

- ψ must be continuous
- ψ must have a continuous slope
- ψ must be a single-valued function
- ψ must be square-integrable; that is, $\int_{\Delta x} |\psi(x)|^2 dx$ must have a finite value

2.3 Observables and Operators

Aside from information regarding the particle's position, a wavefunction also encodes information pertaining to other *observables*, or measurable properties of the system. A few examples of observables are momentum and electric dipole

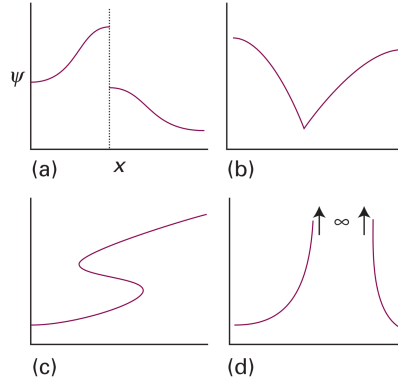


Figure 5: The wavefunction must satisfy stringent conditions for it to be acceptable. (a) Unacceptable because it is not continuous; (b) unacceptable because its slope is discontinuous; (c) unacceptable because it is not single-valued; (d) unacceptable because it is infinite over a finite region.^[2]

moment. The value of an observable must be calculated from an eigenvalue equation containing the wavefunction. In general, an *eigenvalue equation* has the following form:

$$\hat{\Omega}\psi = \omega\psi$$

where ψ is the wavefunction, ω is the value of the observable, and $\hat{\Omega}$ is the operator corresponding to the observable. An *operator* carries out a mathematical operation on the function ψ . An example of an operator is the differential operator, $\frac{d}{dx}$. The differential operator applies the operation of differentiation to the function it acts upon, returning its first derivative:

$$\frac{d}{dx}(\psi(x)) = \psi'$$

where ψ' is the first derivative of ψ . In quantum mechanics, an operator is denoted by the circumflex (“hat”) symbol, as is seen above the Ω in $\hat{\Omega}$. Listed below are the fundamental operators for position and momentum:

$$\hat{x} = x \times$$

$$\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$$

where \hbar is Planck’s constant divided by 2π , and i is the imaginary unit. These operators are used in eigenvalue equations to determine the position and momentum of a given particle governed by the wavefunction of interest. For example, to calculate the momentum of a particle with wavefunction ψ , the following equation would be solved for p :

$$\hat{p}\psi = p\psi.$$

The above equation can be expanded to:

$$\frac{\hbar}{i} \frac{d}{dx}(\psi) = p\psi$$

which is equivalent to:

$$\frac{\hbar}{i} \frac{d\psi}{dx} = p\psi.$$

The value p determined from this differential equation is the linear momentum of the particle with wavefunction ψ .

Another crucially important operator in quantum mechanics is the Hamiltonian operator, \hat{H} . The *Hamiltonian operator* is the operator corresponding to a particle's total energy (that is, the sum of its kinetic and potential energy):

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

Where m is the mass of the particle. The $V(x)$ term represents the particle's potential energy as a function of position, while the $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ portion of the Hamiltonian operator corresponds to the particle's kinetic energy. The kinetic contribution can be derived using the classical definition of kinetic energy and the above expression for the momentum operator:

Recall that the kinetic energy of a particle can be represented classically by

$$E_k = \frac{p^2}{2m},$$

as discussed in the *Wavefunctions* section above. By substituting in the momentum operator, $\frac{\hbar}{i} \frac{d}{dx}$, for p , the expression for kinetic energy becomes the kinetic energy operator:

$$\hat{H}_k = \left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 \frac{1}{2m}$$

which simplifies to the recognizable kinetic energy term of the Hamiltonian:

$$\hat{H}_k = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}.$$

Solving the eigenvalue equation for the Hamiltonian operator ($\hat{H}\psi = E\psi$) is of great importance, since it yields the particle's total energy—in the context of atoms and molecules, it yields the different energy levels that electrons can occupy. The Hamiltonian eigenvalue equation is so central to quantum chemistry that it is given its own name: the Schrodinger equation.

2.4 Schrodinger Equation

The Schrodinger Equation is used to determine the energy of a particle in a quantum system. The Schrodinger equation is the eigenvalue equation for the Hamiltonian operator:

$$\hat{H}\psi = E\psi.$$

Expanding the Hamiltonian gives:

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right) \psi = E\psi$$

which upon simplification, yields the classic form of the Schrodinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

The kinetic energy term of the Schrodinger equation, $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}$, shows that kinetic energy is correlated with the second derivative of the wavefunction. The second derivative of a function is related to its curvature: functions with large second derivatives are sharply curved. This result arises from the fact that the second derivative is the rate of change of the slope (first derivative)—a large second derivative thus corresponds to a rapidly changing slope, and a sharply curved function. Because the kinetic energy is related to the second derivative of the wavefunction, sharply curved wavefunctions will have a high kinetic energy magnitude, whereas less sharply curved wavefunctions will have a lower kinetic energy magnitude.

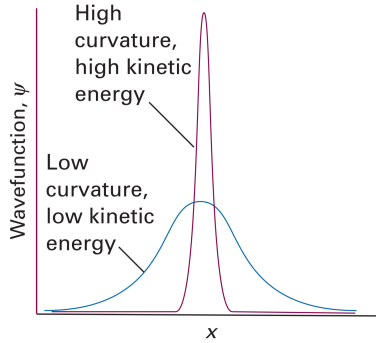


Figure 6: This illustration shows two wavefunctions: the sharply curved function corresponds to a higher kinetic energy than the less sharply curved function. ^[2]

The intuition relating curvature to kinetic energy is also corroborated by the de Broglie relation. If a wavefunction has a very small wavelength, then its momentum will be very high (by $\lambda = h/p$). Since a high momentum corresponds to a high kinetic energy (via $E_k = \frac{p^2}{2m}$), the particle will have a high magnitude of kinetic energy. Alternately, from the Schrodinger point of view, wavefunctions with small wavelengths are sharply curved; thus, their second derivatives are large, and their kinetic energies must also be large. Both equations (de Broglie and Schrodinger) therefore confirm the relationship between curvature and kinetic energy.

Because the energy of a particle is probabilistic (by nature of the Born interpretation of the wavefunction), it is often useful to compute the *expectation value* for the particle's energy; that is, the weighted average of a large number of observations of the energy. The expectation value of the energy, $\langle E \rangle$, can be computed with the following integral:

$$\langle E \rangle = \int \psi^* \hat{H} \psi dx$$

which, for real wavefunctions, where the wavefunction (ψ) equals its complex conjugate (ψ^*), is equivalent to

$$\int \psi \hat{H} \psi dx.$$

The following argument (which makes use of the relation, $\hat{H}\psi = E\psi$) demonstrates why the above integral equals the expectation value of the energy:

$$\langle E \rangle = \int \psi \hat{H} \psi dx = \int \psi (\hat{H}\psi) dx = \int \psi (E\psi) dx = E \int \psi \psi dx = E$$

The integral, $\int \psi \psi dx$ is equal to one, assuming the wavefunction is normalized.

To facilitate future discussion, it may be useful to introduce some notation that simplifies the integral expressions that arise in quantum mechanics:

$$\int \psi_i \psi_j dx = \langle \psi_i | \psi_j \rangle$$
$$\int \psi_i \hat{H} \psi_j dx = \langle \psi_i | \hat{H} | \psi_j \rangle$$

3 Structure of Atomic Orbitals

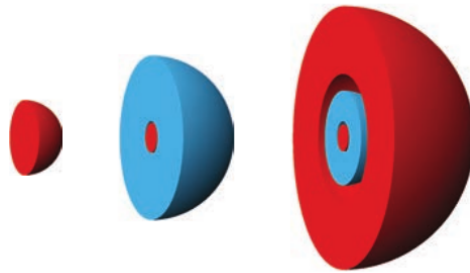
Unfortunately, we can't analytically solve the Schrodinger equation for atoms larger than hydrogen. However, we can look at hydrogenic orbitals to get a visual idea of what these orbitals look like. In order to do this though, we need to understand quantum numbers.

3.1 Quantum Numbers

Atomic orbitals can be described by three integral quantum numbers: the principal quantum number n , angular quantum number l , magnetic quantum number m_l . In addition, the electrons in each atomic orbital can be described by their electron spin quantum number m_s .

3.1.1 Principal Quantum Number n

The principal quantum number describes the size of the atomic orbital. The larger n is, the larger the orbital is. For any particular element, n is upper by it's period in the Periodic Table p ($1 \leq n \leq p$).



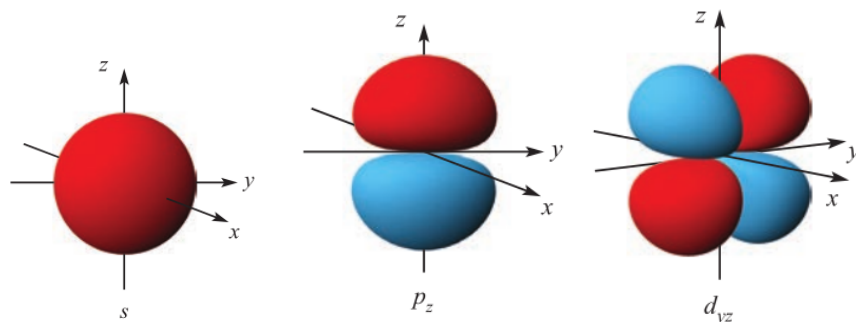
s orbitals of $n = 1, 2, 3$

3.1.2 Angular Quantum Number l

The angular quantum number describes the shape of the atomic orbital. The available orbitals for any principal quantum number are $0 \leq l < n$.

Each value of l is associated with a letter which stands for the orbital's name:

l	0	1	2	3
Name	s	p	d	f



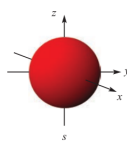
s ($l = 0$), p ($l = 1$), and d ($l = 2$) orbitals

3.1.3 Magnetic Quantum Number m_l

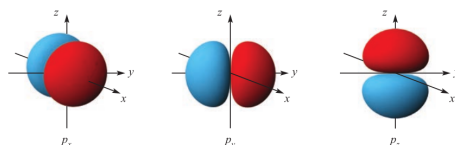
The magnetic quantum number describes the orbital's orientation in space. For angular quantum number l , $-l \leq m_l \leq l$.

This results in a total of $2l + 1$ orbitals per any l .

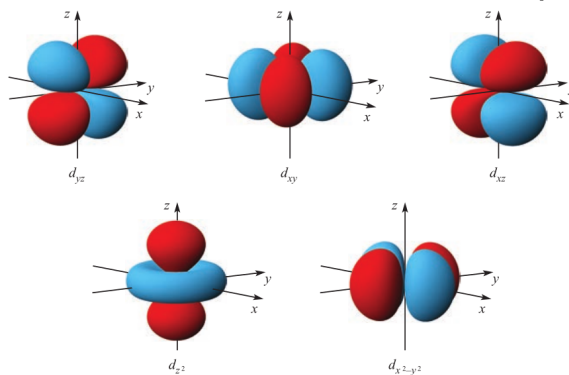
These $2l + 1$ also each have their own names which are derived from spherical coordinate transforms.



s orbitals have only one m_l value, which makes sense because of their spherical symmetry



p orbitals have three m_l values: -1, 0, 1. These manifest as p_x , p_y , p_z orbitals



d orbitals have five m_l values: -2, -1, 0, 1, 2. These manifest as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$, and d_{z^2} .

3.1.4 Electron Spin Quantum Number m_s

The electron spin quantum number is independent of the other three quantum numbers, and describes the spin of the electrons in any given orbital. This value is restricted to $\pm\frac{1}{2}$, which means that only two electrons can occupy an orbital at

any given time, with both electrons having different spins. $m_s = +\frac{1}{2}$ is referred to as "up" spin, and $m_s = -\frac{1}{2}$ is referred to as "down" spin.

3.2 Hydrogenic Wavefunctions

With these quantum numbers, we can understand the hydrogenic wavefunctions. These are derived by analytically solving the Schrodinger equation for hydrogen.

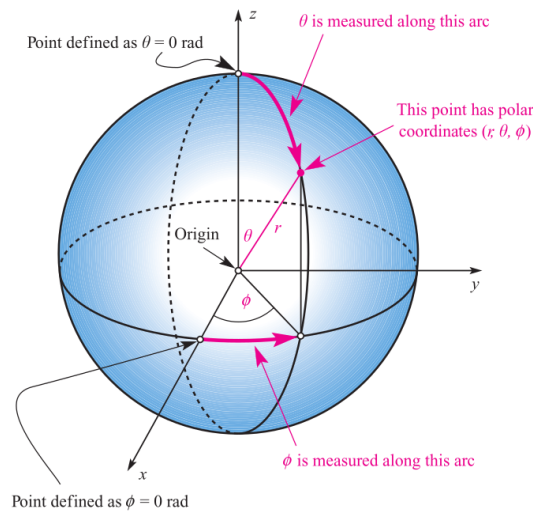
$$\psi_{\text{Cartesian}}(x, y, z) \equiv \psi_{\text{radial}}(r)\psi_{\text{angular}}(\theta, \phi) = R(r)A(\theta, \phi)$$

Table 1.2 Solutions of the Schrödinger equation for the hydrogen atom which define the 1s, 2s and 2p atomic orbitals. For these forms of the solutions, the distance r from the nucleus is measured in atomic units.

Atomic orbital	n	l	m_l	Radial part of the wavefunction, $R(r)^\dagger$	Angular part of wavefunction, $A(\theta, \phi)$
1s	1	0	0	$2e^{-r}$	$\frac{1}{2\sqrt{\pi}}$
2s	2	0	0	$\frac{1}{2\sqrt{2}}(2-r)e^{-r/2}$	$\frac{1}{2\sqrt{\pi}}$
$2p_x$	2	1	+1	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\cos\phi)}{2\sqrt{\pi}}$
$2p_z$	2	1	0	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\cos\theta)}{2\sqrt{\pi}}$
$2p_y$	2	1	-1	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\sin\phi)}{2\sqrt{\pi}}$

[†] For the 1s atomic orbital, the formula for $R(r)$ is actually $2\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$ but for the hydrogen atom, $Z = 1$ and $a_0 = 1$ atomic unit. Other functions are similarly simplified.

Notice that we split the wavefunction into two parts, a radial function and an angular function. Describing wavefunctions in spherical coordinates simplifies the mathematics of orbital calculations, and also aids us in the analysis of nodes.

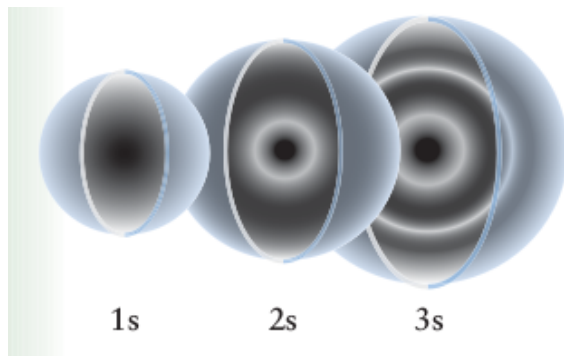


3.3 Nodes

Nodes are areas of orbitals where the wavefunction is 0, meaning there is 0 electron density in those areas. There are two types of nodes, radial nodes and angular nodes.

3.3.1 Radial Nodes

Radial nodes occur when the radial portion of the wavefunction equals 0. These nodal surfaces have spherical characteristic, which can be most prominently seen in the s orbitals as n grows larger.



However, this can also be seen in the radial function. We observe this by plotting $4\pi r^2 R(r)^2$ vs r , which plot the relative electron density at any distance r from the nucleus.

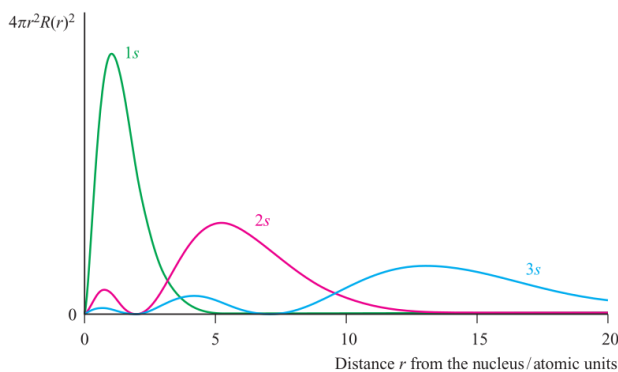
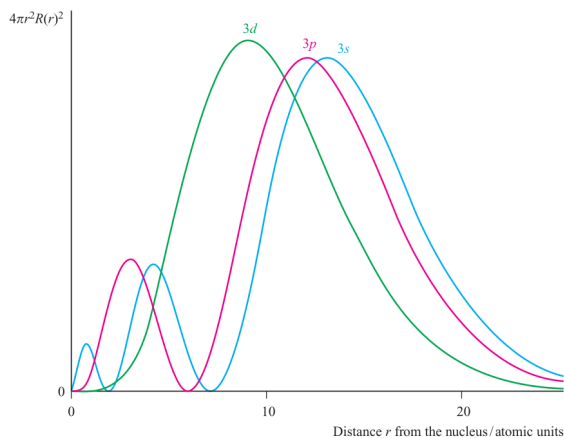


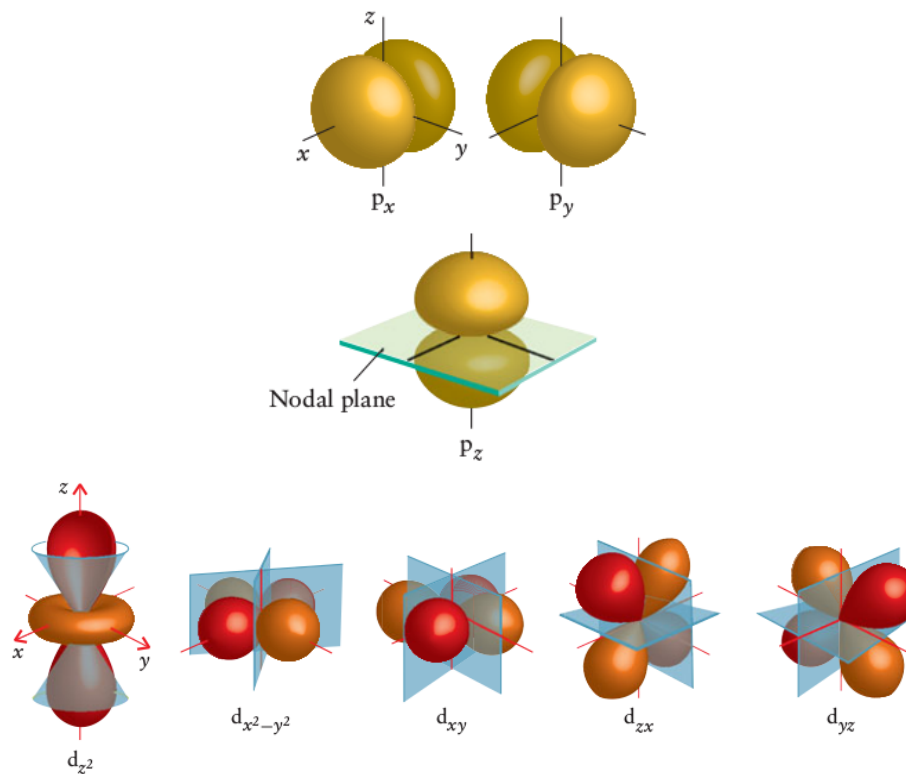
Fig. 1.7 Radial distribution functions, $4\pi r^2 R(r)^2$, for the 1s, 2s and 3s atomic orbitals of the hydrogen atom.



An orbital with principal quantum number n and angular quantum number l will have $n - l - 1$ radial nodes.

3.3.2 Angular Nodes

Angular nodes occur when the angular portion of the wavefunction equals 0. These nodal surfaces tend to have either planar or conical character, which arises from setting θ constant and allowing ϕ to rotate from 0 to 2π



An orbital with angular quantum number l will have l angular nodes.

4 Valence-Bond Theory

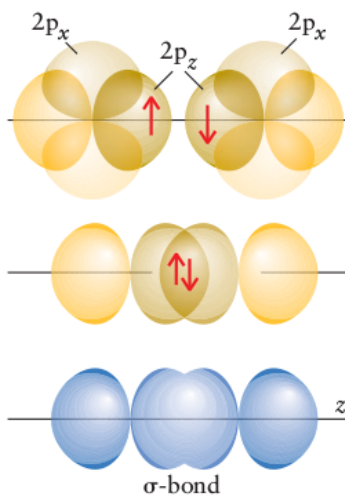
We now know what atomic orbitals look like. What do bonds look like? A more primitive model of bonding is explained by valence-bond (VB) theory.

4.1 Types of bonding

In VB theory, a bond is formed by the overlap of two atomic orbitals, with the two atoms involved in the bond sharing two electrons. Depending on how they overlap, a different type of bond is formed.

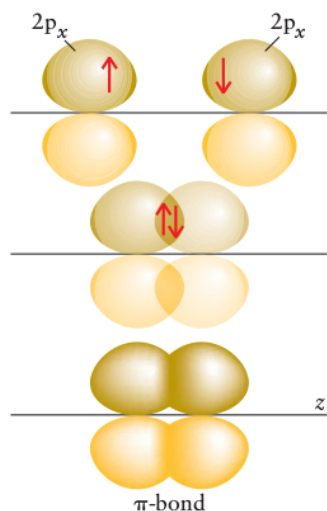
4.1.1 σ bonds

A σ bond is a bond where orbitals overlap head on, as shown below.



4.1.2 π bonds

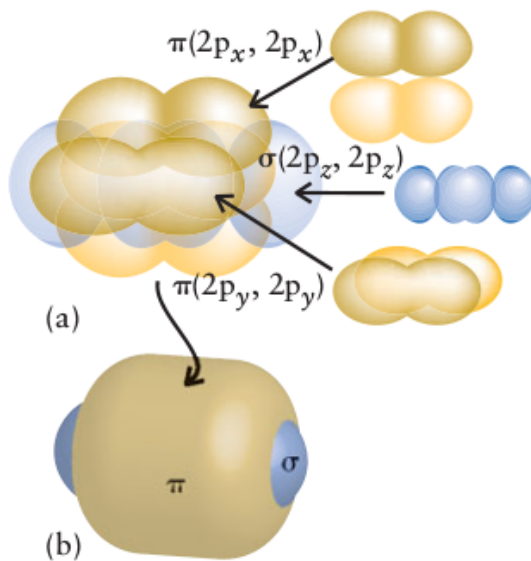
A π bond is a bond where orbitals have sideways overlap. Note that due to the symmetry of s orbitals, π bonds cannot be formed with an s orbital.



4.1.3 Orders of bonding

Given these definitions of bonds, we can define some common Lewis diagram bonds as follows:

- A single bond consists of one σ bond
- A double bond consists of one σ bond and one π bond
- A triple bond consists of one σ bond and two π bonds



N_2 , a molecule with one σ bond and two π bonds, or a triple bond

4.2 Hybridization

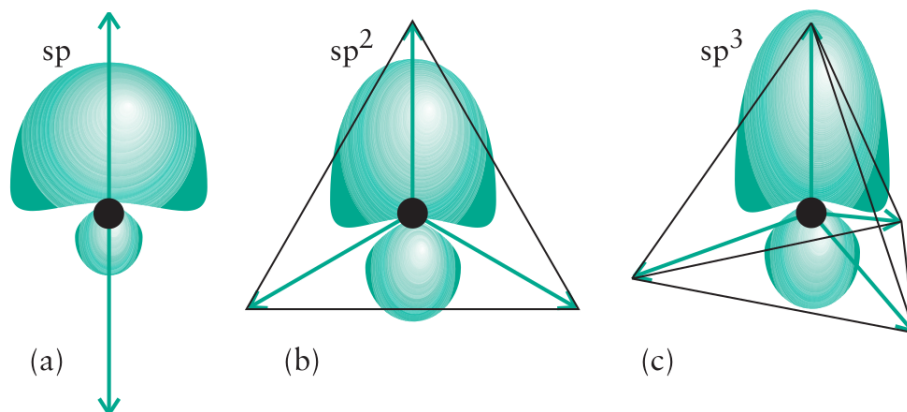
If VB theory was accurate, we would expect methane (CH_4) to have particular bond angles: three long $\text{H}_{1s}\text{-C}_{2p}$ 90° to each other and one short $\text{H}_{1s}\text{-C}_{2s}$ 135° to the other three bonds. However, methane has four equal bonds, each 109.5° to each

other. Hybridization of orbitals is used to make up for this shortcoming of VB theory.

4.2.1 Hybridization of s and p orbitals

Generally, we create hybridized orbitals out of s and p orbitals. Given any set of n orbitals, we generate n equal "hybrid" orbitals, each of which can be used in bonding.

For example, if we use 1 s orbital and 3 p orbitals, we generate 4 new hybrid orbitals, which are known as sp^3 orbitals. Similarly, hybridizing 1 s orbital and 2 p orbitals form 3 sp^2 orbitals, and hybridizing 1 s orbital with 1 p orbital forms 2 sp orbitals.



5 Linear Combinations of Atomic Orbitals and Molecular Orbital Theory

5.1 Introduction to Molecular Orbital Theory

In valence bond theory, electrons are confined to localized bonds that are constrained between groups of adjacent atoms. However, in molecular orbital theory, electrons occupy orbitals that are spread throughout the entirety of the molecule—that is, they are *delocalized* throughout the molecule. To create molecular orbitals, it is necessary to combine the atomic orbitals from each atom in the molecule. Wavefunctions for these new molecular orbitals can be generated with a weighted sum of the wavefunctions of the constituent valence atomic orbitals. Within this sum, each atomic orbital wavefunction is multiplied by a distinct weighting coefficient, or *orbital coefficient*, that quantifies how much each atomic wavefunction contributes to the molecular wavefunction. These orbital coefficients can be either positive or negative.

The weighted sum discussed above is mathematically described below:

$$\psi = \sum_{i=1}^N c_i \phi_i$$

where ψ is the wavefunction of the molecular orbital, N is the number of participating valence atomic orbitals, and c_i is the weighting coefficient for the i th atomic orbital corresponding to the atomic wavefunction ϕ_i . This weighted sum is called a **linear combination of atomic orbitals**, or **LCAO** for short. The molecular orbitals generated from a LCAO are known as LCAO-MOs.

As an introductory example, consider the MOs for diatomic hydrogen (H_2). Let one hydrogen atom be atom A and the other be atom B. The relevant atomic orbitals that will participate in bonding are the 1s orbitals from each atom, which will be denoted with A1s and B1s. The molecular orbitals for the H_2 molecule will be a weighted sum of the wavefunctions for the two 1s orbitals, ϕ_{A1s} and ϕ_{B1s} :

$$\psi = c_{A1s}\phi_{A1s} + c_{B1s}\phi_{B1s}$$

Because both hydrogen atoms are identical, each orbital will contribute equally to the new molecular orbitals. In other words, the magnitudes of their weighting coefficients will be equal: $|c_{A1s}| = |c_{B1s}| = c$.

However, there are two possible combinations for the signs of the coefficients: one where the coefficients have the same sign, and one where they have opposite sign. This multiplicity thus generates two molecular orbital wavefunctions—one in which the atomic wavefunctions are added together, and another in which one atomic wavefunction is subtracted from the other:

$$\psi_+ = c\phi_{A1s} + c\phi_{B1s}$$

$$\psi_- = c\phi_{A1s} - c\phi_{B1s}$$

The orbital designated with ψ_+ is called the *bonding orbital*—it results from the in-phase combination of the two wavefunctions and the constructive overlap of the two atomic orbitals. In contrast, The orbital designated with ψ_- is called the

antibonding orbital—it results from the out-of-phase combination of the two wavefunctions and the destructive overlap of the two atomic orbitals.

The bonding orbital is characterized by a wavefunction with *increased* amplitude between the two nuclei, resulting from the constructive addition of the two atomic wavefunctions. In contrast, the antibonding orbital is characterized by a wavefunction with *decreased* amplitude between the two nuclei, as a result of the destructive subtraction of the two atomic wavefunctions. In fact, in the antibonding orbital, the wavefunction must change sign somewhere between the two nuclei—thus, it must be equal to zero at some point, and there must be a node (with zero probability of finding the electron) dividing the internuclear axis. The bonding and antibonding orbitals are depicted visually in the diagrams below:

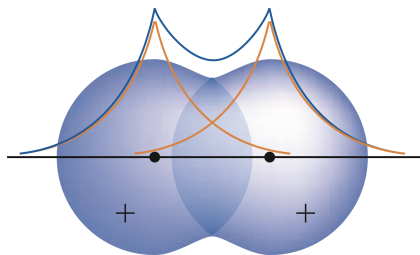


Figure 7: When two 1s-orbitals overlap in the same region of space in such a way that their wavefunctions have the same signs in that region, their wavefunctions (red lines) interfere constructively and give rise to a region of enhanced amplitude between the two nuclei (blue line).^[1]

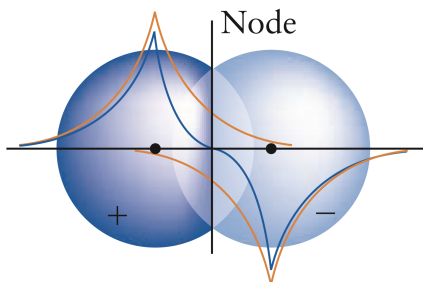


Figure 8: When two 1s-orbitals overlap in the same region of space in such a way that their wavefunctions have opposite signs, the wavefunctions interfere destructively and give rise to a region of diminished amplitude and a node between the two nuclei (blue line).^[1]

In general, with respect to the initial atomic orbitals, a bonding molecular orbital is lowered in energy, while its antibonding counterpart is raised in energy. This result can be proven rigorously using the Schrodinger equation.

5.2 Schrodinger Equation for MOs and the Variational Principle

Since a wavefunction generated from a LCAO is only an approximation (albeit a very good one) of the true molecular orbital wavefunction, the LCAO approach is unable to give exact solutions that satisfy the Schrodinger equation. However, it is still possible to find very good approximate solutions to the Schrodinger equation using LCAO by implementing what is known as the variational principle.

First, recall that the expectation value of the energy corresponding to a particular normalized wavefunction can be represented with the following expression:

$$\langle E \rangle = \int \psi^* \hat{H} \psi dx.$$

However, the molecular orbitals generated from LCAO may not be normalized; thus, the above expression must be divided by the probability of finding the electron over all space, $\int \psi^* \psi dx$, to account for normalization:

$$\langle E \rangle = \frac{\int \psi^* \hat{H} \psi dx}{\int \psi^* \psi dx}.$$

Since the integral is now being taken over three dimensional space (since real orbitals are 3D), the length element dx is now replaced with the volume element, $d\tau$. Additionally, the atomic orbitals of interest have strictly real wavefunctions, so $\psi^* = \psi$:

$$\langle E \rangle = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau}$$

The *variational principle* states that, if any arbitrary approximate wavefunction is substituted into the above expression, the value of $\langle E \rangle$ will always be greater than the true energy of the exact solution. Thus, the best approximate wavefunction can be determined by choosing a wavefunction that minimizes the value of $\langle E \rangle$.

To determine molecular orbital wavefunctions using the variational principle, implement the following process:

1. Determine which atomic orbitals will contribute to the molecular orbitals of interest, and construct a summation for the MO wavefunction:

$$\psi = \sum_{i=1}^N c_i \phi_i$$

2. Obtain an expression for $\langle E \rangle$ by substituting the summation for ψ into

$$\langle E \rangle = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau}.$$

3. Determine the orbital coefficients c_1, c_2, \dots that minimize $\langle E \rangle$.
4. Determine the orbital energies corresponding to the MOs by calculating the minimized values of $\langle E \rangle$.
5. Generate wavefunctions for the MOs by substituting the newly found orbital coefficients back into the summation.

Consider again the MOs resulting from the overlap of two atomic orbitals. Let ϕ_1 correspond to the wavefunction of one atomic orbital, and ϕ_2 correspond to the wavefunction of the other. The summation equation for the LCAO-MO becomes:

$$\psi = \sum_{i=1}^N c_i \phi_i = c_1 \phi_1 + c_2 \phi_2.$$

Substitution of the above sum into the expression for $\langle E \rangle$ gives:

$$\langle E \rangle = \frac{\int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2)d\tau}{\int (c_1\phi_1 + c_2\phi_2)^2d\tau}.$$

Expansion of the numerator gives:

$$\begin{aligned} \int \psi\hat{H}\psi d\tau &= \int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2)d\tau \\ &= c_1^2 \int \phi_1\hat{H}\phi_1d\tau + c_1c_2 \int \phi_1\hat{H}\phi_2d\tau + c_2c_1 \int \phi_2\hat{H}\phi_1d\tau + c_2^2 \int \phi_2\hat{H}\phi_2d\tau \end{aligned}$$

Each of the integrals in the above expansion is an expectation energy term corresponding to different orbital interactions:

- $\int \phi_1\hat{H}\phi_1d\tau$ simply represents the energy of an electron in atomic orbital 1. However, the value of this integral is (to a small degree) influenced by the molecular environment—the nearby electrostatic effects of the other nucleus and additional electrons change the energy slightly. Nonetheless, this integral is called a *Coulomb integral*, and will be represented with α_1 for simplicity. Its value will be negative, since it is energetically favorable for an electron to occupy an orbital.
- $\int \phi_1\hat{H}\phi_2d\tau$ and $\int \phi_2\hat{H}\phi_1d\tau$ are known as *resonance integrals* and will be represented by β_{12} and β_{21} , respectively. They both represent the energy change due to the shared orbital overlap of orbitals 1 and 2. This energy change is a consequence of the increase in the space available for electrons to occupy: in a bonding interaction, electrons from each atom have a greater probability of occupying the region of orbital overlap (due to the increase in wavefunction amplitude resulting from constructive interference), thus allowing them to extend into a region of space beyond their original atomic orbitals. If the electrons occupy more space, their wavefunctions get stretched out, making them less sharply curved and lowering their energy according to the Schrodinger equation (recall that the Schrodinger equation correlates the second derivative of the wavefunction with the kinetic energy of the electron). This lowering of energy due to constructive overlap explains why bonding interactions are favorable. In contrast, the destructive interference of antibonding interactions reduces the space available for electrons to occupy (between the two nuclei), thus raising their kinetic energy, and making the interaction less energetically favorable. The resonance integral is negative—it is associated with the energy decrease of shared orbital space. Since these atomic wavefunctions are real, and the Hamiltonian operator is hermitian, β_{12} and β_{21} are equivalent.
- $\int \phi_2\hat{H}\phi_2d\tau$ corresponds to the energy of an electron in atomic orbital 2 (it is another Coulomb integral), with negative sign. It will be denoted as α_2 .

The numerator can now be simplified to:

$$\int \psi\hat{H}\psi d\tau = c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2$$

Now expand the denominator of the expression for $\langle E \rangle$:

$$\begin{aligned} \int \psi^2 d\tau &= \int (c_1\phi_1 + c_2\phi_2)^2 d\tau \\ &= c_1^2 \int \phi_1^2 d\tau + c_1c_2 \int \phi_1\phi_2 d\tau + c_2c_1 \int \phi_2\phi_1 d\tau + c_2^2 \int \phi_2^2 d\tau \end{aligned}$$

Each of the integrals in the above expansion represents the extent of physical overlap between two orbitals. Note that these integrals do *not* represent energies—they do not contain the Hamiltonian operator (\hat{h}). Rather, they represent a value from 0 to 1, where 0 indicates that there is no net overlap between the two orbitals (over all space) and 1 indicates that the orbitals overlap completely (that is, they are in phase and fully coincide).

To visualize these *overlap integrals*, consider the plots of two generic wavefunctions, ϕ_1 and ϕ_2 , below:

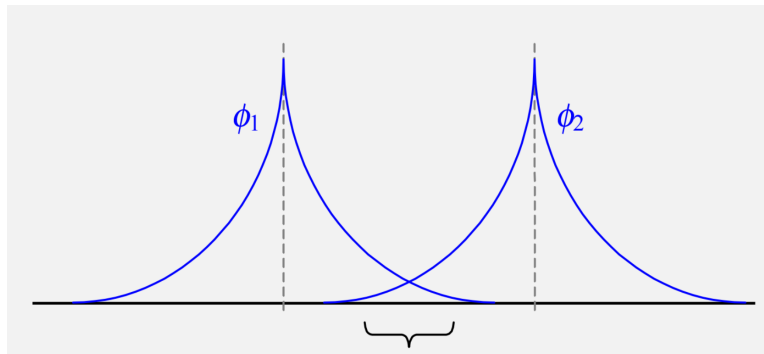


Figure 9: Plot of two generic wavefunctions, ϕ_1 and ϕ_2 , with overlap

The overlap integral, $\int \phi_1\phi_2 d\tau$, of these two wavefunctions will have a nonzero value where the product of both wavefunctions is nonzero. The bracketed section in the above diagram highlights the region where both wavefunctions (and their product) are nonzero—in other words, the bracketed section shows where they overlap. Integrating this product over all space gives a nonzero (in this case, positive) value of the overlap integral, indicating that the orbitals do indeed overlap.

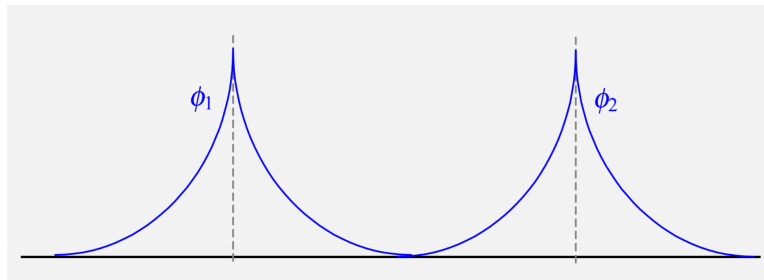


Figure 10: Plot of two generic wavefunctions, ϕ_1 and ϕ_2 , with negligible overlap

Because the two orbitals in this second example are far enough apart, both wavefunctions are very close to zero in the center—thus, their product is very close to zero in this region. Integrating the product over all space gives a value of approximately zero for the overlap integral, indicating that the two orbitals essentially do not overlap.

Reverting back to our discussion of molecular orbitals, the integrals from the denominator of the $\langle E \rangle$ expression have the following physical interpretations:

1. $\int \phi_1^2 d\tau$ represents the overlap integral of orbital 1 with itself. Because orbital 1 completely coincides with itself, the overlap integral will be maximum (that is, a value of 1). Another interpretation of this integral is that it represents the probability of finding the electron over all space; because the wavefunction is normalized, the integral has a value of 1. By a similar argument, $\int \phi_2^2 d\tau$ equals 1 as well.
2. $\int \phi_1 \phi_2 d\tau$ and $\int \phi_2 \phi_1 d\tau$ are equivalent, and represent the overlap integral between orbitals 1 and 2. With reference to the diagrams given above, this integral should have a value between 0 and 1, because the two atomic orbitals have spatial overlap. These integrals will be represented by S for simplicity.

It is worth mentioning that the resonance integral, β (the energy change due to overlap), and the overlap integral, S (the extent spatial overlap), are very often roughly proportional to each other. Thus, orbitals with great spatial overlap often produce very favorable bonding interactions. This is a crucial, fundamental principle of MO theory.

The expression in the denominator can be simplified to the following:

$$\int \psi^2 d\tau = c_1^2 + 2c_1c_2S + c_2^2$$

Combining the expressions for the numerator and denominator yields a simplified expression for $\langle E \rangle$:

$$\langle E \rangle = \frac{c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2}{c_1^2 + 2c_1c_2S + c_2^2}$$

To determine the energies that correspond to the bonding (in-phase) and antibonding (out-of-phase) orbitals, it is necessary to determine the constants c_1 and c_2 that minimize $\langle E \rangle$, in line with the variational principle.

To do so, rearrange the expression of $\langle E \rangle$ to the following ($\langle E \rangle$ will be replaced simply with E for simplicity):

$$E(c_1^2 + 2c_1c_2S + c_2^2) = c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2.$$

Then, to minimize E with respect to c_1 and c_2 , set $\frac{\partial E}{\partial c_1}$ and $\frac{\partial E}{\partial c_2}$ equal to zero:

$$\frac{\partial E}{\partial c_1} = c_1(\alpha_1 - E) + c_2(\beta_{12} - ES) = 0$$

$$\frac{\partial E}{\partial c_2} = c_1(\beta_{12} - ES) + c_2(\alpha_2 - E) = 0$$

The two simultaneous equations listed above are called the *secular equations*, and must be solved for c_1 and c_2 in order to determine the minimized energies. To find nontrivial solutions to the secular equations (that is, solutions other than $c_1 = c_2 = 0$), the following *secular determinant* must be equal to zero:

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

Solving this determinant will yield the values of E for which nontrivial solutions exist for the secular equations. These values of E will be the minimized, best approximate solutions to the Schrodinger equation.

For the case where the two atomic orbitals are identical (as in H_2), $\alpha_1 = \alpha_2 = \alpha$. β_{12} will also be denoted with β for simplicity. The secular determinant now becomes

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

and can be expanded to

$$(\alpha - E)^2 - (\beta - ES)^2 = 0.$$

This equation can be manipulated to yield the possible energy values:

$$(\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$(\alpha - E)^2 = (\beta - ES)^2$$

$$\alpha - E = -(\beta - ES) \text{ or } \alpha - E = +(\beta - ES)$$

$$E - \alpha = +(\beta - ES) \text{ or } E - \alpha = -(\beta - ES)$$

$$E(1 + S) = (\alpha + \beta) \text{ or } E(1 - S) = (\alpha - \beta)$$

Giving the following two energy solutions:

$$E_+ = \frac{\alpha + \beta}{1 + s}$$

$$E_- = \frac{\alpha - \beta}{1 - s}$$

These E values can be substituted back into the secular equations, allowing the values for c_1 and c_2 to be calculated. If this is done, it is found that E_+ corresponds to $c_1 = c_2$, while E_- corresponds to $c_1 = -c_2$.

Thus, the wavefunction with energy E_+ is

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

which corresponds to the bonding molecular orbital. Similarly, the wavefunction with energy E_- is

$$\psi_- = c_1\phi_1 - c_2\phi_2,$$

which corresponds to the antibonding molecular orbital.

Upon examining the expressions for E_+ and E_- , it can be noted that E_+ is lower in energy than E_- , since β is negative. Additionally, the energy expressions can be rearranged to better portray their values relative to the original atomic orbital

energies, α :

$$E_+ = \frac{\alpha + \beta}{1 + s} = \alpha + \frac{\beta - S\alpha}{1 + S}$$
$$E_- = \frac{\alpha - \beta}{1 - s} = \alpha - \frac{\beta - S\alpha}{1 - S}$$

Since $S > 0$, $(1 - S) < (1 + S)$. Necessarily, $\frac{\beta - S\alpha}{1 - S} > \frac{\beta - S\alpha}{1 + S}$, thus requiring that $(E_- - \alpha) > (\alpha - E_+)$. Therefore, *the antibonding orbital is more destabilizing than the bonding orbital is stabilizing.*

This result is of crucial importance to MO theory and chemical bonding. For example, it explains why the molecule He_2 cannot exist: each atom donates 2 electrons to the molecule, so the molecular orbitals have to accommodate 4 electrons. Two electrons enter the bonding orbital, and two electrons enter the antibonding orbital. However, because the antibonding orbital is more destabilizing than the bonding orbital is stabilizing, there is a net energy *increase*, making H_2 an unfavorable species.

If a generic molecule has N atomic orbitals, then there must be N orbital coefficients. Thus, there will be N variables with respect to which E can be minimized by the via the variational principle. Thus, there will be N secular equations: $\frac{\partial E}{\partial c_1} = 0, \frac{\partial E}{\partial c_2} = 0, \dots, \frac{\partial E}{\partial c_N} = 0$. The N secular equations will generate an N by N secular determinant that will ultimately give N different possible values of E . Thus, *N atomic orbitals combine to give N molecular orbitals.* This fundamental rule is highly pervasive throughout all of MO theory.

The remainder of this section will discuss LCAO-MO from a more qualitative, intuitive point of view, with more focus on visual orbital interaction and MO diagram construction. The mathematical principles elucidated here continue to underpin the MO theory that follows, and hopefully serve to provide a more fundamental understanding of the subsequent material.

5.3 Orbital overlap and mixing

Orbital overlap measures how much 2 orbitals overlap with each other. Note that most orbitals (such as p, d) have “positive” and “negative” lobes. Any two orbitals that overlap will mix with each other, with the extent of mixing determined by the extent of overlap. Orbitals that have a total of 0 net overlap (generally resulting from cancellation of positive and negative interactions) are called **orthogonal** and do not mix.

With 2 orbitals, we will always form one bonding (lower in energy) and antibonding (higher in energy) orbital.

5.4 Two orbital problem (degenerate case)

Bonding orbitals will have constructive overlap of wavefunctions, while antibonding orbitals will have destructive interference. This makes sense! We see that constructive overlap means that there is higher electron density in between the two atoms, while destructive overlap means that there is less electron probability between the atoms and more on the other

sides. Our chemical intuition should tell us that a bond means that the electrons are between the two atoms, so this is consistent with the principles that we know.

Notice that the bonding orbital consists of in-phase mixing and the antibonding orbital consists of out-of-phase mixing. In-phase mixing is a result of constructive overlap of the two orbitals (the two positive lobes of the H 1s orbitals are combining together). Out-of-phase mixing is a result of destructive overlap of the two orbitals (one positive lobe is overlapping with another negative lobe, so they cancel each other out in the middle, forming a node (area of 0 electron probability)).

Generally, the more nodes, the higher energy the orbital. This is even true of atomic orbitals (if we consider angular nodes only), as we know that $s < p < d < f$ in energy!

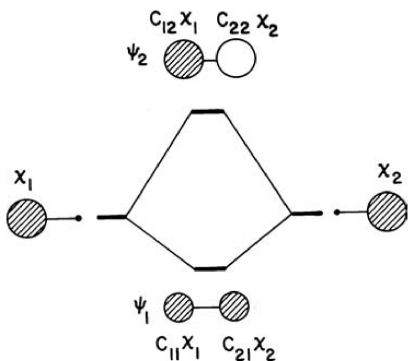


Figure 11: MO diagram for hydrogen, H_2

5.5 Two orbital problem (nondegenerate case)

When the two orbitals are not degenerate (different in energy) and not orthogonal, they will also mix. In this case, one orbital will be lower than both original orbitals (again, constructive interference/bonding) and one will be higher (destructive interference/antibonding). The bonding orbital will be closer in both energy and shape to the lower energy atomic orbital, while the antibonding one will more closely resemble the higher energy atomic orbital.

Notice that when we draw the MOs, for the bonding one we start with the lower energy orbital and then constructively mix in the higher energy one. This makes the lobe on the lower energy atom (He, in this case) bigger, so the electrons are polarized toward He in the bonding MO. Similarly, for the antibonding one we start with the H 1s orbital and destructively mix in the He 1s, so the antibonding orbital will have electrons polarized toward H.

In any 2 orbital mixing problem, the antibonding orbital increases in energy more than the bonding one decreases by (normally just a little bit more). This means that two filled atomic orbitals never want to interact with each other (total energy is increased by interaction).

However, it is important to remember that the lower energy orbital is **not** 100% He in character and the higher energy orbital is **not** 100% H in character! The lower energy bonding orbital is a combination of wavefunctions, albeit with a higher coefficient for He, so it represents a mixture of the two orbitals. Similarly, the higher energy antibonding orbital is also a mixture of the two orbitals, but with a higher coefficient for H.

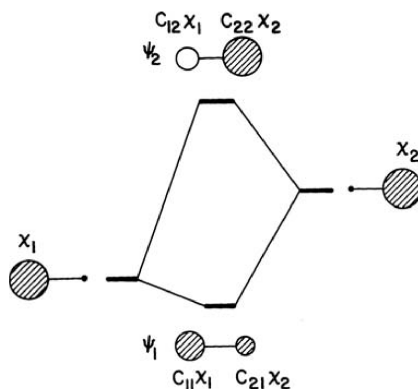


Figure 12: MO diagram of H-He (He 1s is lower in energy, so it is on the left)

The amount of mixing is also correlated with how close in energy the atomic orbitals are: the closer in energy, the more mixing (so larger energy gap). This also means that two orbitals with energies very far apart will experience such little mixing that it can be neglected. We generally assume that if the energies are more than 1 Rydberg (13.6 eV, or the IE of a hydrogen atom) apart, the mixing is negligible. Orbitals such as the fluorine 2s (-46.4 eV) are so low in energy that they will virtually never interact with anything else.

While most molecules will have more than two orbitals interacting, many problems can actually be reduced to the two orbital case! Due to many orbitals being orthogonal and the fact that orbitals far apart in energy mix negligibly, sometimes we only need to mix 2 AOs at a time to form the corresponding MOs. For example, let us consider F_2 .

5.5.1 F_2 molecular orbitals

First, we consider the F 2s orbitals. Being so low in energy, they can only mix with each other, so they split to form the bonding and antibonding pair (note that because the original 2s orbitals are so low in energy, these will still be substantially lower in energy than any other orbitals).

Now consider the F 2p orbitals. Note that the only pairs of 2p orbitals that overlap are the two $2p_z$ s with each other, the two $2p_x$ s with each other, and the two $2p_y$ s with each other; the rest of the pairs are all orthogonal (for example, when interacting one $2p_z$ with one $2p_x$, the interaction with the positive lobe of $2p_x$ exactly cancels that with the negative lobe). We will introduce a concept called symmetry later - only orbitals with the same symmetry can have nonzero overlap and mix.

Note that the $2p_z$ orbitals interact head-on (by default, the bond-axis is the z-axis), forming a bonding and antibonding pair. Similarly, the $2p_x$ s can interact with each other in a π -fashion, so this is another 2 orbital problem. Finally, $2p_y$ s also interact in a π -fashion, forming another 2 orbital problem. Note that x and y are symmetric in this molecule (consider a rotation by 90 degrees that sends x to y; nothing else about the molecule changes, so x and y should be equivalent chemically), so the π_x and π_x^* orbitals are placed at the same energies as the π_y and π_y^* orbitals.

Finally, we know that σ bonds are stronger than π bonds (which are stronger than delta bonds) because there is stronger overlap between the lobes (σ is head-on, π is from a distance), so there is more mixing in the $2p_z$. This means that the σ goes down in energy more (lower) and the σ^* goes up in energy more (highest energy).

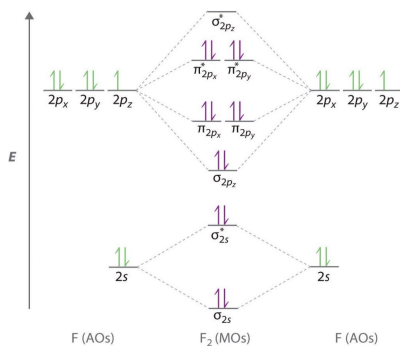


Figure 13: MO diagram of F_2

5.6 Three (or more) orbital mixing problem

Now suppose we have 3 orbitals that can mix with each other. Consider hydroxide, OH^- (by default, the bond axis is the z-axis). Both the $2s$ and $2p_z$ orbitals of the hydroxide can interact with the $1s$ of hydrogen. In this case, the O $2s$ is the lowest in energy, then the O $2p_z$, then the H $1s$. These energy orderings can be obtained from the Valence Orbital Ionization Energy (VOIE) chart, which can be found in most inorganic textbooks or through a Google search.

Most of the time, 3 orbital mixing resembles the hydroxide case - the 2 lower orbitals are both on the same atom, with the higher one on the other atom (generally because the lower atom is much more electronegative and has lower-energy orbitals). The exact resulting energies actually depends on the ordering of the 3 orbitals, but that is not too important here. The main takeaway is that, while the $2s$ and $2p_z$ on O are orthogonal to each other, both of their characters will be present in all the mixed MOs. This can be seen as follows: suppose we just mix the O $2s$ with the H $1s$ to form 2 orbitals. Now because these orbitals have H $1s$ character, they are no longer orthogonal to the O $2p_z$, so the O $2p_z$ will mix with these hybrid orbitals to form the final set of molecular orbitals.

To determine the energy levels of the final orbitals, we start with the lowest one (O $2s$) and lower it. We then take the highest one (H $1s$) and raise it. The middle orbital will probably go down in energy due to the interaction with the H $1s$, but it will also mix with the O $2s$, which will force it up in energy a bit. This is known as secondary orbital mixing, because

the O 2s doesn't directly interact with the O $2p_z$ (contrast this to primary mixing, which is between 2 originally non-orthogonal orbitals). This part is not easy to see and isn't too important, but the idea that the O 2s actually contributes to the MO is important. Either way, it will be fairly similar to the starting energy, so now we know the relative orbital energies.

These principles extend to interactions between any number of molecular orbitals. However, it can be quite difficult to interact many different orbitals with each other. For example, consider the case of N_2 . Each nitrogen atom has 2 orbitals that can interact with orbitals on the other nitrogen atom: 2s and $2p_z$. One method we can use is to first mix the 2 pairs separately, and then mix the resulting MOs with each other. This works because **any** set of non-orthogonal orbitals will mix - they don't have to be atomic orbitals. While the "final" molecular orbitals must be orthogonal, we can make the first set of MOs through this pairwise mixing and then mix the orbitals in this set (which will not be orthogonal). Let's see this in action.

5.6.1 N_2 molecular orbitals

As in the F_2 case above, the $2p_x$ s and $2p_y$ s form π and π^* orbitals. Now note that both nitrogen atoms have a 2s and $2p_z$ orbitals, all of which can mix, because they are much closer in energy. The easiest way is to just create the σ/σ^* pairs from the 2s's and $2p_z$'s, and then mix these with each other. Note that the σ from 2s and σ from $2p_z$ are clearly not orthogonal (both have a ton of electron density in between the two nitrogen atoms), so they will mix. Since the $\sigma(2s)$ is much lower than the $\sigma(2p_z)$ in energy (2s much lower to begin with), it goes down, while the σ from $2p_z$ goes up. Similarly, $\sigma^*(2s)$ mixes with $\sigma^*(2p_z)$, and it goes down while the $\sigma^*(2p_z)$ goes up.

Now we note that the $\sigma(2s)$ is orthogonal to the $\sigma^*(2p_z)$. This is a little tricky to see, but we can decompose the interactions into the interaction of the left N with $2p_z$ and the right N with $2p_z$. Since $2p_z$ is antisymmetric and the two s orbitals are symmetric, the total overlap will be 0.

Now we get our final MO diagram! Notice that the $\sigma(2p_z)$ has actually increased in energy enough (due to the mixing with $\sigma(2s)$) that it is higher in energy than the π set of orbitals. This is a different order than F_2 ! In fact, all period 2 elements at N_2 or earlier have the same ordering as N_2 , while O_2 and Ne_2 have the same ordering as F_2 . This is because, from Li-N, the s and p orbitals are closer in energy, so there is more mixing, pushing $\sigma 2p_z$ higher than π_x and π_y (we will not discuss reasons for the s-p gap here).

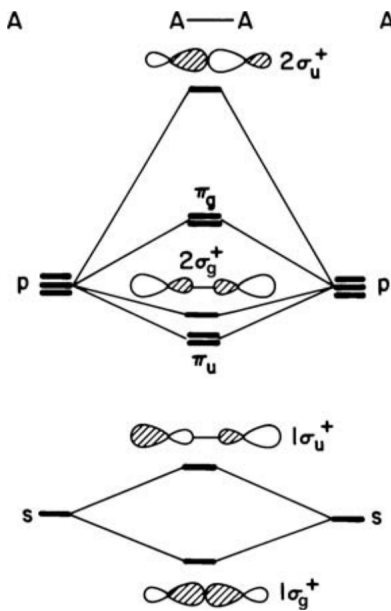


Figure 14: MO diagram of N_2

6 Constructing MOs from Fragments and Perturbation Theory

While molecular orbitals for diatomic molecules are generally constructed from overlapping atomic orbitals, this can be much more difficult for larger molecules. Instead, we generally construct MOs for larger molecules by combining the MOs of different fragments. The rules for combining fragments are the same as those for combining atomic orbitals; in fact, the same orbital mixing principles - that orbitals will mix if they are not orthogonal - hold for all cases. We consider the molecular orbitals for square H_4 , shown in Figure 15 below.

First, note that we have already determined the MOs for H_2 , but it can seem quite difficult to imagine how all four s orbitals can interact with each other. One intuitive way to approach this problem could be to find the MOs for two H_2 fragments and then combine them. For the sake of description, suppose we are mixing the left half with the right half.

Note that if both fragments are in-phase, they will have net overlap and will be able to mix. Similarly, if both fragments are out-of-phase, they will have net overlap and mix. However, the in-phase and out-of-phase fragments are orthogonal to each other, so this nicely simplifies as two 2-orbital problems.

The middle two orbitals are drawn as degenerate (equal in energy). One way to easily tell is that the two orbitals are basically identical - just rotated 90 degrees apart from each other - so they should have the same energy. Another method would be to use symmetry determinations - which we cover in the next section.

Now suppose we distort the square to a rectangle by shrinking the vertical distance and elongating the horizontal distance.

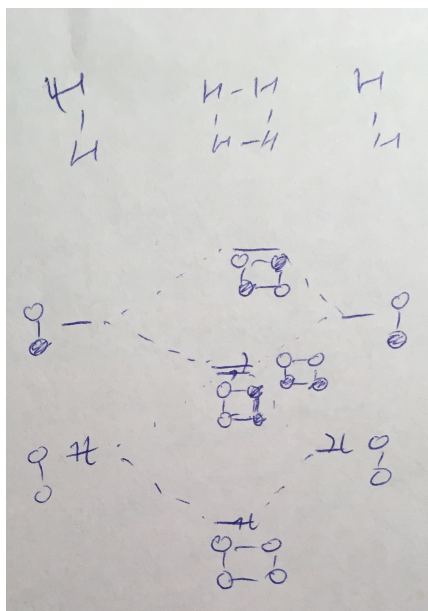


Figure 15: MO diagram of H_4

This increases the orbital overlap between the two “vertical” pairs and decreases the orbital overlap between the two “horizontal” pairs. Note that the lowest fully-bonding orbital stays roughly the same, because it gains bonding interactions from the vertical pair and loses bonding interaction from the horizontal pair. Similarly, the top orbital stays roughly constant. However, the two middle orbitals no longer stay degenerate. Note that one will gain bonding interactions and lose antibonding interactions, causing it to go down in energy, while the other does the opposite, causing it to go up in energy. This is shown in Figure 16 below:

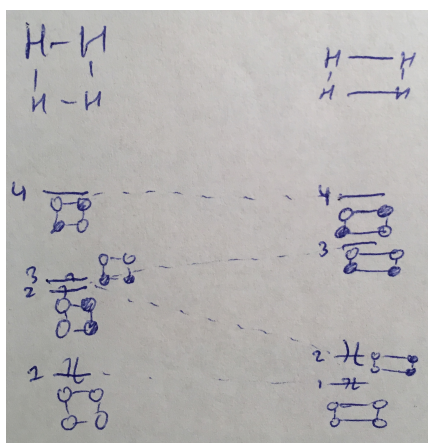


Figure 16: Square H_4 vs rectangular H_4

Note that for neutral H_4 , the molecule prefers a rectangular configuration, because it occupies the two lower bonding orbitals. However, for H_4^{2-} (6 electrons), it prefers the square configuration. This is because of Walsh’s rule, which dictates that the molecule distorts to minimize the energy of the HOMO. Walsh’s rule is very difficult to rationalize in the general case, so we just state it here without intuition behind it.

We may also construct a Walsh diagram - which demonstrates how the orbital energies change as the molecule distorts - for this transition from square to rectangular, which is shown in Figure 17 below:

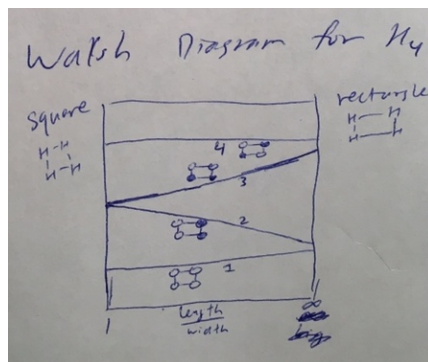


Figure 17: Walsh diagram for the transition from square H₄ to rectangular H₄

While we won't go into much more detail about perturbation theory here, it can be an extremely powerful technique. For example, when constructing the MOs of ammonia, we can first start trigonal planar ammonia and then consider what happens to the MOs as the hydrogen atoms bend downwards. If one of the hydrogen atoms of ammonia was substituted with a Cl, we could still apply perturbation theory to the MOs to see how their energy levels would change (though this is called *electronegativity perturbation*, which is a bit different than what we have discussed so far).

7 Molecular Symmetry and Group Theory

7.1 Symmetry operations

A symmetry operation is an operation that moves an object into an indistinguishable orientation. For example, if we consider a rectangular prism, one symmetry operation could be a reflection down the middle plane or a rotation of 180 degrees. For any object, all the possible symmetry operations comprise a group (a mathematical structure that can be manipulated using group theory). There are 5 different types of symmetry operations. By convention, we also let the z-axis be the principal rotation axis (largest rotational symmetry).

The first is **E**, or the identity operation. Under **E**, everything stays in the same place. The next one is σ , or a plane of reflection. For example, a reflection across the xy-plane would send point (x_1, y_1, z_1) to point $(x_1, y_1, -z_1)$. If the reflection contains the z-axis, it is a reflection across a vertical mirror plane (σ_v). If it is perpendicular to the z-axis, it is a reflection across a horizontal mirror plane (σ_h). The third type is **i**, or inversion. Inversion is equivalent to a reflection across the origin, meaning that point (x_1, y_1, z_1) gets sent to $(-x_1, -y_1, -z_1)$. The fourth type is **C_n**, or a proper rotation. This refers to the rotation of a point about a line by $\frac{2\pi}{n}$ **clockwise** (note that this is opposite to the standard mathematical convention of counterclockwise rotations). Finally, the last type is **S_n**, or an improper rotation. Under **S_n**, a point is first rotated about the line by $\frac{2\pi}{n}$ and then reflected across the plane perpendicular to the rotation axis (equivalent to first doing a **C_n** and then a σ_h).

We can also perform multiple symmetry operations on the same molecule. For example, performing a **C₂** about the z-axis and then a σ_h would be equivalent to an inversion. If we do operation *a* followed by operation *b*, we write the *direct product* as *ba* (this is because we are multiplying *ba* by some matrix representing the state of the molecule, meaning that *a* gets multiplied first, followed by *b*).

All the symmetry operations described above can be written as matrices, which can sometimes help with determining the image of the molecule after performing multiple operations. However, we will not go into much detail about that here.

7.2 Basic Group Theory

A group must satisfy the following four properties:

- Closure - all binary products (product between 2 not-necessarily-distinct operations) must be in the group
- Identity - the group must contain the identity operation
- Inverse - all elements must have an inverse, meaning that for all operations *a*, there exists an a^{-1} such that $a \cdot a^{-1} = a^{-1} \cdot a = E$
- Associativity - for any operations *a*, *b*, and *c*, we must have $(a \cdot b) \cdot c = a \cdot (b \cdot c)$

Groups also *may* satisfy commutativity (for any operations a, b , we have $a \cdot b = b \cdot a$), though most do not. A group is called **Abelian** if it does indeed satisfy commutativity. A subgroup is a subset of the group which contains the same properties as the group. For example, the even integers are a subgroup of the integers under addition (note that the odd integers, however, are not a subgroup, because the sum of 2 odd integers is not odd). A property of subgroups is that the number of items in each subgroup is a divisor of the number of elements of a group. We may now begin to discuss how to determine the point group of a particular object or molecule.

7.3 Assigning point groups

Assigning the point group of a molecule can be very useful in determining its molecular orbitals. In many symmetric molecules (such as octahedral metal complexes or even trigonal pyramidal molecules like ammonia), we can first determine the molecular orbitals of the ligand fragment (ignoring the central atom) and their symmetries, and then mixing these orbitals with those of the central atom to determine the final molecular orbitals of the molecule.

Unfortunately, learning and internalizing the rules can be quite difficult. We try to make it as intuitive as possible here, and we also provide a flowchart to help with this process. Ideally, point group assigning should ultimately be done without the flowchart, but it is not the most pressing skill to acquire either.

First, we check if the molecule is a special point group. A linear molecule is either D_h (symmetric, such as H_2 or CO_2) or C_h (not symmetric, such as HF). A sphere is K_h , though no actual molecule with more than one atom can have this symmetry. Tetrahedral (T_d), octahedral (O_h), and icosahedral (I_h) are the other special point groups (there are slightly different variants of these, which are T, T_h , O, I, but these are extremely rare and will probably never come up in real molecules).

Then we look for the highest order (principal) rotational axis of the molecule (the C_n with the highest n). If there is no rotational axis at all, then we look for a mirror plane (if yes, the molecule has C_s symmetry) or inversion symmetry (if yes, the molecule has C_i symmetry). If it has neither of these as well, it cannot possess any non-identity symmetry operations and is just C_1 .

If the molecule does have a rotational axis, we then look for a mirror plane. These tend to be fairly easy to see. If the molecule does not have a mirror plane, we check for collinear S_{2n} . This refers to S_{2n} with the same axis as the principal rotation axis. If the molecule has collinear S_{2n} , then the point group of the molecule is simply S_{2n} .

If the molecule is not S_{2n} (meaning it either has a mirror plane or has no collinear S_{2n}), we then check for perpendicular C_2 axes. This can be very obvious in molecules such as benzene while very tricky to spot in molecules such as allene. Also note that if you find one perpendicular C_2 axis, there must be $n-1$ more of them (for odd n , the molecule is symmetric with respect to rotation by $\frac{2\pi}{n}$ radians, giving n total C_2 axes; for even n , rotating by $\frac{2\pi}{2n} = \frac{\pi}{n}$ still gives another C_2 axis, but

since each axis is coincident with itself after a rotation of π radians, there are still n total axes. If the latter seems a bit strange, consider structures with an even-fold rotation axis, such as a square pyramid or a hexagon).

If the molecule has such a perpendicular C_2 axis, it is of the D class. Then we check for a horizontal mirror plane (if yes, the molecule is D_{nh}) or a vertical mirror plane (if yes, the molecule is D_{nd}). If it has neither, it is D_n (note that we already checked for a mirror plane, so this part should be easy).

If the molecule does not have such a perpendicular C_2 axis, it is of the C class. Similarly, we check for a horizontal mirror plane (if yes, the molecule is C_{nh}) or a vertical mirror plane (if yes, the molecule is C_{nv}). If it has neither, it is C_n .

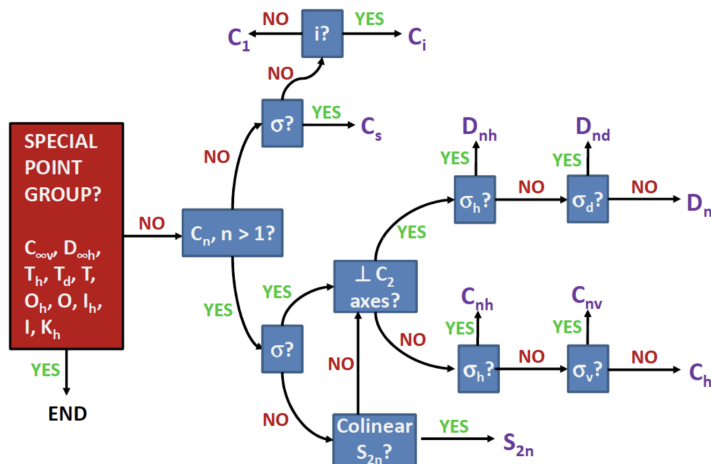


Figure 18: Flowchart for point group determination; image courtesy of the notes of Yogesh Surendranath

To build a deeper intuition for the point groups, we also describe certain characteristics of some of the more common point group classes.

7.3.1 C_n point group

C_n : C_n is actually not very common, as it possesses no mirror planes at all. Most objects of C_n symmetry look like propellers, as shown below:



Figure 19: C_5 symmetry propeller; image courtesy of performacepropsinc.com

7.3.2 C_{nv} point group

C_{nv} : C_{nv} is one of the most common point group classes. Any pyramid with a regular polygon base, such as ammonia, falls into this category. C_{2v} is probably the most common point group, consisting of all bent molecules (e.g. water).

7.3.3 C_{nh} point group

C_{nh} : C_{nh} is not nearly as common as C_{nv} , though many substituted planar molecules such as trans-dichloroethene fall under this class.

7.3.4 D_n point group

D_n : D_n is also quite a rare point group. An example molecule is given below, though there are not many:

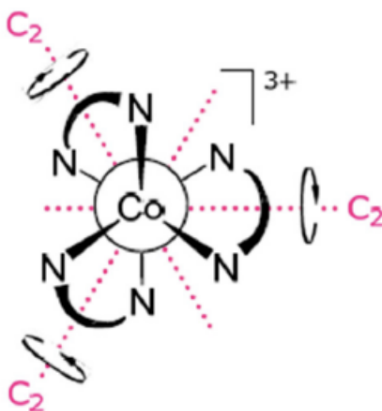


Figure 20: D_3 molecule; image courtesy of notes of Yogesh Surendranath

Note that the C_2 axes are not very easy to see sometimes! For a molecule like this, it can be easier to look at it from the angle above (instead of just the normal octahedral configuration).

7.3.5 D_{nh} point group

D_{nh} : D_{nh} is also one of the most common point groups. It consists of all symmetrically substituted planar molecules (e.g. benzene, ethylene, 1,4-dichlorobenzene) as well as prism-shaped molecules, such as the one below:

7.3.6 D_{nd} point group

D_{nd} : D_{nd} is also a fairly common point group, with most of the molecules being antiprismatic in shape (meaning the top face is offset from the bottom face). Examples include allene (the two $C-H_2$ planes are offset by 90 degrees) and ferrocene:

7.3.7 O_h and T_d point groups

O_h and T_d : of course, most symmetric metal-ligand complexes are either O_h (octahedral, hexavalent) or T_d (tetrahedral, tetravalent). These will be explored in greater detail in the section about ligand field theory!

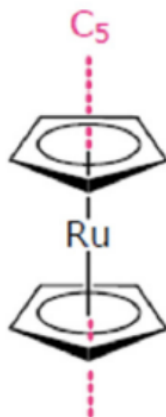


Figure 21: D_{5h} molecule; image courtesy of notes of Yogesh Surendranath

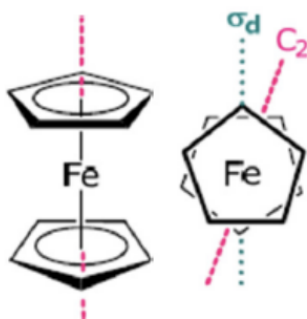


Figure 22: Ferrocene - D_{5d} molecule; image courtesy of notes of Yogesh Surendranath

7.4 Similarity transformations and classes

Operations a and b are considered conjugates of each other if there exist an operation x such that $x^{-1}ax = b$ (conjugacy is commutative). A class of operations is a set of operations that are conjugates of each other. One way to determine the class that a particular symmetry operation is in is to compute $x^{-1}ax$ for all x in the group; the resulting products make up its conjugacy class.

It must hold that each operation is in exactly one class, and that the order of each class is a divisor of the number of elements in the class. After partitioning the group elements into classes, we can begin to determine the representations of the group. Though this may still seem fairly arbitrary, the final irreducible representations (cannot be decomposed any farther) can be used to determine the molecular orbitals of any molecule in that symmetry group.

7.5 Group representations

A representation of the group is a series of coefficients for each of the conjugacy classes of the group. The dimensionality of a representation is the largest (absolute value of) coefficient, which is also the coefficient under the identity operation (must be a positive integer). To clarify things, we use the following notations:

- $h = \#$ of elements in the group
- $\Gamma_i = \text{IRR } i$
- $l_i = \text{dimensionality of } \Gamma_i$
- $g(R) = \#$ elements in conjugacy class R
- $\chi_i(R) = \text{coefficient of } \Gamma_i \text{ in class R}$

We then use the following 5 rules to determine all the irreducible representations (IRR) of a point group:

1. $\#$ of classes = $\#$ of IRRs
2. Determine dimensionality of the IRRs, given that $\sum_i l_i^2 = h$
3. All groups contain one totally symmetric IRR (all coefficients are 1)
4. All IRRs are orthogonal (for any Γ_i and Γ_j , $\sum_R g(R)\chi_i(R)\chi_j(R) = 0$)
5. Sum of squares of each character in any specific IRR (multiplied by the coefficient of the conjugacy class) is equal to the number of elements in the group

This may seem very complicated, but it is actually fairly intuitive and comes fairly quickly with repeated practice. We consider the example of the C_{3v} point group. We first determine the different conjugacy classes of the point group, which are $\{\mathbf{E}\}$, $\{\mathbf{C}_3, \mathbf{C}_3^2\}$, and $\{\sigma_v, \sigma'_v, \sigma''_v\}$ (derivation is left as an exercise to the reader). Since there are three classes, there must be three IRRs.

We already know one of them is fully symmetric from rule 3. From rule 2, we know that the sum of squares of the dimensions must equal 6 ($\#$ of elements in the group). The only way 3 integers squared can sum to 6 is if they are 1, 1, and 2. We also know the other IRR with dimensionality 1 must be orthogonal to the fully-symmetric one, and that all the other coefficients must be either 1 or -1 (the dimensionality is the largest coefficient, and by rule 5, the sum of squares multiplied by the order of the classes must be 6, so we cannot have any 0s). Thus, for it to be orthogonal to the fully symmetric representation, it must have a 1 under the second class and a -1 under the third class. Finally, for the IRR with dimensionality 2, it must have a -1 under the second class and a 0 under the third class to maintain orthogonality with the fully-symmetric IRR. Also note that this is orthogonal to the second IRR and satisfies rule 5. The full character table is shown below:

IRRs are given symmetry labels called *Mulliken symbols*. The following rules help to determine the Mulliken symbol for any given IRR.

- If the character for the IRR under the identity column (E) is 1, then the Mulliken symbol will be either A or B. If it is 2, then the symbol will be E. If it is 3, then the symbol will be T.

$C_{3v};$	E	$2C_3$	$3\sigma_v$	Linear	Binomial
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y) (R_x, R_y)$	$(x^2-y^2, xy) (xz, yz)$

Figure 23: C_{3v} point group character table; image courtesy of notes of Yogesh Surendranath

- If the identity character is 1, and the character under the C_n (principal rotation axis) class is +1, the Mulliken symbol is A. If the character is -1 with respect to the principal rotation axis, then the Mulliken symbol is B.
- If there exists an inversion center (that is, if the i operation is visible in the character table), then if the character in the i column is +1, add a "g" subscript to the Mulliken symbol. If the character is -1, then add a "u" subscript.
- If there is a perpendicular C_2 axis, a character of +1 yields a subscript "1", and a character of -1 yields a subscript "2". If there is no perpendicular C_2 axis, use the character related to the σ_v reflection plane instead.
- If there is a σ_h plane, then a character of +1 adds an apostrophe ('), while a character of -1 adds a double apostrophe (").

A few examples of Mulliken symbols are A_1g , T_{2g} , E_g , and A'' .

8 Symmetry-Adapted Linear Combinations

8.1 Determining molecular orbitals from character tables

Now that we have the character tables for the point groups, we can finally construct some molecular orbitals! Since we generated the character table for C_{3v} , let us consider ammonia (which has point group C_{3v}). We first consider the H_3 fragment and determine its reducible representation in the point group. To do this, we perform each of the group operations on the 3 hydrogen atoms, and each one that stays in place contributes +1, each one that moves contributes 0, and each one that inverts contributes -1 (note that s orbitals don't have inversion symmetry, so this can't happen; however, this may occur for p orbitals). Under the identity transformation, all 3 stay in place, so the character is 3. Under a rotation, all 3 move, so the character is 0. Under each reflection, exactly 1 stays in place, so the character is 1. Our reducible representation is then just $3 \mid 0 \mid 1$.

We now decompose this into irreducible representations. One way to do this is by inspection - since these numbers are small, it is not hard to see that this is a sum of A_1 and E. For larger groups, however, we may need to use the reduction formula, which is as follows:

$$n(\Gamma_i) = \frac{1}{h} \sum_i g(R) \chi_{IRR}(R) \chi_{RR}(R)$$

Applying this to each representation, we get $1A_1 + 0A_2 + 1E$. We then use the projection operator for each of these representations. To do this, we take any N-H bond and consider where it moves upon each symmetry operations. For example, σ_1 moves to σ_1 under E , σ_2 under C_3 , σ_3 under C_3^2 , σ_1 under σ_v , σ_2 under σ'_v , and σ_3 under σ''_v (arbitrary designations of the mirror planes, but all that matters is that σ_1 goes to all 3 N-H bonds under the three mirror planes).

We then consider the dot product between this and the IRR A_1 . Since A_1 has all 1s, the total dot product is $3(\sigma_1 + \sigma_2 + \sigma_3)$, so the orbital is fully in-phase. Similarly, when we take the dot product with the IRR E, we get $2\sigma_1 - \sigma_2 - \sigma_3$. Since E is a doubly degenerate set, we need 2 orbitals. To do this, we then project a different N-H bond (say σ_2) and get $2\sigma_2 - \sigma_1 - \sigma_3$. Note that these orbitals must be orthogonal, so we need to apply a technique called Schmidt Orthogonalization. While we won't go into much detail here, it basically takes an orthogonal linear combination of the two. The resulting orbitals for the E set become $2\sigma_1 - \sigma_2 - \sigma_3$ and $\sigma_2 - \sigma_3$. Upon normalization (multiplication by a coefficient to make the norm 1), these are the MOs for the H_3 fragment!

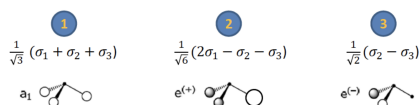


Figure 24: MO diagram of H_2O

8.2 Molecular orbitals of H₂O

We now apply this technique to determine the molecular orbitals of H₂O. We first construct the SALCs for the H₂ fragment in C_{2v} symmetry (the point group of water). While we could do this rigorously, in this case it would be simpler to say that they can either be in-phase or out-of-phase. In fact, the SALCs for a system are equivalent to the MOs of an H_x molecule (x H atoms) in that exact geometry, so if we have already solved for the MOs of that molecule, we do not need to solve for the SALCs again. The in-phase combination transforms as A₁, while the out-of-phase combination transforms as B₂. We then mix the SALCs with the atomic orbitals on oxygen. The O 2s transforms as A₁ symmetry (while low in energy, it does technically mix a little bit; we show it mixing here, but ignoring it would be acceptable as well). The O 2p orbitals transform as A₁, B₁, and B₂. The O 2s and the A₁ and B₂ (in this case, p_z and p_x) p orbitals will then interact with the two H₂ SALCs, as shown in Figure 24.

Note that the 2A₁ orbital is raised a bit in energy due to the antibonding mixing of the O 2s orbital (secondary mixing), so it is higher in energy than the 1A₂ orbital. Also note that H₂O only has 1 fully nonbonding lone pair - a stark contrast from what valence bond theory would predict!

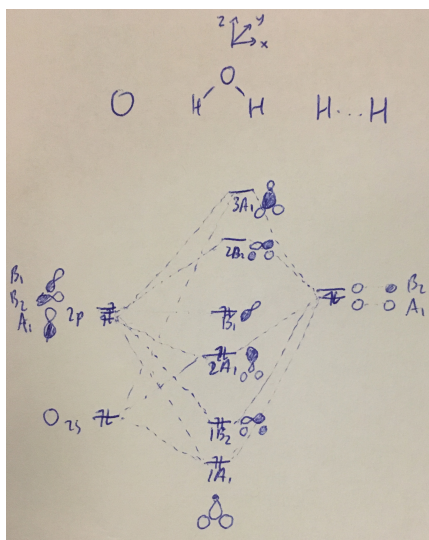


Figure 25: MO diagram of H₂O

9 Crystal Field Theory

Crystal field theory (CFT) is a model used to determine the energy levels of the various d orbitals in a metal-ligand complex. In CFT, we assume that all ligands are (negative) point charges. These point charges repel the electrons in d orbitals, which will raise their energies. As a result, CFT can be used to determine splitting diagrams for different ML_x complexes.

We determine the relative energy levels of the d orbitals by comparing the amount of repulsion that each exhibits with the point charges. First, we consider the octahedral field. As the d_{z^2} and $d_{x^2-y^2}$ interact head-on with the ligands, they will be destabilized the most (greatest repulsive interactions). The d_{xy} , d_{xz} , and d_{yz} are at 45 degree angles to the point charges, so they will be less repelled. Note that from our discussion of symmetry above, we can decompose the d orbital set in the octahedral point group into a T_{2g} and E_g set, which explains the degeneracy of orbitals that we see in Figure 25.

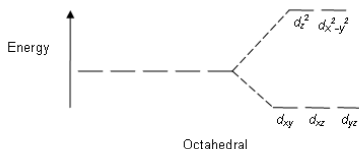


Figure 26: Octahedral field splitting diagram; image courtesy of Wikipedia

Now we consider the tetrahedral field. Here, we have that the d_{xy} , d_{xz} , and d_{yz} orbitals have greater interactions with the ligands than the d_{z^2} and $d_{x^2-y^2}$ orbitals. However, the orbital levels are reversed here (T_2 higher than E). Notice that the energy splitting for tetrahedral is smaller than octahedral (by a factor of around $\frac{4}{9}$). This is because the octahedral interactions are head-on (greater repulsion) and that there are simply more ligands in the octahedral complex (more total interactions). We can apply similar processes to attain orbital splitting energies for other complexes, such as trigonal bipyramidal or square planar; the results are left as an exercise to the reader.

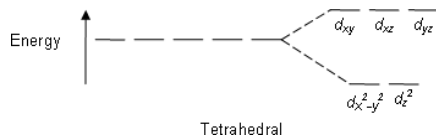


Figure 27: Tetrahedral field splitting diagram; image courtesy of Wikipedia

10 Ligand Field Theory

Here's where the real fun begins! With ligand field theory, the ligands are no longer negative point charges - we actually take into account their orbital interactions with the metal d orbitals. For the simplest case, we can first assume that the ligands are σ -donors only, so they can be represented by just one orbital lobe along their respective axes. We also assume that the metal is a third-row transition metal. We first derive the SALCs of the octahedral ligand basis. The result is shown below in Figure 27 (the derivation is left as an exercise for the interested reader; the answer derived by hand may be slightly different than the one displayed below, though the interactions will remain the same).

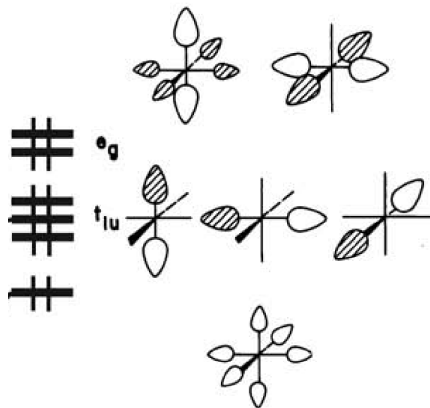


Figure 28: SALCs of an octahedral ligand set^[3]

Now we use these SALCs and mix them with the metal's s, p, and d orbitals. Note that the A_{1g} orbital set (the lowest-energy SALC) will mix with the metal 4s orbital, the T_{1u} set will mix with the metal 4p orbitals, and the E_g set will mix with the metal's d_{z^2} and $d_{x^2-y^2}$ orbitals. Additionally, note that the ligand orbitals will generally be lower in energy than the metal d orbitals (due to ligands being electronegative in nature and having lower-lying lone pairs), which lie below the metal 4s orbital, which lies below the 4p orbitals. The result is shown in Figure 28 below.

Note that each of the interactions described above leads to a bonding and antibonding pair, as we discussed previously. Also note that the T_{2g} metal d orbitals do not interact with any ligand orbitals and are completely non-bonding orbitals. This contrasts with crystal field theory, where the ligand "point charges" do have weak repulsive interactions with the T_{2g} set. Finally, this can also explain the 18-electron rule (which states that a metal complex can take on 18 electrons in bonding/non-bonding orbitals) in the octahedral configuration, as there are 18 total electrons that can fill the T_{2g} orbitals and lower.

However, most ligands are not only σ donors! Even halides or amide (NH_2^-) can interact with the metal d orbitals in a π -fashion using the p_x or p_y orbitals, as shown below:

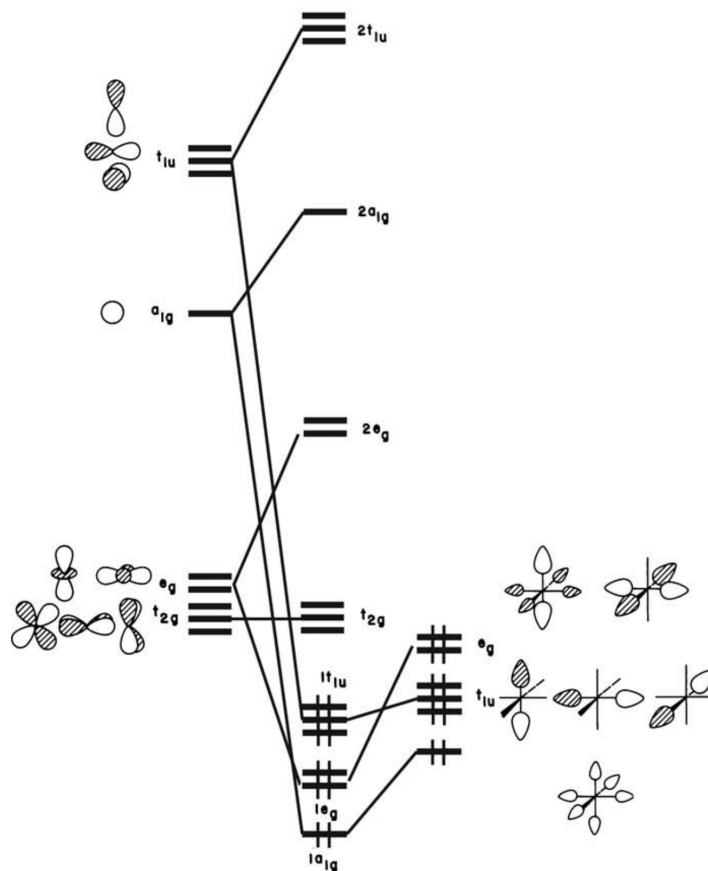


Figure 29: MO diagram for an octahedral ML_6 complex with pure σ -donor ligands^[3]

10.1 π -donating effects

While our previous model works well for pure σ -donor ligands, most ligands are not pure σ -donors. Consider halides or amide, for example, which can also interact with the metal in a π -fashion using one of their lone pairs. This is called π -donation, because the ligand orbitals are interacting with the metal orbitals to form a π bond, which transfers some of the electron density from the ligand to the metal.

The above case shows the interaction of the d_{xy} orbital with one of the ligands in the xy plane. This would cause the lone pair on the ligand to decrease (forms a bonding interaction), while raising the energy of the d_{xy} orbital. Of course, since the T_{2g} set is symmetric, if all 6 ligands are identical, they will all increase in energy by the same amount. We say that the T_{2g} orbital set has π symmetry, since it interacts in a π -fashion, while the E_g set has σ symmetry, since it interacts in a σ fashion.

Note that this raising of the energy of the T_{2g} set brings the T_{2g} and E_g orbitals closer in energy, reducing the octahedral field splitting energy. We thus refer to halides **weak-field** ligands, because they reduce the octahedral field splitting energy.

10.2 π -accepting effects

While halides can donate electrons to the metal in π -fashion (using filled p orbitals), some species can accept electrons from the metal in a π -accepting fashion (using empty π^* orbitals). These species include alkenes, alkynes, CO, CN^- , and almost anything with a double or triple bond. The interaction is shown in Figure 29 below:

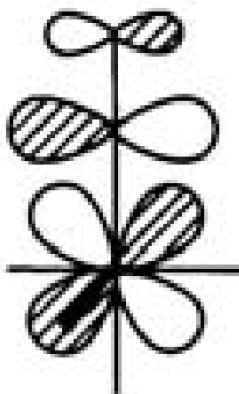


Figure 30: Interaction between metal d orbital and π^* orbital of CO^[3]

Note that while filled ligand orbitals tend to be lower in energy than metal orbitals, unfilled ligand orbitals are generally higher in energy than metal orbitals, by virtue of being antibonding in character. This interaction then causes the metal d_{xy} orbital to decrease in energy, while the π^* orbital increases in energy. Similarly, since the T_{2g} set is degenerate (if the ligands are identical), the entire orbital set will decrease in energy in the presence of these π -acceptor ligands, increasing the octahedral field splitting energy. As a result, we also refer to π -accepting ligands as **strong-field** ligands.

10.3 Spectrochemical Series

We can also quantify the relative amount of π -donor or π -acceptor character in different ligands.

As discussed previously, the amount of mixing between two orbitals depends both on the spatial overlap and the energetic difference. As we move down the halogens, the orbitals become much more diffuse and higher in energy. The diffuse-ness allows the larger halides to have a greater spatial overlap with the metal d orbitals, which extend quite far out; the increased energy of the lone pairs brings their energy closer to the energies of the metal d orbitals. Both of these factors serve to increase the amount of mixing between the orbitals, causing the energy of the T_{2g} set to increase more with the larger halides. This makes the larger halides weaker-field ligands than the smaller halides, so we get $\text{I} < \text{Br} < \text{Cl} < \text{F}$ in order of increasing field strength.

With π -acceptor ligands, the same factors - spatial overlap and energetic proximity - also dictate the extent of mixing. When we have an electronegative atom in the ligand (e.g. CO, CN^-), the energies of the orbitals tend to be much lower.

This is because the electronegative atom has a much lower-lying orbital, so the bonding orbital also decreases in energy. Additionally, because the energy gap is larger, there is less mixing, so the antibonding energy is less destabilized and lower in energy as well. Furthermore, we know that the bonding orbital is primarily the electronegative atom in character, while the antibonding orbital is primarily the electropositive atom in character. In the case of CO or CN^- , the π^* orbital is strongly polarized toward the C, which is the end that interacts with the metal d orbitals. This increases the spatial overlap between the π^* orbital and the metal orbitals compared to that of a generic alkene interacting with the metal. Both this factor and the lower energy of the π^* orbital cause CO/ CN^- to mix more strongly with the metal d orbitals than an alkene, causing the T_{2g} set to decrease by a larger amount in the case of CO/ CN^- . This makes CO/ CN^- a much stronger-field ligand than alkenes.

While there can be a few other factors at play, this analysis gives us a pretty good idea of the field strength of different types of ligands, with π -donors being the weakest field ligands, pure σ -donors being in the middle, and π -acceptors being the strongest-field ligands. These are collectively ordered into the spectrochemical series (though it is important to note that this is determined experimentally and that our rationalizations may not be perfect) as follows: $\text{O}_2^{2-} < \text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- (\text{S-bonded}) < \text{Cl}^- < \text{N}_3^- < \text{F}^- < \text{NCO}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- (\text{N-bonded}) < \text{CH}_3\text{CN} < \text{gly} (\text{glycine}) < \text{py} (\text{pyridine}) < \text{NH}_3 < \text{en} (\text{ethylenediamine}) < \text{bipy} (2,2'\text{-bipyridine}) < \text{phen} (1,10\text{-phenanthroline}) < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$ (courtesy of Wikipedia).

Of course, you do not need to memorize this by any means, but knowing where it comes from can be very useful!

10.4 Other effects

There are also two other important factors in determining the octahedral field splitting energy: oxidation state of the metal and the period of the metal.

As the oxidation state of the metal increases, the electrostatic attraction of the nucleus and the ligands/electrons increases, drawing everything toward the nucleus of the metal center. This causes all the orbitals to come into closer proximity, which increases the orbital overlap and thus extent of mixing. As a result, this will increase the octahedral field splitting energy.

As the period of the metal increases, the metal orbitals become much more diffuse, allowing them to better overlap with ligand orbitals. Furthermore, the larger metal radius reduces the steric clash between the ligands, allowing them to get closer to the metal. Both of these effects increase the extent of mixing, which increases the octahedral field splitting energy.

Finally, the octahedral field splitting can help us determine the electron configuration of the complex. Complexes that are strong-field, or low spin (typically involving strong-field ligands, metals with charge 3+ or in periods 4 or 5, or both), prefer to fully fill the T_{2g} before filling the E_g set (they would rather incur the energy of spin pairing rather than that of the octahedral field splitting energy), while complexes that are low-field, or high spin, prefer to keep parallel spins rather

than pair spins (the octahedral field splitting is smaller than the energy associated with pairing electrons). This allows us to determine the electron configuration of d orbitals!

While we won't go into the specifics, these techniques can be applied to other geometries, such as square planar, trigonal bipyramidal, and tetrahedral.

11 References

[1]: *Chemical Principles: The Quest for Insight*, by Peter Atkins, et al. 6th edition.

[2]: *Physical Chemistry*, by Peter Atkins and Julio de Paula. 9th Edition.

[3]: *Orbital Interactions in Chemistry*, by Thomas Albright, et al. 2nd Edition.