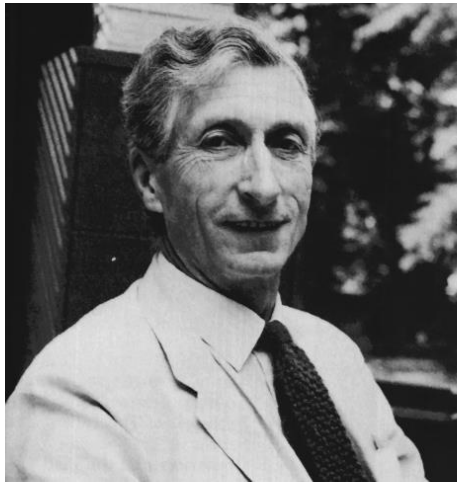
What's a chemical bond?

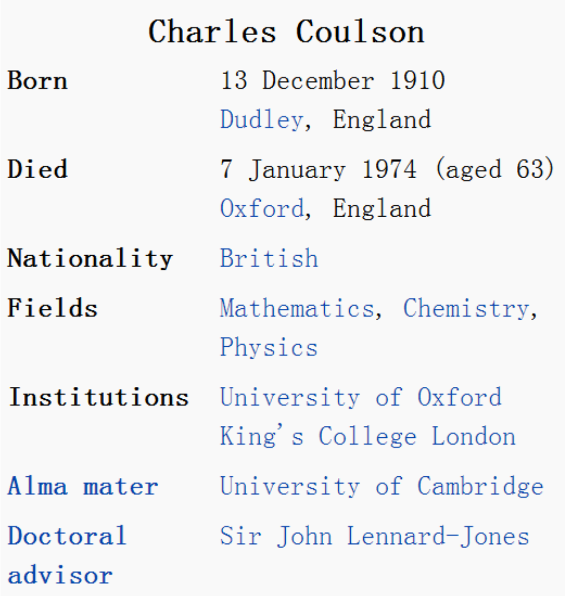
Chemical bonding occurs when one or more electrons are simultaneously attracted to *two* nuclei.

"SOMETIMES IT SEEMS to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it. Then I awake with a little shock, for a chemical bond is not a real thing. It does not exist. No one has ever seen one. No one ever can. It is a figment of our own imagination."

--C.A. Coulson (1910-1974)



The molecular orbital theory that Coulson developed is an extension of atomic quantum theory and deals with 'allowed' states of electrons in association with two or more atomic nuclei, treating a molecule as a whole. He was thus able to explain properly phenomena such as the structure of benzene and other conjugated systems, and invoked what he called partial valency to account for the bonding in such compounds as diborane.
He wrote three best-selling books: Waves 1941, Electricity 1948, and Valence 1952.



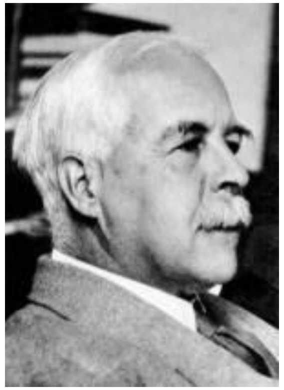
Charles Coulson	
Born	13 December 1910 Dudley, England
Died	7 January 1974 (aged 63) Oxford, England
Nationality	British
Fields	Mathematics, Chemistry, Physics
Institutions	University of Oxford King's College London
Alma mater	University of Cambridge
Doctoral advisor	Sir John Lennard-Jones

Quantum mechanical theory for chemical bonding

- **Molecular Orbital (MO) Theory**
  a) Proposed by Hund, Mulliken, Lennard-Jones et al. in 1930s.
  b) Further developments by Slater, Hückel and Pople et al.
  c) MO-based softwares are widely used nowaday, e.g., Gaussian
- **Valence Bond (VB) Theory**
  a) Proposed by Heitler and London 1930s, further developments by Pauling and Slater et al.
  b) Programmed in later 1980s, e.g., latest development--XMVB!
- **Density Functional Theory**
  a) Proposed by Kohn et al.
  b) DFT-implemented QM softwares are widely used, e.g., ADF.

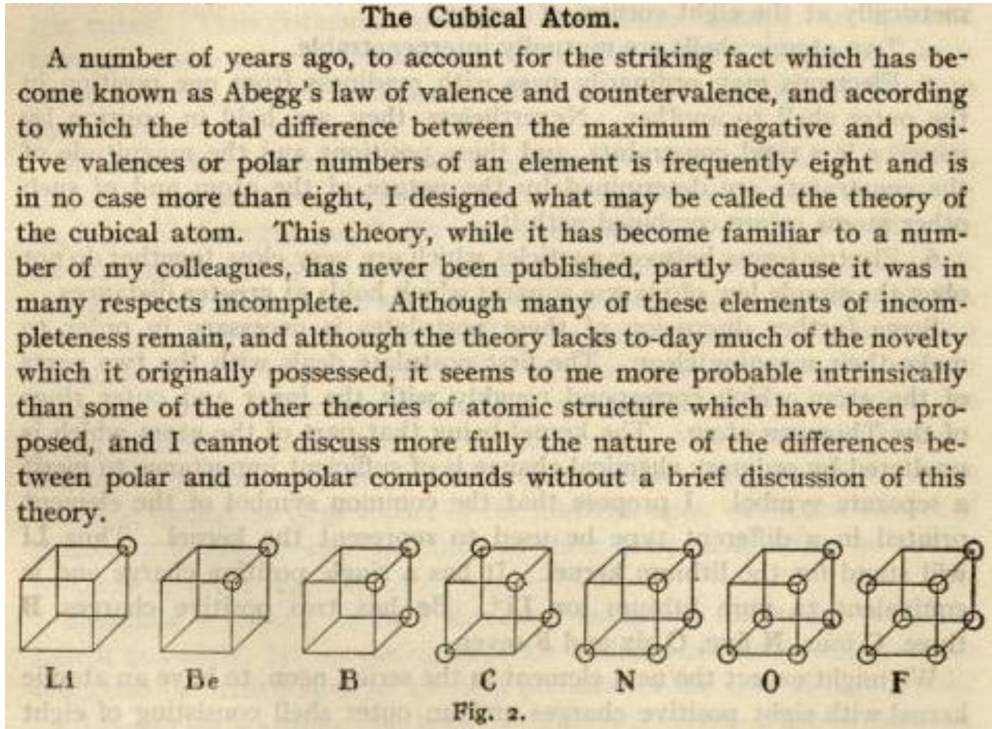
The discovery of the covalent bond and the concept of electron pairs

He introduced the notions of electron-pair bonding and the octet rule.



G. N. Lewis

nominated 41 times for Nobel prize



The Cubical Atom.

A number of years ago, to account for the striking fact which has become known as Abegg's law of valence and countervalence, and according to which the total difference between the maximum negative and positive valences or polar numbers of an element is frequently eight and is in no case more than eight, I designed what may be called the theory of the cubical atom. This theory, while it has become familiar to a number of my colleagues, has never been published, partly because it was in many respects incomplete. Although many of these elements of incompleteness remain, and although the theory lacks to-day much of the novelty which it originally possessed, it seems to me more probable intrinsically than some of the other theories of atomic structure which have been proposed, and I cannot discuss more fully the nature of the differences between polar and nonpolar compounds without a brief discussion of this theory.

Fig. 2.

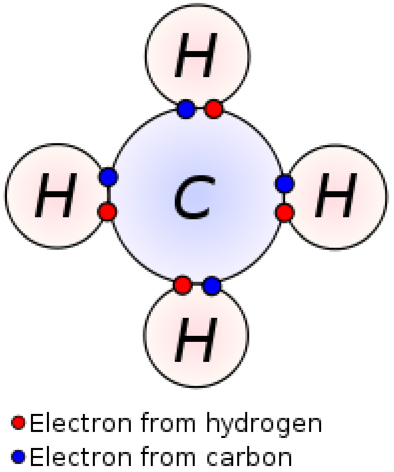
The Atom and the Molecule JACS, 1916, 38, 762

The covalent bond consists of a shared pair of electrons

“covalence”

The term "covalence" in regard to bonding is proposed firstly

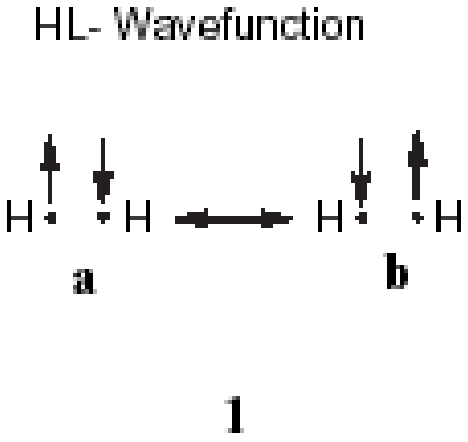
I. Langmuir



The Arrangement of Electrons in Atoms and Molecules.
JACS, 1919, 41, 868–934

The naissance of VB and quantum chemistry

W. Heitler



F. London

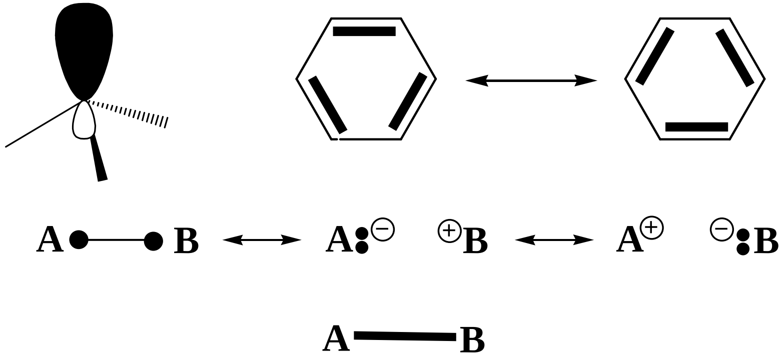
Zeits. für Physik. 44, 455 (**1927**).

Interaction Between Neutral Atoms and Homopolar

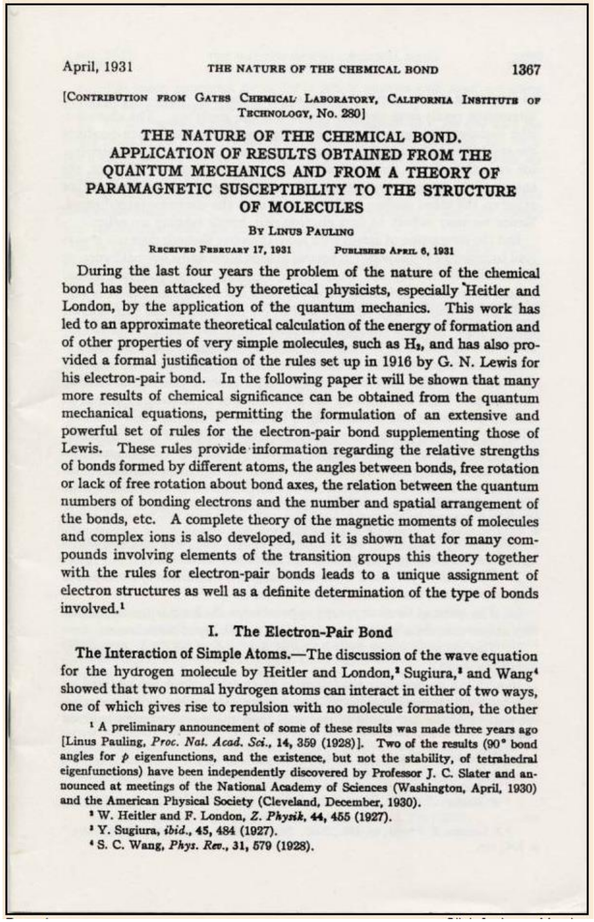
In 1927 the Heitler–London theory was formulated to show how two hydrogen atom wavefunctions join together, with plus, minus, and exchange terms, to form a covalent bond.

The contributions of Pauling

L. Pauling



Pauling constructed a general quantum chemical theory for polyatomic molecules. He developed the notion of hybridization, the covalent-ionic superposition, and the resonating benzene picture.



April, 1931 THE NATURE OF THE CHEMICAL BOND 1367

[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 280]

THE NATURE OF THE CHEMICAL BOND. APPLICATION OF RESULTS OBTAINED FROM THE QUANTUM MECHANICS AND FROM A THEORY OF PARAMAGNETIC SUSCEPTIBILITY TO THE STRUCTURE OF MOLECULES

By Linus Pauling

Received February 17, 1931 Published April 6, 1931

During the last four years the problem of the nature of the chemical bond has been attacked by theoretical physicists, especially Heitler and London, by the application of the quantum mechanics. This work has led to an approximate theoretical calculation of the energy of formation and of other properties of very simple molecules, such as H_2, and has also provided a formal justification of the rules set up in 1916 by G. N. Lewis for his electron-pair bond. In the following paper it will be shown that many more results of chemical significance can be obtained from the quantum mechanical equations, permitting the formulation of an extensive and powerful set of rules for the electron-pair bond supplementing those of Lewis. These rules provide information regarding the relative strengths of bonds formed by different atoms, the angles between bonds, free rotation or lack of free rotation about bond axes, the relation between the quantum numbers of bonding electrons and the number and spatial arrangement of the bonds, etc. A complete theory of the magnetic moments of molecules and complex ions is also developed, and it is shown that for many compounds involving elements of the transition groups this theory together with the rules for electron-pair bonds leads to a unique assignment of electron structures as well as a definite determination of the type of bonds involved.[1]

I. The Electron-Pair Bond

The Interaction of Simple Atoms.—The discussion of the wave equation for the hydrogen molecule by Heitler and London,[2] Sugiura,[3] and Wang[4] showed that two normal hydrogen atoms can interact in either of two ways, one of which gives rise to repulsion with no molecule formation, the other

[1] A preliminary announcement of some of these results was made three years ago [Linus Pauling, *Proc. Nat. Acad. Sci.*, 14, 359 (1928)]. Two of the results (90° bond angles for *p* eigenfunctions, and the existence, but not the stability, of tetrahedral eigenfunctions) have been independently discovered by Professor J. C. Slater and announced at meetings of the National Academy of Sciences (Washington, April, 1930) and the American Physical Society (Cleveland, December, 1930).

[2] W. Heitler and F. London, *Z. Physik*, 44, 455 (1927).

[3] Y. Sugiura, *ibid.*, 45, 484 (1927).

[4] S. C. Wang, *Phys. Rev.*, 31, 579 (1928).

The Nature of the Chemical Bond, Cornell University Press, Ithaca New York,1939 (3rd Edition, 1960).

Classical VB theory

- The pair bonding ideas of Lewis
- The Heitler–London theory
- Resonance (1928)
- Hybrid orbitals (1930)

Molecular orbital theory

R. S. Mulliken

Originally called the Hund-Mulliken theory, introduced by Mulliken in 1932.

J. C. Slater; F. Hund; J. Lennard-Jones…

The first accurate calculation of a molecular orbital wavefunction was that made in 1938 on the hydrogen molecule.

From 1950s….

共振论与化学键概念直接联系，成功地应用到所有化学结构和所有化学问题

L. Pauling, *The Nature of the Chemical Bond,* Cornell University, Press, Ithaca New York, 1939 (3rd Edition, 1960).

G.W. Wheland, *Resonance in Organic Chemistry*， Wiley, New York, 1955.

相反地，MO理论直接与已有的化学思想概念抵触

VB理论统治着人们对化学的理解

1950 年中期，

MO方法　　Huckel规则得到实验验证

1952年Fukui发表了前线分子轨道理论

光谱，化学反应等应用的成功，

计算方法的发展（EHMO, 半经验方法）

1965年Woodward和Hoffmann发表轨道对称守恒原理

对化学反应的研究取得巨大的成功

VB方法停滞不前，没有给出新东西，无法应用于较大分子体系

Density functional theory

The Hohenberg-Kohn Theoremm
Density Is Everything

Kohn played the leading role in the development of density functional theory, which made it possible to calculate quantum mechanical electronic structure by equations involving the electronic density (rather than the many-body wavefunction).

$$\hat{H} = -\frac{1}{2}\sum \nabla_i^2 + \sum v(r_i) + \sum_{i<j} \frac{1}{r_{ij}}$$

external field

$$v(r_i) = -\sum_{\alpha} \frac{Z_\alpha}{r_{i\alpha}}$$

Once *v*(r_i) and N are specified, wave function is determined.

There exists a one-to-one correspondence between the electron density of a system and the energy

Proof by contradiction

If the theorem is wrong, one ρ(r) must correspond to least two external potential, v(r) and v'(r), so there must be two Hamiltonian system:

$H = T + V + V_{ee}$

$H' = T' + V' + V'_{ee}$

(1)The operator $T = T'$, $V_{ee} = V'_{ee}$

so we have $H = H' + V - V'$

(2) $H\Psi = E\Psi$

$H'\Psi' = E'\Psi'$

For system 1: $\rho(r) = |\Psi(r)|^2$

2: $\rho(r) = |\Psi'(r)|^2$

(3) According to variation principle:

If the exact ground state Ψ(r) is found, the energy is

$$E = \langle\Psi|H|\Psi\rangle$$

$$E' = \langle\Psi'|H'|\Psi'\rangle$$

If the ground state Ψ(r) is not fully optimized, then $E < \langle\Psi|\mathrm{H}|\Psi\rangle$

$$E = \langle\Psi|H|\Psi\rangle$$
$$< \langle\Psi'|H|\Psi'\rangle$$
$$= \langle\Psi'|\, H' + V - V' \,|\Psi'\rangle$$
$$= \langle\Psi'|\, H' \,|\Psi'\rangle + \langle\Psi'|\, V - V' \,|\Psi'\rangle$$
$$= E' + \langle\Psi'|\, V - V' \,|\Psi'\rangle$$

Because:

$$\langle \Psi' | V - V' | \Psi' \rangle = \int dr \Psi'(r)(V - V')\Psi'(r)$$
$$= \int dr (V - V')\Psi'(r)\Psi'(r)$$
$$= \int dr (V - V')\rho(r)$$

So we have: $E < E' + \int dr (V - V')\rho(r)$ (*)

$$\begin{aligned} E' &= \langle \Psi' | \mathrm{H}' | \Psi' \rangle \\ &< \langle \Psi | \mathrm{H}' | \Psi \rangle \\ &= \langle \Psi | \, \mathrm{H} - (V - V') | \Psi \rangle \\ &= \langle \Psi | \, \mathrm{H} \, | \Psi \rangle - \langle \Psi' | \, V - V' \, | \Psi' \rangle \\ &= E - \langle \Psi' | \, V - V' \, | \Psi' \rangle \end{aligned}$$

$$E' < E - \int dr (V - V') \rho(r) \qquad (**)$$

Sum of eqs (*) and (**), we have:

$E + E' < E + E'$

The conclusion is wrong.

So the theorem is right.

(1)Instead of dealing with the formidable 3N degrees of freedom, only 3 degrees of freedom are necessary to be studied in any physical or chemical system since the electron density normally is a 3-dimensional variable.

This theorem grantees that a quantum theory based on the particle density is not only possible but also promising.

(2) The nuclear geometry => $V(r)$ => $\rho(r)$ => H

It determines the physical and chemical nature of the system.

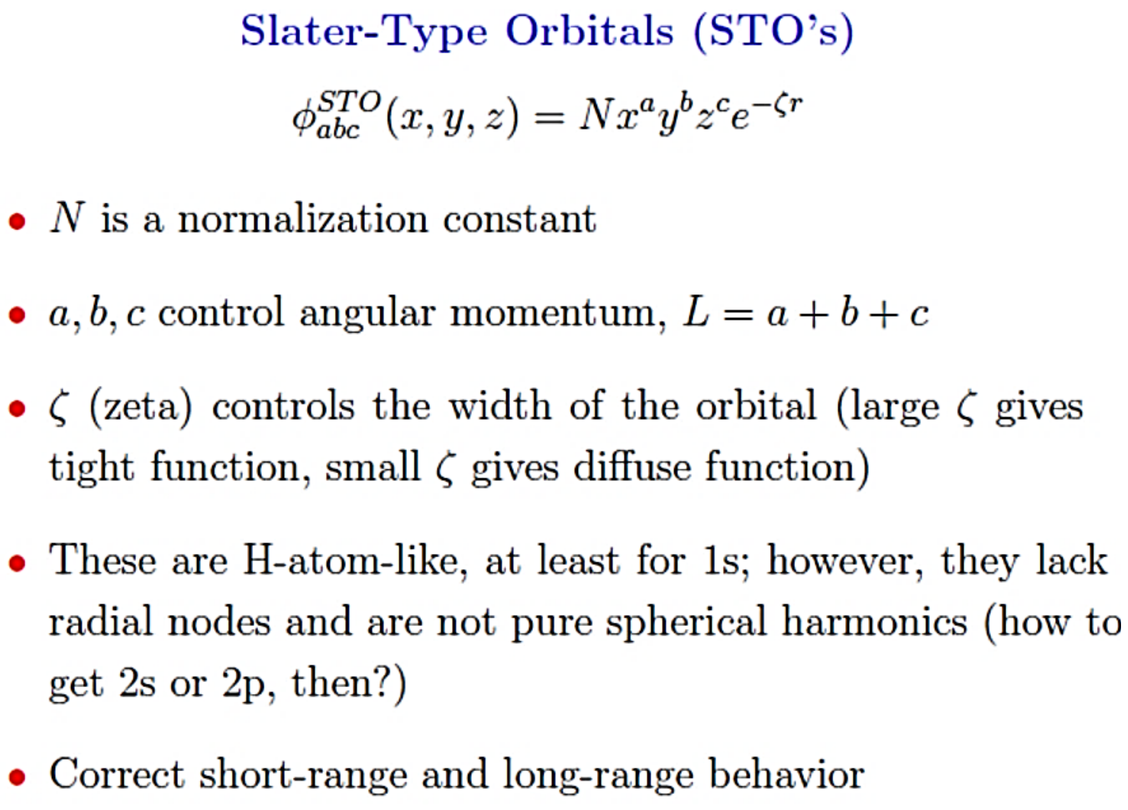
Structure determine everything.

8. Diatomic molecules

For calculations on larger molecules it is necessary to use a linear combination containing many more functions. The set of functions that we use is called a *basis set*. The simplest basis set contains, for each atom, the atomic orbitals up to and including its valence shell. This *minimal basis* for any first-row atom contains the $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals. For a first-row diatomic this gives 10 functions, and leads to secular equations for the 10 coefficients — an eigenvalue equation involving a 10×10 matrix.

This basis set can be improved by adding more functions. A *split-valence* basis uses two each of the $2s$ and $2p$ functions, one a bit more contracted and one a bit more diffuse than the single function of the minimal basis. This allows the wavefunction on a particular atom to be more contracted if it carries a net positive charge, or more diffuse if it carries a net negative charge.

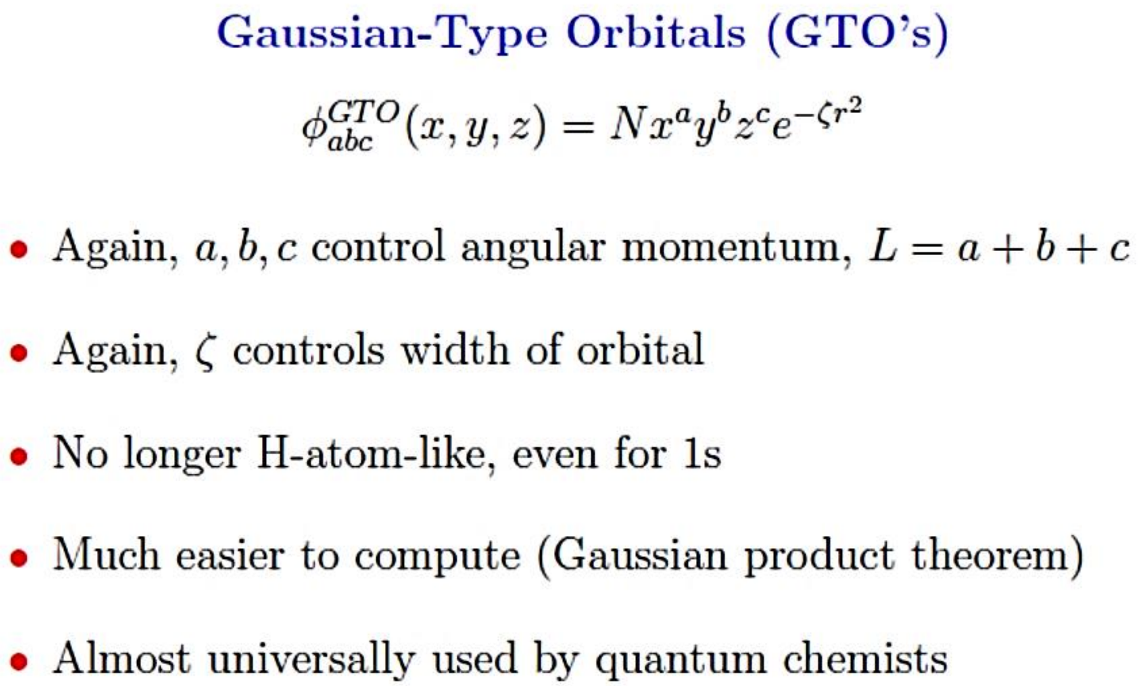
Modern accurate wavefunction calculations use even bigger basis sets, and the secular equations can then only be solved using a computer. However valuable insights may be obtained using the much simpler approach of Hückel theory, combined with the use of symmetry to simplify the problem.



Slater-Type Orbitals (STO's)

$$\phi_{abc}^{STO}(x,y,z) = N x^a y^b z^c e^{-\zeta r}$$

- N is a normalization constant
- a, b, c control angular momentum, $L = a + b + c$
- ζ (zeta) controls the width of the orbital (large ζ gives tight function, small ζ gives diffuse function)
- These are H-atom-like, at least for 1s; however, they lack radial nodes and are not pure spherical harmonics (how to get 2s or 2p, then?)
- Correct short-range and long-range behavior



Gaussian-Type Orbitals (GTO's)

$$\phi_{abc}^{GTO}(x,y,z) = N x^a y^b z^c e^{-\zeta r^2}$$

- Again, a, b, c control angular momentum, $L = a + b + c$
- Again, ζ controls width of orbital
- No longer H-atom-like, even for 1s
- Much easier to compute (Gaussian product theorem)
- Almost universally used by quantum chemists

Homonuclear diatomic molecules

The two-orbital picture can be applied to diatomic molecules. Let's consider the F_2 molecule.

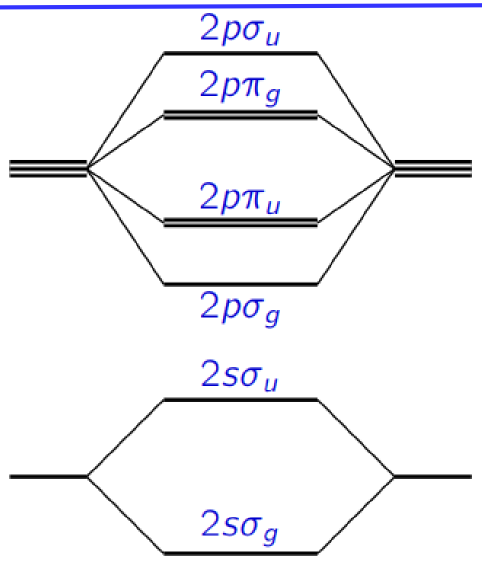
The $1s$ atomic orbitals are far removed in energy from the other orbitals, so they don't mix with them. Also they are very compact, so they overlap with each other only very slightly — β is very small. However $\Delta\alpha$ is zero, so the molecular orbitals are sum and difference of the atomic orbitals.

Molecular orbitals in diatomics are labelled σ if they have no nodes containing the molecular axis, π if they have one such node, and so on.

Orbitals are described as g (for German *gerade*, 'even') if they are unchanged by inversion through the centre of mass — that is, if $\psi(-x,-y,-z)=\psi(x,y,z)$.
They are u (for German *ungerade*, 'odd') if inversion changes the sign, i.e. if $\psi(-x,-y,-z)=-\psi(x,y,z)$.

Thus the $1s$ atomic orbitals generate a $1s\sigma_g$ orbital and a $1s\sigma_u$ one

Orbitals in diatomic molecules: F_2



In F_2 the $2s$ orbitals are some way below the $2p$ in energy, and as a first approximation we can ignore sp mixing. There is a bonding combination ($2s\sigma_g$) and an antibonding one ($2s\sigma_u$). The overlap is much larger than for the $1s$ orbitals, so β is bigger and the difference in energy is substantial.

Finally, the $2p$ orbitals can be classified into $2p\sigma$ (pointing along the bond) and $2p\pi$ (perpendicular to the bond). The σ and π orbitals don't mix with each other — the β integral between σ and π is zero because positive and negative regions cancel. Consequently we get bonding and antibonding $2p\sigma$ orbitals — $2p\sigma_g$ and $2p\sigma_u$ respectively. From the $2p\pi$ orbitals we get a pair of $2p\pi_u$ bonding orbitals and a pair of $2p\pi_g$ antibonding orbitals. The resulting orbital energy level pattern is the familiar picture shown. (The $1s\sigma_g$ and $1s\sigma_u$ levels have been omitted.)

N_2

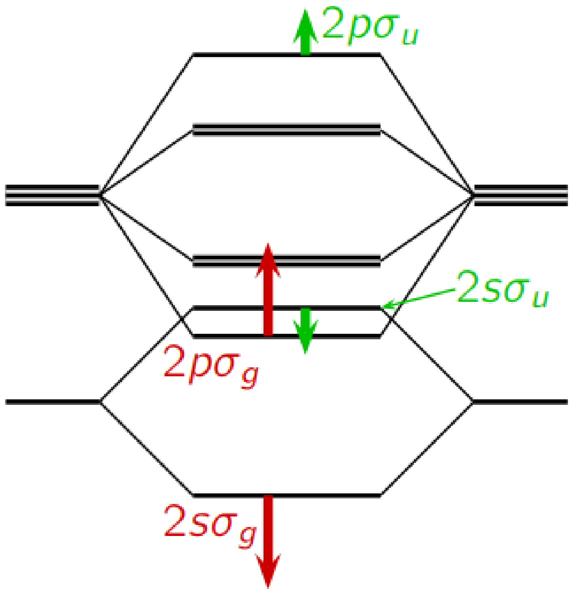
In the fluorine atom, the $2s$ and $2p$ orbitals are well separated because of screening effects.

Further to the left in the periodic table, screening has less effect in separating the $2s$ and $2p$ orbital energies, and we have to allow for *sp* mixing. This can again be treated as a set of two-orbital problems, one for each symmetry.

The $2s\sigma_g$ and $2p\sigma_g$ orbitals mix, pushing each other apart so that the $2s\sigma_g$ becomes more strongly bonding and the $2p\sigma_g$ more weakly bonding.

Similarly, the $2s\sigma_u$ and $2p\sigma_u$ orbitals mix and push each other apart.

The $2p\pi$ orbitals are unaffected.

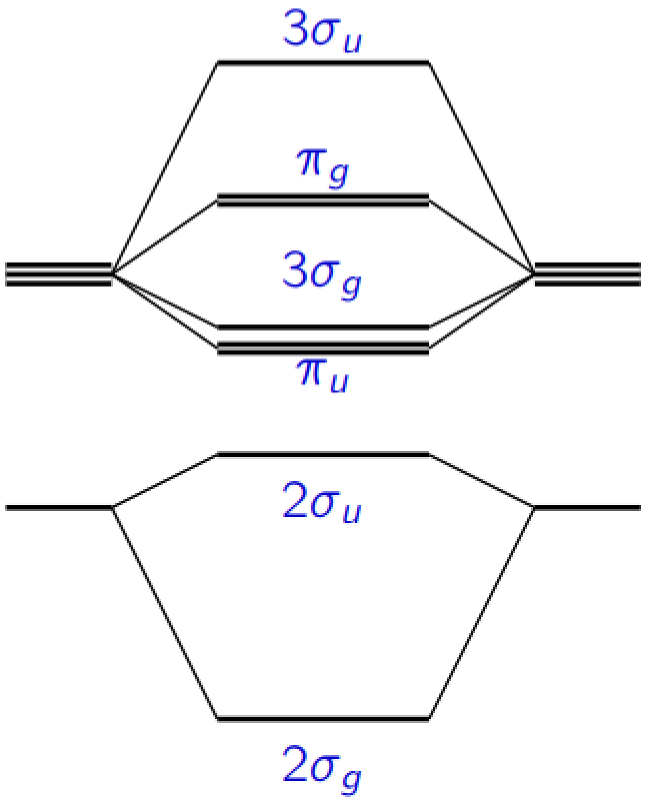


Because the σ orbitals are now mixtures of *s* and *p*, it is usual to label them sequentially from lowest energy upwards. Sometimes the core orbitals are included in the numbering, sometimes not. Here we count them as $1\sigma_g$ and $1\sigma_u$.

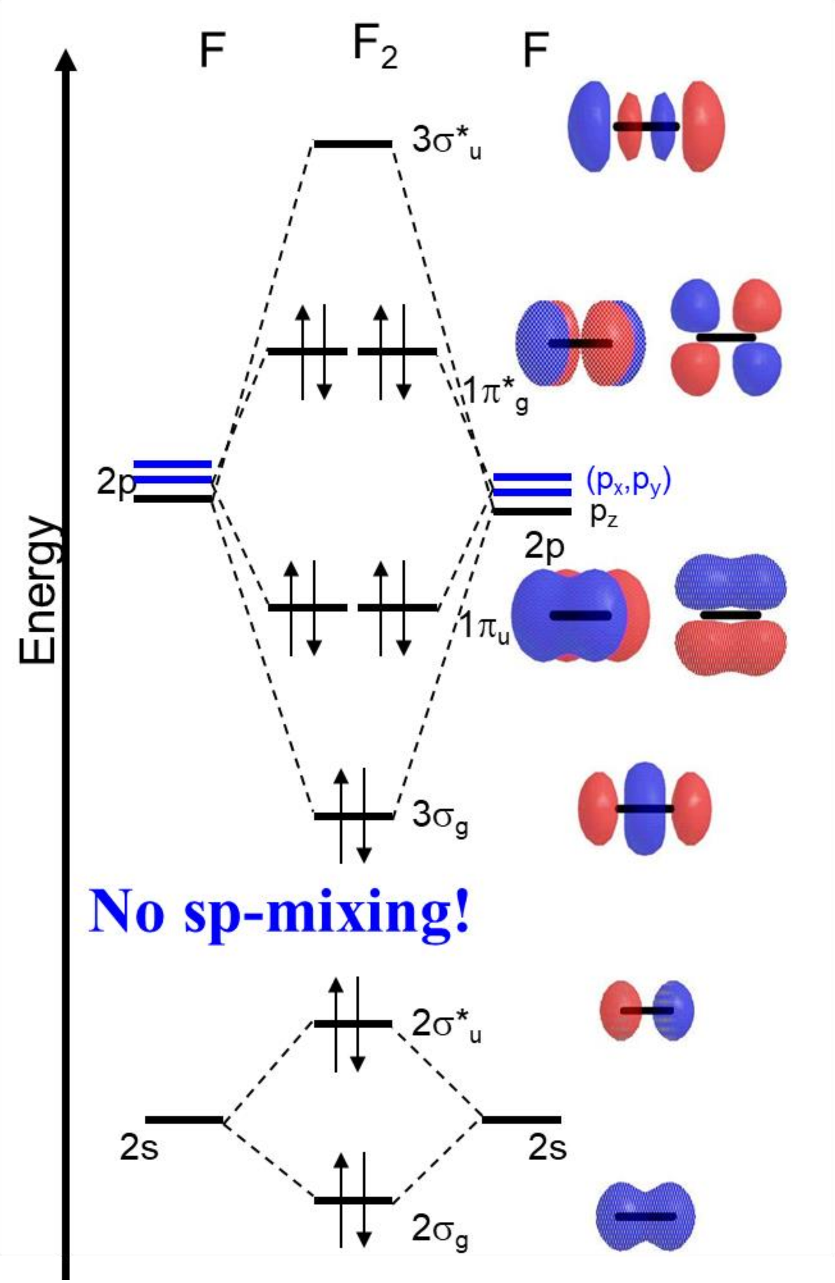
The outcome of all this is that for N_2,

- The $2\sigma_g$ orbital is very strongly bonding.
- The $3\sigma_g$ orbital lies *above* the π_u and is relatively weakly
- bonding.
- The $2\sigma_u$ orbital is only weakly antibonding.

These effects are present in O_2 but the screening effects are intermediate between N_2 and F_2. In particular, the $3\sigma_g$ orbital lies below the π_u in O_2.

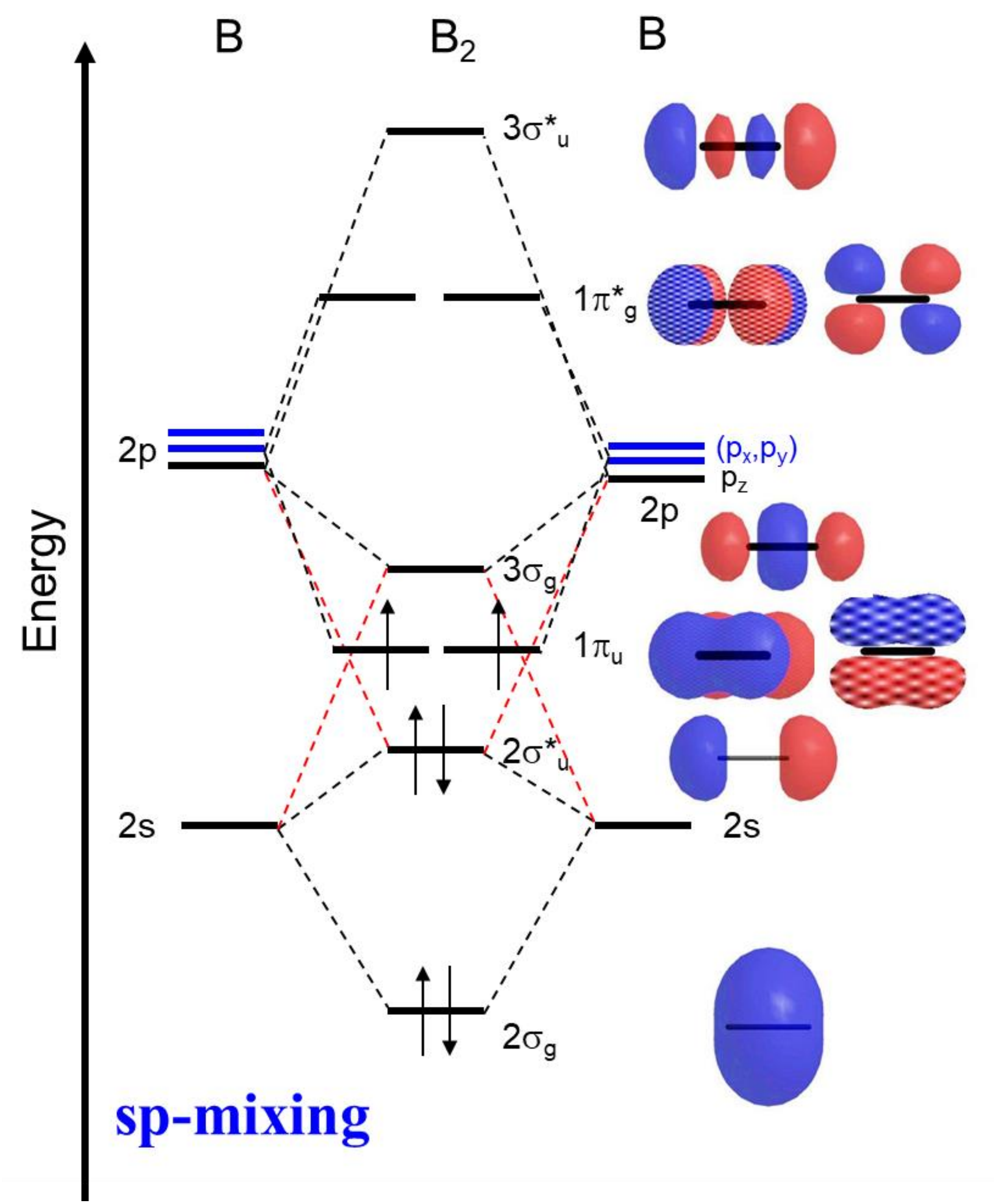


MO diagram for F_2

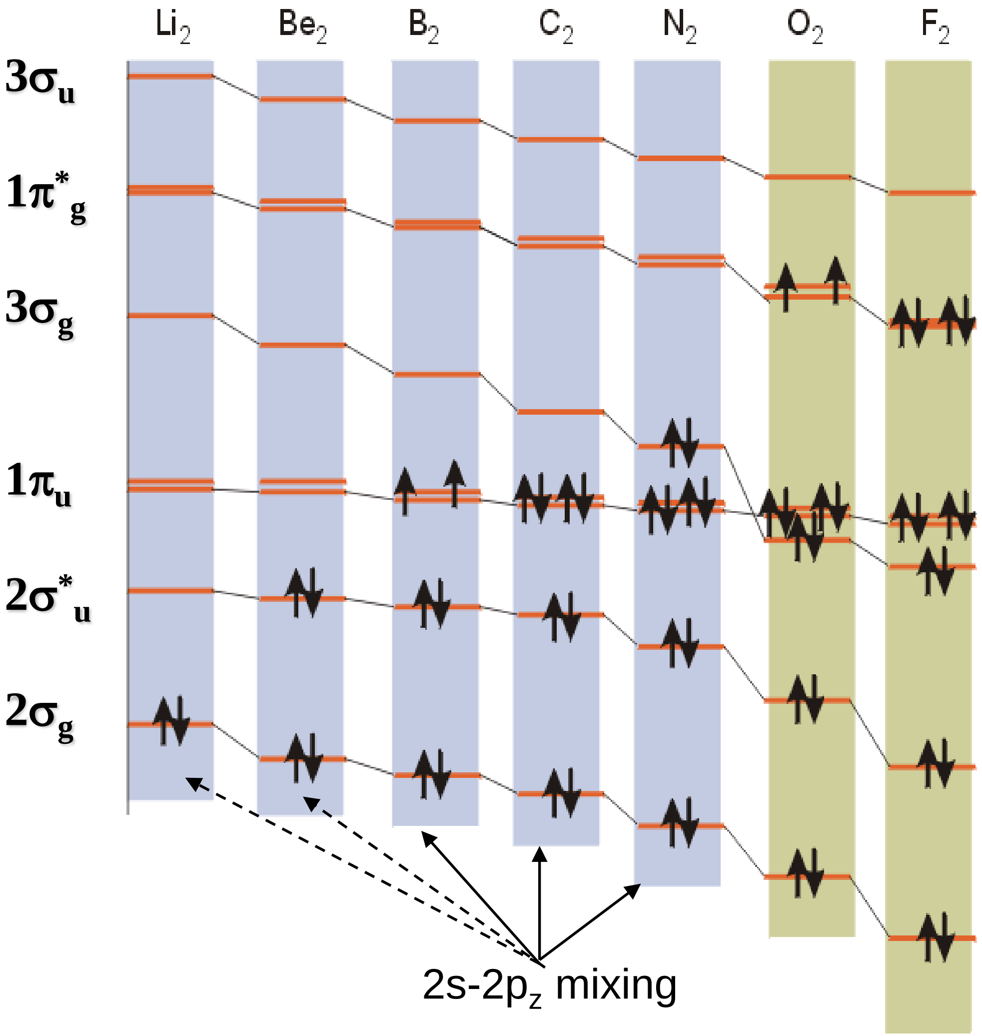


No sp-mixing!

MO diagram for B_2



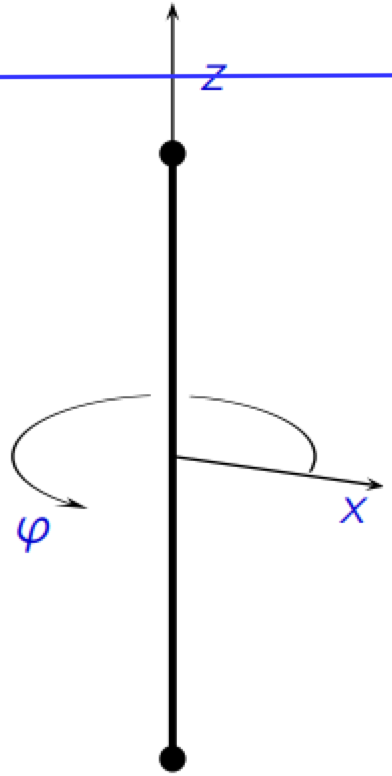
sp-mixing



Electronic configurations

H_2	2	$(1\sigma_g)^2$
He_2^+	3	$(1\sigma_g)^2(1\sigma_u)^1$
Li_2	6	$KK(2\sigma_g)^2$
B_2	10	$KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2$
C_2	12	$KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$
N_2^+	13	$KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^1$
N_2	14	$KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$
O_2^+	15	$KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_g)^4(1\pi_u)^1$
O_2	16	$KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_g)^4(1\pi_u)^2$
F_2	18	$KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_g)^4(1\pi_u)^4$

Angular momentum in diatomics



Angular momentum is an important property of diatomics and other linear molecules. We take the z axis to coincide with the internuclear axis. The orbital angular momentum operators for an electron are the components $\hat{l}_x$, $\hat{l}_y$ and $\hat{l}_z$ and $\hat{\boldsymbol{l}}^2 = \hat{l}_x{}^2 + \hat{l}_y{}^2 + \hat{l}_z{}^2$, but only $\hat{l}_z$ commutes with the Hamiltonian and only it can have a definite value. It is customary to use greek letters for diatomics, and the quantum number associated with $\hat{l}_z$ is called λ. We can assign a λ value to each occupied molecular orbital, and we just add these up to get the total angular momentum Λ for all the electrons.

As before, $\hat{l}_z = \frac{\partial}{\partial\varphi}$. For orbitals to have definite angular momentum they need to be expressed in complex form. The value of λ is identical to m in those equations, so $\lambda=0$ for ψ_{2p0} and ±1 for ψ_{2p1} and $\psi_{2p_{\bar{1}}}$ respectively. Orbitals with $\lambda=0$ are called σ, those with $\lambda=\pm1$ are π, and so on; the letters are the Greek equivalents of the $s, p, d, f,$ etc., that we use for $l = 0, 1, 2, 3,$ etc., in atoms.

Term symbols for diatomics

Term symbols are used for diatomics in the same way as for atoms — to label states and to specify their angular momenta and other symmetry characteristics. The central item represents the quantum number Λ, but it is expressed as a greek letter: Σ, Π, Δ, Φ, etc., for $\Lambda = 0, 1, 2, 3$, etc.

$$X^{2S+1}\Lambda^{(\pm)}_{g/u}$$

There may be a prefix letter: usually X for the ground term, then A, B, etc., for higher-energy terms with the same multiplicity and a, b, etc., for terms with different multiplicity.

The right subscript is g if the overall molecular wavefunction is unchanged by inversion of all the electron coordinates in the centre of mass, or u if inversion changes the sign

Constructing diatomic term symbols

- We get Λ by adding up the λ values for the occupied orbitals.
- If the number of electrons in u orbitals is odd, the overall inversion symmetry is u, otherwise it is g.
- Hund's rule determines the spin and hence the multiplicity for the ground term, but other values may be possible for excited states.
- For Σ states only, there is a superscript $+$ or $-$ which describes the effect of reflecting the entire wavefunction in a plane containing the internuclear axis, or (equivalently) the effect of changing the sign of the φ coordinates of all the electrons. The $-$ case can only arise in *open-shell* Σ states.

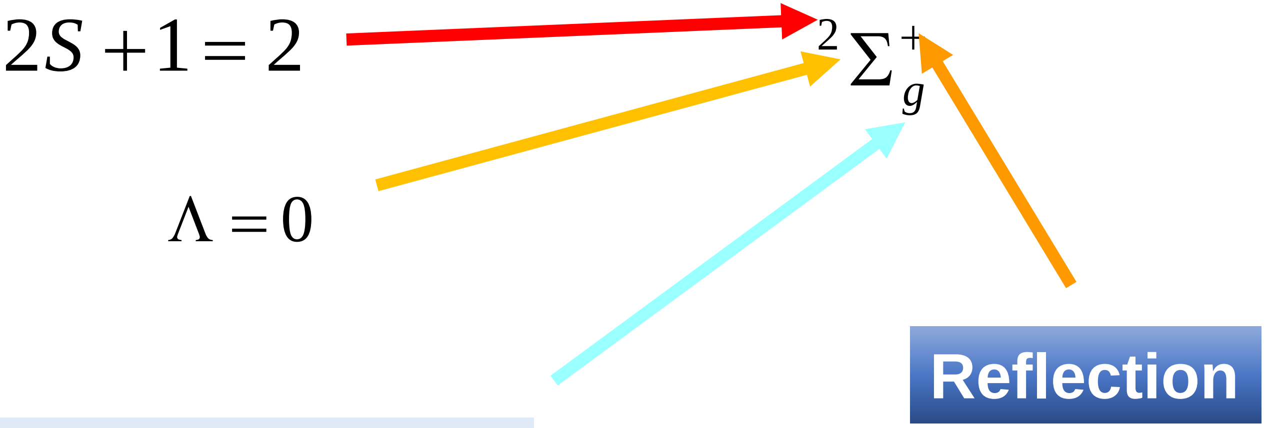
Molecule	Configuration
H_2^+	$(1\sigma_g)^1$

↑ or ↓

$m = 0$

$m_s = \pm 1/2$

$\Lambda = 0$, $S = 1/2$



$2S + 1 = 2$

$\Lambda = 0$

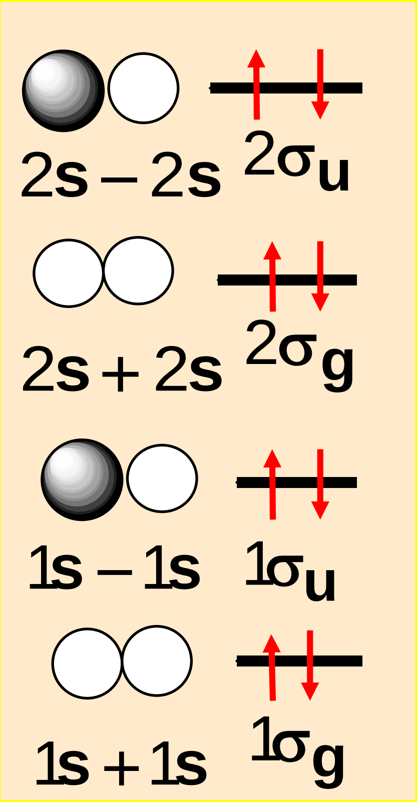
$^2\Sigma_g^+$

Reflection

e.g., $(1\pi_u)^2 \rightarrow (1\pi_{+1})^1 (1\pi_{-1})^1$

$\Lambda = +1 - 1 = 0$, $S = 1$, $u \times u = g$

Molecule	Configuration	Term symbol
H_2	$(1\sigma_g)^2$	$^1\Sigma_g^+$
H_2^-	$(1\sigma_g)^2(1\sigma_u)^1$	$^2\Sigma_u^+$
He_2	$(1\sigma_g)^2(1\sigma_u)^2$	$^1\Sigma_g^+$
Li_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$	$^1\Sigma_g^+$
Be_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2$	$^1\Sigma_g^+$



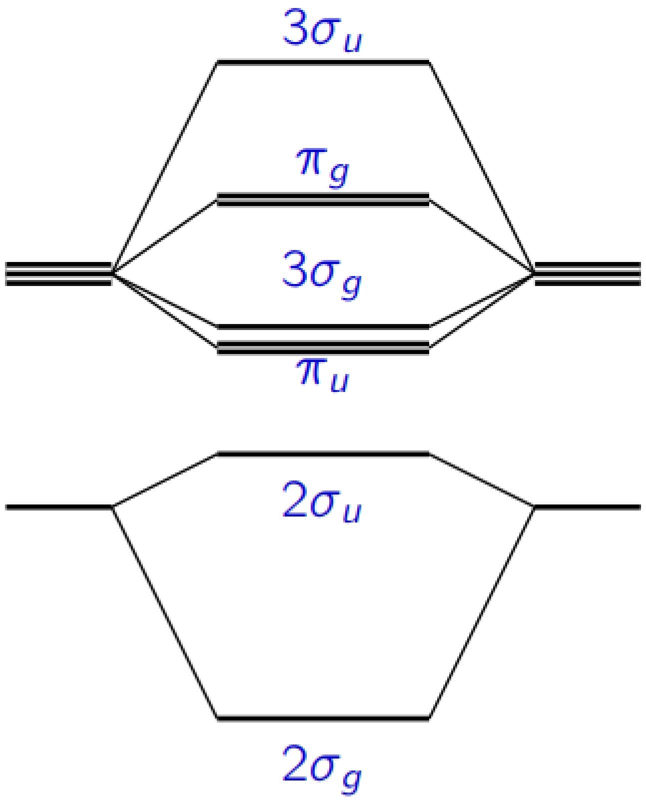
- For homonuclear diatomics, a closed-shell electronic configuration has ***S* = *0*** and ***Λ* =*0***, giving rise to the spectral term $^1\Sigma_g^+$.
- **The spectral terms of molecules with open shell(s) are determined by the electrons in the open shell(s)!**

Examples of diatomic term symbols

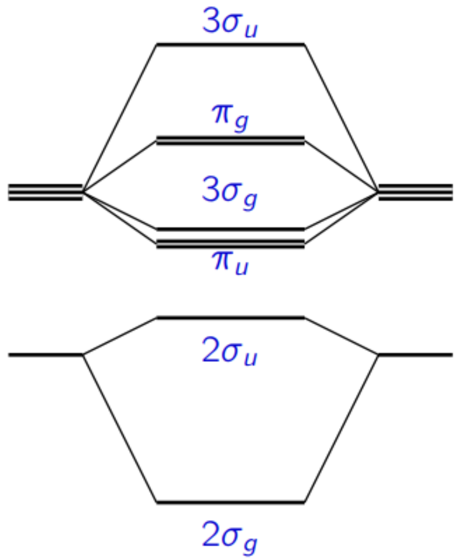
Let us find the ground terms of some of the first-row homonuclear diatomics.

Li_2 There are 2 valence electrons. They occupy the $2\sigma_g$ orbital ($\lambda = 0$), so $\Lambda = 0$. The spins are paired, so $S = 0$. There are no u orbitals occupied, so the term symbol is ${}^1\Sigma_g^+$.

N_2 There are 10 electrons. All the bonding orbitals are occupied. The π_u orbitals have $\lambda = \pm 1$, but there are two electrons in each, so the total $\Lambda = 0$ as before. Once again we have a ${}^1\Sigma_g^+$ term.



Diatomic term symbols: N_2^+

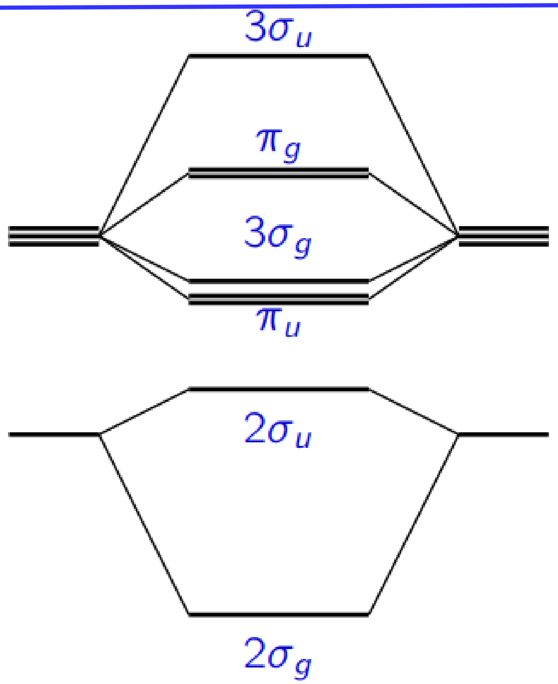


In the photoelectron spectrum of N_2, we observe states of N_2^+. The lowest of these has an electron removed from the $3\sigma_g$ orbital, leaving the configuration $\ldots 2\sigma_u^2\pi_u^4 3\sigma_g^1$. There is only a single σ_g electron outside closed shells, so $\Lambda = 0$ and $S = \frac{1}{2}$, and the term symbol is $X^2\Sigma_g$.

Other possibilities observed in the photoelectron spectrum include the ionisation of an electron from the π_u shell ($\lambda = \pm 1$), to give a state with $\Lambda = \pm 1$, the $A^2\Pi_u$ term. Removal of an electron from the $2\sigma_u$ orbital leaves a single σ_u electron apart from closed shells, and gives the $B^2\Sigma_u$ term.

The photoelectron spectrum, together with other spectroscopic data, provides experimental evidence for the theoretical expectation that the $2\sigma_u$ orbital is only weakly antibonding and the $3\sigma_g$ only weakly bonding.

Diatomic term symbols: C_2



C_2 is an interesting case. The obvious candidate for the ground state has the configuration $...(2\sigma_g)^2(2\sigma_u)^2(\pi_u)^4$, which is a closed shell, with term symbol $^1\Sigma_g^+$.

However the energy difference between π_u and $3\sigma_g$ is small, so there is the possibility of promoting an electron, giving the configuration $...(2\sigma_g)^2(2\sigma_u)^2(\pi_u)^3(3\sigma_g)^1$. The promotion energy can be compensated by making the spins parallel (triplet state).

Two of the π electrons can have $\lambda = 1$ and the other $\lambda = -1$, or vice versa, so $\Lambda = \pm 1$ and we have a Π term. The number of occupied u orbitals is now odd, so the overall g/u symmetry is u, and the overall term symbol is $^3\Pi_u$.

For some years it was not known which of these states is the ground state. It is now established to be the $^1\Sigma_g^+$, but the $^3\Pi_u$ is only about $700\ \text{cm}^{-1}$ higher

Diatomic term symbols: O_2

The oxygen molecule is a more complicated case. There are 2 electrons in addition to the N_2 closed shell, and they go in the shell. There are several possibilities.

	$a^1\Delta_g$	$b^1\Sigma_g^+$	$X^3\Sigma_g^-$
$E =$	7918 cm^{-1}	13195 cm^{-1}	0 cm^{-1}

Hund's first rule tells us that the ground state is the one with the highest spin, i.e. the $^3\Sigma_g^-$ state.

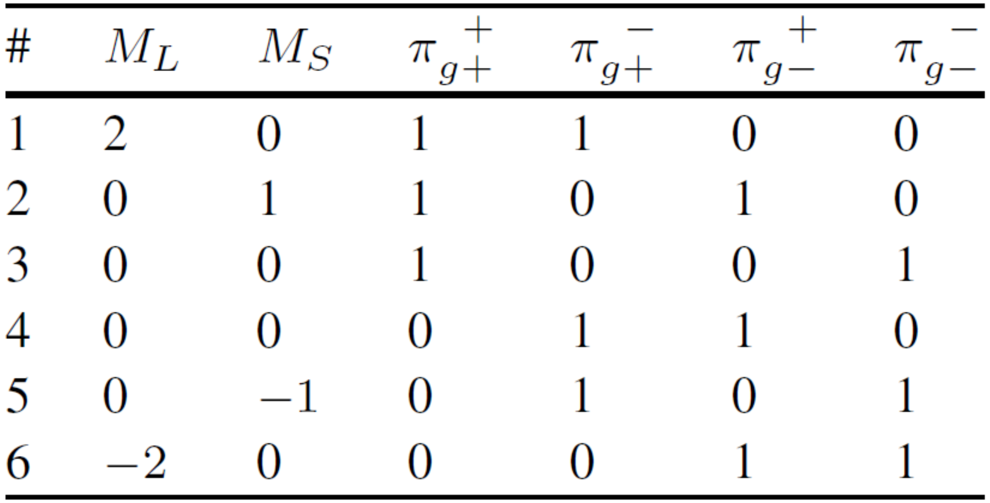
Term symbols for π^2 configurations

To complete the term symbols for O_2, or for any state with two electrons in a π shell, we have to examine the wavefunctions in a bit more detail. We only need to consider the φ-dependent part of the wavefunction, and the spin.

For equivalent electrons in an open shell: π_g^2 has in total $C_4^2 = 6$ microstates. (e.g., O_2)

m	+1 -1	+1 -1	+1 -1	+1 -1	+1 -1	+1 -1
M_L =	0	0	0	0	2	-2
M_S =	1	-1	0	0	0	0

#	M_L	M_S	π_{g+}^{+}	π_{g+}^{-}	π_{g-}^{+}	π_{g-}^{-}
1	2	0	1	1	0	0
2	0	1	1	0	1	0
3	0	0	1	0	0	1
4	0	0	0	1	1	0
5	0	-1	0	1	0	1
6	-2	0	0	0	1	1



#	M_L	M_S	π_{g+}^{+}	π_{g+}^{-}	π_{g-}^{+}	π_{g-}^{-}
1	2	0	1	1	0	0
2	0	1	1	0	1	0
3	0	0	1	0	0	1
4	0	0	0	1	1	0
5	0	−1	0	1	0	1
6	−2	0	0	0	1	1

$$\pi_{g+}^{+} = \pi_{g+}(1)\alpha(1)$$
$$\pi_{g+}^{-} = \pi_{g+}(1)\beta(1)$$
$$\pi_{g-}^{+} = \pi_{g-}(1)\alpha(1)$$
$$\pi_{g-}^{+} = \pi_{g-}(1)\alpha(1)$$

$$\varphi_2 = \left|\pi_{g+}(1)\alpha(1)\pi_{g-}(2)\alpha(2)\right|$$

$${}^3\Sigma_g$$

$$\varphi_2 = \frac{1}{\sqrt{2}}\left(\pi_{g+}(1)\pi_{g-}(2) - \pi_{g-}(1)\pi_{g+}(2)\right)\alpha(1)\alpha(2)$$

$$\varphi_5 = \left|\pi_{g+}(1)\beta(1)\pi_{g-}(2)\beta(2)\right|$$

$$\varphi_5 = \frac{1}{\sqrt{2}}\left(\pi_{g+}(1)\pi_{g-}(2) - \pi_{g-}(1)\pi_{g+}(2)\right)\beta(1)\beta(2)$$

Angular Momentum: $|M_L| = (+1) + (-1) = 0$

Symmetry: g×g = g

$$\varphi_3 = \left|\pi_{g+}(1)\alpha(1)\pi_{g-}(2)\beta(2)\right|$$

$$\varphi_4 = \left|\pi_{g-}(1)\beta(1)\pi_{g+}(2)\alpha(2)\right|$$

φ3 <=> φ4

$^3\Sigma_g$

$$\varphi_t = \frac{1}{\sqrt{2}}(\varphi_3 + \varphi_4) = \frac{1}{\sqrt{2}}\left(\pi_{g+}(1)\pi_{g-}(2)\text{-}\pi_{g-}(1)\pi_{g+}(2)\right)\cdot\left(\alpha(1)\beta(2)+\beta(1)\alpha(2)\right)$$

$^1\Sigma_g$

$$\varphi_s = \frac{1}{\sqrt{2}}(\varphi_3\text{-}\varphi_4) = \frac{1}{\sqrt{2}}\left(\pi_{g+}(1)\pi_{g-}(2)+\pi_{g-}(1)\pi_{g+}(2)\right)\cdot\left(\alpha(1)\beta(2)\text{-}\beta(1)\alpha(2)\right)$$

Angular Momentum: $|M_L|$ = (+1) + (-1) = 0
Symmetry: g×g = g

Consider the Σ wave functions and make the substitution $\pi_{g+} \rightarrow \pi_{g-}$ notice that the triplets change sign while the singlet does not.

$^3\Sigma_g^-$

$^1\Sigma_g^+$

#	M_L	M_S	π_{g+}^{+}	π_{g+}^{-}	π_{g-}^{+}	π_{g-}^{-}
1	2	0	1	1	0	0
2	0	1	1	0	1	0
3	0	0	1	0	0	1
4	0	0	0	1	1	0
5	0	−1	0	1	0	1
6	−2	0	0	0	1	1

$$\varphi_1 = \left|\pi_{g+}(1)\alpha(1)\pi_{g+}(2)\beta(2)\right|$$

$$\varphi_6 = \left|\pi_{g-}(1)\alpha(1)\pi_{g-}(2)\beta(2)\right|$$

φ1 <=> φ6

$^{1}\Delta_g$

$$\psi = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_6)$$

$$\psi' = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_6)$$

Angular Momentum: $|M_L| = 2$

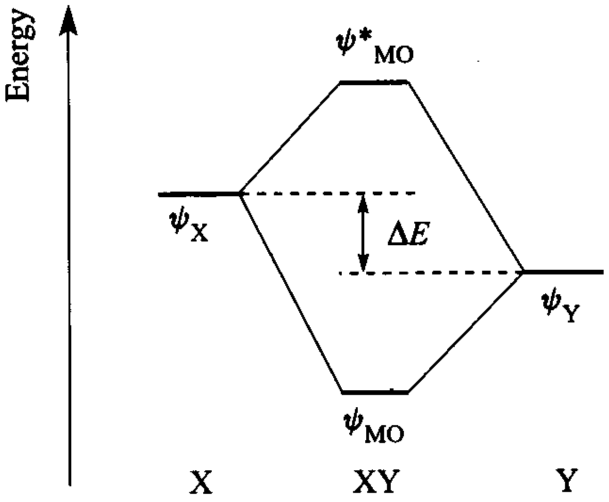
Symmetry: g×g = g

Term Symbols	**Atoms** $^{2S+1}L_J$	**Molecules** $^{2S+1}\lvert M_L \rvert_{g/u}$
Orbital Momentum - along z axis	Choice of z axis is arbitrary for spherical atom m_l = component along z axis for individual electron $M_L = \Sigma m_{l,i}$	z-axis defined as internuclear axis, p_o m_l = component along z axis for individual electron $M_L = \Sigma m_{l,i}$ $\lvert M_L \rvert$ = 1: Σ (s = sigma) 2: Π (p= pi) 3: Δ (d = delta)
- total	L = 1: S 2: P 3: D $M_L = L,\ L\text{-}1, \ldots 0 \ldots, -L$	L not fully applicable for molecules due to lower symmetry of molecules (not spheres)
Electron Spin - along z axis	$m_s = \pm 1/2$ $M_S = \Sigma m_{s,i}$	$m_s = \pm 1/2$ $M_S = \Sigma m_{s,i}$
- total	$M_s = S,\ S\text{-}1, \ldots -S$ Spin multiplicity = 2S+1	$M_s = S,\ S\text{-}1, \ldots -S$ Spin multiplicity = 2S+1
Total Combined Angular Momentum	$J = L + S$ $J = L + S,\ L+S\text{-}1, \ldots \lvert L\text{-}S \rvert$	
Inversion Symmetry		If inversion symmetry exists: $g_i * g_j = g$, $g_i * u_j = u$, $u_i * u_j = g$

MO Theory for Heteronuclear Diatomics

- MO’s will no longer contain equal contributions from each AO.
  - AO’s interact if symmetries are compatible.
  - AO’s interact if energies are close.
  - No interaction will occur if energies are too far apart. A nonbonding orbital will form.

Y_X makes a greater contribution to the Y^*_{MO}



Y_Y makes a greater contribution to the Y_{MO}

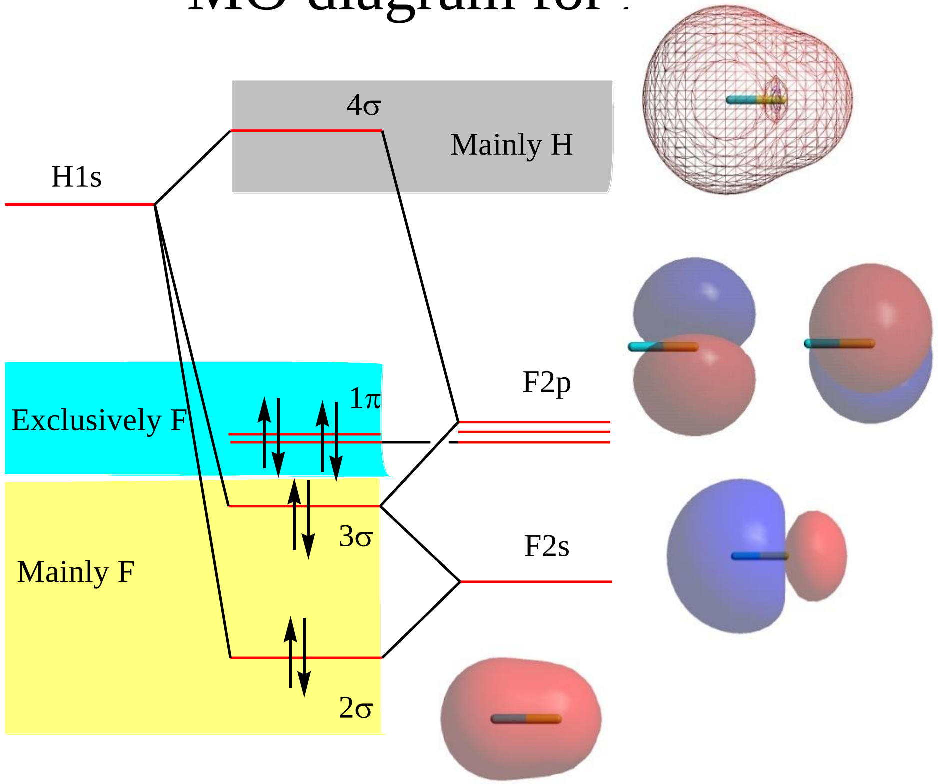
Heteronuclear diatomics: CO

We can think of CO as a modified N_2, in which we have moved a proton charge from one nucleus to the other. There is no centre of symmetry in a heteronuclear diatomic, so the *g/u* labels don’t apply. Several differences result:

- The core orbitals are far removed in energy from each other as well as from the other orbitals, so they don't mix. The 1σ is wholly on the O atom and the 2σ wholly on the C.
- The difference in electronegativity causes bonding orbitals to have their electron density mainly on the O atom, while the antibonding ones have their electron density mainly on the C.
- What were the $2\sigma_u$ and $3\sigma_g$ orbitals of N_2 can now mix with each other. The resulting 4σ orbital is essentially a lone-pair on the oxygen, while the 5σ is a diffuse lone-pair orbital on the carbon.
- The π_u now labelled 1π, has its density mainly on the O atom. The unoccupied 2π, formerly the π_g, is primarily on the C atom, where it is an effective π-acceptor orbital.

Heterogeneous diatomic molecules, HX

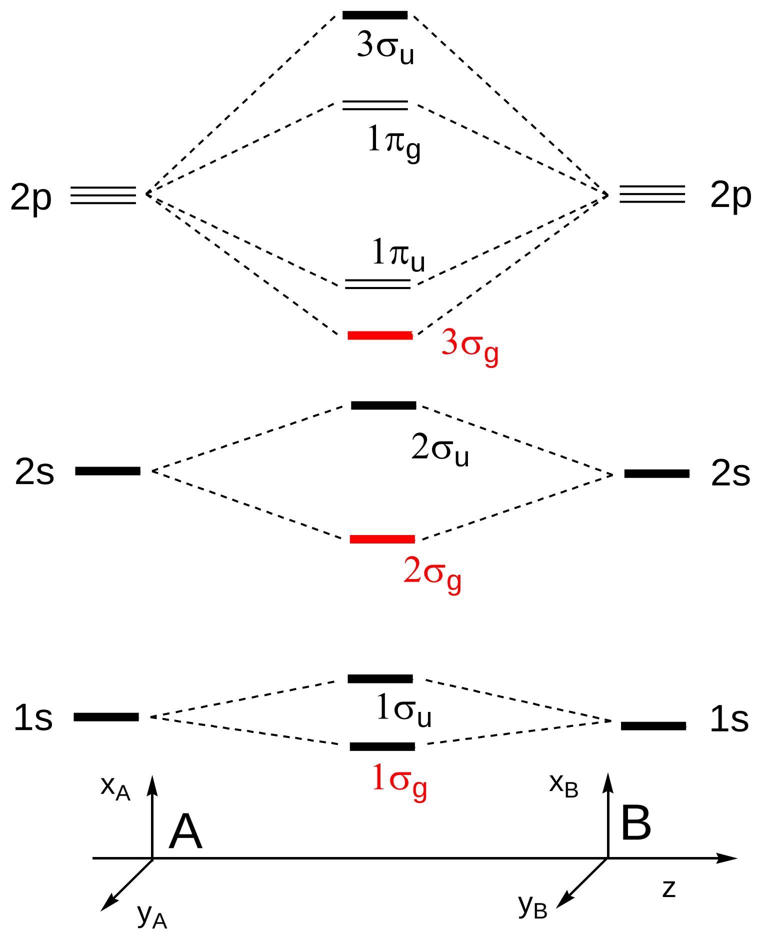
MO diagram for HF

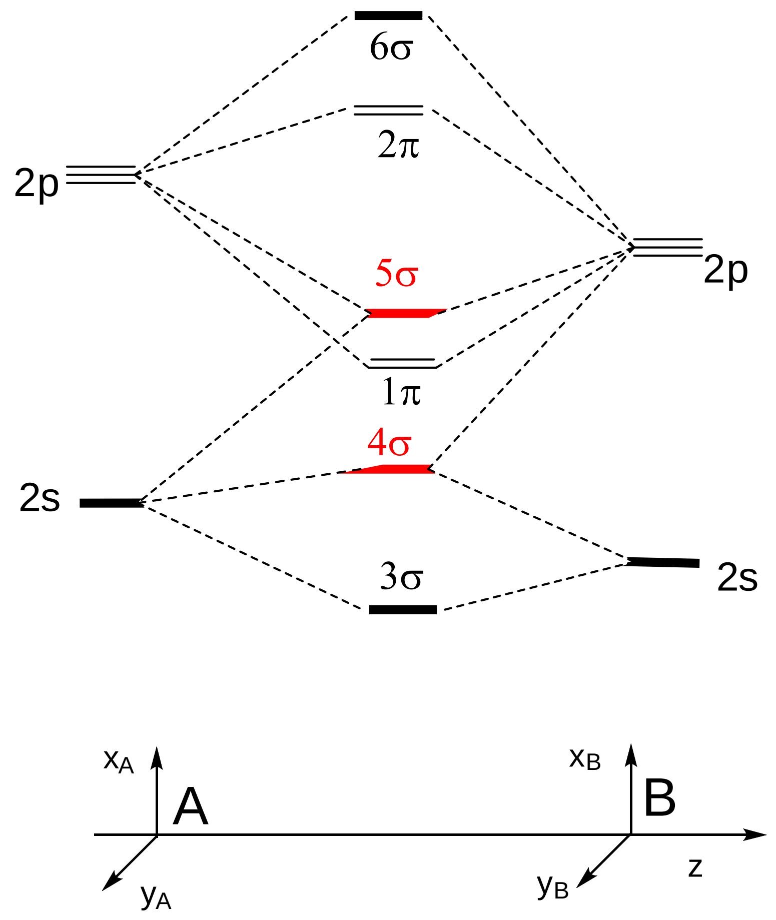


Electronic configurations

LiH	4	$K(2\sigma)^2$
BeH	5	$K(2\sigma)^2 (3\sigma)^1$
CH	7	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^1$
NH	8	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^2$
OH	9	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^3$
HF	10	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^4$

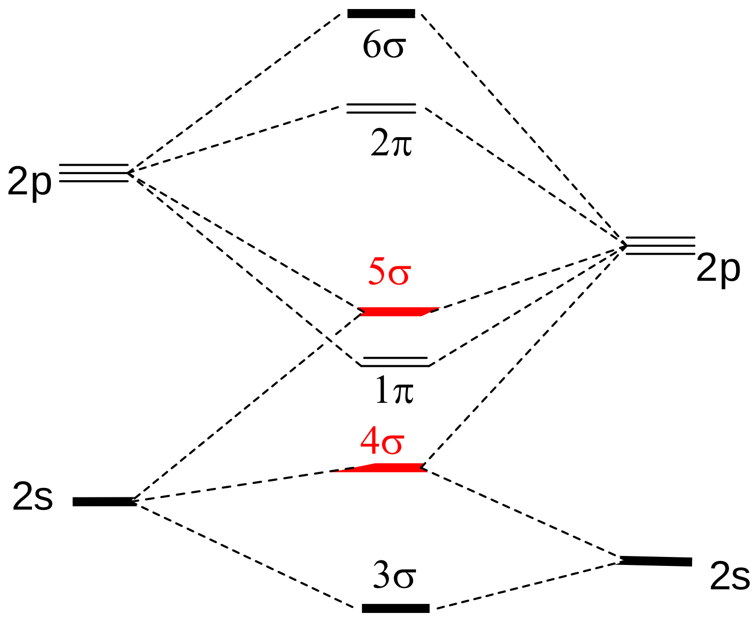
Simplified MO diagram of heteronuclear diatomic molecules





A = B ↔ **A ≠ B**

Heterogeneous diatomic molecules, YX



Isoelectronic rule:

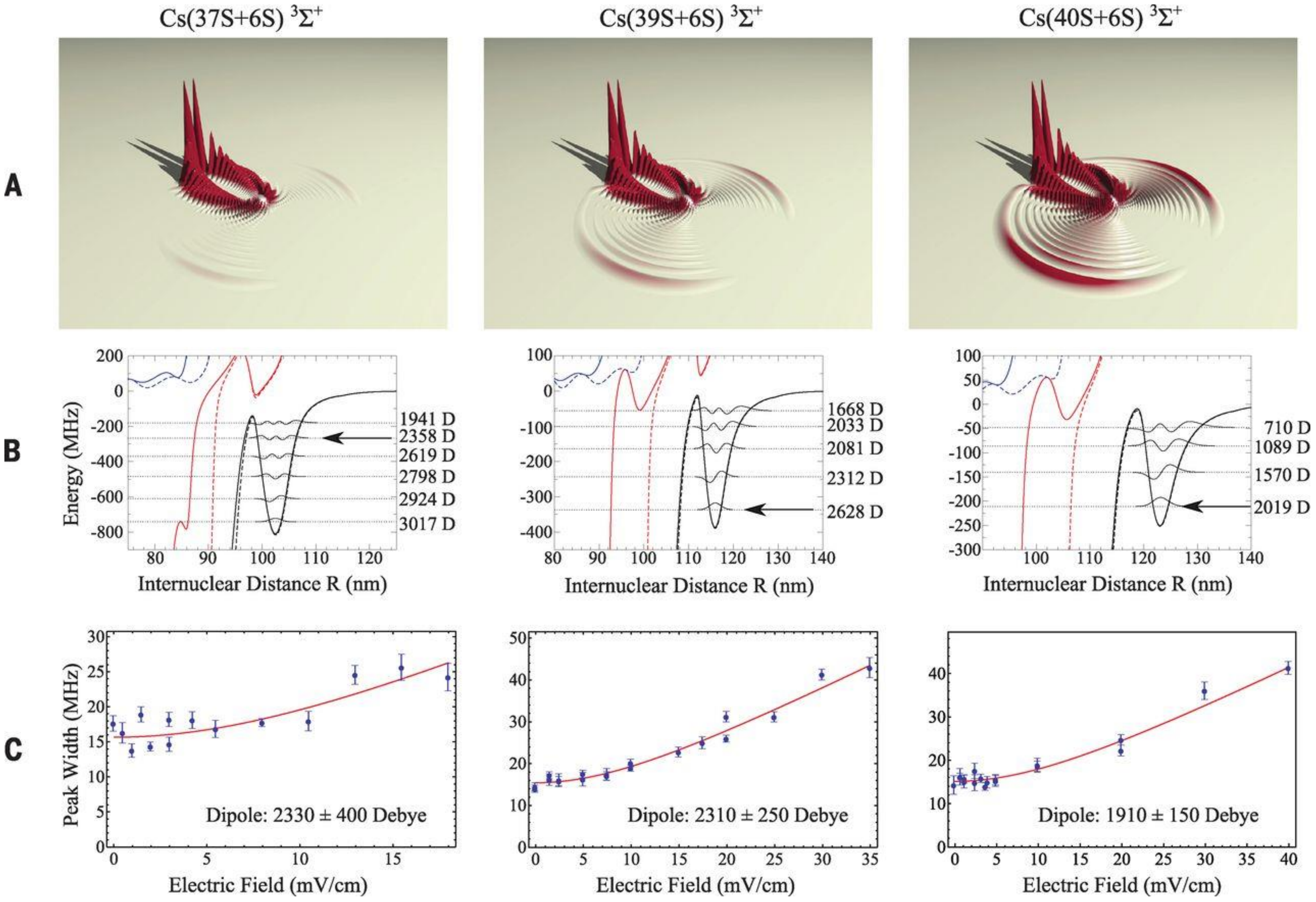
The MO's bond formation and electronic configurations are similar among the isoelectronic diatomic molecules.

CO is isoelectronic with N_2.

KK$(3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^2$

BeO	12	KK$(3\sigma)^2 (4\sigma)^2 (1\pi)^4$
CN	13	KK$(3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^1$
CO	14	KK$(3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^2$
NO	15	KK$(3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^2 (2\pi)^1$

LiH	4	$K(2\sigma)^2$	$^1\Sigma^+$
BeH	5	$K(2\sigma)^2 (3\sigma)^1$	$^2\Sigma^+$
CH	7	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^1$	$^2\Pi$
NH	8	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^2$	$^3\Sigma^-$
OH	9	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^3$	$^2\Pi$
HF	10	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^4$	$^1\Sigma^+$
BeO , BN	12	$KK(3\sigma)^2 (4\sigma)^2 (1\pi)^4$	$^1\Sigma^+$
CN , BeF	13	$KK(3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^1$	$^2\Sigma^+$
CO	14	$KK(3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^2$	$^1\Sigma^+$
NO	15	$KK(3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^2 (2\pi)^1$	$^2\Pi$



D. Booth et al. Science 2015;348:99-102