

# Molecular orbital

In [chemistry](#), a **molecular orbital** (or **MO**) explains what happens to [electrons](#) when [atoms](#) join together in a [molecule](#). A MO is a [mathematical function](#) which describes the [wave](#)-like behaviour of an [electron](#) in a [molecule](#). The functions can tell the [probability](#) of finding an [electron](#) in any specific [region](#). [Chemists](#) use such functions to [predict](#) or explain [chemical](#) and [physical properties](#).

Chemists usually build [mathematical models](#) of molecular orbitals by combining [atomic orbitals](#). [Hybrid](#) orbitals from each [atom](#) of the molecule, or other molecular orbitals from groups of atoms can also be used. [Computers](#) can work on these functions. Molecular orbitals allow chemists to apply [quantum mechanics](#) to study molecules. MOs answer questions about how the atoms in molecules stick together. The various rounded shapes in an orbital diagram indicate where electrons would most likely be found in an atom.

Figure 1: Complete [acetylene](#) ( $\text{H-C}\equiv\text{C-H}$ ) molecular orbital set

## History

[[change](#) | [change source](#)]

The word *orbital* was first used in English by [Robert S. Mulliken](#). The [German](#) physicist [Erwin Schrödinger](#) wrote about MOs earlier. Schrödinger called them *Eigenfunktion*.

Physicist [Max Born](#) described the theory behind molecular orbitals in 1926. Today, it is known as Born's rule and is part of the [Copenhagen interpretation](#) of [quantum mechanics](#). When initially proposed, this theory did not agree with the [atom model](#) of [Niels Bohr](#). Bohr's model described electrons as "orbiting" the nucleus, as they moved around in circles. However, the Born model eventually gained popular support because it was able to describe the locations of electrons within molecules and explained a number of previously inexplicable [chemical reactions](#).

## Overview

[[change](#) | [change source](#)]

Atomic orbitals [predict](#) the position of an electron in an atom. Molecular orbitals are created when atomic orbitals are brought together. A molecular orbital can give information about the [electron configuration](#) of a molecule. The electron configuration is the most likely position, and the energy of one (or one pair of) electron(s). Mostly a MO is represented as a [linear combination of atomic orbitals](#) (the LCAO-MO method), especially in [approximate](#) use. This means that chemists [assume](#) the chance of an electron being at any point in the molecule is the sum of the [probabilities](#) of

the electron being there based on the individual atomic orbitals. LCAO-MO is a simple model of [bonding](#) in molecules, and is important for studying [molecular orbital theory](#).

[Theoretical chemists](#) use [computers](#) to calculate the MOs of different molecules (both [real](#) and [imaginary](#)). The computer can draw [graphs](#) of the "cloud" to show how likely the electron will be in any region. The computers can also give information about the [physical properties](#) of the molecule. They can also say how much [energy is required to form the molecule](#). This helps chemists say whether some small molecules can be combined to make bigger molecules.

Most present-day ways of doing [computational chemistry](#) begin by calculating the MOs of a system. Each MO's [electric field](#) is generated by the [nuclei](#) of all the atoms and some average distribution of the other electrons.

## Analogy

[[change](#) | [change source](#)]

Calculating the MOs is like predicting the location of each employee in a home improvement store.

Understanding MOs is like the task of knowing where each [employee](#) is in a large home improvement store (without looking inside the store). An analyst knows the number of employees working at the store and each employee's department. He also knows that employees do not step on each other's toes and employees stand in the [aisle](#) rather than on the [merchandise shelves](#). Employees leave their own department to help customers locate merchandise in other departments or to check [inventory](#). An analyst giving the location of all employees in the store at a selected moment without looking inside is like a chemist calculating the MOs of a molecule. Just as MOs cannot tell the exact location of each electron, the exact location of each employee is not known. An MO having a nodal [plane](#) is like the conclusion that employees walk down aisles and not through shelves. Although electrons are contributed from a specific [atom](#), the electron fills an MO without regard to its source atom. This is like an employee leaving his department to walk elsewhere in the store during the day. So, an MO is an incomplete description of an electron just as the analyst's calculations about the unseen store is an incomplete [guess](#) about employee locations.

## Formation of molecular orbitals

[[change](#) | [change source](#)]

Theoretical chemists have invented rules for calculating MOs. These rules come from an understanding of [quantum mechanics](#). Quantum mechanics helps chemists to use what [physics](#) said about electrons to work out how the electrons behave in molecules. Molecular orbitals form from "allowed" [interactions](#) between [atomic orbitals](#). The interactions are "allowed" if the [symmetries](#) (determined from [group theory](#)) of the atomic orbitals are

[compatible](#) with each other. Chemists study atomic orbital interactions. These interactions come from the [overlap](#) (a [measure](#) of how well two orbitals constructively interact with one another) between two atomic orbitals. The overlap is important if the atomic orbitals are close in energy. Finally, the number of MOs in a molecule must [equal](#) the number of atomic orbitals in the atoms being brought together to form the molecule.

## Qualitative approach

[[change](#) | [change source](#)]

Chemists need to understand the geometry of MOs in order to discuss molecular structure. The LCMO (Linear combination of atomic orbitals molecular orbital) method gives a rough but good description of the MOs. In this method, the molecular orbitals are expressed as [linear combinations](#) of all of the [atomic orbitals](#) of each atom in the molecule.

### Linear combinations of atomic orbitals (LCAO)

[[change](#) | [change source](#)]

Electron [wavefunctions](#) for the [1s orbital](#) of the hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H<sub>2</sub> molecule. The [real part](#) of the wavefunction is the blue curve, and the [imaginary part](#) is the red curve. The red dots mark the locations of the protons. The electron wavefunction oscillates according to the [Schrödinger wave equation](#), and orbitals are its [standing waves](#). The standing wave frequency is proportional to the orbital's energy. (This plot is a one-dimensional slice through the three-dimensional system.)

Molecular orbitals were first introduced by [Friedrich Hund](#)<sup>[1][2]</sup> and [Robert S. Mulliken](#)<sup>[3][4]</sup> in 1927 and 1928.<sup>[5][6]</sup>

The linear combination of atomic orbitals or "LCAO" approximation for molecular orbitals was introduced in 1929 by [Sir John Lennard-Jones](#).<sup>[7]</sup> His ground-breaking paper showed how to derive the electronic structure of the [fluorine](#) and [oxygen](#) molecules from quantum principles. This qualitative approach to molecular orbital theory is part of the start of modern [quantum chemistry](#).

Linear combinations of atomic orbitals can be used to guess the molecular orbitals that are made when the molecule's atoms bond together. Similar to an atomic orbital, a [Schrodinger equation](#), which describes the behavior of an electron, can be constructed for a molecular orbital as well. Linear combinations of atomic orbitals, (the sums and differences of the atomic [wavefunctions](#)) provide approximate solutions to the molecular Schrodinger equations. For simple [diatomic molecules](#), the wavefunctions that you get are represented mathematically by the equations

$$\Psi = c_a \psi_a + c_b \psi_b$$

and

$$\Psi^* = c_a \psi_a - c_b \psi_b$$

where  $\Psi$  and  $\Psi^*$  are the molecular wavefunctions for the bonding and [antibonding](#) molecular orbitals, respectively,  $\psi_a$  and  $\psi_b$  are the atomic wavefunctions from atoms a and b, respectively, and  $c_a$  and  $c_b$  are adjustable [coefficients](#). These coefficients can be positive or negative, depending on the energies and symmetries of the individual atomic orbitals. As the two atoms become closer together, their atomic orbitals overlap to produce areas of high electron density. So, molecular orbitals are formed between the two atoms. The atoms are held together by the [electrostatic](#) attraction between the positively charged nuclei and the negatively charged electrons occupying bonding molecular orbitals. [\[8\]](#)

## Bonding, Antibonding, and Nonbonding MOs

[\[change\]](#) | [change source](#)

When atomic orbitals interact, the resulting molecular orbital can be of three types: [bonding](#), antibonding, or nonbonding.

Bonding MOs:

- Bonding interactions between atomic orbitals are constructive (in-phase) interactions.
- Bonding MOs are lower in energy than the atomic orbitals that combine to produce them.

Antibonding MOs:

- Antibonding interactions between atomic orbitals are destructive (out-of-phase) interactions.
- Antibonding MOs are higher in energy than the atomic orbitals that combine to produce them.

Nonbonding MOs:

- Nonbonding MOs are the result of no interaction between atomic orbitals because of lack of compatible symmetries.
- Nonbonding MOs will have the same energy as the atomic orbitals of one of the atoms in the molecule.

## HOMO and LUMO

[\[change\]](#) | [change source](#)

See the main article: [HOMO/LUMO](#)

Each molecular orbital has its own energy level. Chemists sort the MOs by energy levels. Chemists assume that the electrons will fill the lowest energy level MOs first. For example, if a molecule has electrons to fill 15 orbitals, the 15 MOs with the lowest energy levels will be filled. The 15th MO on the list would be called the "highest occupied molecular orbital" (HOMO) and the 16th MO on the list would be the "lowest unoccupied molecular orbital" (LUMO). The difference in the HOMO's energy level and the LUMO's energy level is called the [band gap](#). The band gap can sometimes serve as a [measure](#) of the [excitability](#) of the molecule: the smaller the energy, the more easily it will be excited. When the electron is excited, it will jump to an unoccupied MO. For example, this can help guess whether something will give out [light](#) ([luminescence](#)).

## References

[[change](#) | [change source](#)]

1. [↑](#) Hund F. 1926. Zur Deutung einiger Erscheinungen in den Molekelspektren [On the interpretation of some phenomena in molecular spectra]. *Zeitschrift für Physik*. **36**, 657-674.
2. [↑](#) Hund F. 1927. Zur Deutung der Molekelspektren. *Zeitschrift für Physik*, Part I, **40**, 742-764; Part II, **42**, 93-120 (1927); Part III, vol. **43**, 805-826 (1927); Part IV, **51**, 759-795 (1928); Part V, vol. 63, pages 719-751 (1930).
3. [↑](#) Mulliken R.S. 1927. Electronic states. IV. Hund's theory; second positive nitrogen and Swan bands; alternate intensities. *Physical Review*, **29**, 637-649.
4. [↑](#) Mulliken R.S. 1928. The assignment of quantum numbers for electrons in molecules. *Physical Review*. **32**, 186-222.
5. [↑](#) Kutzelnigg, Werner 1996. [Friedrich Hund](#) and Chemistry, on the occasion of Hund's 100th birthday. *Angewandte Chemie International Edition*. **35**, 573-586, (1996)
6. [↑](#) [Robert S. Mulliken](#) 1967. Robert S. Mulliken's Nobel Lecture. *Science*, **157**, 3785, 13-24. [Nobelprize.org Archived](#) 2011-06-29 at the [Wayback Machine](#)
7. [↑](#) John Lennard-Jones 1929. The electronic structure of some diatomic molecules. *Transactions of the Faraday Society*. **25**, 668-686 (1929).
8. [↑](#) Gary L. Miessler; Donald A. Tarr. Inorganic Chemistry. Pearson Prentice Hall, 3rd ed., 2004.

## Other websites

[[change](#) | [change source](#)]

- [Java molecular orbital viewer](#) shows orbitals of hydrogen molecular ion.
- [The orbitron](#), a visualization of all atomic, and some molecular and hybrid orbitals
- [xeo](#) Visualizations of some atomic and molecular atoms
- [Simulations of molecules with electrons caught in molecular orbital](#) (Simulations run on PC only.)

<div> <div>• <a href="#">v</a></div> <div>• <a href="#">t</a></div> <div>• <a href="#">e</a></div> </div> <div> <b><a href="#">Chemical bonding theory</a></b> </div>		
<div> <div>•</div> <div>•</div> </div> <div> <div><a href="#">Atomic orbital</a></div> <div><a href="#">Quantum mechanics</a></div> </div>		
Types of bonds	By symmetry	<div> <div>• <a href="#">Sigma (<math>\sigma</math>)</a></div> <div>• <a href="#">Pi (<math>\pi</math>)</a></div> <div>• <a href="#">Delta (<math>\delta</math>)</a></div> <div>• <a href="#">Phi (<math>\varphi</math>)</a></div> </div>
	By <a href="#">multiplicity</a>	<div> <div>• <a href="#">2 (double)</a></div> <div>• 3 (triple) (see <a href="#">/triple bond</a>)</div> <div>• <a href="#">1 (single)</a></div> <div>• <a href="#">4 (quadruple)</a></div> <div>• <a href="#">5 (quintuple)</a></div> <div>• <a href="#">6 (sextuple)</a></div> </div>
	By <a href="#">spin</a>	<div> <div>• <a href="#">Triplet</a></div> <div>• <a href="#">Singlet</a></div> <div>• <a href="#">Exchange-coupled</a></div> </div>
<a href="#">Valence bond theory</a>	Concepts	<div> <div>• <a href="#">Lewis structure</a></div> <div>• <a href="#">Hybrid orbital</a></div> <div>• <a href="#">Resonance</a></div> </div>
	Constituent units	<div> <div>• <a href="#">Covalent bond</a></div> <div>• <a href="#">Lone pair</a></div> </div>
<a href="#">Molecular orbital theory</a>	Concepts	<div> <div>• Molecular orbital</div> <div>• <a href="#">LCAO</a></div> <div>• <a href="#">MO diagram</a></div> </div>
	Constituent units	<div> <div>• <a href="#">Bonding MO</a></div> <div>• <a href="#">Non-bonding MO</a></div> <div>• <a href="#">Antibonding MO</a></div> </div>

Retrieved from "[https://simple.wikipedia.org/w/index.php?title=Molecular\\_orbital&oldid=9293111](https://simple.wikipedia.org/w/index.php?title=Molecular_orbital&oldid=9293111)"